PROPERTY PREDICTION AND RESIDUAL STRESSES IN
ALUMINIUM ALLOY 7010

BY

ROBERT JOSEPH FLYNN

THESIS SUBMITTED FOR THE AWARD OF
DOCTOR OF PHILOSOPHY
AT THE FACULTY OF SCIENCE AND ENGINEERING
UNIVERSITY OF LIMERICK

SUPERVISED BY:

DR. J. S. ROBINSON
DEPARTMENT OF MECHANICAL, AERONAUTICAL AND BIOMEDICAL
ENGINEERING
UNIVERSITY OF LIMERICK

SUBMITTED TO THE UNIVERSITY OF LIMERICK 2013
Declaration

This is entirely my own work and it has not been previously submitted to this or any other institution of higher education for this or any other academic award.

Where use has been made of the work of other people, it has been acknowledged and has been fully referenced.

Signed: [Signature]  
Date: 6.6.2013

Robert J. Flynn
DEDICATION

For Catherine and Hugo
Abstract

This project investigates the development of C-curves for aluminium alloy 7010 under various tempers and processing conditions and the subsequent use of quench factor analysis (QFA) for property prediction. Statistical evaluation and comparison of both the isokinetic (classical Quench Factor Analysis) and the non-isokinetic property prediction models using both fixed and variable values for the minimum property values was carried out. It was concluded that the non-isokinetic property prediction model with a variable minimum property value provided the most accurate method for property prediction of the techniques evaluated for aluminium 7010 alloy in an overaged temper. C-curves were then successfully developed for 0.2% proof stress, Vickers hardness and electrical conductivity. The validity of these C-curves was proved using multiple isothermal holds and multiple quenchants demonstrating the effectiveness of the models at up to 67% strength loss with a recorded error of only 4.6%. The use of the Jominy end quench method to provide a relatively quick source of continuous cooled data for C-curve construction for aluminium alloy 7010 in the peak aged, overaged and a cold compressed+overaged condition was demonstrated. It was shown that that the method provides a good indicator of alloy quench sensitivity. The method also revealed that in the cold compressed+overaged condition, that 7010 cold compressed prior before artificial aging demonstrates greater quench sensitivity than the alloy in the peak aged and overaged conditions. The influence of post-quench delay prior to cold compression on residual stress was evaluated using x-ray diffraction and was found to be non-conclusive.
Acknowledgments

It would not have been possible to finish this doctoral thesis without the help and support of numerous people both in and out of the University of Limerick. I would like to thank first and foremost Dr. Jeremy Robinson for his unending patience and guidance, putting up with my tendency to procrastinate and for listening to my constant diatribe of "next week". Mark Twain summed it up perfectly when he said "Never put off until tomorrow what you can do the day after tomorrow.". I would also like to thank Professor Stuart Hampshire and my former colleagues at the Materials Ireland Research Centre. I would like to thank Enterprise Ireland for providing me with the funds in the earlier days of this work. I'd like to say special thanks to Dr. Gerald Dolan and to Dr. David Tanner for endless conversations over numerous cups of early morning coffee about aluminium alloys, residual stress etc. and for help with the TFM. I would also like to mention and thank Dr. Wynette Reddington for her help with X-ray diffraction. A big thank you also goes to all the technicians and other academic staff in the former Materials Science and Technology department which, sadly, is no more. In the latter years, I would like to thank Dr. Imelda Lambkin for giving me the scope and time in my current role to finally get this over the line. I'd also like to thank my parents for their support over the years for their unwavering support for me in whatever I wanted to do.

This acknowledgement would not be complete without mention of Catherine, my late wife who passed away during the course of this work. For lost weekends in the lab and late nights at the computer, that time in retrospect was precious and only wish she had been here to see it finished...this work I dedicate to her and of course to my son Hugo.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_0)</td>
<td>Number of nucleation sites per unit volume</td>
</tr>
<tr>
<td>(C_{\text{max}})</td>
<td>Maximum concentration</td>
</tr>
<tr>
<td>(C_{\text{min}})</td>
<td>Minimum concentration</td>
</tr>
<tr>
<td>(C_{\text{AQ}})</td>
<td>As quenched concentration</td>
</tr>
<tr>
<td>(t_c)</td>
<td>Critical time required to precipitate a constant amount of solute (s)</td>
</tr>
<tr>
<td>(d_{\theta})</td>
<td>Interplanar spacing in the direction defined by (\phi) and (\psi)</td>
</tr>
<tr>
<td>(d_{\theta}')</td>
<td>Interplanar spacing for unstressed material (m)</td>
</tr>
<tr>
<td>(\Delta G_n)</td>
<td>Activation energy for nucleation (J.mol(^{-1}))</td>
</tr>
<tr>
<td>(\Delta G_v)</td>
<td>Driving force for precipitation (J.mol(^{-1}))</td>
</tr>
<tr>
<td>(\Delta G_m)</td>
<td>Activation Energy (J.mol(^{-1})) (Also Q)</td>
</tr>
<tr>
<td>(\Delta G_s)</td>
<td>Misfit strain energy per unit volume (J.mol(^{-1}))</td>
</tr>
<tr>
<td>(\Delta \sigma_i)</td>
<td>Incremental amount of strength loss (MPa)</td>
</tr>
<tr>
<td>(\epsilon)</td>
<td>Engineering strain</td>
</tr>
<tr>
<td>(\epsilon^{\text{eq}})</td>
<td>Elastic strain</td>
</tr>
<tr>
<td>(\epsilon^{\text{pl}})</td>
<td>Plastic strain</td>
</tr>
<tr>
<td>(E)</td>
<td>Young's Modulus (GPa)</td>
</tr>
<tr>
<td>(k)</td>
<td>Boltzmann's constant</td>
</tr>
<tr>
<td>(k_1)</td>
<td>Constant that equals the natural log of the fraction untransformed during quenching</td>
</tr>
<tr>
<td>(k_2)</td>
<td>Constant related to the reciprocal of the number of nucleation sites (s)</td>
</tr>
<tr>
<td>(k_3)</td>
<td>Constant related to the energy required to form a nucleus (J.mol(^{-1}))</td>
</tr>
<tr>
<td>(k_4)</td>
<td>Constant related to the solvus temperature (K)</td>
</tr>
<tr>
<td>(k_5)</td>
<td>Constant related to the activation energy for diffusion (J.mol(^{-1}))</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Wavelength (m)</td>
</tr>
<tr>
<td>(N_{\text{he}})</td>
<td>Nucleation Rate (number.m(^{-3}).s(^{-1}))</td>
</tr>
<tr>
<td>(N_0)</td>
<td>Term related to the number of nucleation sites</td>
</tr>
<tr>
<td>(\psi)</td>
<td>Angle between the normal to the surface and the bisector of the incident and diffracted beams (°)</td>
</tr>
<tr>
<td>(R)</td>
<td>Universal gas constant (J.mol(^{-1}) K(^{-1}))</td>
</tr>
<tr>
<td>(R_{0.2})</td>
<td>0.2% proof stress (MPa)</td>
</tr>
<tr>
<td>(Q_0)</td>
<td>Activation energy for diffusion (J.mol(^{-1}))</td>
</tr>
<tr>
<td>(Q_s)</td>
<td>Enthalpy of precipitation (J)</td>
</tr>
<tr>
<td>(\sigma_{\text{min}})</td>
<td>Minimum Strength (MPa)/mechanical property</td>
</tr>
<tr>
<td>(\sigma_{\text{max}})</td>
<td>Maximum Strength (MPa)/mechanical property</td>
</tr>
<tr>
<td>(\sigma_m)</td>
<td>Measured strength (MPa)</td>
</tr>
<tr>
<td>(\sigma_p)</td>
<td>Predicted strength (MPa)</td>
</tr>
<tr>
<td>(S_{\text{eq}}(T))</td>
<td>Equilibrium solute concentration at temperature T</td>
</tr>
<tr>
<td>(T)</td>
<td>Absolute temperature (K)</td>
</tr>
<tr>
<td>(\theta)</td>
<td>Angle between the x-ray source and the detector (°)</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Stress (Pa)</td>
</tr>
<tr>
<td>(\nu)</td>
<td>Poisson's ratio</td>
</tr>
<tr>
<td>(\Psi)</td>
<td>Angle between the specimen normal surface and the normal diffracting crystallographic plane (°)</td>
</tr>
<tr>
<td>(\phi)</td>
<td>The angle of rotation of the sample about its surface normal (°)</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Resistivity ((\Omega)m)</td>
</tr>
<tr>
<td>(s)</td>
<td>Volume fraction transformed</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
</tr>
<tr>
<td>$t$</td>
<td>Quench Factor</td>
</tr>
<tr>
<td>$n'$</td>
<td>Strengthening metastable phase 7000 series alloys</td>
</tr>
<tr>
<td>$Q_d$</td>
<td>Activation energy for diffusion (J.mol$^{-1}$)</td>
</tr>
<tr>
<td>$K$</td>
<td>Constant related to the free energy change of nucleus formation</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Solvus temperature ($^\circ$C)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Strain energy (J)</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>Time interval (s)</td>
</tr>
<tr>
<td>$\sigma_{min(T)}$</td>
<td>Minimum strength (MPa) at Temperature $T$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Factor related to vibration frequency of atom the critical nucleus area</td>
</tr>
</tbody>
</table>
In the novel “From the Earth to the Moon” (1865) the French author Jules Verne, often regarded as the father of modern science fiction describes the use of a giant gun to launch a space craft to the moon. The protagonist of the novel, Impey Barbicane, president of the elite Baltimore Gun Club, decides there is only one material which is ideally suited to the application – aluminium.

"This valuable metal possesses the whiteness of silver, the indestructibility of gold, the tenacity of iron, the fusibility of copper, the lightness of glass. It is easily wrought, is very widely distributed, forming the base of most of the rocks, is three times lighter than iron, and seems to have been created for the express purpose of furnishing us with the material for our projectile."
1 Introduction

1.1 Aluminium and Aluminium Alloys - A Historical Perspective

In 1808, the French chemist Antoine Lavoisier identified an oxide of a yet undiscovered metal from a material known simply as “alum”. Seventeen years later, in 1825, a Danish chemist, Hans Christian Oersted, isolated the first small amounts of metallic aluminium. This was followed by the chemical production of the first ingots by Sainte-Claire Deville in France in 1855. The first recorded aeronautical use of an aluminium alloy (Al-8% Cu) was an Alcoa (Aluminium Company of America) casting used in the engine crankcase of the Wright Brother’s Flyer in 1903 [Gayle & Goodway 1994]. In 1909, a German metallurgist at the Dürmer Metallwerke Aktien Gesellschaft, Alfred Wilm, credited with discovery of the precipitation process, patented the first age-hardenable aluminium alloy of 3.5% copper and 0.5% magnesium [Dwight 1999]. The material later became known as “Duralumin” and its most illustrious application was in that of the dirigibles developed by Count Ferdinand von Zeppelin in the early 1900’s.

The first aeronautical application of this new alloy was by Dr. Hugo Junkers in the fuselage and wings of the sesquiplane known as the J4 [Gibbs-Smith 1985]. This alloy is now classified as a 2000 series alloy as designated by the aluminium association. This was followed by a US Navy contract with Alcoa to develop an aerospace sheet alloy, known as 17S-T (2017-T4). This alloy found extensive use in another Junkers aircraft, the F13 in 1920. As an understanding into precipitation hardness mechanisms were discovered, Alcoa began developing newer higher strength alloys such as 2024-T3 and 2010-T6 (up to 350MPa) alloys by increasing the alloy content and modification of the heat treatments. The importance of corrosion resistance was subsequently demonstrated by the development of Al clad 2024-T3 in 1931 (used in the B-17 and B-24). During World War II, the higher strength Al-Zn-Mg-Cu alloy designated 7075-T6
was developed and because of its high strength, found applications in both commercial and military aircraft. This was followed by the development of the higher strength 7178-T6 which was first used on the Boeing 707, however; stress-corrosion cracking (SCC) problems appeared when thicker mill products began to be used in larger aircraft. The SCC problems were solved by the development of overaged 7075-T73 but with a resulting loss in strength. This alloy was first used in the McDonald-Douglas DC10.

Figure 1-1  Aerospace aluminium alloy usage (Alcoa-www.alcoa.com)

During the late 1960's and early 1970's, alloy selection was influenced by the requirement for greater durability and damage tolerance. Alcoa developed high strength 7175-T74 forgings which were comparable to the strength of 7075-T6 in thin sections but provided an improved resistance to SCC. Alcoa also commercialised the alloy 7049-T73, developed in Germany and first used on the undercarriage of the US B52 bomber. The need for SCC resistant high strength thick section materials continued with the US Navy and Air Force funding Alcoa to develop alloy 7050-T74. Alloy
7050-T74 plate was first used to retrofit 7079-T6 components in the A6 intruder and was chosen for the bulk of the aluminium structure in the F18. Shortly after, alloy 7010-T74 was developed under a UK Ministry of Defence contract in association with HDA Forgings Ltd. (now Mettis Aerospace) and Alcan and is currently used for strength critical components such as wing spars in the Airbus family of aircraft, in the outer wing of the Airbus 380 and the landing gear of the new A400M tactical air lifter (see Figure 3-1) [Aerospace Materials Specifications 1989]. The alloy was chiefly developed as a plate and forging alloy with a reduced quench sensitivity allowing for use in large sections [Reynolds & Baxter 2000]. The combination of strength, fracture toughness and SCC resistance was an improvement compared to alloys such as Alcoa’s 7075-T651 and 7079-T6. 7010 differed in composition from these alloys in that zirconium (Zr) was used instead of chromium (Cr) and/or manganese (Mn) to control the grain growth during heat treatment. It achieved this through the pinning action of the Al3Zr dispersoids, which acted to retard recrystallisation during thermomechanical processing. The combined iron (Fe) and silicon (Si) content was also kept below 0.27wt% which improved the materials toughness; [Reynolds et al. 2000]. 7010 is very similar in composition to Alcoa’s 7050 and its compositional detail with respect to a range of 7000 series alloys is outlined in Table 1-1. A comprehensive comparison of the similarity in properties between 7010 and 7050 is offered by Schra et al. [Schra & Hart 1983]. Further strength increases were brought about by the development of 7449 which is now available in the T76 temper for gauges up to 10cm thick. 7449 is used for very high-strength wing panels for the A340-500/600 [Alcan International 2007]. A compositional comparison of 7010, 7050 and 7075 with respect to the Mg-Cu components of the alloy phase diagram is shown in Figure 1-2.
Figure 1-2  Magnesium (Mg) versus Copper (Cu) composition for 7010, 7050 and 7075

Other alloys such as Alcan’s 7040 and 7140 provide an improved strength to toughness balance compared to 7050 and 7010 with a lower quench sensitivity and a claimed reduced residual stress providing reduced distortion after machining and excellent surface quality though the mechanism of how these alloys achieve a low residual stress is currently unclear [Alcan International 2007].

Table 1-1 7000 series alloys-nominal chemical compositions

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>7010</td>
<td>0.12*</td>
<td>0.15*</td>
<td>1.50-2.00</td>
<td>0.10*</td>
<td>2.10-2.60</td>
<td>0.05*</td>
<td>6.70-7.10</td>
<td>0.60*</td>
<td>0.10-0.16</td>
</tr>
<tr>
<td>7050</td>
<td>0.12*</td>
<td>0.15*</td>
<td>2.00-2.60</td>
<td>0.10*</td>
<td>1.90-2.60</td>
<td>0.10*</td>
<td>5.70-6.70</td>
<td>0.60*</td>
<td>0.08-0.15</td>
</tr>
<tr>
<td>7140</td>
<td>0.10</td>
<td>0.13</td>
<td>1.3-2.3</td>
<td>---</td>
<td>1.5-2.4</td>
<td>---</td>
<td>6.2-7.0</td>
<td>0.06*</td>
<td>0.05-0.12</td>
</tr>
<tr>
<td>7085</td>
<td>0.08*</td>
<td>0.15</td>
<td>1.3-2.0</td>
<td>---</td>
<td>1.2-2.0</td>
<td>---</td>
<td>7.0-8.0</td>
<td>---</td>
<td>0.08-0.15</td>
</tr>
<tr>
<td>7075</td>
<td>0.40*</td>
<td>0.50*</td>
<td>1.20-2.00</td>
<td>0.30*</td>
<td>2.10-2.90</td>
<td>0.20*</td>
<td>5.10-6.10</td>
<td>0.20*</td>
<td>0.05*</td>
</tr>
<tr>
<td>7040</td>
<td>0.10*</td>
<td>0.13*</td>
<td>1.5-2.4</td>
<td>0.04</td>
<td>1.7-2.3</td>
<td>0.04</td>
<td>5.70-6.70</td>
<td>0.06*</td>
<td>0.05-0.12</td>
</tr>
<tr>
<td>7178</td>
<td>1.6-2.4</td>
<td>0.40</td>
<td>0.5</td>
<td>0.3</td>
<td>2.4-3.1</td>
<td>6.3-7.3</td>
<td>0.18-0.35</td>
<td>0.20</td>
<td>---</td>
</tr>
<tr>
<td>7475</td>
<td>0.10</td>
<td>0.12</td>
<td>1.2-1.9</td>
<td>0.06</td>
<td>1.9-2.6</td>
<td>0.08-0.25</td>
<td>5.2-6.2</td>
<td>0.06</td>
<td>---</td>
</tr>
</tbody>
</table>

*a maximum [Davis 1992], [AMS4408 2007], [Chakrabati, Liu, Sawtell, & Venema 2004], [Starink & Wang 2003]
Newer alloys such as the Alcoa alloy 7085 with very low quench sensitivity combined with high strength and damage tolerance are continuing to be developed for the latest generation of aircraft such as the Boeing 787 Dreamliner and is already being used in the Airbus A380 [Chakrabati et al. 2004]. A typical example, of which, is shown in Figure 1-4. These improvements in properties are brought about by modification of the alloy chemistry. Alloy 7085 has increased zinc content and a decreased magnesium and copper content compared to 7050. Other new alloys developed for use in the aerospace industry include alloys such as 7056 and 7449. Both these alloys are used in the A380 for the upper wing panels (plate) and upper wing stringers respectively.

1.2 Heat Treatment of Aluminium Alloys

Heat treatment of aluminium alloys is generally carried out in order to increase the strength and/or to impart particular properties for specific applications. In 7000 series alloys, it is primarily carried out using a process known as precipitation hardening.
(aging) which takes advantage of an increase in the solid solubility of the alloying additions with corresponding increases in temperature. The process consists of three main stages:

**Solution Heat Treatment** - Solution heat treatment (SHT) allows the hardening alloying elements to become fully soluble in the aluminium matrix resulting in the formation of a solid solution (ss) (see example in Figure 1-5 for Aluminium - Copper). The treatment consists of heating the component to the appropriate temperature for the alloy and soaking for a defined period to produce a homogenous solid solution. The recommended temperature and subsequent soakage arc times are both alloy and size dependant.

![Figure 1-5](image-url)  
Aluminium-rich end of the aluminium-copper phase diagram illustrating 3 stages and resulting microstructures [Askeland 1994]

**Quenching** – Quenching is whereby rapid cooling (>100°C/min) from the solution heat treatment temperature is carried out in order to preserve or “trap” the solid solution formed during solution heat treatment at room temperature to form a supersaturated
solid solution. The quenching stage is critical, as slow cooling allows the hardening alloying additions to precipitate out from the matrix as coarse precipitates resulting in a reduction of the maximum achievable mechanical properties. The degree of this property loss is known as “quench sensitivity”. Over-rapid cooling on the other hand is not always desirable due to the creation of detrimental residual stresses through the imposition of large thermal gradients.

**Aging** – Aging is the process where the supersaturated solid solution formed as a result of the quench can be decomposed by holding at room temperature (natural) or elevated temperatures (artificial) to produce a fine dispersion of precipitates, thus increasing the mechanical properties of the alloy. As with solution heat treatment, the schema of the aging processes differs for each alloy and the final properties required. The ASM Metals Handbook provides a comprehensive source of detail with respect to industrial heat treatment regimes and processes for aluminium alloys [Davis 1992].

### 1.3 Quench Factor Analysis

Quench Factor Analysis or QFA is a technique developed by Staley *et al.* in 1977, which allows the prediction of alloy properties following the heat treatment process. The technique uses the quench cooling path in conjunction with Time-Temperature-Property (TTP) curves known as “C”-curves. These are similar to the TTT curves developed for steels, which allow the identification of regions where rapid precipitation can occur. To-date, the widespread use of QFA has been hindered by the lack of publicly available C-curves for individual aluminium alloys and tempers.

### 1.4 Residual Stresses

Residual stresses are defined as those which “remain in a body which is stationary and at equilibrium with its surroundings and are a consequence of manufacturing processes
such as rolling, drawing, forging, extruding and bending as well welding/joining and subsequent heat treatment processes. Heat treatment induced residual stresses can lead to stress corrosion cracking, distortion, fatigue cracking and premature failures in manufactured components. In aluminium alloys, methods available for residual stress reduction include modification of the quench rate by the use of alternative quenchants to cold water or by the introduction of a plastic deformation (stretching or compression) stage after the quench and it is the modification of quench rate that links QFA with the characterisation of residual stresses.
2 Objectives

The objective of the current work is to investigate the quench sensitivity of Aluminium Alloy 7010 primarily in an overaged temper by the creation of C-curves or Time-Temperature Property (TTP) curves, and their application for the prediction of properties in thick forgings. The project has involved the production of C-curves for both 0.2% proof stress (Rp0.2), hardness (Hv20) and electrical conductivity/resistivity using both the classical Evancho and Staley Quench Factor Analysis (QFA) model and subsequent developed models based on a non-isokinetic approach (i.e. where the nucleation and growth rate are assumed to be non-linear). One of the limitations of classical Quench Factor Analysis is that if the loss in properties during heat treatment exceeds approximately 10% of the maximum attainable property for the alloy and temper, the accuracy of the predictions decreases due to assumptions which were introduced in to the classical model in order to simplify the mathematical complexity of the transformations taking place. With the general trend in the aviation industry towards larger and larger aircraft (e.g. Airbus A380/Boeing 747-8), there is now a commercial requirement to produce aluminium alloy in thicker sections, in which it is possible that the loss in property can exceed this 10% limit. Thus, the technological requirement for a model, which would extend the ability to accurately predict this further loss in properties, was required and the full extent of the quench sensitivity of the alloy determined. Throughout the course of this work, limitations on the current methods for the theoretical extrapolation of the C-curves have been examined and C-curves obtained by Quench Factor Analysis and subsequent modifications and advances to the classical Evancho and Staley model compared and evaluated using overaged aluminium alloy 7010. Another limitation of all the models developed to date is the effect of cold compression on the final properties of the alloy and to date none of the
models have taken this into account. In addition, the use of the Jominy end quench technique has been explored as a technique for the determination of producing continuously cooled data and for the production of C-curves for alloys in the cold compressed tempers.

The objective of the current work can be divided and summarised into two parts:

1) In relation to property prediction, the objectives can be summarised as follows:
   - Determination, comparison and evaluation of \( R_{p0.2} \), Vickers hardness and electrical conductivity C-curves for 7010 in the overaged condition using classical and improved Quench Factor Analysis (QFA) models for 7010.
   - Determination of \( R_{p0.2} \), mechanical and electrical conductivity C-curves using QFA for 7010 in the cold compressed condition.
   - Evaluation of the Jominy end quench test method as a source of continuous cooled data for the production of C-curves for property prediction.

2) In commercial production of aluminium alloy forgings, a period of natural aging is often carried out prior to cold compression. The current work has examined the effect of introducing various periods of natural aging prior to the cold compression process and its affect on residual stress magnitudes.
3 Literature Review

3.1 Wrought Aluminium Alloys

Wrought, as opposed to cast products are those which have been shaped by some form of plastic deformation process. This includes both hot and cold working processes such as forging, rolling and extruding to transform a cast ingot to a finished product such as sheet, foil, plate, wire, rod and bar.

Figure 3-1 Composite of micrographs of forged 7010 showing structure directionality [J.R. Robinson Private Communication] [Robinson, Whelan, & Cudd 1999]

These processes change the microstructure from a cast structure to a wrought product with a radically changed grain structure which depends on both the thermal and mechanical history of the alloy. For large wrought forms such as forgings, heavy extrusions and plate which are hot worked; the changes to the microstructure are relatively minor. With increasing hot and cold working, the changes to the
microstructure become more pronounced. These changes include deformation of the original cast grain structure with subsequent recovery or recrystallisation and fragmentation of the brittle intermetallic phases into more equiaxed grains which align themselves in the direction of the deformation (that direction in which the product was extended or lengthened the most during working). A composite micrograph of a forged 7010 block showing structural directionality is shown in Figure 3-1.

As a consequence of this, the longitudinal direction (L) generally has the most superior tensile and compressive properties as well as superior stress-corrosion cracking resistance and resistance to fatigue stresses. In the short transverse (ST) direction, the properties are generally the lowest with the long transverse (LT) showing intermediate properties between the L and ST directions.

Wrought aluminium alloys are designated by a 4 digit numerical system based on an Aluminium Association of the United States classification known as the International Alloy Designation System (IADS) as shown in Table 3-1 [AS 2848.1 1986, Polmear 1995].

Table 3-1  Wrought Aluminium Alloy Designations

<table>
<thead>
<tr>
<th>Four Digit Series</th>
<th>Al content or main alloying elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1xxx</td>
<td>99.00% minimum</td>
</tr>
<tr>
<td>2xxx</td>
<td>Copper (Cu)</td>
</tr>
<tr>
<td>3xxx</td>
<td>Manganese (Mn)</td>
</tr>
<tr>
<td>4xxx</td>
<td>Silicon (Si)</td>
</tr>
<tr>
<td>5xxx</td>
<td>Magnesium (Mg)</td>
</tr>
<tr>
<td>6xxx</td>
<td>Magnesium (Mg) and Silicon (Si)</td>
</tr>
<tr>
<td>7xxx</td>
<td>Zinc (Zn) (most others contain Magnesium (Mg) with Copper (Cu), Chromium (Cr) and Zirconium (Zr))</td>
</tr>
<tr>
<td>8xxx</td>
<td>Others e.g. Lithium (Li)</td>
</tr>
<tr>
<td>9xxx</td>
<td>Unused</td>
</tr>
</tbody>
</table>
3.1.1 Aluminium Alloys - Effect of Alloying Element Additions

The following provides details of the solubility of the major alloying elements and impurities in aluminium and their resulting effect on the final properties of aluminium alloys:

**Zinc:** Zinc is the major alloying element in 7000 series alloys and has a solubility limit in aluminium of 66.4 at.% (82.8 wt.%) [Polmear 1995]. When zinc is coupled with percentages of magnesium ranging from 2.1 to 2.6 wt.% in 7010 and copper, it results in heat-treatable alloys of very high strength. Yield strengths of up to 625MPa have been attained for 7001-T6 [AS 2848.1 1986]. Zinc containing alloys such as 7010 and 7050 are susceptible to intergranular corrosion, stress-corrosion cracking, and exfoliation corrosion [AS 2848.1 1986; Puiggali, Zielinski, Olive, Renaud, Desjardins, & Cid 1998; Wanhill, Schra, & Van Leeuwen 1979; Yan, Chunzhi, Jigang, & Minggao 1991].

**Magnesium:** Magnesium has a solubility limit of 17.4 wt% in aluminium though does not usually exceed 5.5 wt% in commercial wrought alloys. It provides substantial strengthening to the work-hardening characteristics of the alloy and is also added in conjunction with other elements such as zinc in 7000 series alloys and/or copper for further increases in strength. The addition of magnesium also acts to reduce the low temperature solubility of zinc. Magnesium precipitates preferentially at the grain boundaries as Mg₅Al₇ or Mg₅Al₈. These are highly anodic phases which can result in an increased susceptibility to intergranular corrosion and stress corrosion [Andreatta, Terryn, & De Wit 2004; Jones, Baer, Danielson, & Vetrano 2001].
**Iron:** Iron has a very high solubility (~0.91 at.%-3.4 wt.%) in the liquid state and in combination with silicon forms the largest level of impurities found in 7000 series aluminium alloys. The solubility of iron in the solid phase is very low (~0.025 at.%-0.04 wt.%) resulting in iron in excess of this amount appearing as an intermetallic secondary phases in combination with aluminium (FeAl3) or other elements present in the alloy [Mondolfo 1976]. Iron has the effect of reducing the grain size in wrought alloys as well as producing a slight decrease in strength, elongation and fracture toughness. Alloys such as 7010 and 7050, are specified with a maximum iron and silicon content due to their relationship to quench cracking and more importantly to fracture toughness [Earle, Robinson, & Colvin 2004].

**Silicon:** Silicon like iron, has a high solubility in the molten state (12.6 at.%) and a maximum solubility of 1.58 at.% in aluminium at room temperature. In wrought alloys, silicon is used with magnesium at up to 1.5 wt.% to produce Mg2Si in the 6000 series of heat treatable alloys. In 7000 series alloys, the formation of Mg2Si (β phase) removes magnesium from the solid solution resulting in a reduction of the amount of magnesium available for precipitation of the strengthening phase, MgZn17(17) [Bussu & Dunn 2006; Mondolfo 1976; Van Horn 1967].

**Copper:** Many alloys contain copper either as the major alloying addition such as in 2000 series alloys or as an additional alloying element such as in 7000 series. Copper has a high solid solubility of 2.4 at.%-5.65 wt.% and introduces significant changes in the precipitation process and consequently in the age-hardening behaviour of the alloy where it promotes the rapid nucleation of the strengthening phase MgZn2 [Chinh, Lendvai, Ping, & Hono 2004; Maloney, Polmear, & Ringer 2000]. In general,
copper increases the quench sensitivity, reduces the resistance to general corrosion of Al-Zn-Mg alloys but increases the resistance to stress corrosion cracking.

**Chromium:** Chromium is added to many of the Al-Zn-Mg-Cu alloys in amounts generally not exceeding 0.15 wt.%. Chromium has a slow diffusion rate and forms fine (<1μm) intermetallic phases (Al12Mg5Cr) known as dispersoids in wrought products which act to inhibit recrystallisation [Tiryakioglu & Staley 2003]. Chromium also increases an effect known as the *quench sensitivity* which refers to the extent to which slower quench rates can be tolerated such that there is no precipitation occurs during cooling. Chromium also improves resistance to stress corrosion cracking [Tiryakioglu & Staley 2003].

**Manganese:** Manganese has a limited solid solubility in aluminium of 1 wt.%. Up to the 1.25 wt.% level manganese is the main alloying addition of the 3000 series alloys in which it is added alone or with magnesium. Manganese increases strength as a finely precipitated intermetallic phase and in a similar way to chromium, controls grain growth and is effective in slowing recovery [Tiryakioglu & Staley 2003].

**Zirconium:** An increasing number of alloys particularly in the 7000 series (e.g. 7050, 7010), use zirconium to reduce the as-cast grain size. Additions in the range 0.1 to 0.3 wt.% form dispersoids that also inhibit recovery and recrystallisation during processing. Zirconium additions also act to further reduce the quench sensitivity of alloys compared to those containing just chromium [Lloyd & Chaturvedi 1982; Thomson, Subramanya, & Levy 1971].

A comprehensive review on the metallurgical effects of alloying editions to aluminium is offered by Tiryakioglu and Staley [Tiryakioglu & Staley 2003].
3.2 Precipitation Hardening – Background and Overview

The increase of strength of 7000 series wrought aluminium alloys is obtained through a process known as precipitation hardening. The basic principle of the process is to create in the alloy, a dense and fine dispersion of precipitated particles in a matrix. Precipitation hardening was first observed in an aluminium-copper alloy known as Duralumin (Al-3.5Cu-0.5Mg-0.5Mn), patented by Alfred Wilm (Germany 1903-1911) while searching for a method to improve the hardness of aluminium in a similar method to that used for steels [Wilm 1911]. A theoretical explanation for this hardening effect was proposed by Merica, Waltenburg and Scott in 1919. They proposed that if an aluminium-copper alloy is heated to -540°C, the copper dissolves to form an α-Al face centred cubic (fcc) solid solution. If the alloy is then rapidly quenched to room temperature, the separation of the β-phase (~CuAl₂) is suppressed, leading to a supersaturated solid solution as shown in Figure 3-2 [Polmear 1995].

![Aluminium-copper phase diagram](image)

Figure 3-2 Aluminium-copper phase diagram [Polmear 1995]
The type of solid solution formed in aluminium alloys is known as a substitutional solid solution where atoms share a single common array of atomic sites. The factors which control the formation of this solid solution are known as the Hume and Rothery rules \citep{Cottrell1975, Hume-Rothery1954}. This supersaturation of copper in aluminium provides the driving force for precipitation of the $\theta$-CuAl$_2$ equilibrium phase. If the quenched alloy is then “aged” for a period of time, a precipitate in the form of a sub-micron sized dispersion is precipitated from the aluminium matrix resulting in the hardening of the alloy \citep{Martin1968}. Jeffries and Archer attempted to explain the mechanism for this age-hardening effect based on a “slip interference” theory \citep{Jeffries1921}. They proposed that strengthening was obtained by slip interference within grains due to a “keying” effect of the particles (see Figure 3-3). The effect increases with the fineness of the sub-division of particles (for a given amount of phase) suggesting that the strengthening reached a maximum at an average particle size and is denoted by the term “critical dispersion”.

![Figure 3-3](image)

Figure 3-3 Slip planes keyed by small hard particles, (B) large hard particles \citep{Jeffries1921}
These ideas were further developed upon, after the precipitates responsible for hardening were identified following the development of small-angle x-ray scattering (SAXS). These are known today as Guinier-Preston zones or GP zones and are named after their co-discoverers, André Guinier and George Preston [Preston 1938]. The exact shape and size of the GP zones depend on the specific alloy and on the thermal and mechanical history of the product. GP zones are typical small, spherical particles that are approximately two atomic layers thick, 10nm in diameter with spacing in the order of 10nm.

Their formation requires movement of atoms over very short distances and their densities can approach $10^{17}$ to $10^{18}$ cm$^{-3}$. GP zones cannot be observed directly by transmission electron microscopy but the resulting strain fields can be resolved as shown in Figure 3-4. In the majority of metallurgical systems, as the aging temperature and/or time is increased, the GP zones grow or are replaced by more stable transition
phases followed eventually by the stable equilibrium phase. The transitional or intermediate phases have lower activation energies of formation than the equilibrium phase and have a distinct crystalline structure to that of the solid solution matrix.

It was not however until the introduction of the concept of dislocations by Mott and Nabarro that a fundamental understanding of the strengthening process was achieved \[\text{Mott \\& Nabarro 1940}\]. This was followed by Orowan’s theories on strengthening by non-deformable particles in 1948 [Orowan 1948b]. Further reviews by Kelly and Nicholson [Kelly \\& Nicholson 1963], Brown and Ham [Brown \\& Ham 1971] who focussed on particle-dislocation interaction and Ardell [Ardell 1985], form the basis of today’s understanding of the strengthening mechanisms occurring during precipitation hardening.

The current interpretation of precipitation hardening is that the strength increases are derived from the interaction of moving dislocations and the internal stresses developed by particles/precipitates and their resulting misfit. The precipitates form during aging at either ambient or elevated temperatures; in alloy systems which have a decreasing solid solubility with decreasing temperature. Depending on the size, spacing and degree of coherency (a quantitative term used to describe the degree of interfacial bonding between the matrix and the precipitate – see Figure 3-9), precipitate particles are sheared, looped or bypassed by the dislocations during plastic deformation (see Figure 3-5). Consideration of the critical stresses for cutting and looping shows that there is an optimum particle size for hardening precipitates. Osamara observed that for three 7000 series alloys, the dislocations cut through the precipitates when the average precipitate radius is less than 2nm. When the precipitates grow to approximately 5-6 nm, the yield stress is dominated by the Orowan looping mechanism [Osamura, Ochiai, \\& Uehara 1984; Osamura, Okuda, Amemiya, \\& Hashizume 1988].
Significant numbers of the lattice positions in most crystalline solids are not occupied by atoms. These vacant lattice sites are known as vacancies. Diffusion of the substitutional solid-solution forming elements, as well as self-diffusion is believed to occur primarily by a vacancy exchange mechanism as well as having a significant role in the formation of GP Zones. Interactions between vacancies and various solute atoms influence aging kinetics and make the effect of trace element additions important. The vacancy concentration increases exponentially with temperature so that when the alloy is quenched a supersaturation of vacancies is frozen into the structure. The overall availability of these vacancies had a marked effect on precipitation kinetics and strengthening potential.

### 3.2.1 Precipitation Thermodynamics

#### 3.2.1.1 Homogenous nucleation in solids

According to Gibbs, the basic idea of nucleation is that work is necessary for the formation of new surface phases.
If we consider the precipitation of a B rich β phase from a supersaturated A-rich α phase solid solution as shown in Figure 3-6, for the nucleation of β, B atoms within the A matrix must first diffuse together for to form a small volume with the β composition. If necessary, the B atoms must rearrange into the β crystal structure. This requires the creation of a new α/β interface and leads to an activation energy barrier.

The free energy change associated with the nucleation process will have 3 different contributions:

1. At temperature where the β phase is stable, the creation of a volume $V$ of β will cause a free energy reduction of $V\Delta G$.

2. If we assume that the α/β interfacial energy is isotropic the creation of an area $A$ of interface will give a free energy increase of $A\gamma$.

3. In general, the transformed volume will no longer fit into the original space occupied by the matrix, this gives rise to a misfit strain energy $\Delta G$, per unit volume of β which is proportional to the volume of the inclusion.
Therefore the total free energy change is the summation of these 3 energy contributions, thus:

$$\Delta G = -V\Delta G_e + A\gamma + V\Delta G$$ \hspace{1cm} \text{Equation 3-1}

For nucleation in solids, the value of $\gamma$ can vary from low values for a coherent interface to high values for interfaces of a non-coherent nature (see section 3.2.1.2); therefore, the term $A\gamma$ should be replaced by a summation over all the surfaces of the nucleus, therefore:

$$\Delta G = -V\Delta G_e + \sum A_i\gamma_i + V\Delta G$$ \hspace{1cm} \text{Equation 3-2}

If the variation of $\gamma$ with respect to the orientation of the interface is ignored and we assume that the nucleus is spherical with a radius $r$, Equation 3-2 becomes:

$$\Delta G = -\frac{4}{3} \pi r^3 (\Delta G_e - \Delta G_i) + 4\pi r^2 \gamma$$ \hspace{1cm} \text{Equation 3-3}

Where volume of a sphere $= \frac{4}{3} \pi r^3$ and the surface area $= 4\pi r^2$.

For the critical radius $r^*$, we can set $\Delta G = 0$ or $\frac{\partial \Delta G}{\partial r} = 0$ for critical condition $r = r^*$, therefore, differentiating with respect to $r$:

$$\frac{\partial \Delta G}{\partial r} = 4\pi r^2 (\Delta G_e - \Delta G_i) + 8\pi r \gamma = 0 \text{ at } r^*$$ \hspace{1cm} \text{Equation 3-4}

Therefore:

$$r^* = \frac{2\gamma}{(\Delta G_e - \Delta G_i)}$$ \hspace{1cm} \text{Equation 3-5}

Substituting for $r^*$ in Equation 3.3:
Where \( r^* \) = the critical nuclei radii and \( \Delta G^* \) = the free energy barrier to nucleation. This is illustrated in Figure 3-7.

\[
\Delta G^* = -\frac{16\pi r^6}{3(\Delta G^*_e - \Delta G^*_v)^2} \tag{Equation 3-6}
\]

**Figure 3-7** Free energy curves for homogenous nucleation

For nucleus with a radius of \( r > r^* \), the Gibbs free energy will decrease if the nucleus grows. \( r^* \) is the critical nucleus size and represents the minimum size of a stable spherical nucleus. The concentration of the critical sized nuclei \( C^* \) will be given by:

\[
C^* = C_0 \exp \left( -\frac{\Delta G^*}{kT} \right) \tag{Equation 3-7}
\]**
$N_{\text{hom}} = f C^*$

Equation 3-8

$f$ depends on how often a critical nucleus can receive an atom from the $\alpha$ matrix and will depend on the surface area of the nucleus and rate at which diffusion can occur. If the activation energy for diffusion is $\Delta G_m$ per atom, $f$ can be written as:

$$f = \omega \exp \left( -\frac{\Delta G_m}{kT} \right)$$

Equation 3-9

$\omega$ is a factor that includes the vibration frequency of the atoms and the area of the critical nucleus. The nucleation rate therefore can be described by the following equation:

$$N_{\text{hom}} = \omega C_v \exp \left( -\frac{\Delta G^*}{kT} \right) \exp \left( -\frac{\Delta G_m}{kT} \right)$$

Equation 3-10

In order to evaluate this equation as a function of temperature, $\omega$, $\Delta G^*$ and $\Delta G_m$ can be assumed constant but $\Delta G^*$ will be strongly temperature dependent. The main factor controlling $\Delta G^*$ will be $\Delta G_v$. Since composition is a variable, the magnitude of $\Delta G_v$ must be obtained from the free energy composition diagram. The magnitude of the driving force for precipitation, $\Delta G_v$, increases with increasing undercooling, $\Delta T$ below the equilibrium solvus temperature $T_e$. The temperature dependence on the nucleation rate is shown in Figure 3-8a, with the corresponding TTP or "C"-curve shown in Figure 3-8b.
Figure 3-8  

a) Temperature dependence of Nucleation Rate and b) subsequent TTT or 'C-curve'

In summary, at small degrees of undercooling nucleation is difficult although diffusion, i.e. growth of the critical nuclei is fast. Hence the overall rate of nucleation is controlled by the slowest process:

\[ \text{i.e. exp} \left( -\frac{\Delta G^*}{kT} \right) \]

At a large degree of undercooling, although nucleation is not difficult (\(\Delta G^*\) small) diffusion or growth is slow and therefore the overall rate of nucleation is controlled by the rate of growth:

\[ \text{i.e. exp} \left( -\frac{Q}{kT} \right) \]

3.2.1.2 Types of precipitate/matrix interface

In order to describe the thermodynamic processes which occur during precipitation hardening, the case of the simple Al-Cu alloy will be used. GP zone formation as previously mentioned can be explained on the basis of the relative activation energy barriers for nucleation. GP zones are described as being fully coherent (see Figure 3-9h) with the matrix and hence possess a very low interfacial energy.
It can be seen from Equation 3.6 that $\Delta G^*$ is proportional to $\gamma$, thus interfaces having low values of $\gamma$ are preferred. A coherent interface has the lowest surface energy as illustrated in Figure 3.9b. In this type of interface there is a good matching of the precipitates and matrix plane across the interface.

In the binary Al-Cu system, the equilibrium $\theta$ phase has a tetragonal structure which presents an incoherent face to the matrix (Figure 3.9d) and possesses a very high interfacial energy. GP zones also minimise their strain energy by forming a disc shape perpendicular to the elastically weak $<100>$ direction in the face centred cubic aluminium matrix. Therefore, although the driving force for the precipitation of GP zones is less than that for the equilibrium phases, the barrier to nucleation is less, which means that the zones will nucleate rapidly. GP zones are the initial precipitate formed during low temperature aging of many of the heat treatable aluminium alloys. GP zone formation as previously mentioned is followed by precipitation of the intermediate or
transitional precipitates. The transitional phases have a lower activation energy barrier for nucleation than the equilibrium phases.

3.2.2 Precipitation Hardening - Methodology

Commercial precipitation hardening heat treatment of aluminium alloys is carried out in three stages:

1) Solution heat treatment within the single phase solid solution region.

2) Quenching to room temperature to obtain a supersaturated solid solution. The quench rate used is dictated by the commercial necessity to obtain a balance between solute depletion thus reducing the final mechanical properties and quench induced residual stress.

3) Controlled decomposition of the supersaturated solid solution to form a distribution of precipitates by aging at one or two intermediate temperatures.

A detailed review of each of the stages is offered in the following sections.

3.2.2.1 Solution heat treatment

Solution heat treatment (SHT) involves the heating of the alloy to a temperature above the solvus known as the solution heat treatment temperature, where the main constituent alloying elements, such as zinc and magnesium in the case of 7000 series alloys, dissolve to form a single phase solid solution. The time required for complete solution treatment is dependent upon the phase distribution and composition of the alloy, the method of fabrication and the size and shape of the component which is being heat treated [Bates, Totten, & Jarvis 1994]. Inadequate solution heat treatment time can result in not all of the solute being in solution at the time of quench. Over exposure at the solution heat treatment temperature can result in the diffusion of hydrogen from
moisture causing surface blistering with 7050 forgings being particularly sensitive to this effect. The use of ammonium fluoroborate is often used to overcome the occurrence of this problem with respect to 7000 series alloys [Howard, Bogh, & Mackenzie 2003].

3.2.2.2 Quenching

After solution heat treatment, the alloy is quenched to a temperature below the solvus temperature in order to form the supersaturated solid solution. Quenching is carried out with the aid of an appropriate cooling fluid, the quenchant. Rapid quenching (>300°C.min⁻¹) is usually achieved by quenching into cold water (~20°C); however this can result in distortion or warping, especially for thinner sections such as plate or sheet due to retained residual stresses [Bates 1987; Bates & Totten 1988; Earle et al. 2004; Robson 2004b]. In contrast, if the alloy is cooled too slowly, solute atoms (such as zinc and magnesium in 7000 series alloys) will precipitate out of solution to form coarse non-strengthening phases resulting in a reduction of mechanical properties [Godard, Archambault, Aeby-Gautier, & Lapasset 2002; Hall & Mudawar 1995; Sawtell 1984]. This effect is known as quench sensitivity and is discussed in greater detail in section 3.2.5.

Quenching parameters selected for forgings represent a compromise between the cooling rates needed to minimise the residual stresses that affect quench distortion and machining performance and quench sensitivity. There are two types of quenching in general use for the commercial heat treatment of aluminium alloys: direct immersion and spray quenching: direct immersion where the component is submerged in a quench bath and spray quenching where the quenchant is sprayed at high velocity onto the component [Howard, Bogh, & Mackenzie 2003].
Several quenchant and material factors influence the rate of heat removal from a component being quenched. The cooling rates, in practise are controlled by the vapour blanket formation [Bernardin & Mudawar 1995], boiling characteristics, flow velocity/agitation, temperature, specific heat, heat of vapourisation, conductivity, density, viscosity and wetting characteristics of the quenchant. The difference in temperature between the boiling point of the medium and actual temperature of the medium being the major factor influencing the rate of heat transfer in liquid quenchants [Bates, Totten, & Clinton 1993]. The surface finish of the component and component thickness also have an influence, the lowest quench rates being obtained with freshly machined or bright-etched clean surfaces with surface staining or oxide layers increasing the cooling rate [Bates 1987; Croucher & Butler 1981: Higgins 1970]. Various quenchants have been employed to control the quench rate. Alternative quenchants to cold water include hot water (65 to 80°C), boiling water, oil, fused salts [Thompson, Singleton, McGowan, & Spangler 1970], forced air and polymer quenchants. Polymer quenchants such as Poly (alkylene glycol) or PAG copolymer solution was first reported by Blackwood and Chessman [Blackwood & Chessman 1965]. PAG is inversely soluble in water i.e. its solubility decreases with increasing temperature, and works by the formation of a film on the surface which, surrounds the component during quenching [Tensi, Stich, & Totten 1995]. This reduces the “rewetting” time of the aluminium compared to that of water. Rewetting times refers to the time when the entire surface is covered by the quenchant and can be measured using specially developed quench probe type systems [Maniruzzaman, Chaves, McGee, Ma, & Sisson 2002]. Tensi et al. provides a comprehensive review of rewetting for water and polymer quenchants using this method [Tensi, Stitzelberger-Jakob, & Totten 1999]. The most common PAG quenchants used in the aerospace industry
today are designated as Type I quenchants and their properties are outlined in AMS3025A [Totten, Bates, & Jarvis 2004]. The distortion reduction advantages of these quenchants have been detailed by Blackwood et al. [Blackwood, Jarvis, Totten, Webster, & Narumi 1996]. Other quench media reported in the literature include liquid nitrogen [Il'yushko & Bedarev 1968] yeast media [Krotov, Khamidullin, & Anan' in 1989] and clay-based quenchants [Rauche 1981]. However, hot and cold water and aqueous polymer solutions are the quenchants most frequently used for the quenching of aerospace alloy parts [Totten, Webster, & Bates 2003a].

Alcoa have produced a proprietary quench known as Alcoa Proprietary Quench (APQ) which claims to eliminate dimensional distortion frequently encountered when machining high-strength aluminium alloy closed-die forgings. It also claims to reduce residual stresses in alloys such as 7050 by up to 55% compared with a warm water quench [Nicol, Seaton, Kuhlman, Yu, & Pishko 1996]. Other quenching processes designed to reduce residual stresses include the Alcoa developed "uphill quenching" or "deep freezing" [Hill & Willey 1960]. The general principle is based on the theory that residual quenching stresses result from thermal gradients induced in the materials during cooling therefore it should be possible to develop residual stresses of an opposite nature by subjecting the component to a rapid heating i.e. an uphill quench thus counteracting the originally induced stresses. The alloy is quenched normally in cold water then immersed in dry ice or liquid nitrogen followed by immersion in boiling water or exposure to superheated steam [Rein 1970]. This type of quench has proven to be effective at reducing residual stress for parts quenched in cold water, though less success has been achieved with PAG and hot water quenched parts with low residual stresses [Totten, Webster, & Bates 2003a].
The severity of various quenchants is often expressed in terms of Grossmann number or H-value which is related to the coefficient of heat transfer between the quenchant and the component, and the thermal conductivity of the alloy [Grossmann & Bain 1964]. The heat transfer coefficient is essentially the effective film coefficient of the quenchant. Unagitated water at 25°C has a film coefficient of ~3.9 Wm⁻²K⁻¹ with film coefficients generally decreasing with increasing water temperature (70-80°C) to 0.35-1.3 Wm⁻²K⁻¹. Polymer quenchants depending on quenchant concentration generally have film coefficients <1.6 Wm⁻²K⁻¹ [Totten, Webster, & Bates 2003a]. Quench factors, numerical values derived during the process of classical Quench Factor Analysis have also been used to quantify the quenchant severity [Totten, Webster, Bates, Han, & Kang 2008].

### 3.2.2.3 Aging

Aging is where the alloy undergoes decomposition of the metastable supersaturated solid solution created during the quench to form a fine dispersion of precipitates. This process results in an increase of the final mechanical properties of the alloy. 7000 series alloys go through a range of precipitation sequences to precipitate from the matrix the strengthening MgZn₂ (η') phase [Park & Ardell 1983; Park & Ardell 1988]. Progression of this sequence can be achieved by either natural aging at room temperature or at an accelerated rate known as artificial aging carried out at elevated temperatures (>room temperature (RT)).

#### 3.2.2.3.1 Natural aging

Natural aging refers to the spontaneous and rapid formation of precipitates that have formed by diffusion of solute into clusters or Guinier-Preston (GP) zones from the solid solution and from quenched-in vacancies at room temperature. These tempers are
designated T3 and T4 by the industry. Natural aging leads to an increase in properties but the period of time an alloy is left to age naturally can have a detrimental effect on any subsequent aging process applied to the alloy [Calatayud, Ferrer, Amigo, & Salvador 1997]. Electrical conductivity has been shown to decrease with natural aging supporting the theory that GP zones are forming instead of “true” precipitates. The properties achieved from natural aging are not stable, with the alloy exhibiting significant changes even after several years. For 2000 series alloys, improvements in properties are generally minor up to 4-5 days at room temperature, 7000 series alloys on the other hand are more unstable with aging occurring very rapidly. Tanner et al. have shown that refrigeration at -20°C is still not sufficient to retard the natural aging processes in 7010 over long periods [Tanner & Robinson 2004]. For industrial use, refrigeration is not rapid enough to cool the parts. In these situations, dry ice and methanol have also been used along with a paraffin derivative know as Stoddard’s solvent (white spirit) at -40°C [Totten, Xie, & Funatani 2004]. Natural aging curves for tensile properties of several 7000 alloys are available in the literature [Davis 1992; Tanner & Robinson 2006]. Alloys which are naturally aged are designated T3 and T4 tempers by the industry. Natural aging has been show to have no significant effect on residual stress magnitudes thought the effect of natural aging prior to cold compression in 7000 series alloys has not been studied and forms one of the objectives of the current work.

3.2.2.3.2 Artificial aging

Artificial aging is defined as aging at an elevated temperature. 7000 series alloys are artificially aged to a wide range of tempers consisting of one or more time/temperature stages, depending on the final properties required. 7010 alloy for example, is often used commercially in an overaged form. Overaged tempers (T7x) refer to treatments where
the alloy has been artificially aged beyond the maximum strength (T6). These types of treatments were originally developed to improve certain characteristics of the alloys such as the naturally aged T3 temper for improved stress corrosion cracking (SCC) resistance in 7075 thick sections and the T76 temper for improved exfoliation corrosion resistance of alloys such as 7010, 7075 and 7178. To achieve the T76 temper, a two-stage heat treatment is required. A typical T76 industrial aging regime includes a first stage at 120°C, followed by a second stage heat treatment at 172°C. T7x tempers have also been developed for 7475, 7049 and 7050. The relationship between the underaged, the peak aged T6 temper and the overaged tempers is shown in Figure 3-10. The full range of tempers applied to wrought aluminium alloys is defined within ANSI H35.1 with SAE AMS2772D (formally US Military specification MIL-H-6088G) providing extensive data on recommended aging temperatures and times.

Figure 3-10  T6x-T7x Tempers [Kaufman 2004]

The general effect on the mechanical and corrosion properties of a selection of the T7x overaged tempers are shown in Figure 3-11.
3.2.2.4 Plastic deformation tempers

The T8 temper refers to alloys that have been solution heat treated, cold worked and artificially aged and the T9 temper to alloys that have been solution treated but where the cold work is carried out after artificial aging. Additional T tempers for heat treatable alloys include tempers of the form Tn5x which refer to products which have been stress relieved by stretching, compression or a combination of the two respectively (Tn54). In the Tn52 condition, products can be stress relieved by up to 5% by compression after heat treatment or cooling from an elevated temperature and is generally carried out in the ST direction. Because this process deforms the alloy, a large number of dislocations are introduced into the material which can dramatically affect the precipitation process [Allen & Sande 1980; Embury & Nicholson 1965].

On a microscopic scale this process has been studied in detail by Allen, Vander and Sande who demonstrated that the growth of precipitates is faster on dislocations than in the bulk [Allen et al. 1980; Allen & Sande 1978]. At elevated temperatures such as during aging (120-160°C) the presence of an increased number of dislocations results in the acceleration of the precipitation kinetics [Deschamps & Brechet 1999] though a slowing down of precipitation kinetics has been observed at room temperature due to
the annihilation of quenched-in vacancies on the dislocations [Ceresara & Fiorini 1972]. Waterloo et al. have shown that 10% pre-deformation in tension carried out on alloys 7108 and 7030 in the “as quenched” condition can reduce the yield strength in the artificially aged hardened T6 condition by up to 10%. This is due to nucleation of the non-strengthening equilibrium phase i.e. overaging, occurring on the dislocation network [Waterloo, Hansen, Gjonnes, & Skjervold 2001]. The final strength after artificial aging is directly related to the amount of plastic strain performed on the alloy [Davis 1992; Escobar, Gonzalez, Ortiz, Nguyen, Bowden, Foyos, Ogren, Lee, & Es-Said 2002; Torgerson & Kropp 1977]. This effect has been shown to be reduced where a natural aging step is introduced prior to deformation [Conserva, Buratti, Di Russo, & Gatto 1973]. Plastic deformation of aluminium alloys can result in an effect known as the “Bauschinger effect”. This is where after an alloy has been subjected to 1 or 2% plastic deformation (i.e. elongation or cold compression), a higher strength is observed in the direction of deformation as opposed to against the deformation direction where a lower strength is observed. This is illustrated schematically in Figure 3-12.

![Diagram of Stress-Strain curves demonstrating the Bauschinger effect](https://example.com/diagram.png)

**Figure 3-12 Stress-Strain curves demonstrating the Bauschinger effect**

[Conserva et al. 1973; Gedeon 1999]
The Bauschinger effect has been found to be a function of the initial material microstructure as well as the strain rate [Thakur, Nemat-Nasser, & Vecchio 1996]. An extensive attempt at modelling the Bauschinger effect and its applications to wrought aluminium alloys has been conducted by Chun et al. [Chun, Jin, & Lee 2002; Chun, Kim, & Lee 2002].

### 3.2.3 Microstructural Phases in 7000 Series Alloys

The different phases which may occur in alloys of the 7000 series can be divided into three categories:

*Intermetallics* - e.g. Fe-Si phases.

*Dispersoids* - which control the phenomena of recrystallisation.

*Hardening Precipitates* - which control the engineering properties such as yield strength and hardness.

These categories of phases are produced at one of several stages during the initial wrought production and subsequent heat treatments. The resulting phases and their morphology, along with the kinetics of their formation have been investigated by several authors using a multitude of analytical techniques and are discussed in detail in the following sections.

### 3.2.4 Initial Wrought Production

Several types of coarse intermetallic precipitates are formed during initial ingot casting. Elements present as impurities such as iron and silicon, form extremely stable intermetallic compounds such as the phases Mg$_2$Si and Al$_2$Cu$_2$Fe. Those containing copper and iron are have been shown to be cathodic with respect to the matrix and tend to promote dissolution of the matrix [Wei, Liao, & Gao 1998]. Thermomechanical treatments (rolling etc.) used in the production of the wrought material results in severe
distortion of their morphology. The particles also break during these operations. The size of the particles have been observed at between 1 and 10μm and have a tendency to form very slim clusters, aligned according to the direction of deformation as shown in Figure 3-13.

![Figure 3-13](image)

**Figure 3-13** Mg$_2$Si (03) and Al$_3$Cu$_2$Fe (01) aligned with rolling direction in 7010 (Backscattered Electron Image)

Also formed during initial thermomechanical processing of the wrought alloy are the dispersoid phases. Their resultant size and spacing also have an influence on the grain structure with small closely packed dispersoids having the greatest effect. Dispersoids of less than 0.4μm in diameter, such as spherical Al$_2$Zr with a diameter of ~20nm in 7010 for example, act by pinning the grain boundaries. The affect of these dispersoids on the precipitation process and their affect on the final properties are discussed in greater detail in the following sections.
3.2.5 Precipitation of 7000 Series Alloys During Quenching

Precipitation which takes place during the quenching of the 7000 series - Al-Zn-Mg-Cu family of alloys, such as 7010, occurs in a similar manner to that which has been observed in Al-Zn-Mg alloy systems [Deschamps & Brechet 1998b]. Deschamps et al. has shown quite clearly that all cooling rates between 5 and 40°C.min⁻¹ experience quench-induced precipitation [Deschamps, Texier, Ringeval, & Delfaut-Durut 2009].

In order to achieve the best achievable properties in heat treatable aluminium alloys, the occurrence of precipitation during the quench is something that in commercial terms is generally avoided due to the detrimental effect on the age-hardening response of the alloy [Holl 1969; Huchner & Loeffler 1985; Tiryakioglu 1999]. This precipitation has been shown by several authors, through studies based on interrupted quenching studies to severely reduce the final mechanical properties such as yield strength, ductility and fracture toughness [Evancho & Staley 1974; Staley 1986; Staley, Doherty, & Jaworski 1993]. This effect is known as quench sensitivity and has been an issue for the modern aerospace industry, where the use of less than optimised quench rates using hot water and polymer quenchants following solution heat treatment are often used in order to reduce quench-induced stresses in thick plates and forgings [Sainfort, Gomiero, Raynaud, & Sigli 1997]. From a metallurgical viewpoint, quench sensitivity has been attributed to the precipitation of coarse heterogeneously nucleated particles forming on both the dispersoids as well as on both the grain and sub-grain boundaries. This results in a reduced level of supersaturation following the quench, and also to the loss of vacancies to sinks, to a level such that the rate of GP zone formation during any subsequent aging is reduced [Conserva, Di Russo, & Caloni 1971; Deschamps & Brechet 1998a; Polmear 1995; Thomson et al. 1971]. The varying degree of quench sensitivity which occurs within 7000 series alloys is mainly controlled
by the presence of the minor elemental additions such as chromium, manganese, vanadium and zirconium in the dispersoid phases which act to inhibit recrystallisation. The presence of copper in 7000 series alloys on the other hand is known to increase the quench sensitivity by reducing the solubility of zinc and magnesium in aluminium [Bryant 2003; Dumont, Deschamps, & Brechet 2003; Fink & Willey 1948; Thomson et al. 1971; Vruggink 1968]. The effect of dispersoid type on quench sensitivity for two Al-Zn-Mg-Cu alloys containing manganese (Al₂₅Mn₃Cu₂) and chromium (Al₁₂Mg₃Cr) as dispersoid formers is shown in Figure 3-14 [Tiryakioglu & Staley 2003].

The chromium containing phases have a much greater influence on increasing quench sensitivity than manganese. Alloys that contain chromium and manganese dispersoid forming elements such as 7075 provide very efficient nucleation sites and are much more quench sensitive than those such as 7010 that contain zirconium (Al₃Zr) [Polmear 1995]. This is due to the way in which the dispersoids present themselves to the
aluminium matrix. The chromium containing dispersoids present an incoherent interface to the aluminium matrix (Figure 3-9d) while zirconium presents a coherent interface (Figure 3-9b). Nucleation is more difficult on coherent interfaces, so alloys such as 7010 and 7040 containing zirconium dispersoids (Al₂Zr) are less quench sensitive than alloys containing incoherent dispersoids such as Al₂₅Mn₂Cu₂ and Al₁₂Mg₃Cr which are less effective.

Depending on the quench rate, several types of precipitate which nucleate during the quench from the solution heat treatment temperature have been observed. A nucleation diagram for 7010 constructed by Godard et al. based on transmission electron microscopy studies is shown in Figure 3-15 [Godard et al. 2002].

Figure 3-15  Nucleation diagram determined from microstructural observations for 7010 [Godard et al. 2002]

3.2.5.1 η-phase

The most influential phase in terms of its effect on the final properties of the alloy, which precipitates during the quench is the equilibrium η phase-Mg(Zn₂AlCu). This is
a non-strengthening phase (as opposed to the strengthening η' phase), which precipitates when intermediate or slow quench rates (<100°C/sec) are used, at temperatures of between 440°C—the η-phase solvus temperature and 250°C. The η phase solvus temperature has previously been measured by differential scanning calorimetry (DSC) as 440°C [Godard & Archambault 2000] in 7010 though this temperature is dependent on the alloy composition. The phase precipitates as plate shaped type structures on the dispersoids such as Al₃Zr in 7010 as shown by transmission electron microscopy in Figure 3-16.

![Figure 3-16 η precipitate on a spherical Al₃Zr dispersoid during air cooling [Deschamps & Brechet 1998b]](image)

Further TEM studies have shown the η phase precipitating in long parallel bands due to the homogenous distribution of the dispersoid phase (see Figure 3-17. This has been ultimately attributed to the location of the Al₃Zr dispersoids in 7010 following solidification of the dendrite arms which become flattened during the rolling process, the low diffusivity of Zr being responsible for retaining this segregation during subsequent solution heat treatment.
The thickness of these bands has been observed to be approximately 1-2μm and up to 100μm in length. [Conserva et al. 1971; Deschamps & Brechet 1998b; Robson 2004b]. The size of the precipitates formed has been shown using SAXS to be almost independent of the quench rate though the quench rate has been found to have an effect on the immediate surroundings of the precipitate resulting in formations known as a precipitate free zone (PFZ) [Deschamps & Brechet 1998a; Dumont, Deschamps, Brechet, Sigli, & Ehrstrom 2004; Thomson et al. 1971]. The presence of these precipitate free zones or PFZ's after slow quenching and aging as shown in Figure 3-18 is attributed to the depletion of solute atoms adjacent to particles and to the migration of vacancies from the region during the quench. The width of the PFZ has been shown to be a both a function of the solution heat treatment temperature and the aging temperature [Newkirk, Mahoney, Mackenzie, & Ganapathi 1999]. The width of the PFZ has also been shown to be inversely proportional to the quench rate [Mackenzie 2003]. The η phase has a hexagonal structure with $a = 0.521$nm and $c = 0.860$nm [Li, Hansen, Gjonnes, & Wallenberg 1999]. The phase has and can present several orientations to the aluminium matrix [Gjonnes & Simenson 1970; Loffler, Kovaes, & Lendvai 1983; Park et al. 1983]. Neutron scattering studies have revealed twelve orientation relationships between the η phase and the aluminium matrix depending on
when nucleation occurs [Auger, Bernole, Blaschko, Ernst, Quittner, Just, & Roth 1978].

![Precipitate Free Zone](image)

**Figure 3-18 Precipitate Free Zone [Deschamps 2003]**

At lower temperatures, between 200-100°C, the η' precipitates are formed. This is the strengthening metastable phase which is primarily associated with aging and is discussed in section 3.2.6. The η' and η are sometimes referred to in the literature as M' and M phases respectively.

### 3.2.5.2 S phase

S phase has a relatively fixed composition of Al₃CuMg. It has been observed in 7070 at long isothermal hold times at temperatures between 300 and 200°C and has been observed to be lath-shaped as shown by the transmission electron microscopy micrograph in Figure 3-19 [Godard et al. 2002]. DSC measurements have shown that S forms via a metastable precursor S' though other researchers have shown by transmission electron microscopy that the S' and S phase can be considered the same
phase [Starink & Gregson 1995]. S is a large and brittle phase and needs to be avoided in commercial applications [Radmilovic, Thomas, Shiflet, Starke, & Jr. 1989]. S phase has been determined to have an orthorhombic structure with lattice parameters of $a=0.403 \text{ nm}$, $b=0.930 \text{ nm}$ and $c=0.708 \text{ nm}$ [Radmilovic, Kilaas, Dahmen, & Shiflet 1999].

Figure 3-19  S'- Precipitates observed at 250°C in 7010 [Godard et al. 2002]

3.2.5.3  T phase

T is a cubic phase and has the composition $\text{Al}_{12}(\text{Mg, Zn})_4\text{Si}_6$. The T phases has been observed in 7010 at temperatures between 300 and 250°C for isothermal holding times of over 1000s [Godard et al. 2002]. The phase has an irregular globular morphology with a cuboid coherent T' phase precursor. The presence of copper has been shown to suppress the formation of T in favour of $\eta$. 
3.2.6 Precipitation in 7000 Series Alloys During Aging

During the commercial aging of 7000 series alloys, the metastable $\eta'$ and stable $\eta$ phases have been identified as the most important precipitates as forming from the supersaturated solid solution.

The development of the equilibrium $\eta$ phase ($\text{Mg(Zn}_2\text{AlCu})$) proceeds through a succession of stages as shown in Figure 3-20 [Degischer, Lacom, Zahra, & Zahra 1980].

![Precipitation sequence 7000 Alloys](image)

Figure 3-20 Precipitation sequence 7000 Alloys [Werenskold, Deschamps, & Bréchet 2003]

After solution heat treatment and quenching, two types of zones or clusters are formed at room temperature, the aforementioned Guinier-Preston (GP(I)) zones and Vacancy Rich Clusters (VRC), depending on aging conditions and pre-treatment [Dlubek, Krause, Bruemmer, & Plazaola 1986; Löffler et al. 1983]. In most crystalline solids a significant number of lattice positions are not occupied by atoms and are known as vacancies. The vacancy rich clusters are thought to be formed right after or during the quench to room temperature and to be quite stable at this temperature. They are assumed to constitute the main route to the semicoherent $\eta'$ with GP(II) zones as an intermediate phase as shown in Figure 3-20. At above 120°C, the GP zone solvus, GP(II) transforms into $\eta'$, while GP(I) either dissolves back into solution or transforms into $\eta'$ if it has reached some critical size [Löffler et al. 1983]. $\eta'$ is usually associated
with producing the maximum strength T6 condition. In the overaged T76 condition, the 
\( \eta' \) phase is replaced by the equilibrium non-hardening, \( \eta \) phase. In order to achieve this 
progression, a two stage heat treatment is required. Aging at the lower of the dual 
temperature aging stages (120°C or a slow ramp to 170°C for the T76 temper for 7010) 
allows the formation of a large number of the GP zones that are stable at the higher 
temperature second stage. Poole et al. have described a model for the age hardening 
response of a 7000 series alloy that describes a two step aging treatment and its effect 
on the kinetics of aging [Poole, Shercliff, & Castillo 1997].

The size and structure of the precipitation in 7000 series alloys during aging has been 
characterised using Transmission Electron Microscopy (TEM) by several researchers. 
GP (I) zones have been identified as equiaxed structures ranging from 1-1.5 nm in size 
and GP (II) zones as thin discs, 2-3 nm wide and 1-2 atoms in thickness [Berg, Gjonnes, 
Hansen, Li, Knutson-Wedel, Waterloo, Schryvers, & Wallenburg 2003]. The 
metastable \( \eta' \) has been identified as disc shaped with lattice parameters of \( a=0.496 \text{ nm} \) 
and \( c=1.405 \text{ nm} \) [Li et al. 1999]. Bigot et al. determined the compositions and volume 
fractions of \( \eta' \) and \( \eta \) by 3D atomic probe in a 7050 alloy [Bigot, Denoix, & Augier 
1996]. They found that \( \eta' \) and \( \eta \) contain approximately 55 and 40 at.% aluminium 
respectively. The Zn:Mg ratio was found to be 1:1.

The precipitation hardening process in 7000 alloys had been well characterised using a 
variety of other techniques. Electrical resistivity has been used to characterise the 
depletion of the solid solution during quenching as well as to determine the change in 
concentration of vacancies with respect to temperature [Godard et al. 2000; 
Mackenzie 1996]. Atom Probe Field Ion Microscopy (APFIM) has been used to 
investigate GP zone and \( \eta' \) phase formation during the early stages of precipitation in 
aluminium alloy 7050 [Sha & Cerezo 2004]. Small Angle Neutron Scattering (SANS)
has been used to study the structural changes which occur during the precipitation of G.P. zones [Osamura et al. 1988] and Positron Annihilation Spectroscopy (PAS) has been used to examine the association between GP zones and vacancies in 7010 [Dlubek, Lademann, Krause, Krause, & Unger 1998].

3.2.7 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) [Jiang, Noble, Holme, Waterloo, & Tafto 2000: Lloyd et al. 1982: Park & Ardell 1989] has been used by several researchers to examine the phase transformation and transformation kinetics in 7000 series alloys [Hausen, Karlsen, Langsrud, & Gjonnes 2004]. Lloyd et al. has determined the temperature of dissolution of the η phase in 7000 series alloys [Lloyd et al. 1982]. DSC has also been combined with transmission electron microscopy to investigate the low-temperature decomposition processes taking place in an Al-Zn-Mg alloy and to confirm the existence of the two types of GP zones, i.e., GP(I) (solute-rich clusters) and GP(II) (from vacancy-rich clusters) [Jiang et al. 2000].

3.3 Electrical Conductivity

The electrical conductivity (the reciprocal of resistivity) of aluminum alloys is dependent on the concentration of atoms in solid solution. The concentration of dissolved atoms in the matrix, the precipitation in 7xxx alloys and the resulting microstructures significantly influence the change of conductivity through the aging process. Surface electrical conductivity measurement provides a rapid and cost-effective, non-destructive method for assessing the properties of aluminium alloys and is particularly responsive to changes in alloy composition and temper. The measurement technique takes advantage of the Eddy current effect whereby electrical currents are induced in an electrically conductive material in the presence of an
alternating magnetic field. These Eddy currents then subsequently produce their own magnetic field in opposition to the generating magnetic field. Measurements are acquired by using commercially available probes applied to the surface of the alloy. The changes in the magnetic field detected by the surface probe are directly related to the conductivity of the material being analysed. The most typical use of surface electrical conductivity measurement is in the development of heat treatment processes for aluminium alloys and the subsequent measurement of the final products for quality control. The common designation for electrical conductivity is the %IACS or International Annealed Copper Standard. The %IACS is the relative conductivity of a material compared to the conductivity of alloyed, annealed copper at 20°C. Copper under these conditions is assigned a conductivity of 100% [Hunt Jr., Stiffler, & Green 1998] and is outlined under AMS 4149D [SAE AMS 4149D:2002 2002]. The SI unit of electrical conductivity is MegaSiemens per meter (M.Sm⁻¹) where 100%IACS = 58 MS.m⁻¹ as defined under EN 2004-1:1993 [BS EN 2004-1:1993 1993]. The conductivity of aluminium alloys spans the range 25 to 60%IACS with pure aluminium having a conductivity of 64.94%IACS (26.5MS.m⁻¹). Resistivity is defined as the reciprocal of conductivity and has the unit Ωm. A model that predicts conductivity as a function of microstructure was proposed by Guyot and Cottignies [Guyot & Cottignies 1996]. They proposed that the variation of electrical conductivity with aging is due to the scattering of conduction electrons within the alloy by the coarsening precipitation. A number of factors influence this scattering including alloy composition, quenched in vacancies, G.P. zones with similar dimensions to that of the electron wavelength as well as dislocations and coherency strains at the boundaries of zones or clusters [Ferragut, Somoza, & Torriani 2002]. The effect of the various alloying elements both in and out of solution on the electrical conductivity of aluminium alloys is shown in Table 3-2.
Table 3-2 Decrease in conductivity (% IACS) per wt% addition [Hunt Jr. et al. 1998]

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>In solution (% IACS)</th>
<th>Out of solution (% IACS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>7.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Mg</td>
<td>11</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn</td>
<td>2.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Si</td>
<td>18.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Fe</td>
<td>32.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn</td>
<td>34.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Cr</td>
<td>39.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Zr</td>
<td>25.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Ti</td>
<td>33.9</td>
<td>2.9</td>
</tr>
<tr>
<td>V</td>
<td>37.2</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Electrical conductivity of most heat treatable alloys increases as the solid solution solute content decreases [Sawtell & Staley 1983]. The quenching of an alloy after solution heat treatment (W-temper) results in the lowest electrical conductivity due to the formation of the supersaturated solid solution. The electrical conductivity then progressively increases due to precipitation as the alloy is artificial aged as the solute atoms are removed from the solid solution. The general effect of heat treatment and temper on electrical conductivity and its relationship to the alloy strength is illustrated in Figure 3-21.

Figure 3-21 Effect of heat treatment on electrical conductivity [Hunt Jr. et al. 1998]
Table 3-3 shows specific electrical conductivity data for a selection of 7000 series alloys over a range of applied tempers. At a microstructural level, a decrease in conductivity indicates that GP zones are forming instead of true precipitates. This decrease in conductivity is related to the consumption of vacancies by the GP zones.

Table 3-3 Electrical conductivity values (%IACS) for 7000 series alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Electrical Conductivity %IACS Temper</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7010</td>
<td>40-44</td>
<td>-</td>
</tr>
<tr>
<td>7075</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>7050</td>
<td>41</td>
<td>40.5</td>
</tr>
</tbody>
</table>

The electrical conductivity decreases with natural aging which is the opposite of artificially aged alloys. This is due in part to the gradual increase in the number and size of the GP zones. Electrical conductivity has also been used as an indication of SCC resistance particularly from near peak aged-T6 to the overaged-T3 temper [Park & Ardell 1991].

Changes due to plastic deformation increase the dislocation density. Dislocations also scatter electrons and thus an increase in the number of dislocations lowers the conductivity. Previous research has also shown that there is a non-linear correlation between conductivity and yield strength for a full range of 7010 temper conditions [Salazar-Guapuriche, Zhao, Pitman, & Greene 2006].

3.4 Mechanical Properties - Tensile and Vickers Hardness

Hardness provides a useful indication of the condition of the alloy after heat treatment. In general, the correlation between hardness and yield strength or proof stress-Rp0.2 for aluminium alloys is good though care must be taken where anisotropy exists. A ratio of
yield strength: Vickers hardness of 3:1 in the LT direction, has been suggested as a good approximation. Several researchers have suggested that the approach of substituting hardness for strength should be approached with caution [Bernardin et al. 1995; Bratland, Grong, Shercliff, Myhr, & Tjotta 1997; Hall, Mudawar, Morgan R.E., & Ehlers 1997; MIL-H-6088G 2004; Rometsch, Starink, & Gregson 2003; Shercliff & Ashby 1990; Shuey, Tiryakioglu, & Lippert 2003]. Previous research has demonstrated that a good linear correlation is observed between strength and hardness if the same aging treatment is carried out following the application of different continuous cooling quench rates. If dissimilar aging treatments are used, differences in work hardening lead to a poorer correlation [Rometsch & Schaffer 2002]. A similar study has shown that this linear relationship is only true for aging to the T6 temper and that deviations from linearity are observed for the over and underaged tempers due to strain hardening at the indenter/metal interface [Tiryakioglu, Campbell, & Staley 2000].

Ives et al. have studied yield strength-hardness relationships in aluminium alloy 2024 with different tempers and found a curvilinear relationship [Ives, Swartzendruber, Boettinger, Rosen, Ridder, Biancanello, Reno, Ballard, & Mehrabian 1983]. These non-linear variations between hardness and yield strength underline the importance of tensile testing for property prediction as opposed to the easier approach of tensile information extrapolated from assumptions based on hardness data. 0.2% proof stress ($R_{p0.2}$), tensile strength and hardness ($H_v$) for a range of commercially available 7000 alloys and tempers are shown in Table 3-4.
Table 3-4  R_p0.2, Tensile strength, R_p0.2 and Vickers hardness for a range of 7000 series alloy and tempers (Alcan International)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temper</th>
<th>R_p0.2 (Proof Stress) (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Hardness (Hv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7010</td>
<td>T651</td>
<td>530</td>
<td>580</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>T7651</td>
<td>485</td>
<td>545</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>T7451</td>
<td>460</td>
<td>530</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>T7351</td>
<td>410</td>
<td>500</td>
<td>---</td>
</tr>
<tr>
<td>7475</td>
<td>T651</td>
<td>480</td>
<td>531</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>T7351</td>
<td>414</td>
<td>490</td>
<td>155</td>
</tr>
<tr>
<td>7075</td>
<td>T651</td>
<td>480</td>
<td>550</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>T7351</td>
<td>420</td>
<td>500</td>
<td>---</td>
</tr>
</tbody>
</table>

3.5 Property Prediction - Introduction

There have been a number of methods reported in the literature for the prediction of physical properties in aluminium alloys. The first systematic attempt to correlate properties with quench rate was carried out by Fink and Wiley who studied the effects of quenching on the strength of 7075-T6 and on the corrosion behaviour of 2024-T4 [Fink et al. 1948]. They used the technique of using isothermal quenching to develop Time-Temperature-Property (TTP) (or C-curves) which are similar to the Time-Temperature-Transformation curves used in the steel industry and describe the isothermal holding time at a particular temperature required to obtain a given property value. The technique was based on using an average quench rate to describe the quench but which was proved unsuitable where variation in the quench cooling rate occurred.

This led to the subsequent development of Quench Factor Analysis (QFA) by Evancho and Staley in the early 1970s, to predict the effect of continuous cooling on the yield strength and the mode of corrosion in 2024-T4 [Evancho et al. 1974]. C-curve coefficients were determined such that integration of the QFA equations over a series of
isothermal laboratory quench paths best matched the obtained corresponding property data. These coefficients were then used to predict properties after arbitrary quenches.

A theoretical justification for QFA was presented by Staley in 1987 [Staley 1987], and an improved quench factor model was published in 1993 [Staley et al. 1993]. This has since been followed by various refinements [Staley & Tiryakioglu 2001; Tiryakioglu & Shuey 2010; Tiryakioglu & Shuey 2003] and suggestions for improvements [Rometsch et al. 2003].

Since its development, QFA has been applied to a wide range of wrought aluminium alloys to predict properties such as hardness, yield strength and electrical conductivity as well as to optimise industrial quenching procedures [Bates et al. 1994; Bernardin et al. 1995; Flynn & Robinson 2001; Ives et al. 1983; Sewarzendruber, Boettinger, Ives, Coriell, Ballard, Laughlin, Clough, Biancamiello, Blau, Cahn, Mehrabian, Free, Berger, & Mordfin 1980]. It has also been applied to steels [Bates 1988] and aluminium casting alloys [Gao, Wang, Wen, & Li 2012; Rometsch & Schaffer 2000; Rometsch, Schaffer, Yao, & Couper 1998], and is now recognised as an important technique for modelling property losses during continuous cooling [Bates, Totten, & Brennan 1991; Brooks 1991]. Attempts have also been made to use QFA to predict elongation and fracture toughness [Shuey, Tiryakioglu, Bray, & Staley 2006; Staley et al. 1993].

3.5.1 Quench Factor Analysis - Overview

Quench Factor Analysis (QFA) is based on the principle of using isothermal transformation kinetics to predict transformations under non-isothermal conditions such as continuous cooling. By representing a quenching curve as a series of consecutive isothermal transformation events and adding together the amount transformed during each isothermal step, the effect of temperature on transformation rate can be determined
for virtually any step quenching or continuous cooling thermal path. Consequently, the
effect of quench rate on properties can be modelled much more accurately than the
average quench rate approach adopted by Fink and Wiley. The use of isothermal data
to make non-isothermal transformation predictions was originally proposed by Avrami
and Scheil who stated that the approach was valid only for a very limited number of
additive type reactions [Avrami 1940; Scheil 1935]. Further work by Cahn showed
that heterogeneously nucleated transformations which are typically observed during
quenching of aluminium alloys also tended to obey the rule of additivity, suggesting
that a wider range of reactions were additive [Cahn 1956]. Since then, a broad range of
non-isothermal transformations have been successfully modelled under the assumption
that the reactions are additive [Bjorneklett, Grong, Myhr, & Klukken 1998; Grong &
Myhr 2000; Park, Yue, & Jonas 1992; Pham, Hawbolt, & Brimacombe 1995a;
Pham, Hawbolt, & Brimacombe 1995b; Verdi & Visintin 1987], despite the fact that
the precise conditions for additivity are still disputed [Lusk & Jou 1997;

3.5.2 Quench Factor Analysis – Theory

3.5.2.1 Time–Temperature–Property (TTP) curves or “C” curves

Isothermal precipitation kinetics of equilibrium precipitates, transition precipitates and
GP zones all tend to follow a C-shaped behaviour. The C-shape curve is essentially the
combined effect of the two processes: nucleation and diffusion (see Figure 3-22) as
described in section 3.2.1.1.
Figure 3-22 Schematic illustration of the C-curve shaped behaviour of precipitation [Staley & Tiryakioglu 2001]

A. At higher temperatures close to the solvus temperature, nucleation rates are slow due to the low level of supersaturation resulting in a thermodynamic driving force low precipitation rate despite the high rate of diffusion.

B. At intermediate temperatures, the degree of supersaturation increases and the diffusion rate remains high resulting in a high precipitation rate and approach to equilibrium. The precipitates formed are usually are of a size and distribution which do not contribute to increasing the strength of the alloy and deplete the level of remaining solute to a level that adversely effects the strength following aging.

C. At low temperatures, the level of supersaturation is high but a low diffusion rate results in a slow precipitation rate.
The C-curve illustrates the time required to produce equal amounts of precipitation and identification of the critical temperature range where the precipitation rate is at its maximum. This in turn allows the determination of the time required to attain the desired physical properties for a particular alloy and temper. The final shape and position of the C-curve with respect to time and temperature depends on the alloy composition and temper as well as several other factors including, the nucleation and growth rate, the density and distribution of the nucleation sites as well as the occurrence of any physical impingement between transformed adjacent regions.

### 3.5.2.2 Analytical description of C-curve

For use within computerised Quench Factor Analysis models there is a requirement for an analytical description of the C-curve. As previously derived in section 3.2.1.1, the simplified classical rate equation for nucleation in solids is shown in Equation 3-11. [Evancho et al. 1974; Porter & Easterling 1992].

\[
N = ω_0 C_n \exp \left( - \frac{\Delta G^*}{RT} \right) \exp \left( - \frac{Q_d}{RT} \right)
\]

Equation 3-11

where:

- \(ω_0\) = Factor related to vibration freq. of the atoms and the critical nucleus area
- \(C_n\) = Number of nucleation sites per unit volume
- \(\Delta G^*\) = Activation energy barrier for nucleation
- \(Q_d\) = Activation energy for diffusion
- \(R\) = Universal Gas Constant (8.3143 J.K\(^{-1}\).mol\(^{-1}\))

If a precipitation hardenable alloy is cooled from above the solvus temperature, the change in free energy of the system increases as the difference between the temperature
and the solvus temperature increases. This change in the free energy of the system with undercooling is the driving force for participation of the new phases. For a particular alloy, $\Delta G_i$ (as defined in section 3.2.1) is proportional to the degree of undercooling and can be expressed as a function of temperature [Evansco et al. 1974; Porter & Easterling 1992].

\[
\Delta G_i = \frac{K(T_s - T)}{T_c}
\]

Equation 3-12

where:

- $K$: Constant
- $T$: Absolute temperature (K)
- $T_c$: Solvus temperature (K)

For heterogeneous nucleation which is observed for temperatures above the GP zone solvus temperature, strain energy can be ignored, thus $\Delta G^*$ can be expressed as a function of temperature:

\[
\Delta G^* = \frac{K T_s^2}{(T_s - T)^2}
\]

Equation 3-13

By substitution of this equation into the reciprocal form of Equation 3-11, the $C_i$ function, which mathematically describes the C-curve and consequently the precipitation kinetics, can be represented by [Evansco et al. 1974]:

\[
C_i(T) = -k_i k_s \exp\left(\frac{k_s k_s^2}{RT(k_s - T)^2}\right) \exp\left(\frac{k_s}{RT}\right)
\]

Equation 3-14

where:

- $C_i$ = Critical time required to precipitate a constant amount of solute (s)
\[ k_1 = \text{Constant that equals the natural log of the fraction untransformed during quenching (no units)} \]
\[ k_2 = \text{Constant related to the reciprocal of the number of nucleation sites (s)} \]
\[ k_3 = \text{Constant proportional to the energy required to form a nucleus (J.mol}^{-1}) \]
\[ k_4 = \text{Constant related to the solvus temperature (K)} \]
\[ k_5 = \text{Activation energy for diffusion, } Q_\text{h} (\text{J.mol}^{-1}) \]
\[ R = \text{Universal gas constant (J.mol}^{-1} \text{K}^{-1}) \]
\[ T = \text{Absolute temperature (K)} \]

A full mathematical derivation of the \( \zeta \) function from the above nucleation rate equation (Equation 3.11) is offered by Bratland et al. [Bratland et al. 1997].

### 3.5.2.3 Isothermal transformation kinetics

The kinetics for isothermal transformations have been assumed by previous researchers to follow a Johnson-Mehl-Avrami-Kolmogorov (JMAK) type transformation [Avrami 1940; Johnson & Mehl 1939] (The JMAK equation is sometimes referred to as the Avrami, the JMA or JMAK equation). The general form of this equation for diffusion controlled growth is shown in Equation 3-15.

\[
\zeta = 1 - \exp\left[-k_{171} t^n\right]
\]

Equation 3-15

where:

\[ \zeta = \text{Volume fraction transformed} \]
\[ n = \text{Constant (Avrami exponent)} \]
\[ k_{171} = \text{Temperature dependant constant} \]
\[ t = \text{Time} \]
Isothermal precipitation kinetics indicate that at a given temperature during a quench, the fraction transformed or precipitated \( \zeta \), is dependent on the actual time \( t \) dictated by the rate of cooling to the critical time for precipitation \( (C_t) \) determined from the \( C_t \)-curve.

Christian stated that \( 1-n<1.5 \) for the diffusion controlled growth of particles that have an appreciable starting diameter [Christian 1975]. This case can be approximated by the growth of a precipitate that has nucleated on a dispersed particle. Additionally a value of \( n=1 \) is predicted for needle or plate-like precipitates which are small in comparison with their separations and for thickening of long cylinders after impingement (see Table 3-5). This type of precipitate morphology is typically observed in the matrix and grain boundaries of slowly cooled aluminium alloys.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>All shapes growing from small dimensions, increasing nucleation rate</td>
<td>&gt;2½</td>
</tr>
<tr>
<td>All shapes growing from small dimensions, constant nucleation rate</td>
<td>2½</td>
</tr>
<tr>
<td>All shapes growing from small dimensions, decreasing nucleation rate</td>
<td>1½-2½</td>
</tr>
<tr>
<td>All shapes growing from small dimensions, zero nucleation rate</td>
<td>1½</td>
</tr>
<tr>
<td>Growth of particles of appreciable volume</td>
<td>1-1½</td>
</tr>
<tr>
<td>Needles and plates of finite long dimensions, small in comparison with separation</td>
<td>1</td>
</tr>
<tr>
<td>Thickening of long cylinders (needles) (e.g. after complete end impingement)</td>
<td>½</td>
</tr>
<tr>
<td>Thickening of very large plates (e.g. after complete edge impingement)</td>
<td>½</td>
</tr>
<tr>
<td>Precipitation on dislocations (very early stages)</td>
<td>-2/3</td>
</tr>
</tbody>
</table>

By assuming that the value of \( n \) in the JMAK equation (Equation 3-15) has a value of 1, the precipitation kinetics for continuous cooling of aluminium alloys can be rewritten [Evancho et al. 1974] as:

\[
\zeta = 1 - \exp \left( \frac{k_t}{C_t} \right)
\]

Equation 3-16
where: $k_i = \text{constant}$

Cahn’s analyses of transformation kinetics during continuous cooling showed that reactions at different temperatures are additive whenever the growth rate is proportional to the nucleation rate (i.e. isokinetic) [Cahn 1956]. A theoretical example of an isokinetic transformation is shown in Figure 3-23.

![Image of Figure 3-23: Example of an isokinetic transformation where $\Delta \log t = \text{constant and } A > B$](image)

Although the successful application of QFA relies on the assumption that the transformations occurring during quenching are largely additive, there is still a lack of conclusive evidence regarding the additivity or non-additivity of such reactions. Rometsch et al. state that this continues to be a major assumption at the core of QFA [Rometsch et al. 2003]. For these types of reactions, Cahn demonstrated that under non-isothermal conditions, the fraction transformed is given by the integral:
where:

\[ t_0 = \text{Quench start time (s)} \]

\[ t_f = \text{Quench finish time (s)} \]

\[ t_C = \text{Critical time as a function of temperature (s)} \]

\[ \tau = \text{Quench factor (the quench factor } \tau \text{ is often assigned the letter "Q" in the literature)} \]

Precipitation kinetics for continuous cooling can therefore be described by the equation:

\[ \zeta = 1 - \exp(k_1 \tau) \quad \text{Equation 3-18} \]

When \( \tau = 1 \), the fraction transformed \( \zeta \) equals the fraction transformed by the C-curve.

In Equation 3-14, the empirically determined constants \( k_2-k_5 \) defines the C-curve with the most critical temperature being represented by the minimum or "nose" of the curve.

For commercial applications, recommendations have been made that the cooling rate through this critical temperature range should exceed 100°C.min\(^{-1} \) with some of the more quench sensitive alloys such as 7075 requiring up to 300°C.min\(^{-1} \) which is not achievable in thick sections [Totten, Webster, & Bates 2003b].

Based on a continuous cooling quench curve, the quench factor can be summated mathematically by the following formulas:
or

$$
\tau = \frac{N_1}{C_1} + \frac{N_2}{C_2} + \frac{N_3}{C_3} + \cdots + \frac{N_{n+1}}{C_{n+1}}
$$

Equation 3-20

This is illustrated graphically in Figure 3-24 [Evancho et al. 1974].

![Quench Factor Determination](image)

**Figure 3-24 Quench Factor Determination [Evancho et al. 1974]**

Equations 3-19 and 3-20 assumes that the transformation reaction is additive which means that the reaction rate is a function only of temperature and the amount transformed. The quench factor calculated using this method is a single number describing the quench severity based on a C-curve and the actual quench path. Slow quench rates produce high quench factors as opposed to rapid quench rates which give low quench factors.

### 3.5.2.4 Yield strength prediction

The attainable yield strength of 7000 series alloys is a function of the amount of solute available for precipitation remaining in solid solution after the quench, as long as aging
is carried out so that GP zones nucleate prior to the appearance of the η' phase. By assuming that the relationship between yield strength and the solute available for precipitation of the hardening phase is linear and by substituting: \[ \frac{\sigma_x - \sigma_{\text{min}}}{\sigma_{\text{max}} - \sigma_{\text{min}}} \text{ for } 1 - \zeta \]

Equation 3-18, the yield strength of the alloy can be predicted from:

\[ \frac{\sigma_x - \sigma_{\text{min}}}{\sigma_{\text{max}} - \sigma_{\text{min}}} = \exp(k_1 \tau) \]  

Equation 3-21

where:

\( \tau \) = Quench factor

\( k_1 \) = Constant that equals the natural log of the fraction untransformed during quenching (no units)

\( \sigma_x \) = Predicted \( \sigma_{0.2} \) after heat treatment (MPa)

\( \sigma_{\text{min}} \) = Minimum \( \sigma_{0.2} \) (this may be 0, a constant or a temperature dependant variable depending on the model used) (MPa)

\( \sigma_{\text{max}} \) = Maximum \( \sigma_{0.2} \) after an “infinitely” fast quench (MPa)

The theoretical justification for Equation 3-21 is presented in Appendix 1. In terms of yield strength, a quench producing a quench factor of 1 (based on a 99.5% of \( \sigma_{\text{max}} \)) will achieve an offset yield strength or Proof Stress (\( \sigma_{0.2} \)) of 570 MPa for \( \sigma_{\text{max}} = 600 \) MPa.

This model can be equally applied to both hardness and electrical conductivity (resistivity) as shown in Equation 3-22 and Equation 3-23 [Hall et al. 1995] [Swarzendruber et al. 1980].
Due to the inverse relationship between strength and electrical conductivity, the reciprocal, electrical resistivity ($\rho$) is often used as shown in Equation 3-23.

$$\frac{\rho_s - \rho_{\text{max}}}{\rho_{\text{max}} - \rho_{\text{min}}} = \exp(k_T) \quad \text{Equation 3-23}$$

Though the models apply equally well to hardness and electrical conductivity/resistivity, property prediction based on the previously discussed limitations of assuming a linear relationship between tensile and hardness data needs to be considered. Shuey and Tiryakioglu [Shuey et al. 2006] have stated that it is the underlying quench precipitates which ultimately effects all the alloy properties. Since the development of the original strength prediction methods by Evancho & Staley [Evancho et al. 1974], the equations have generally been applied to multiple properties independently of each other. The first attempt at joint modelling of strength and fracture toughness by Staley et al. [Staley et al. 1993] used a single C-curve plus a parameter for the ratio between the hold time for the drop in toughness and the hold time for a drop in strength but did not account for when the toughness rises at long isothermal holds at low temperatures. Further work by Shuey and Tiryakioglu [Shuey et al. 2006] using multiple C-curve models on 7075-T76 and several other data sets have shown excellent strength prediction with a significantly improved toughness prediction.
3.5.2.5 Influence of $\sigma_{\text{min}}$

In the original QFA model, Evancho and Staley set $\sigma_{\text{min}} = 0$ in order to utilise Cahn’s model of predicting the extent of transformation under non-isothermal conditions. This has the problematic effect of predicting 0.2% proof stress for alloys isothermally held for infinitely long times equal to 0. For many industrial applications this provides adequate results when the expected loss in strength is less than 10%. Based on that assumption, Equation 3.21 is redefined as:

$$\sigma_s = \sigma_{\text{max}} \exp(k_r t)$$

Equation 3-24

Later models set $\sigma_{\text{min}}$ to a constant value or as a minimum value as a function of isothermal holding temperature where the precipitate growth has reached its limit at a particular temperature [Ives et al. 1983].

3.5.2.6 Influence of Avrami exponent (n)

Evancho and Staley showed that when interrupted quench data generated by Fink and Wiley [Fink et al. 1948] to determine yield strength C-curves for alloy 7075 is plotted in the form time versus $-\log(\sigma_s \sigma_{\text{max}})$. (This is known as an Avrami transformation plot) a linear relationship is observed when the isothermal hold time is $<1000$s as illustrated in Figure 3-25 [Evancho et al. 1974]. This provided an experimental vindication for Figure 3-21 and that the assumption that the Avrami exponent n in Equation 3-15 equals 1 is valid and has subsequently been used as a reasonable approximation for a range of aluminium alloys [Bates et al. 1988; Dolan, Robinson, & Morris 2001; Kim, Hoff, & Gaskell 1991; Staley 1987].
Figure 3-25  Avrami transformation plot for Fink and Wiley 7075-T6 data [Evancho et al. 1974]

Though this provides a good approximation for growth in the early stages of the reaction, deviations from linearity have been noticed for values of t > 1000s. For 7010, no deviation from linearity was observed below 1000s (see section 5.9.5.2 - Figure 5-36) but for times > 1000s, slight divergence from the linear isokinetic model was observed [Flynn & Robinson 2003]. The $R_{p0.2}$ C-curve coefficients for the calculation of the quench factor at 99.5% of the maximum attainable strength for a selection of heat treatable alloys and tempers obtained using classical QFA are shown in Table 3-6 with the resultant C-curves shown in Figure 3-26.

Table 3-6  Tensile C-curve coefficients for various aluminium alloys and tempers

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$k_2$ (s)</th>
<th>$k_3$ (J/mol°C)</th>
<th>$k_4$ (K)</th>
<th>$k_5$ (J/mol°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7050-T76</td>
<td>2.21-19</td>
<td>5190</td>
<td>850</td>
<td>1.81-5</td>
<td>[Staley 1974]</td>
</tr>
<tr>
<td>7075-T73</td>
<td>1.371-13</td>
<td>1069</td>
<td>737</td>
<td>1.371-5</td>
<td>[Swarzendruber et al. 1980]</td>
</tr>
<tr>
<td>7075-T6</td>
<td>4.11-13</td>
<td>1050</td>
<td>780</td>
<td>1.41-5</td>
<td>[Staley 1974]</td>
</tr>
<tr>
<td>7010-T76</td>
<td>5.81-20</td>
<td>7370</td>
<td>899</td>
<td>1.81E+15</td>
<td>[Flynn &amp; Robinson 2003]</td>
</tr>
</tbody>
</table>
Figure 3-26 Yield strength C-curves for a selection of Aluminium alloys and tempers

This figure illustrates for example that alloy 7075-T6 is more quench sensitive than alloy 7050-T76. QFA has proved very successful as a predictive modelling tool, where the loss in properties is <10%, though as yet is still to be accepted as a useful commercial tool beyond this limit.

3.5.2.7 Assumptions and limitations of classical quench factor analysis

Since its inception, researchers have identified several assumptions, limitations and points of contention in relation to the classical model of Quench Factor Analysis developed by Evans and Staley, these include:

- Transformation kinetics are described adequately by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation with the Avrami exponent n=1 [Starink 1997]
- Strength varies linearly with solute concentration [Rometsch et al. 2003]
- $\sigma_{min}$ is negligible with respect to $\sigma_{max}$ for artificially aged tempers (see Equation 3-22) [Rometsch et al. 2003]
• The effect of quenched in vacancies and vacancy related defects is ignored
[Rometsch et al. 2003]

• The influence of multiple precipitates [Tiryakioglu & Shuey 2010a]

When Evancho and Staley [Evancho et al. 1974] originally analysed aluminium alloys 7075-T6 and 2024-T4 interrupted quenching data from Fink and Willey [Fink et al. 1948], they obtained linear correlations with a slope of 1 on logarithmic plots of \(-\log(\sigma_d/\sigma_{max})\) versus isothermal hold time as previously shown in Figure 3-25. All subsequent published QFA models have assumed that the Avrami exponent \(n\) equals 1 and can hence be omitted from Equation 3-21 irrespective of the material the QFA model is being applied to [Rometsch et al. 2003]. Current diffusion-controlled nucleation and growth theories indicate that \(n<1.5\) is not possible for reactions that involve growth through diffusion in 3 dimensions (e.g., precipitates nucleating and growing within grains) [Christian 1965; Christian 1975; Starink 1997]. Hence the use of \(n=1\) in classical QFA contradicts the notion that quench sensitivity is mostly related to the formation of non-hardening precipitates within the grains during quenching. Although, Staley acknowledged that \(n\) can vary with nucleation rate and precipitate morphology, it was not included as a possible variable in Equation 3-21 [Staley 1987]. Other researchers who have taken a more pragmatic approach have found no statistically significant requirement for inclusion of an \(n\) exponent [Shuey & Tiryakioglu 2006]. Starink has also demonstrated that in many situations, the JMAK equation does not describe diffusion-controlled precipitation reactions [Starink 1997] which highlights another shortcoming in the classical QFA model. Besides assuming that \(n=1\), the equation also assumes that impingement of diffusion fields (i.e. soft impingement) can be described by the JMAK equation, which is valid for hard
impingement but has not been proven for soft impingement [Lee & Kim 1990: Starink 1997]. Impingement is defined as either “hard” impingement—physical contact between particles or soft impingement—the overlapping of solute depleted zones. While the JMAK equation may be valid for relatively rapid quenches yielding limited amounts of widely spaced precipitates, there could be numerous instances (e.g., during slow cooling, long isothermal holds or for a high density of nucleation sites) where impingement becomes more critical. According to Starink et al., if certain preconditions are met, the JMAK kinetic equation has been shown to provide sufficient accuracy. These preconditions include randomly distributed product phases, isotropic growth and constant equilibrium state. Mechanisms causing deviation from these preconditions include capillary effects also known as Gibbs-Thomson effects which can cause small particles to grow less rapidly than large ones [Robson 2004a], vacancy annihilations and blocking (also known as shielding) due to anisotropic growth [Song & Liu 2012: Starink 2001]. In order to overcome some of these limitations, several modifications and new models have been proposed by a number of researchers [Dorward 1997: Rometsch et al. 2003: Rometsch, Wang, Harriss, Gregson, & Starink 2002: Staley & Doherty 1989: Staley et al. 1993: Staley & Tiryakioglu 2001: Tiryakioglu & Shuey 2010a].

3.5.3 Non-Isokinetic Models - Overview

As stated previously, in order to use Cahn’s existing model for isokinetic transformations, $\sigma_{\text{min}}$ was neglected from Evancho and Staley’s classical QFA model as they assumed $\sigma_{\text{min}}>\sigma_{\text{max}}$ [Evancho et al. 1974]. The effect of this is that as the $\sigma_{\text{v}}/\sigma_{\text{max}}$ ratio decreases, the QFA model loses accuracy predicting the strength of very slowly cooled components from close to the equilibrium phase solvus temperature approaching an unrealistic zero as illustrated in Figure 3-27A.
Figure 3-27  Effect of: A) \( \sigma_{\text{min}} = 0 \) and B) \( \sigma_{\text{min}} = \text{Constant } \sigma_0 \); on property prediction [Cahn 1956; Staley & Tiryakioğlu 2001]

Ives et al. assumed that \( \sigma_{\text{min}} \) was a non-temperature dependant constant \( \sigma_0 \) (Figure 3-27B) which could be calculated along with \( k_2-k_5 \) to minimise the RMSE (Root Mean Square Error) value [Ives et al. 1983]. Using this model they were able to extend the use of QFA to ~15% loss of property.

Research conducted by Grong and Myhr of transformations that involve nucleation and growth of precipitates by diffusion, determined that Cahn’s additively model was not suitable for all possible quench paths in aluminium alloys. They concluded that the rate of precipitation at a particular temperature depends on the amount of solute remaining in the alloy [Grong et al. 2000]. This then subsequently influences the amount of precipitation that can occur at that temperature. This is opposed to the Cahn model which requires that the precipitation rate is just a function of the temperature and the amount transformed [Grong et al. 2000]. Based on this approach Staley et al. developed a non-isokinetic model, which, allows property prediction from very rapid quench conditions, beyond the 15% loss in properties to very slow cooling conditions such as those which may occur at the centre of large forgings or during annealing [Staley & Doherty 1989; Staley et al. 1993].
3.5.3.1 Staley and Doherty non-isokinetic model

The maximum strength of an aluminium alloy is usually achieved when quenched at an infinite rate from the solution temperature to retain the maximum amount of solute available for precipitation hardening. If an alloy is quenched to a temperature below the solvus temperature and held isothermally until equilibrium is reached and subsequently quenched, a proportionate amount of solute will be lost from the alloy. The solute remaining is proportional to the maximum strength attainable and is equivalent to the strength that would be obtained if the alloy was solution treated at this temperature. Therefore the lower the isothermal hold temperature below the solvus temperature, the greater the solute loss. This model is again based on the assumption that strength and solute content show a linear relationship and that the alloy loses an incremental amount of the ability to develop the property over each individual time interval, thus:

\[
\frac{ds}{dt} = A(T)(S - S_{\text{eq}}(T))
\]

Equation 3.25

where:

\[S\] = Solute concentration in solution

\[t\] = Time at temperature, T

\[A(T)\] = Kinetic constant

\[S_{\text{eq}}(T)\] = Equilibrium solute concentration at temperature T

Based on the previous assumption that solute and strength show a linear relationship, Equation 3.25 can be rewritten as:
\[ \frac{d\sigma}{dt} = k(T)(\sigma - \sigma_{\text{min}}(T)) \]  

Equation 3-26

The term \( k(T) \) can be replaced by:

\[ k(T) = \frac{1}{C_i(T)} \]  

Equation 3-27

where \( C_i(T) \) is the critical time as previously described (the theoretical validation of this substitution is presented in Appendix 2). Therefore, the attainable property over any quench path can be described as:

\[ \frac{d\sigma}{dt} = (\sigma - \sigma_{\text{min}}(T)) \frac{1}{C_i(T)} \]  

Equation 3-28

For a constant \( T \), integration of the above expression gives:

\[ \Delta \sigma_i = (\sigma_{i+1} - \sigma_{\text{min}T_i}) \left[ 1 - \exp\left( - \frac{\Delta t_i}{C_i(T_i)} \right) \right] \]  

Equation 3-29

where:

- \( \sigma_{i+1} \), \( \Delta \sigma_i \), \( \Delta t_i \) are functions of the equilibrium concentration at each incremental isothermal hold temperature. For each subsequent incremental isothermal step, \( \sigma_{i+1} \) is a function of the
amount transformed during the previous incremental isothermal step (i.e. \( \sigma_{i-1} \)) is set equal to the predicted value of \( \sigma \) from the previous isothermal step. The \( R_{p0.2} \) after quenching is thus defined as the: \textit{maximum obtainable} \( R_{p0.2} (\sigma_{\text{max}}) - \text{sum of the incremental strength losses} (\Delta \sigma) \) as described in Equation 3-30:

\[
\sigma = \sigma_{\text{max}} - \sum_{i=1}^{n} \Delta \sigma_i
\]

Equation 3-30

This model is used extensively throughout the course of this work for property prediction. Staley and Tiryakioglu have also presented a similar model which relates \( \sigma_{\text{max}} \) to the equilibrium solvus curve on the equilibrium phase diagram \cite{Tir}. This method has been shown to be successful for aluminium alloys such as 6061 and D357.

3.5.3.2 Multiple quench precipitates models

Shuey and Tiryakioglu have recently shown that it is possible to model multiple quench precipitates overcoming the limitation of where the models to date have considered only one type of quench precipitate \cite{Tir}. Using the data set provided by Swarzendruber et al. for 2219-T87 \cite{Swarz}, the original QFA model was modified by introducing a new unitless variable, \( S \) to describe the evolution of the amount of each type of quench precipitate \cite{Tir, Shi}. At an infinite cooling rate where no quench precipitation occurs, \( S=0 \) and conversely \( S=1 \) when the cooling rate is slow enough to result in the complete loss of solute at the end of quench. For arbitrarily long isothermal holds, in the absence of any competing precipitates, the limiting value, \( S_{\text{qr}} \), is:

\[
S_{\text{qr}} (T) = 1 - \exp \left[ \frac{Q_e}{R} \left( \frac{1}{k_4} - \frac{1}{T} \right) \right] \text{for} T \leq k_4
\]

Equation 3-31
Where, \( k_4 \) is the lesser of the solution treatment and solvus temperatures and \( Q_s \) is the enthalpy of precipitation. \( S_{eq} \) represents the equilibrium amount of \( S \) at a given temperature. The evolution of quench precipitates is modelled by:

\[
\frac{dS}{dt} = \frac{S_{eq} - S}{C_e}
\]

Equation 3-32

On integrating:

\[
\Delta S_i = S_{eq} - S_i \left[ 1 - \exp\left( -\frac{\Delta f_i}{C_e} \right) \right]
\]

Equation 3-33

At the end of the quench, \( S \) is determined as:

\[
S = \sum_i \Delta S_i
\]

Equation 3-34

Property can then be predicted by:

\[
\sigma = \sigma_{max} = \sum_j k_j S_j
\]

Equation 3-35

Where \( j \) is for the quench precipitates modelled and \( k \) = strength coefficient. This new model allows the concurrent modelling of multiple properties and/or multiple tempers.

### 3.5.3.3 Rometsch and Starink model

Other work by Rometsch and Starink debates the linear relationship between peak aged strength and solute concentration which is the major underlying theoretical principle of the classic QFA model and the subsequent non-isokinetic models developed by Staley and Doherty [Staley et al. 1993]. They state the assumption is inconsistent with current strengthening theory. They suggest that Equation 3-21 be rewritten as:

\[
\frac{\sigma_{max} - \sigma_{min}}{\sigma_{max} - \sigma_{min}} = \exp(k_1 \tau)^{1/2}
\]

Equation 3-36
This gives a similar predicted T6 strength but provides more realistically positioned C-curved. Rometsch and Starink have also suggested that the exponent n=1 used in the Avrami equation maybe questionable since possible deviation due to the impingement issue needs to be considered. They suggested the applicability of an equation developed by Starink and Zahra [Christian 1975: Rometsch et al. 2003: Starink & Zahra 1997].

\[
\zeta = 1 - \left[ \left( \frac{k t}{\eta_i} + 1 \right)^{\frac{1}{n}} \right]^{n_i}
\]

Equation 3-37

Where:

\( \zeta \) = Fraction transformed

\( k \) = Temperature dependant constant

\( n_i \) = Avrami component

\( \eta_i \) = Impingement Factor

This equation is based on the Austin-Rickett (AR) [Austin & Rickett 1939] equation which has been shown to have a better fit for diffusion-controlled precipitation reactions than the JMAK equation [Starink 1997]. By adapting Equation 3-37 to Quench Factor Analysis the following model was obtained (see Equation 38).

\[
\frac{\sigma_{\text{AV}} - \sigma_{\text{MIN}}}{\sigma_{\text{MAX}} - \sigma_{\text{MIN}}} = 1 - \left[ \left( \frac{k t}{\eta_i} + 1 \right)^{\frac{1}{n_i}} \right]^{\frac{n_i}{2}}
\]

Equation 3-38

Using Fink and Wiley’s interrupted quench data set [Fink et al. 1948] and by iteratively adjusting the constants \( k_i \), \( \sigma_{\text{MIN}} \), \( \sigma_{\text{MAX}} \) and \( \eta_i \) to minimise the root mean square error (RMSE), Rometsch and Starink obtained an Avrami exponent of \( n=1.5 \) [Rometsch et
Christian stated that value of $n \geq 1.5$ describes particles of any shape growing through diffusion in three dimensions under conditions where negligible nucleation occurs [Christian 1975]. In the limit of $\eta_i$ approaching infinity, Equation 3-37 is identical to the JMAK equation but when $\eta_i$ is small ($\eta_i < 10$) the fraction transformed will differ significantly from that predicted by the JMAK equation especially in the later stages of transformation where impingement is likely to occur.

Researchers have also shown that the non-isokinetic empirical approach of the determination of $\sigma_{\text{min}}$ used by Evancho and Staley may be improved by including a regular solution model to describe the slope of the solvus [Christian 1975; Rometsch et al. 2003]. This method eliminates the minimum strength altogether and replaces strength with concentrations as shown in Equation 3-39.

$$\frac{C_{\text{AQ}} - C_{\text{max}(T)}}{C_{\text{max}(T)} - C_{\text{min}(T)}} = 1 - \left(\frac{(kr)^*}{\eta_i} + 1\right)^{-\eta_i/2}$$  \text{Equation 3-39}

Where:

- $C_{\text{AQ}}$ = As quenched concentration (local)
- $C_{\text{max}}$ = Maximum concentration (local)
- $C_{\text{min}}$ = Minimum concentration (local)

This model is only really suitable for aging to the peak T6 condition. Rometsch and Wang have shown the success of this approach for 6082-T6 [Rometsch et al. 2002].

### 3.5.3.4 Dynamic quench model

A dynamic quench model that predicts strength under continuous cooling conditions was developed by Doward using step-quenching data obtained by cooling to successively lower temperatures at one rate followed by quenching at a faster rate [Doward 1997]. According to Doward, a procedure based on quench rate has
advantages in many practical situations since it circumvents the assumptions involved with applying established TTP diagrams to continuous cooling.

### 3.6 Residual Stress - Overview

Residual stresses or internal stresses are defined as ‘those existing in bodies upon which no external forces are acting’ [Orowan 1948a]. They primarily originate from non-uniformities occurring in the alloy due to mechanical, thermal and/or metallurgical factors introduced during manufacturing processes such as rolling, drawing, forging, extruding, bending and quenching. Residual stresses can result in quench cracking and distortion during machining operations [Davis 1992; Torgerson et al. 1977], as well as reducing the stress corrosion cracking resistance and fatigue resistance of the alloy [Bussu & Dunn 2006; Stewart-Jones 1969; Webster & Ezeilo 2001]. Residual stress can be divided into two main types:

**Macrostresses:** Macrostresses are defined as those which extend over distances that are large compared to the material grain size. These stresses are referred to as type I stresses [Withers & Bhadeshia 2001].

**Microstresses:** Microstresses are defined as stresses associated with strains within the crystal lattice that extend over distances, which are of the same order or smaller than the grain size [Prevey 1986]. These stresses are referred to as type II and type III stresses [Withers et al. 2001].

For 7000 series aluminium alloys, rapid quenching (>100°C/s) is carried out in order to develop the maximum possible allowable properties in the alloy from the subsequent precipitation hardening process. This rapid quenching induces high levels of residual stress within the component due to inhomogeneous plastic flow caused by the creation of large temperature differentials between the internal and external surfaces of the part during the quench.
The final result is that the surface develops a compressive stress while the core develops a tensile stress. This effect is graphically described in Figure 3-28. The magnitude of these stresses is directly related to the temperature gradient generated during the quench. An early description of the magnitude of these stresses in heat treated aluminium alloys was provided by Klint and Janney [Klint & Janney 1958]. Further work by Becker et al. quantified these residual stresses as well as the resulting distortion which occurs during cold water quenching [Becker, Karabin, Liu, & Smelser 1996]. For cold water as-quenched 7010, surface compressive stresses in the order of 160-200MPa have been observed [Robinson & Tanner 2002].

3.6.1 Residual Stress Control – Overview of Methods

Several methods are commonly employed for residual stress reduction/control in heat treated aluminium alloy components:

- Thermal Methods - modification of the quench path (quenchant type, uphill quenching) and post-quench treatments such as regression re-aging
• Mechanical methods - shot peening and plastic deformation (stretching/compression).

3.6.1.1 Quench path modification

In order to reduce residual stresses created during the quench process, the quench rate is lowered by quenching in boiling water or other polymer based quenchants such as PAG as previously described in section 3.2.2.2. Reduced quench rates for 7010 have been shown to reduce the residual stress by up to 95% though with a resulting trade off in properties [Tanner et al. 2006]. The reduced cooling rate of boiling water is due to the formation of what is known as a "vapour blanket". The water in contact with the metal surface rapidly vaporises forming a vapour blanket around the block or component. This reduces the heat transfer from the block effectively slowing the rate of cooling.

This is followed by a vigorous boiling of the water, in which rapid cooling then occurs. This stage is known as "nucleate boiling". When the nucleate boiling has ceased, the block is then cooled by simple convection. The reduction in cooling rates is provided by the vapour blanket at the beginning of the quench and is sustained until the temperature of the block reaches about 300°C [Bryant 2003]. All these quench path modification methods have the detrimental effect of reducing the final mechanical properties due to effect of the precipitation of non-hardening precipitates on the aging response [Deschamps & Brechet 1998b].

3.6.1.2 Post-quench thermal methods

Thermal methods for stress relief in 7000 series alloys, such as those typically used for steels are essentially limited in their application since the temperature for effective stress relief is above that used for artificial aging. Relief which does occur within the material is essentially due to the plastic flow caused by the movement of dislocations.
Stress relief at the artificial aging temperatures has been shown to give a reduction of only 10 to 20% [Van Horn & Kent, R 1967]; though there is some evidence to suggest that stress relief in the range of 10%-35% may occur at the peak aged T6 aging temperature with some alloys. In general, the degree of reduction or relaxation is very dependent on the time and temperature of the precipitation heat treatment as well as the alloy composition. This has led to the application of retrogression and re-aging (RRA) type treatments, which have been shown to be effective for reducing residual stress in 7010 by 15-20% where plastic deformation methods have not been used [Robinson, Tanner, & Whelan 1999]. Some attempts at reduction in quench distortions of castings has been reported using gas quenching methods [Rose, Kessler, Hoffmann, & Zoch 2006]. The effect of natural aging has been shown to have little effect on the residual stress magnitudes in 7010 as shown in Figure 3-29 [Robinson & Tanner 2002].

![Figure 3-29 Residual stress vs natural aging time for 7010 and 5251](Robinson & Tanner 2002)
In light of these limitations, quenched induced residual stresses are typically relieved using mechanical methods.

### 3.6.1.3 Plastic deformation

The relief of quench induced residual stresses is most often successfully carried out through plastic deformation at room temperature of components after initial quenching. [Kleint et al. 1958]. The deformation can be:

- Tensile deformation or stretching designated **T**x51
- Compressive deformation designated **T**x52
- Re-striking cold (closed die forgings) designated **T**x54

The direction of plastic deformation (tensile or compressive) used is often due to practical considerations such as sample geometry and size, and the aim of achieving uniform stress relief throughout the component. Tensile deformation of components such as plates, bars and extrusions can be stress relieved from 1 to 5% by post-quench compression and is generally carried out in the ST direction [Van Horn & Kent.R 1967]. In general, both compression and stretching processes have been shown to reduce residual stresses by more than 90% [Koc, Culp, & Altan 2006].

![Figure 3-30](image)

*Figure 3-30*  The effect of compression and stretching on residual stress magnitudes. [Robinson, Hossain, Truman, Oliver, Hughes, & Fox 2009]
This is illustrated in Figure 3-30 where OS-OC-OS pertains to the as quenched residual stress distribution from the surface to core while 1s-1c-1s is the reduced stress distribution after compression but before the removal of the load. 2s-2c-2s represents the remaining residual stress distribution after load removal. Previous researchers have shown that for 7075 for tensile deformation, the majority of residual stresses can be relieved after just 0.5% deformation with essentially complete relief occurring at 2% [Altschuler, Knaatz, & Cina 1988; Robinson et al. 2009]. This differs from compression where approximately 4% is required for practically complete stress relief in the transverse direction to be obtained. The effect of cold compression on the residual stress in a 7000 series alloy on both the 1-ST and 1-LT surfaces is shown in Figure 3-31. The practical use of cold compression is limited to open die forging or specially closed dies which have been designed to account for the large thermal expansion mismatch between steel and aluminium.

![Graph showing residual stresses on ST and LT surfaces deformed in compression](image)

**Figure 3-31** Residual stresses on ST and LT surfaces deformed in compression [Altschuler et al. 1988]
Finite Element (FE) Analysis of cold compression of 7010 open die forgings has revealed that cold compression of 2-3% should relieve the majority of residual stress. Compression of greater than 3% deformation has been shown to lead to increased residual stress with greater than 5% leading to wrinkling and cracking in 7010 [Tanner, Robinson, & Cudd 2000]. Tanner and Robinson have also used the finite element method in conjunction with a layer removal technique to analyse the effect that varying process parameters during the cold compression procedure have on the magnitude of the final residual stress [Tanner & Robinson 2000; Tanner & Robinson 2003; Tanner et al. 2000]. For commercially processed 7000 series alloys, plastic deformation is usually carried out as soon as possible following the quench. This is primarily due to the subsequent increase in strength of the alloy brought on by natural aging. This has practical implications with respect to the ability to physically compress the component as the strength increases. To date very little work has been carried out on the effect of this post-quench delay on the overall efficiency of the cold compression stress relief and the magnitude of the final residual stress.

3.6.1.3.1 Influence of friction during cold deformation

Frictional effects between the compression platens and the forging surface occurring during cold compression can result in the occurrence of significant levels of stress existing at different locations throughout the forgings. This friction is usually reduced by the introduction of suitable lubricants though previous researchers have shown that frictional effects cannot be completely eliminated. Papirno et al. have stated that the effect of friction on the stress and strain distributions is only of consequence above 10% compression though laboratory testing has shown the onset of the “orange peel effect” at 5% though this is very grain size and alloy dependant [Papirno, Mescall, & Hansen]
1983]. Insufficient lubrication can also result in "barrelling" of forgings, which can have a detrimental effect on any subsequent surface residual stress measurement.

3.7 Residual Stress Measurement – Overview

There are several methods, both destructive and non-destructive techniques available for the measurement of residual stress including the hole drilling technique [ASTM 2008], x-ray diffraction [Fitzpatrick, Fry, Holdway, Kandil, Shackleton, Suo, & Suominen 2005], neutron diffraction [Albertini, G., Bruno, Carrad, Fiori, Rogante, & Rustichelli 1999], the contour technique [Prime & Hill 2002] as well as magnetic, holographic, ultrasonic, thermoelastic, and piezospectroscopic techniques (Raman or fluorescence luminescence) methods. A comprehensive description of the various non-destructive techniques is provided by Withers et al. and the National Physical Laboratory in the UK [Kandil, Lord, Fry, & Grant 2004; Withers et al. 2001]. A summary of the advantages, disadvantages and capabilities of a selection of the most commonly used methods are shown in Table 3-7.

Table 3-7 Comparison of a selection of techniques for Residual Stress measurement

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Penetration</th>
<th>Spatial Resolution</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-Ray Diffraction</td>
<td>Non-Destructive</td>
<td>Surface techniques, Small components/sample geometry</td>
<td>&lt;50μm (Al)</td>
<td>1mm laterally, 20μm</td>
<td>±50MPa</td>
</tr>
<tr>
<td>Neutron Diffraction</td>
<td>Penetration, 3D mapping</td>
<td>Availability</td>
<td>100mm in Al</td>
<td>200 μm</td>
<td>±50 x 10⁻⁶ strain</td>
</tr>
<tr>
<td>Hole Drilling</td>
<td>Portable, rapid, inexpensive, widely available</td>
<td>Semi-destructive, limited spatial resolution, data interpretation</td>
<td>1.2 x hole diameter</td>
<td>1mm</td>
<td>±50MPa</td>
</tr>
</tbody>
</table>

3.7.1 X-ray Diffraction Technique for Residual Stress Analysis

The x-ray diffraction method for the determination of residual stress is a non-destructive technique whereby surface and sub-surface residual stresses (destructively using layer
removal techniques) can be determined indirectly by the strain measurement of the material's atomic lattice (d-spacing). The stress resolved using x-ray diffraction is defined by the irradiated area and is the arithmetic mean stress of a volume of material [Prevey 1986]. This diffraction takes place from a thin layer of approximately 20μm on the surface. The diffractometer angles used in residual stress analysis are:

- $2\theta$ Angle between the incident and diffracted x-ray beams (Bragg angle)
- $\phi$ (Phi) Angle of rotation of the sample about its surface normal
- $\psi$ (Psi) Angles through which the sample is rotated (Sin$^2$ψ method)

A collimated x-ray beam of wavelength $\lambda$ is focused on the sample to be measured and the quantity of the x-rays diffracted recorded as the angle $\theta$ between the x-ray source and the detector is altered thus providing an intensity versus scattering angle $2\theta$ diffraction plot. In conjunction with the Bragg equation (see equation 3-40), this allows determination of the change in lattice spacing due to variations in the residual stress.

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} \text{Equation 3-40}

where:

- $n$ = Order of diffraction
- $\lambda$ = X-ray wavelength (m)
- $\theta$ = Diffraction angle (°)
- $d$ = Lattice spacing (m)

Bragg's equation relates the atomic lattice plane spacings ($d$) to the angle of diffraction ($\theta$) and the incident wavelength ($\lambda$). Changes in lattice spacing caused by elastic strain ($e$) give rise to shifts in the diffracting angle ($\Delta \theta$):
Figure 3-32 shows impingement of the beam on the surface of the specimen for two orientations of the sample. $\psi$ is the angle of the orientation of the stressed surface and is defined as the angle between the normal to the surface and the bisector of the incident and diffracted beams. This is also the normal between the lattice planes and the specimen surface.
Part A shows a sample orientation $\psi = 0$ where the diffracting planes are parallel to the surface. The indicated stress having no effect on the lattice spacing (excluding Poisson's ratio effect) as it is parallel to the diffracting lattice planes.

Part B illustrates where the sample is rotated through a known angle $\psi$ thus, presenting a smaller lattice spacing to the incident x-ray beam than in the non-stressed condition. This is associated with a quantifiable shift of the diffraction peak as illustrated in Figure 3-32B. The resulting stress in the system can then be calculated in conjunction with the Young's modulus ($E$) and the measured strain using Hooke's law (Equation 3-41 and Figure 3-33).

$$\frac{d_{pp} - d_{ss}}{d_{ss}} = \frac{1 + \nu}{E} \sigma_c \sin^2 \psi$$  \hspace{1cm} \text{Equation 3-41}

where:

- $d_{pp}$: Interplaner spacing in the direction defined by $\phi$ and $\psi$
- $d_{ss}$: Interplaner spacing for unstressed material (m)
- $E$: Young's modulus (N/m$^2$)
- $\nu$: Poisson's Ratio
- $\sigma_c$: Angle between the normal to the surface and the bisector of the incident and diffracted beams.

Figure 3-33 $\phi$ coordinate system
If $d_{\text{av}}$ is the spacing between the lattice planes measured in the directions defined by $\phi$ and $\psi$ then the stress can be defined as:

$$\sigma_0 = \left(\frac{E}{v+1}\right) \left(\frac{1}{d_{\text{av}}} \frac{d\delta d_{\text{av}}}{d\sin^2 \psi}\right)$$  \hspace{1cm} \text{Equation 3-42}

For an isotropic material under a bi-axial stress condition, the residual stress can be calculated from Equation 3-42. A typical x-ray diffraction peak is shown in Figure 3-34.

Figure 3-34  Typical x-ray diffraction peak with a superimposed Pearson VII fit

The breadth of this peak has been shown to increase as materials are cold worked [Prevey 1986]. The slope $(m)$ of $d_{\phi}$ versus $\sin^2 \psi$ in conjunction with the elastic constants allows determination of the residual stress. An example of a typical $d_{\phi}$ vs $\sin^2 \psi$ plot is shown in Figure 3-35.
3.7.1.1 Sources of error

3.7.1.1.1 Grain size and texture

Coarse crystal sizes (>100μm) due to for example recrystallisation in aluminium alloys reduces the number of crystals contributing to the diffraction peak (i.e. obeying Bragg's Law). This results in lower peak intensities and reduced peak position accuracy. Previous research has shown that to determine intensity to 1% accuracy at a single point on the diffraction curve, an intensity of $10^4$ (counts/sec$^{-1}$) is required [Prevey 1986]. The affect of texture results in peaks of varying intensity with ψ tilt.
This problem is usually overcome by increasing the irradiated area or through oscillation of the sample through the $\phi$ and $\psi$ angles (rocking) encompassing more grains into the diffracting state.

3.7.1.1.2 Subsurface residual stress gradients

For x-ray diffraction residual stress measurements, the effective depth of penetration is relatively small with nominally only 50% of the diffracted radiation originating from a depth of less than 10$\mu$m [Lamda Research 1991]. Surface measurements are an average of the stress at the surface and in the layers immediately beneath it.

3.7.1.1.3 Sample geometry

Sample geometry effects can have a significant effect on the measured residual stress. Surface roughness, pitting or excessive curvature of the surface due to example “barrelling” in cold worked samples within the irradiated area will result in a systematic error similar to that caused by sample displacement [Withers et al. 2001].

3.7.1.1.4 X-ray elastic constants (XEC’s)

One of the other potential sources of error related to stress measurement by x-ray diffraction is due to the empirically determined x-ray elastic constants as shown in Equation 3-44.

$$\left( \frac{E}{1 + \nu} \right)_{\text{bulk}}$$  \hspace{1cm} \text{Equation 3-44}

The constants are determined using an instrumented 4 point bend method and are proportional to the value of the measured residual stress and can typically be determined to an accuracy of ±1%. The results may differ by as much as 40% from the bulk value due to elastic anisotropy present within the material [Prevey 1986].
aluminium alloy 7010, the elastic constants for the cubic aluminium [Cottignies & Guyot 1996] plane used are those previously determined by Hauk et al. [Hauk & Macherauch 1983].

3.7.1.5 Instrument positioning errors

Errors of ±0.025 in the alignment of the diffracting apparatus or positioning of the specimen can lead to errors in the stress measurement of up to ±14MPa. In general the x-ray diffraction technique is generally considered as a precise measurement method for the determination of residual stress.

3.7.2 Neutron Diffraction Technique for Residual Stress Analysis

The neutron diffraction technique has several advantages over the x-ray diffraction method due to the wavelength atomic spacing similarity of the lattice allowing greater penetration of the sample to the order of centimetres. Neutron diffraction studies of a 7449 aluminium alloy forging before and after cold compression as illustrated in Figure 3-36 show compressive stresses in the order of -200MPa at the surface with a gradual progression to tensile stresses towards the interior of up to 300MPa in the longitudinal direction and stresses in the short transverse of 0-100MPa following quenching [Robinson 2006]. Cold compression in the ST direction results in a significant reduction and a redistribution of the remaining residual stresses.
3.7.3 Other Residual Stress Measurement Techniques

The contour method has been shown to be particularly effective in measuring bi-axial stress distributions [Prime 2001]. Other techniques for residual stress measurement...
include holographic hole-drilling [Lu 1996; Nelson, Makino, & Fuchs 1997]. In
general residual stress measurement with any of the currently available techniques can
be expected to have uncertainties of at least 20 MPa [Lu 1996].

3.8 Review

The classical quench factor analysis model developed by Evancho and Staley [Evancho
et al. 1974] provides limited applications for property prediction where slow quench
rates (<100°C/sec) may occur such as in the centre of large forgings or where slower
cooling rates may be employed in order to reduce residual stresses or cracking. Later
models provide the possibility of applying more accurate property prediction to
situations where property loss of greater than 10% may occur. The non-isokinetic
compositional method developed by Rometch et al. [Rometsch et al. 2003] may
provide a more theoretical approach based to C-curve construction than the more
empirical approach adopted by Evancho and Staley [Evancho et al. 1974]. Also
models developed by Tiryakioglu and Shuey [Tiryakioglu & Shuey 2010a] may
address issues with respect to multiple precipitates. A statistical comparison and the
limitations of some of these methods as applied to aluminium alloy 7010 in an overaged
condition are provided in the following sections. The use of the Jominy end quench
technique is also explored as a source of continually cooled data as well as the influence
of cold compression on the resulting shape of the C-curves. A study regarding the
effect of the introduction of a natural aging step over increasing time periods prior to
cold compression and the resulting effect on residual stresses has also been investigated.
4 Experimental

In order to carry out property prediction using C-curves and evaluate the various methods required for their determination, a tensile, hardness and electrical conductivity data set for 7010 in an overaged temper was required over a range of isothermal hold temperatures and times. In order to compare isothermally held data with continuously cooled data, Jominy specimens were also prepared for analysis. The various experimental methods used for the generation of this data set (i.e. tensile, hardness and electrical conductivity) and the resulting C-curves using the various models for their production is presented, as well as experimental details in relation to sample preparation including cold compression, techniques for microscopy and residual stress measurements using x-ray diffraction.

4.1 Aluminium Alloy

All samples were prepared from a proprietary specification 7010-W52 rectilinear open die forging supplied by Mettis Aerospace U.K. The specific composition of this 7010 alloy forging is shown in Table 4-1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Zr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>7010</td>
<td>0.03</td>
<td>0.06</td>
<td>1.69</td>
<td>&lt;0.01</td>
<td>2.44</td>
<td>&lt;0.05</td>
<td>6.26</td>
<td>&lt;0.06</td>
<td>0.14</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

The forging was manufactured on a 20MN draw down hydraulic press. Heat treated and machined forgings similar to these are commercially used by Airbus to manufacture the wing spar assembly in the A330/A340 family of aircraft. The as-received forgings had dimensions 562 (L-Longitudinal) x 265 (LT-Long Transverse) x 169mm (ST-Short Transverse direction). After forging, the block had been solution heat treated at 475±2°C for 6h followed by cold compression of 2.25±0.5% on a 120MN hydraulic...
press. Both these steps were carried out in-house by Mettis Aerospace. A section of this forging as shown in Figure 4-1 was used for the current work.

Figure 4-1 Section of "as received" 7010-W52 rectilinear open die forging

4.2 C-curve Sample Preparation

Figure 4-2 Forging section
112 tensile test pieces were machined from the forging described in section 4.1. All tensile pieces were cut from the LT direction as shown in Figure 4-2. The tensile specimen sample geometry is illustrated in Figure 4-3.

![Tensile Specimen Geometry](image)

**Figure 4-3 Tensile specimen geometry**

Specimens for hardness and electrical conductivity measurements consisted of 6mm thick, 25×0.1mm square coupons cut from sections of a similar rectilinear forged block as shown in Figure 4-4. Samples were ground and polished using 400 and 1200 grit (15μm) silicon carbide grinding papers respectively to produce a uniform surface finish.
Figure 4-4   Electrical Conductivity and Vickers Hardness specimen geometry

A test matrix of temperatures versus isothermal hold times as shown in Table 4-2 based on a previously determined 7010-T6 peak aged C-curve [Robinson, Cudd, Tanner, & Dolan 2001] was constructed using temperatures ranging from 210 to 440±2°C and at isothermal holding periods from 2 to 15000 seconds.

Table 4-2  Test Matrix - Temperature versus Isothermal Hold Time

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>500</th>
<th>1500</th>
<th>5000</th>
<th>10000</th>
</tr>
</thead>
<tbody>
<tr>
<td>210</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>235</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>260</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>285</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>310</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>335</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>360</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>385</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>410</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
<tr>
<td>440</td>
<td>10</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>500</td>
<td>1500</td>
<td>5000</td>
</tr>
</tbody>
</table>

Note: Isothermal hold times do not include 2 seconds transfer time - 3 seconds to reach equilibrium

Samples were re-solution heat treated at 475±2°C for 2 hours using a Carbolite recirculating fan oven followed by isothermal heat treatment in accordance with the test matrix described in Table 4-2. This was achieved by rapid quenching into a Houghton Durlett salt bath containing approximately 60 litres of AG 140 Degussa specification sodium nitrite/potassium nitrate eutectic mixture. The transfer time was approximately 2 seconds. Salt bath temperature was monitored using an extra type K thermocouple connected to a Labview based PC temperature data recorder. Isothermal hold time
recording commenced 3 seconds after transfer to allow the sample to reach within 5°C of the target temperature. This was followed by a manually agitated cold water quench (±22°C) and artificial aging in an air circulating oven to an overaged condition (10h@120±2°C and 8h@172±2°C). As close as possible to the maximum achievable property values were also determined by solution heat treating the appropriate specimens for 2h at 475±2°C, followed by cold water quenching and overaging as previously described. The complete heat treatment schedule is shown graphically in Figure 4-5. In cases where it was not possible to commence artificial aging immediately following the quench, samples were refrigerated at -25±2°C to suppress natural aging. For each isothermal temperature the specified property was then plotted against time.

![Figure 4-5 Overaged heat treatment schedule](image)

4.3 Cooling Curve Determination

Cooling curves were determined using an embedded K-type thermocouple centrally located within a representative sample. A National Instruments high speed data...
acquisition system was employed to record the temperature data. Previous authors have shown that time intervals above 0.4 seconds may cause significant variation in the resulting quench factors, therefore time–temperature data was recorded at a frequency of 10Hz for the duration of the run and the subsequent cooling curves constructed.

The construction of the isothermal C-curves was based on cooling curves determined independently (as described above) from the actual tensile specimens used for $R_{p0.2}$ measurement using an instrumented tensile sample. Error is inherent in the method since it is impossible to duplicate the exact conditions of the quench experienced by each individual isothermal hold sample. A method to overcome this problem was developed whereby a sample and an instrumented sample of the same geometry were solution heat treated and quenched to the isothermal hold temperature or room temperature by quenching simultaneously both specimens using a specially fabricated sample holder as shown in Figure 4-6.

![Figure 4-6 Clamp for tensile specimens](image)

This simple device allowed an individual cooling curve for each tensile sample to be generated acquiring the exact thermal history of the sample. This method eliminated any problems associated with isothermal hold time corrections, salt bath temperature
variations or precipitation occurring during quenching caused by delays in quenching to
the isothermal hold temperature and/or to room temperature as well as variations
occurring due to the agitation of the quench media. This method was used to carry out
continuously cooled experiments for both tensile and hardness/electrical conductivity
square coupon specimens using a similar fixture at various furnace cooled quench rates
and as well as quenching using alternatives to cold water.

4.4 Mechanical and Electrical Characterisation

Tensile properties were determined using a Dartec 500kN servo hydraulic universal
testing machine in accordance with BS 4A 4:1966 in conjunction with an Epsilon Corp.
extensometer to measure extension. A displacement rate of 0.02mm.min\(^{-1}\) was used for
all tensile testing[BS 4A 4:1966 1966]. Hardness testing was carried out using an
block. Electrical conductivity measurements were carried out using a Verimet M-900C
conductivity meter calibrated using 7010 and 5154 standards of known %IACS
c Conductivity in accordance with ASTM E1004-02 2002 [ASTM E1004-02 2002].
Electrical conductivity, when evaluated with eddy-current instruments, is usually
expressed as a percentage of the conductivity of the International Annealed Copper
Standard (IACS). The conductivity of the Annealed Copper Standard is defined to be
5.8001\times10^7\text{S.m}^{-1} (100\%IACS) at 20°C. Where required, \%IACS was converted to
resistivity (\(\mu\Omega\text{cm}\)) using the formula:

\[
\text{Resistivity (}\mu\Omega\text{cm}) = \frac{172.41}{\%\text{IACS}}
\]

\text{Equation 4-1}
4.5 C-curve Construction

C-curves were constructed using arbitrary percentages of the maximum property value. For these experiments, C-curves were constructed for 95% and 90% and where possible 85% of the cold water quench (CWQ) property value. Using for example, 0.2% proof stress ($R_{p0.2}$) data from the 335°C isothermal hold for 7010-Overaged as shown in Figure 4-7. $R_{p0.2}$ values for 95 and 90% of the maximum attainable $R_{p0.2}$ were obtained (The maximum attainable $R_{p0.2}$ here refers to a cold water quench). For this example 95, 90 and 85% corresponds to 10, 25 and 38s respectively. This was repeated for the range of isothermal holding temperatures and provides the required critical times ($C_t$) for construction of the experimental C-curves for $R_{p0.2}$ Vickers hardness and electrical conductivity. A full description of the C-curve generation process is presented in section 5. A full step-by-step procedure using EXCEL® and Origin® software for generation of the theoretical C-curves and C-curve coefficients is available in Appendix 3.

![Figure 4-7](image-url)  
R$_{p0.2}$ vs Isothermal Hold Time at 335°C
4.6 Jominy End Quench Testing

Jominy end quench testing involves the heating of a cylindrical bar (25mm diameter and 100mm length) to the solution heat treatment temperature followed by rapid transfer to a quench fixture so that the specimen is held vertically 12.7mm above an opening where through which a stream of water is directed at the base of the specimen. This results in a controlled progressive decrease in the rate of cooling along the bar. This test has been widely used by the steel industry though has found limited use in the non-ferrous alloys area.

4.6.1 Jominy End Quench - Sample Preparation

The Jominy end quench method provides a rapid way of obtaining large amounts of thermal cooling data necessary for C-curve construction as well as providing a source of continuously cooled data for comparison with the isothermally obtained data used in classical C-curve construction. Jominy end quench samples were machined from a similar section of the forging described in section 4.1, in accordance with ASTM 255 as shown in Figure 4-8 [ASTM A 255 2007]. The machined flats corresponding to the 1 1/4 surface as indicated Figure 4-9.

Figure 4-8  Jominy End Quench Test Sample
4.6.2 Jominy End Quench – Cooling Curve Determination

Figure 4-9 Instrumented Jominy end quench sample for FE cooling C-curve determination [ASTM A 255 2007; Tanner et al. 2004]

An instrumented Jominy end quench sample prepared by previous researchers was used to obtain cooling curve data required for construction of the C-curves [Dolan, Flynn, Tanner, & Robinson 2005]. Three K-type thermocouples were positioned at 3, 38 and 78mm from the quenched end of the specimen as shown in Figure 4-9. The sample was placed in a Carbolite air recirculating oven and isothermally held at 475±2°C for 2h. The specimen was then rapidly removed (<5s) and placed in a Jominy end quench rig as described in BS EN ISO 642. The specimen remained in the fixture for 3 minutes to allow the sample to cool to room temperature. Using the recorded data, cooling curves at 2mm interval were generated by Tanner using the Finite Element (FE) method.

4.6.3 Jominy End Quench – Overaged

The Jominy end quench sample was placed in a Carbolite air recirculating oven and isothermally held at 475±2°C for 2h. The specimen was then rapidly removed (<5 s) and placed in the Jominy end quench fixture. The specimen remained in the fixture for 3 minutes to allow the sample to cool to room temperature. This was followed by artificial aging to an overaged condition as described in section 4.2. Hardness measurements were carried out on the machined L-LT surface using a Leco M-400-G1 microhardness tester under a 0.5kg load. An average of three measurements was taken.
at 2mm intervals along the length of the specimen from the quenched end. Electrical conductivity was measured by sectioning of the Jominy end specimen at 5mm intervals. Three measurements were taken on both sides of the L-ST plane section and averaged.

4.6.4 Jominy End Quench – Peak aged

The term “peak aged” in the context of this work is used for specimens that have undergone artificial aging, which, under commercial quenching and aging procedures would result in the maximum hardness and tensile strength for the alloy. In this case the specimen was subjected to a single stage heat treatment of 120°C for 24h. The Jominy end quench testing procedure and Vickers hardness measurements were carried out as described above in section 4.6.3.

4.6.5 Jominy End Quench – Cold Compressed+Overaged

A Jominy specimen with pre-machined flats as shown in Figure 4-9 was used for producing a specimen in the cold compressed condition. This was achieved by using the same heat treatment procedure as that used for the overaged specimen but with the addition of a cold compression step introduced after quenching in the Jominy end quench fixture. Cold compression was carried out as soon as possible (~1 min.) after Jominy end quenching to minimise any effects due to natural aging. 2.25±0.1% compression was carried out in the ST direction using the Dartec universal testing machine as described in section 4.7, using two mild steel platens and a light machine oil (3-in-one®) to reduce interfacial friction. Artificial aging was carried out as described for the overaged Jominy specimen in section 4.6.3.

4.6.6 Isothermal σ\text{min} Determination - Overaged

In order to produce the isothermal equilibrium data required for the determination of the σ\text{min} values for C-curve construction using the non-isokinetic methods in the overaged
condition, twelve samples having the same cross sectional geometry as the Jominy end specimen (Figure 4-9) were placed in an air recirculation furnace at 475±2°C for 2h followed by incremental cooling from 440 to 210±2°C in 8 decreasing temperature intervals. Each isothermal hold was maintained for 24h after which time, the samples were assumed to have reached a steady state equilibrium. one sample was subsequently removed, cold water quenched and stored at -25±2°C until artificial aging could be carried out.

4.6.7 Isothermal $\sigma_{\text{min}}$ Determination - Cold Compressed+Overaged

In order to produce the isothermal data required for the determination of the $\sigma_{\text{min}}$ values and $\Delta$-curve construction in the overaged and cold compressed condition, twelve samples having the same cross sectional geometry as the Jominy end specimen (Figure 4-9) were placed in an air recirculation furnace at 475±2°C for 2h followed by incremental cooling from 440 to 210±2°C in 8 decreasing temperature intervals. Each isothermal hold was maintained for 24h after which time the samples were assumed to have reached equilibrium. one sample was subsequently removed and cold water quenched. After quenching, the sample was rapidly transferred to the Dartec universal testing machine for 2.25±0.1% cold compression followed by overaging. The transfer time from quenching, through the cold compression step to the commencement of artificial aging was less than 3 minutes to minimise the affect of natural aging. Sample surfaces were lubricated using a light machine oil to reduce interfacial friction between the specimen and the compression platens. A preload of 2kN was used for all samples. Samples were deformed in the ST direction at a rate 0.033m/min until the limit of proportionality was deemed to have been reached. Using the Data Manager component of the Dartec control software, the elastic strain component ($\epsilon_{\text{el}}$) was determined, and
the additional deformation calculated to provide the required 2.25±0.1% plastic deformation.

4.7 Natural Aging and Cold Compression - Sample Preparation

Samples blocks of 25 (L,T) x 25 (ST) x 35mm (L), were cut from a similar open die W52 forging to that used for the preparation of the C-curves (section 4.2). The sample size used was based on the limited load capacity of the servo hydraulic test equipment used for compression (500kN). Samples were solution heat treated at 475+2°C for 2h followed by quenching into cold water (RT). Samples were naturally aged for periods from 3 to 66240min. (~6 weeks) followed by cold compression. As with the isothermal samples, compression was carried out in the ST direction to provide the required 2.25±0.1% plastic deformation as shown in Figure 4-10 and Figure 4-11. A similar procedure was used for the Jominy samples.

Figure 4-10 Cold compression samples

Figure 4-11 Sample set-up - Dartec
500kN universal testing machine
4.8 The effect of varying % cold compression on residual stress magnitudes

A set of sample blocks were prepared similar to those previously described in section 4.7. Samples were solution heated treated at 475±2°C, cold water quenched and compressed in the ST direction to between 1 and 5±0.1% within 3 minutes of quenching. This experiment was to determine the effect of different levels of cold compression on the resulting residual stress magnitudes on both the L-I.T and L-ST surfaces.

4.9 X-Ray Diffraction Technique for Residual Stress Analysis

Residual stress measurements were carried out using a Philips X’pert x-ray diffractometer in conjunction with Philips PC-APDW (version 4.0e) software. The following scan parameters were used for all measurements (Table 4-3):

Table 4-3 X-ray diffraction analysis scan parameters for residual stress measurements (PC-APDW)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Notes/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength $K_u$ ($\lambda$)</td>
<td>1.54056</td>
<td>Recommended for Aluminium Alloys</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Cottignies et al. 1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Fitzpatrick et al. 2005]</td>
</tr>
<tr>
<td>Irradiated Length (mm)</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Minimum start angle (°2Theta)</td>
<td>136.013</td>
<td></td>
</tr>
<tr>
<td>Maximum end angle (°2Theta)</td>
<td>138.988</td>
<td></td>
</tr>
<tr>
<td>Step size (°2Theta)</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>Time per step size (s)</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Number of scans</td>
<td>16</td>
<td>Recommend ~5 [Fitzpatrick et al. 2005]</td>
</tr>
<tr>
<td>$\psi$ (°)</td>
<td>0°-60°</td>
<td>Positive tilting only</td>
</tr>
</tbody>
</table>

Samples were cleaned using a pH neutral cleaning solution in an ultrasonic bath for 15 minutes to remove any surface contamination and oil residues from the cold compression stage, no further sample surface preparation was deemed necessary [Prevey 1986]. The midpoint of the sample face to be measured was identified and the
sample secured to the flat multipurpose type PW1821 stage with the specimen 1.
direction parallel to the incident x-ray beam. Measurements were carried out at two
locations: 1) the 1-T-T face in immediate contact with the compression platens and 2)
the 1-ST face, a free surface parallel and adjacent to the first. The height of the sample
was adjusted using a precision dial gauge (±0.002 mm). The 20 angles selected:
136°-20°-139° were chosen to encompass the Cu-Kα doublet for the [Cottignies et al.
1996] planes. Based on an optimum scan arrangement and setup parameters for
residual stress in aluminium alloys as determined by previous investigations, 16 scans
were performed at the midpoint of each sample at ψ angles of 0°, 12.92°, 18.43°, 2.79°,
26.57°, 30.00°, 33.21°, 36.27°, 39.23°, 42.13°, 45.00°, 47.87°, 50.77°, 53.73°,
56.79° and 60.00° respectively [Tanner 1999]. Positive ψ angles were used for all
measurements due to the negative angle movement restriction of the goniometer. The
x-ray diffraction spectra was analysed using Residual Philips PC-Stress Software
(Version 2.61) using the parameters outlined in Table 4-4.

<table>
<thead>
<tr>
<th>Parameter/Analysis options</th>
<th>Value</th>
<th>Recommendations /reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>XEC Constants S&lt;sub&gt;1&lt;/sub&gt;</td>
<td>4.97 x 10&lt;sup&gt;-12&lt;/sup&gt; (m&lt;sup&gt;2&lt;/sup&gt;N&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>[Noyan &amp; Cohen 1987]</td>
</tr>
<tr>
<td>Aluminium ½S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>19.07 x 10&lt;sup&gt;-12&lt;/sup&gt; (m&lt;sup&gt;2&lt;/sup&gt;N&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>[Noyan &amp; Cohen 1987]</td>
</tr>
<tr>
<td>Stress Analysis Method</td>
<td>Sin ψ</td>
<td></td>
</tr>
<tr>
<td>Background correction</td>
<td>Linear</td>
<td></td>
</tr>
<tr>
<td>Lorentz-polarisation</td>
<td>On</td>
<td></td>
</tr>
<tr>
<td>Kα₂ Stripping</td>
<td>On</td>
<td>[Noyan &amp; Cohen 2006]</td>
</tr>
<tr>
<td>Absorption Correction</td>
<td>On</td>
<td></td>
</tr>
<tr>
<td>Peak Position Calculation</td>
<td>Pearson VII</td>
<td>[Prevey 1986]</td>
</tr>
</tbody>
</table>
The elastic constants (XEC) used were taken from the literature [Noyan & Cohen 1987]. Shearing stresses were assumed to be negligible when compared with normal stress magnitudes. For statistical purposes, all measurements were repeated a minimum of 3 times. Peak positions were calculated using a Pearson VII fit.

4.10 Optical Microscopy

Samples for optical microstructural analysis were sectioned using a Buehler Isomet precision diamond saw from the heads of the tensile specimens used for yield strength determination. The cut specimens were mounted in conductive Bakelite resin followed by grinding and polishing using a Buehler Motopol 2000 using the procedure outlined in Table 4-5.

<table>
<thead>
<tr>
<th>Buehler Surfaces</th>
<th>Abrasive/Size</th>
<th>Load (N)</th>
<th>Base Speed (rpm)/Direction</th>
<th>Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbimet ULTRA-POI</td>
<td>220-320 (grit) SiC 6μm diamond</td>
<td>22</td>
<td>250 / comp.</td>
<td>Until Plane</td>
</tr>
<tr>
<td>Trident</td>
<td>3μm diamond</td>
<td>27</td>
<td>150 / comp.</td>
<td>6</td>
</tr>
<tr>
<td>Nanocloth</td>
<td>0.05μm Mastermet colloidal silica</td>
<td>27</td>
<td>150 / contra.</td>
<td>4</td>
</tr>
</tbody>
</table>

All samples were subsequently etched using orthophosphoric acid and Keller's Reagent.

4.11 Transmission Electron Microscopy

Samples for transmission electron microscopy were prepared by cutting 3mm slices from the Jonny end quench specimens using a Buehler ISOMET precision saw. These slices were then mounted individually into a handheld milling device and ground to approximately 200μm thick using 1200 grit silicon carbide grit paper. Disks of diameter 3mm were then punched from these slices and further ground down using
another milling jig to a thickness of between 50 and 75 µm. This was followed by thinning to the required electron transparency thickness by electropolishing in a 30% nitric/methanol solution cooled to -20°C. Samples were examined using a Jeol 2010 TEM operated at 200 kV. The electron beam axis was perpendicular to the 1-ST plane.

4.12 Scanning Electron Microscopy

Scanning electron microscopy was carried out using a Jeol 840 Electron Microscopy in conjunction with a PGT elemental analyser (EDX). Samples for microstructural analysis were prepared by mounting in conductive Bakelite and polished in accordance with the regime outlined in section 4.10-Table 4-5. Fracture surfaces were cleaned using isopropyl alcohol prior to examination.
5 Results and Discussion

5.1 Maximum Achievable Property Values

In order to determine the maximum achievable property values for 7010 in the overaged condition, three samples of both the tensile and hardness/electrical conductivity geometries were prepared and subsequently tested using the methods outlined in section 4.4. After solution treatment at 475±2°C, rapid quenching in cold water (-22°C) and aging to an overaged condition using the overaging procedure described in section 4.3, the average (3 samples) maximum attainable Rp0.2 (σmax) and hardness (HV3000) obtained was 524MPa and 189.7Hv3000 respectively. One example of the engineering stress vs engineering strain, tensile test curve obtained for 7010-Overaged is shown in Figure 5-1.

![Tensile Test Curve - 7010-Overaged](image)

The average minimum electrical conductivity obtained was 37.2%IACS (or a maximum resistivity 4.63x10^-6Ωm). The term "maximum" used here and throughout the course of this work refers to the maximum achievable values that it was possible to obtain.
using a cold water quench using the standard geometry test pieces described in Section 4.2 and the laboratory facilities available. These "maximum" property values were used for all subsequent averaged sample calculations.

5.2 Isothermal Quench Cooling Curves

The isothermal quench cooling curves obtained for both tensile and hardness/electrical conductivity sample geometries, solution treated at 475°C ± 2°C and salt bath quenched to the isothermal hold temperatures ranging from 210°C to 440°C ± 2°C are shown in Figure 5-2 and Figure 5-3 respectively. The isothermal hold time recorded for the purpose of these experiments was commenced 3 seconds after quenching to allow the sample to reach within 5°C of the isothermal hold temperature. As can be seen from Figure 5-2 and Figure 5-3, the actual time required for the samples to reach the actual isothermal hold temperatures was in the region of 20-25s.

![Figure 5-2 Tensile specimen - isothermal quench cooling curves](image-url)
This approach can cause errors at the lower temperatures as the sample may not have reached within 5°C of the isothermal holds but was considered the best approach as the duration isothermal hold times were longer (>50 seconds) at the lower and higher temperatures compared to the nose of the curve where the precipitation rate is at its maximum so the effect on the final C-curve was considered minimal.

Other researchers have used aluminium "sheet" where available in order to increase the quench rate to the isothermal hold temperature.

![Graph showing temperature and time correlation](image)

Figure 5.3 Hardness/Electrical Conductivity specimen - isothermal quench cooling curves

5.3 Tensile - Rp0.2

This section presents the acquired tensile data and the construction of the 0.2% proof stress (Rp0.2) C-curve for 7010 in the averaged condition.

5.3.1 Rp0.2 - Isothermal Hold Data

Table 5-1 7010-Overaged - Rp0.2 data (MPa) for T=210-440±2°C (σ_max=524MPa)
Table 5-1 shows the measured $\sigma_{p0.2}$ data obtained for 7010 in the averaged condition at temperatures ranging from 210-440±2°C at isothermal hold times of between 2 and 10000s. $\sigma_{p0.2}$ (MPa) versus isothermal hold time (s) was plotted for each isothermal hold temperature. Figure 5-1, as an example, illustrates the response of the alloy after a quench from the solution heat treatment temperature of 475±2°C to an isothermal hold at 310±2°C. Here we can observe a steady decrease in the measured 0.2% proof stress of the alloy from a maximum of 498MPa at 2s to 190MPa at 500s corresponding to over a 60% loss in strength being measured as the isothermal hold time is increased. This is due to the increasing loss in solute over time at the isothermal hold temperature as described previously in section 3.2.2.2. Slow quenches allow precipitation of coarse non-strengthening precipitates with a consequential depletion of the overall solute, which is then unavailable for the precipitation of the hardening phases during the aging.
process. This loss in strength is observed at various degrees depending on the temperature and the duration of the isothermal hold.

![Graph](image)

**Figure 5-4**  \( R_{p0.2} \) vs Isothermal hold time for 7010-Overaged at 310°C

These plots were used to graphically calculate the time for the alloy to reach 95%, 90% and 85% \( R_{p0.2} \) of the maximum \( R_{p0.2} \). The full set of \( R_{p0.2} \) isothermal hold data for 7010 in the overaged condition at isothermal hold temperatures from 210 to 440±2°C is shown below in Figure 5-5. No error bars are presented due to limitations on the availability of tensile test specimens.
Figure 5.5  $R_{p0.2}$ vs isothermal hold time for T=210 to 440±2°C for 7010-Overaged
5.3.2 Experimental $R_{p0.2}$ C-curves

Using the data obtained in section 5.3.1 in conjunction with the polynomial curve fitting function in Microsoft EXCEL®, the time required to reach 90 and 95% of the maximum $R_{p0.2}$ ($\sigma_{\text{max}}$) was determined allowing the construction of Time-Temperature-Property or C-curves. Experimentally generated C-curves for 90 and 95% of the maximum obtainable $R_{p0.2}$ for 7010-Overaged are shown in Figure 5-6.

![C-curve for 7010-Overaged](image)

**Figure 5-6  Experimental C-curve $R_{p0.2}$ 7010-Overaged**

The resulting isothermal hold time versus temperature data illustrates the characteristic C-shaped TTP curve, the C-curve deriving its shape from competition between the processes of nucleation and diffusional growth. At the lower temperatures, below the nose of the C-curve, the undercooling and, hence the driving forces for nucleation are high; however, diffusion and growth are relatively slow. At higher temperatures, above the nose of the C-curve, diffusion is faster but nucleation more difficult [Sawtell 1984]. It has been shown that the accuracy of this method is excellent as long as the property under examination remains above approximately 85% of the maximum attainable value.
Using data below this value sees the accuracy of the Staley developed classical method of Quench Factor Analysis decrease. The experimental curves also show the possibility of the effect of multiple precipitates (multiple noses). This is discussed further in section 5.9.5.2.

5.4 Vickers Hardness -(Hv)

This section presents the acquired Vickers hardness (HV20) data and the construction of the Vickers harness C-curve for 7010 in the overaged condition.

5.4.1 Vickers Hardness- Isothermal Hold Data

Table 5-2 Table 5-2 shows the average measured HV20 data for 7010-Overaged at temperatures ranging from 210-440±2°C at isothermal hold times of between 2-10000s.

Table 5-2 7010-Overaged HV20 data- (Avg. of 3 Indentations) T=210-440±2°C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>75</th>
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<th>1500</th>
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<td>171'</td>
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</table>

* No data or test failure; 's=15 seconds, '2000, '15000s
Figure 5-7 illustrates the hardness response of the alloy in the overaged condition after a quench from the solution heat treatment temperature of 475±2°C to an isothermal hold at 310±2°C.

![Hardness Response Graph](image)

**Figure 5-7  HV20 vs Isothermal hold time at 310±2°C for 7010-Overaged**

In a similar response to the Rpo.2 experimental results we observe a steady decrease in the measured Vickers hardness of the alloy in the overaged condition from 181HV20 at an isothermal hold time of 3s to 109HV20 at 500s due to the reduction of solute and precipitation of non-strengthening precipitates. This reduction in hardness is due to the precipitation of the coarse equilibrium η phase precipitate and parallels the measured reduction with Rpo.2 with increasing isothermal hold duration. The full set of hardness data acquired over the temperature range 210-440±2°C is shown in Figure 5-8.
5.4.2 Experimental Hardness C-curves

Figure 5-9 shows the subsequently developed experimental C-curves for 90 and 95% of the maximum achievable $HV_{20}$ using the same method as described in section 5-3. Again the curves show the possibility of the effect of multiple precipitates (multiple noses). If we assume a yield strength:Vickers hardness ratio of 3:1, 90 and 95% of the maximum achievable hardness or 10 and 5% loss in hardness corresponds to approximately 56.9 and 28.4MPa respectively.
5.5 Electrical Conductivity - %IACS

This section presents the acquired electrical conductivity data and the construction of the electrical conductivity C-curve for 7010 in the overaged condition.

5.5.1 Electrical Conductivity Isothermal Hold Data

Table 5-2 shows the average (3 measurements) measured electrical conductivity (%IACS) vs isothermal hold time (s) for 7010-Overaged at temperatures ranging from 210-440±2°C at isothermal hold times of between 2 and 10000s.

Table 5-2 7010-Overaged Electrical Conductivity (%IACS) data—(Avg. of 3 Indentations) for T=210-440±2°C

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<th>Isothermal Hold Time (s)</th>
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- No data or test failure: 7*15 seconds, 2690, 15000s

Figure 5-10 shows an example of electrical conductivity (%IACS) vs isothermal hold time (s) for 7010-Overaged isothermally held at 310±2°C. An increase in electrical conductivity is observed from 38% IACS at 3s to 41.9%IACS at 500s. The electrical
conductivity increases over time as opposed to the mechanical properties which decrease as the isothermal hold time is increased.

![Electrical Conductivity and Resistivity Graph](image)

**Figure 5-10** Electrical Conductivity (%IACS) and Resistivity (Ωmx10⁻⁸) vs Isothermal Hold Time (s) for 7010-Overaged at 310±2°C

This is due to the depletion of the solute which increases the conductivity (or decreases the resistivity) of the matrix. In this example at 310±2°C where the precipitation rate is close to its maximum at the peak of the C-curve, the change in the electrical conductivity with increasing isothermal hold duration is rapid (~2%IACS in ~200s).

The full electrical conductivity data set acquired over the temperature range 210-440±2°C is shown in Figure 5-11. All the electrical conductivity versus isothermal hold time plots follow the same trend, i.e. increasing conductivity (decreasing resistivity) with increasing isothermal hold time. An increasing electrical conductivity represents a decrease in the level of solute remaining as the alloying elements precipitate out of the solid solution with increasing isothermal hold time.
In the case of 7010, this is due to precipitation of coarse incoherent non-hardening phases (η, S and T phases) causing a depletion of solute from the matrix increasing the electrical conductivity but reducing the mechanical properties of the alloy.

5.5.2 Experimental Electrical Conductivity/Resistivity C-curves

Figure 5-12 Experimental C-curve - Electrical Conductivity %IACS for 7010-Overaged for 95% of the maximum attainable electrical resistivity converted to conductivity (%IACS)
Figure 5-12 shows the generated C-curve for 95% of the maximum attainable electrical resistivity converted to conductivity (35.3% IACS). As the percentage change of electrical resistivity with respect to the maximum attainable electrical resistivity was less than 10%, it was not possible to generate a complete curve based on 90% or less of the maximum electrical resistivity. As with the yield strength and Vickers hardness data, due to the rapid change in conductivity at some temperatures (i.e. nose of the C-curves), it was not possible to produce C curves experimentally at 99% or above, neither was it possible to produce a 90% experimental C-curve due to the limited change in electrical conductivity over the duration of the isothermal holds. On comparison with the $R_{p0.2}$ and Vickers Hardness C-curves, we see signs of multiple noses as highlighted in Figure 5-12. Again, this would indicate the possible precipitation of multiple phases during the quench.

### 5.6 C-curves - Summary

From the generated experimental C-curves we can observe and deduce that at the higher isothermal hold temperatures (>~335°C) essentially all the solute is maintained in solution at the end of the quench at the shorter isothermal hold times. At temperatures close to the nose of the C-curve solute is lost quite rapidly from the alloy because some of the solute has precipitated out as heterogeneous precipitates, fewer vacancies are being retained which, results in less GP zone formation and the subsequent precipitation of the hardening phases during aging thus reducing the measured $R_{p0.2}$ and $Hv_{50}$. The higher level of quench induced precipitation also results in a higher electrical conductivity. At the nose of the curve (~335°C), there is a rapid decrease in mechanical properties with up to a 49% loss in $R_{p0.2}$ at occurring at a 100s hold time. At increasing isothermal hold times, the mechanical properties are further reduced with a corresponding increase in electrical conductivity, as there are essentially no sites
available for precipitation of the strengthening η' phase during the subsequent artificial aging. At temperatures below the nose of the curve (<-335°C), the diffusion rate is slow hence a slower precipitation rate despite the high degree of supersaturation. C-curves indicate that for commercial operations, the quenching rate can be decreased near the solution heat treatment temperature without unduly affecting the mechanical properties. They allow the development of cooling curves which can provide a large portion of the quench where critical times are short in order to obtain the desired mechanical properties and/or reduction in residual stresses. These experimentally derived C-curves provide the basis for property prediction in the following sections using Quench Factor Analysis.

5.7 Theoretical C-curve Determination

Theoretical C-curves for 90%, 99% and 99.5% of the maximum attainable R_p0.2 and Vickers hardness and the minimum electrical conductivity were determined by using the 95% experimental C-curve data obtained in sections 5.3, 5.4 and 5.5. followed by fitting to the C-curve equation using the regression function in Microsoft EXCEL®. The classic C-curve equation is shown in Equation 5.1.

$$C_1(T) = -k_1 k_2 \exp\left(\frac{k_2 k_{z}^{2}}{RT(k_z - T)^2}\right) \exp\left(\frac{k_2}{RT}\right)$$  \hspace{1cm} \text{Equation 5-1}

In order to simplify and use the EXCEL® regression function, logs of both sides of the equation 5.1 was obtained and rearranged to give:

$$\log C_1(T) = \log(k_1 k_2) + \left(\frac{k_2 k_{z}^{2}}{RT(k_z - T)^2}\right) + \left(\frac{k_2}{RT}\right)$$  \hspace{1cm} \text{Equation 5-2}

Rearranging:
\[
\log C_r(T) = \log(k_1k_2) + \frac{k_1}{RT} \left[ \frac{1}{(1-k_4T)^2} \right] + \frac{k_3}{R \left[ \frac{1}{T} \right]}
\]

**Equation 5-3**

This provides three distinct variables for use with the regression analysis function in the form of two X-variables: \[\frac{1}{T}\] and \[\frac{1}{(1-k_4T)^2}\], and one Y variable: \[\log C_r(T)\].

A value approximating the solution heat treatment temperature was chosen for \(k_4\) and adjusted until the best fit was obtained, regression analysis providing the values for the remaining coefficients. A detailed procedure using Microsoft EXCEL® for this method is presented in Appendix 3. The values obtained using this method for coefficients \(k_2\), \(k_3\), \(k_4\), and \(k_5\) from equation 5-1 are shown in Table 5-4 for Rp0.2, hardness (Hv20) and electrical conductivity respectively.

**Table 5-4 Coefficients \(k_2\), \(k_3\), \(k_4\) and \(k_5\) for Rp0.2 7010-Overaged Curve Fitting Method**

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<th>(k_2) (\text{J.mol}^{-1})</th>
<th>(k_3) (\text{J.mol}^{-1})</th>
<th>(k_4) (\text{K})</th>
<th>(k_5) (\text{J.mol}^{-1})</th>
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<td>Hv20</td>
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<td>2.19E+03</td>
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</table>

These coefficients were then used for the construction of C-curves for 90, 95 and 99.5% of the maximum property values. It was observed that the values obtained for \(k_4\) using this method were notably higher than the solvus temperature for the \(\eta\) phase of 713K and the values for \(k_3\) substantially lower. The values for \(k_5\) which is related to the activation energy for diffusion also vary considerably from between 126000 J.mol\(^{-1}\) to 190000 J.mol\(^{-1}\). The activation energy for Cu and Mg in Al are 133,000 J.mol\(^{-1}\) and 136000 J.mol\(^{-1}\) respectively. Figures 5-13, 5-15 and 5-16 show the experimental and predicted C-curves based on the derived \(k_2\)-\(k_5\) constants obtained for Rp0.2, Hv20 and electrical conductivity of 7010-Overaged using this method.
From Figure 5-13 we can see a good fit of the experimental data to the predicted C-curve for 95% of the maximum attainable hardness. The nose of the curve occurs at -335°C and at a critical time of 0.3s. The fit for 90% of the maximum achievable Rp0.2 is not as good.

Figure 5-14 Comparison of Rp0.2-C-curves for 7000 series alloys.
Figure 5-14 shows a comparison of the obtained C-curve with respect to other 7000 series alloys and tempers. We can observe that the overaged 7010 (designated 7010-T76 in Figure 5-14) is less quench sensitive when compared to some other 7000 series alloys such as 7075-T73 but very similar to the compositionally analogous 7050-T76.

Figure 5-15 shows the C-curve obtained for Vickers Hardness in the overaged condition with the peak of the curve occurring at 325°C which is 10°C lower than observed for \( \text{R}_e \). This slight deviation maybe due to strain hardening at the indenter/metal interface as outlined earlier [Tiryakioglu et al. 2000]. We also see a much poorer fit for the 90% of the maximum attainable hardness compared to the 95% curve. This again highlights the issue with respect to the decreasing accuracy of the method as the % of the maximum achievable property decreases.

Figure 5-15  Hardness Hv210 C-curves for 7010-Overaged

Figure 5-16 shows the 99 and 99.5% theoretical deduced electrical conductivity C-curves for 7010 in the overaged condition.
Figure 5-16  Electrical Conductivity C-curves for 7010-Overaged

Though the hardness and electrical conductivity C-curves as plotted in figures 15 and 16 show C-curves for equal amount of % property loss, they do not represent the same level of precipitation. For example using the data set for the combined hardness/electrical conductivity specimen, at 310°C, a loss of Vickers hardness of 8.27% corresponds to a loss of only 3.37% in resistivity for the same level of precipitation as both properties were measured on the same sample.

5.8 Quench Factor Determination

Quench factors were determined using the combination of the acquired cooling curves and the mathematically generated C-curves as described in Figure 3-24 in section 3.5.2.3. The $C_t$ (critical time) at each temperature is calculated by taking the average temperature over each individual time step from the cooling curve. Then using the previously derived C-curve, the corresponding $C_t$ at that temperature is determined. The time interval $\Delta t$ is subsequently divided by the critical time $C_t$ to calculate the incremental quench factor ($q$). The summation of these incremental quench factors
gives the overall quench factor \((Q\) or \(\tau\)) as the part is cooled through the critical temperature range. For 7010, this has been determined as 425-150°C. This is summarised in the following equation:

\[
\tau = \sum_{i=1}^{n} \frac{\Delta t_i}{C_i(T)}
\]

*Equation 5-4*

The length of the time step \((\Delta t)\) has been shown to have an influential effect on the calculated quench factor. Time intervals of under 0.4s seem to have a negligible effect on the resulting quench factors however; intervals over 0.4s have been shown to cause large variations in the calculated quench factors. In these experiments a time interval of 0.1s was used for all the cooling curves [Totten, Webster, & Bates 2003b] except for isothermal hold times over 5000 seconds where an interval of 0.2s was used due to the large amount of generated data and subsequent calculations required. In order to confirm the accuracy of this method, a range of continuous quenches using alternative quenchants i.e. decreasing cooling rates was carried out.

![Quench paths for tensile specimens using various quenchants](image)

*Figure 5-17* Quench paths for tensile specimens using various quenchants
Quench paths for tensile specimens were obtained using a selection of quench media including cold water (CWQ), hot water (80°C), boiling water, carbonated water, oil, air, and furnace cooled (O temper) as shown in Figure 5-18 with the resultant quench rates varying from 301.5°C.sec⁻¹ for cold water to 0.14°C.sec⁻¹ for furnace cooling over the range 450-150°C shown in Table 5-5.

**Table 5-5**  Quench rates (450-150°C) using different quench media.

<table>
<thead>
<tr>
<th>Quenchant</th>
<th>Quench Rate (°C.sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Water Quench</td>
<td>301.5</td>
</tr>
<tr>
<td>Carbonated Water</td>
<td>132.3</td>
</tr>
<tr>
<td>80°C</td>
<td>126.3</td>
</tr>
<tr>
<td>Oil – Agitated</td>
<td>73.8</td>
</tr>
<tr>
<td>Boiling Water Quench</td>
<td>28.6</td>
</tr>
<tr>
<td>Air- Agitated</td>
<td>1.6</td>
</tr>
<tr>
<td>Furnace cooled</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Using the method described above, quench factors were obtained for a range of continuous cooling quench paths as shown in Table 5-6 with the corresponding measured and predicted $R_{p0.2}$.

**Table 5-6**  Quench Factors and $R_{p0.2}$ predictions for various quench paths

<table>
<thead>
<tr>
<th>Quenchant</th>
<th>Quench Factor</th>
<th>Measured $R_{p0.2}$ (MPa)</th>
<th>Predicted $R_{p0.2}$ (MPa)</th>
<th>Measured $R_{p0.2}$ as % of $R_{p0.2}$ max</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Water Quench (CWQ)</td>
<td>0.80</td>
<td>524</td>
<td>524</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Carbonated Water Quench</td>
<td>1.31</td>
<td>521</td>
<td>522</td>
<td>99.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Hot Water Quench (80°C)</td>
<td>1.49</td>
<td>520</td>
<td>520</td>
<td>99.2</td>
<td>0</td>
</tr>
<tr>
<td>Oil – (Agitated)</td>
<td>2.34</td>
<td>518</td>
<td>499</td>
<td>98.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Boiling Water Quench (BWQ)</td>
<td>9.46</td>
<td>500</td>
<td>497</td>
<td>95.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Air (agitated)</td>
<td>148.6</td>
<td>353</td>
<td>249</td>
<td>67.3</td>
<td>29.5</td>
</tr>
<tr>
<td>Furnace Cool (O)</td>
<td>3274.2</td>
<td>128</td>
<td>0</td>
<td>24.4</td>
<td>-</td>
</tr>
</tbody>
</table>

As we can observe, the calculated quench factor describes the severity of the quench with a cold water quench (CWQ) having a quench factor of less than 1, while an agitated air cooled quench produces a quench factor of 148. The accuracy of the model...
is within ±1 MPa for the measured Rp0.2 above 90% of the maximum achievable Rp0.2. For values of below ~90%, in this case 47.5 and 24.4% for the air cooled and furnace cooled quenches respectively, the predicted property values deviate substantially from the measured values. In general, we see that as that as the quench factor increases, the model loses validity, which, is very evident on examination of the furnace cooled sample (O temper) where an unrealistic Rp0.2 of 0 MPa is predicted. Table 5-7 and Table 5-8 show the predicted Vickers hardness and electrical conductivity respectively and the equivalent quench factors.

Table 5-7  Quench Factors and Hv20 predictions for various quench paths

<table>
<thead>
<tr>
<th>Quench Factor</th>
<th>Measured Hv20</th>
<th>Predicted Hv20</th>
<th>Measured as % of Hv20max</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Water Quench (CWQ)</td>
<td>1.26</td>
<td>188</td>
<td>189</td>
<td>99.1</td>
</tr>
<tr>
<td>Carbonated Water Quench</td>
<td>2.10</td>
<td>187</td>
<td>188</td>
<td>98.6</td>
</tr>
<tr>
<td>Hot Water Quench (80°C)</td>
<td>2.45</td>
<td>186</td>
<td>187</td>
<td>98.9</td>
</tr>
<tr>
<td>Oil – (Agitated)</td>
<td>4.14</td>
<td>186</td>
<td>186</td>
<td>98.0</td>
</tr>
<tr>
<td>Boiling Water Quench (BWQ)</td>
<td>7.08</td>
<td>181</td>
<td>183</td>
<td>95.4</td>
</tr>
<tr>
<td>Air (agitated)</td>
<td>254.44</td>
<td>110</td>
<td>53</td>
<td>58.0</td>
</tr>
</tbody>
</table>

Table 5-8  Quench Factors and Electrical Conductivity predictions for various quench paths

<table>
<thead>
<tr>
<th>Quench Factor</th>
<th>Measured EC (%IACS)</th>
<th>Predicted EC (%IACS)</th>
<th>Measured as % of ECmax</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Water Quench (CWQ)</td>
<td>0.07</td>
<td>37.5</td>
<td>37.2</td>
<td>100.8</td>
</tr>
<tr>
<td>Carbonated Water Quench</td>
<td>0.12</td>
<td>38.1</td>
<td>37.2</td>
<td>102.4</td>
</tr>
<tr>
<td>Hot Water Quench (80°C)</td>
<td>0.15</td>
<td>38.0</td>
<td>37.2</td>
<td>102.2</td>
</tr>
<tr>
<td>Oil – (Agitated)</td>
<td>0.20</td>
<td>38.0</td>
<td>37.2</td>
<td>102.2</td>
</tr>
<tr>
<td>Boiling Water Quench (BWQ)</td>
<td>0.49</td>
<td>38.5</td>
<td>37.3</td>
<td>103.5</td>
</tr>
<tr>
<td>Air (agitated)</td>
<td>12.49</td>
<td>41.7</td>
<td>39.6</td>
<td>112.1</td>
</tr>
<tr>
<td>Furnace Cool (O)</td>
<td>32.58</td>
<td>43.3</td>
<td>38.0</td>
<td>116.4</td>
</tr>
</tbody>
</table>

We can see that again for the lower quench factors (Boiling Water Quench = 7.08), the accuracy of the method is good (within ~2Hv20) but again large deviations (>50Hv20 for
air and furnace cooled samples) are observed for the less than 90% of the maximum achievable hardness.

5.9 C-Curves

This method of C-curve construction suffers from several drawbacks. In order to produce an ideal quench (i.e. a quench at an infinitely fast rate), the samples need to be quenched as fast as possible to the isothermal quench temperature. In practise, this is rarely achievable due to the inherent delay in transferring the sample from the heat treatment furnace to the quench media. For an alloy such as 7075, it has been recommended that the cooling rate to the isothermal hold temperature should be as high as 300°C/sec. at the nose of the curve; however, as we can see from the specimen cooling curves (Figure 5-2 and Figure 5-3), it takes a finite time for the samples to reach thermal equilibrium. To overcome this, a time allowance of 3s was made to allow the sample to reach within 5°C of the isothermal hold temperature. It is inevitable that precipitation will occur during this period. As we can see from the tensile C-curve (Figure 5-9) the critical time and hence the cooling rate required for maximum precipitation at the nose of the curve is <1 second which in a laboratory or an industrial environment practice is very difficult to achieve, this is why a 95% of the maximum property is used experimentally to extrapolate theoretical curves for values above 95%.

If we utilise the C-curve coefficients shown in Table 5-4 as determined using the method described in section 4.5 to generate the quench factors and hence the predicted Rp0.2 values for the complete isothermal data set, large deviations were observed between the actual and predicted values for a significant proportion of the experimental data set. This method also has limitations in that the C-curve obtained is based on fitting a curve to data fitted above 90% of the maximum achievable yield strength which has been suggested is the maximum theoretical limit for Quench Factor Analysis.
for $\sigma_{\text{min}}=0$ ignoring data obtained where the loss in strength is less than 90% [Staley \& Tiryakioglu 2001]. This is illustrated in Figure 5-18 where the Measured versus Predicted $R_{p0.2}$ as a % of the maximum attainable $R_{p0.2}$ are plotted and in Figure 5-19 where the Quench Factor $\tau$ is plotted against measured $R_{p0.2}$ for averaged 7010.

![Figure 5-18 Predicted $R_{p0.2}$ as % of $R_{p0.2\text{(max)}}$ vs measured $R_{p0.2}$ as % of $R_{p0.2\text{(max)}}$](image1)

![Figure 5-19 Measured $R_{p0.2}$ vs Quench Factor Curve Fitting Method $\sigma_{(\text{min})}=0$](image2)
The curve represents values predicted in accordance with the QFA model, while the points represent the measured Rp0.2. From this data we can see that the correlations between the predicted and the measured values are poor beyond 10% loss in property (~470MPa). In order to produce a more realistic C-curve, predicted values were plotted against measured Rp0.2 and the EXCEL® solver function was used to determine optimum values for k2-k3 in order to improve the correlation between the measured and the predicted Rp0.2. The EXCEL® solver uses an iterative non-linear regression engine to determine local minima. Using the solver, the Estimated Standard Deviation (ESD) [Ives et al. 1983] was minimised for various values of k2-k3 using the multiple regression results determined using the curve fitting method as candidate values. The ESD is defined as:

\[
ESD = \sqrt{\frac{\sum_{j=1}^{j=n} (\sigma_{mj} - \sigma_{pj})^2}{DF}}
\]

where:
- \(\sigma_{mj}\) = Measured Rp0.2 as a % of \(\sigma_{max}\)
- \(\sigma_{pj}\) = Predicted Rp0.2 as a % of \(\sigma_{max}\)
- N = Total number of samples
- DF = Degrees of freedom

\[
j = \frac{n}{\sum_{j=1}^{j=n} (\sigma_{mj} - \sigma_{pj})^2} = \text{Sum of the squares (SS)}
\]

The degrees of freedom is defined (DF) as the No. of samples - No. of variables. In this case, 4 variables: \(k_2 - k_3\). Ives et al. used 6 variables by including \(\sigma_{min}\) and \(\sigma_{max}\) as variables in their calculations. As the number of variables increases the computational power and time required to optimise the solution increases. Figure 5-20 shows the correlation between the predicted Rp0.2 (\(\sigma_p\)) and measured Rp0.2 (\(\sigma_m\)) with an ESD of 6.81%.
Figure 5-20 Predicted Rp_{0.2} as % of Rp_{0.2\text{(max)}} vs Measured Rp_{0.2} as % of Rp_{0.2\text{(max)}} (\sigma_{\text{min}}=0) - ESD=6.81%

Figure 5-21 shows the measured Rp_{0.2} (\sigma_m) versus Quench Factor (\tau) for \sigma_{\text{min}}=0. As we can see this provides a much better fit to the data then the curve fitting method especially as the quench factor increases.

Figure 5-21 Measured Rp_{0.2} vs Quench Factor using QFA and EXCEL* solver for \sigma_{\text{min}}=0

Table 5-9 shows the recalculated predicted values when the EXCEL* solver is used.
Table 5-9  Quench Factor, Measured and Predicted Rp₀₂ for different quench media for σ_min=0

<table>
<thead>
<tr>
<th>Quenchant</th>
<th>Quench Factor</th>
<th>Measured Rp₀₂ (MPa)</th>
<th>Predicted Rp₀₂ (MPa)</th>
<th>Measured as % of Rp₀₂ max</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Water Quench (CWQ)</td>
<td>0.80</td>
<td>524</td>
<td>524</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Carbonated Water Quench</td>
<td>1.31</td>
<td>521</td>
<td>523</td>
<td>99.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Hot Water Quench (80°C)</td>
<td>1.49</td>
<td>520</td>
<td>523</td>
<td>99.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Oil – (Agitated)</td>
<td>2.34</td>
<td>518</td>
<td>523</td>
<td>98.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Boiling Water Quench (BWQ)</td>
<td>9.46</td>
<td>500</td>
<td>519</td>
<td>95.4</td>
<td>3.8</td>
</tr>
<tr>
<td>Air (agitated)</td>
<td>148.6</td>
<td>249</td>
<td>435</td>
<td>47.5</td>
<td>74.7</td>
</tr>
<tr>
<td>Furnace Cool (O)</td>
<td>3274.2</td>
<td>128</td>
<td>63</td>
<td>24.4</td>
<td>50.8</td>
</tr>
</tbody>
</table>

5.9.1 Non-temperature Dependant Constant σ_min = σ₀

A solution proposed by Ives et al. assumed that σ_min was a non-temperature dependant constant σ₀, which could be used in conjunction with the iterative method and k₂-k₅ to minimise the ESD [Ives et al. 1983].

Figure 5-22  Predicted Rp₀₂ as % of Rp₀₂(max) vs Measured Rp₀₂ as % of Rp₀₂(max) for σ_min = σ₀ (σ₀=128 MPa) – ESD=3.48%

In this case, σ₀ was assigned the value of 128MPa, the annealed Rp₀₂ for 7010. An ESD of 3.48% between the predicted and measured Rp₀₂ was achieved using this method as
shown in Figure 5-22. A comparison of the C-curves for the curve fitting method, $\sigma_{\text{min}} = 0$ and $\sigma_{\text{min}} =$ constant ($\sigma_{\text{min}} = \sigma_0 = 128 \text{ MPa}$) are shown in Figure 5-23.

![Figure 5-23 95% C-curves for $\sigma_{\text{min}} = 0$ (Original Curve Fitting Method), $\sigma_{\text{min}}=0$ and $\sigma_{\text{min}} =$ constant (128 MPa)]

The three curves show a marked difference at temperatures at the "nose" of the curve and above. The C-curve based on the $\sigma_{\text{min}}$ as a constant $\sigma_{\text{min}} = 128 \text{ MPa}$ showing a better fit to the data over a wider loss in property range (0--75%) as well as demonstrating a more realistic reflection of the quench sensitivity of the alloy when we compare to similar 7000 series alloys. The curve fitting method resulting in an over approximation of the quench sensitivity and the setting of $\sigma_{\text{min}} = 0$ an under approximation of the quench sensitivity. Table 5-10 presents the $k$ coefficients for the 3 methods.

Table 5-10 $k$ coefficients for fixed $\sigma_{\text{min}}$ methods

<table>
<thead>
<tr>
<th>$\sigma_{\text{min}}$</th>
<th>$k_2$</th>
<th>$k_3$</th>
<th>$k_4$</th>
<th>$k_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{min}} = 0$ (curve fitting)</td>
<td>9.06E-15</td>
<td>2945.82</td>
<td>855</td>
<td>1.51E+05</td>
</tr>
<tr>
<td>$\sigma_{\text{min}} = 0$</td>
<td>5.58E-20</td>
<td>6624.84</td>
<td>889.50</td>
<td>1.88E+05</td>
</tr>
<tr>
<td>$\sigma_{\text{min}} = (128 \text{Mpa})$</td>
<td>5.58E-20</td>
<td>4768.34</td>
<td>849.87</td>
<td>1.92E+05</td>
</tr>
</tbody>
</table>
5.9.2 Non-isokinetic Model 7010-Overaged - Rp₀.₂ Data

In order to apply the non-isokinetic model as described in "Non-Isokinetic Models" - section 3.5.3, the minimum Rp₀.₂ (σₘₐₙ) was determined over a range of temperatures. Tensile test specimens were solution heat treated (2h/475±2°C) followed by furnace cooling at 0.2°C/min to temperatures ranging from close to the equilibrium η-phase (MgZn₂) solvus at 440 to 170±2°C in a Carbolite air circulation furnace followed by isothermal holds for up to 450,000 seconds (24h). The assumption was made that the alloy had reached 99% of its equilibrium condition after this time period and that precipitate growth had reached its limit for the isothermal hold temperature. This isothermal hold was followed by cold water quenching and overaging using the schedule previously described. The Rp₀.₂ values obtained represent the minimum Rp₀.₂ (σₘₐₙ) after aging at temperature T. This provides a true value for σₘₐₙ at the isothermal hold temperature as opposed to 0 MPa which was used in the previous models.

5.9.2.1 Boltzmann sigmoidal curve fit to isothermal data

A plot of σₘₐₙ versus temperature was obtained as shown in Figure 5-24. Staley and Doherty suggested that the effect of temperature on σₘₐₙ could be described by a polynomial equation of the form aT² + bT + c [Staley & Doherty 1989]. For the data set generated as part of this work, a sigmoidal relationship was assumed as it provided a better fit to the data over the entire temperature range under consideration. To determine the minimum σₘₐₙ as a function of isothermal hold temperature, the initial hold temperature, was selected as the solution heat treatment temperature (see Figure 5-24). This temperature was selected in preference to the solvus temperature to guarantee full dissolution of second phase as some evidence of precipitation was evident at the 440°C. Using the data obtained, a non-linear Boltzmann sigmoidal curve
fit as described in Equation 5-7 was applied using Origin Pro 8.0 and a value for \( \sigma_{\text{min}} \) for each incremental temperature step determined.

\[
\sigma_{\text{min}} = A_2 + \frac{A_1 - A_2}{1 + \exp \left[ \frac{X - X_0}{dX} \right]}
\]

\textbf{Equation 5-7}

Where:
- \( X_0 \) = Mean temperature range (°C)
- \( dX \) = Change of Rp0.2 with respect to temperature i.e. slope (MPa°C\(^{-1}\))
- \( A_1 \) = Annealed Rp0.2 value (MPa)
- \( A_2 \) = Maximum Rp0.2 value (\( \sigma_{\text{max}} \)) (MPa)

![Figure 5-24  Rp0.2(min) vs Temperature-7010-Overaged](image)

For the 7010-Overaged Rp0.2 data set, the best fit with a \( R^2 \) of 0.9978 was obtained for \( X_0 = 324.2 \) MPa, \( A_1 = 112.3 \) MPa, \( A_2 = 510.7 \) MPa and \( dX \) (slope) = \( 21.27 \) MPa.°C\(^{-1}\) thus providing a mathematical description of \( \text{Rp0.2}-\sigma_{\text{min}} \) for any value of \( T \). Using the model developed by Staley and Doherty as described earlier where:

\[
\text{Figure 5-24  Rp0.2(min) vs Temperature-7010-Overaged}
\]
\[
\Delta \sigma_i = (\sigma_i - \sigma_{\text{int}}) \left[ 1 - \exp \left( -\frac{\Delta t_i}{C_i(T_i)} \right) \right]
\]

Equation 5-8

and by iteratively adjusting the \(k_2-k_3\) constants in the \(C_i\) function using the EXCEL solver, modified C-curves which provide a more accurate property prediction for more than 15\% property loss were obtained. Figure 5-25 illustrates the predicted \(R_{p0.2}(\sigma_p)\) versus measured \(R_{p0.2}(\sigma_m)\) as a \% of \(R_{p0.2(\text{max})}\) for \(\sigma_{\text{min}}\) = a temperature dependant variable as determined using the method described above. The ESD for this method based on the available data set was 2.57\%.

Figure 5-25  Predicted \(R_{p0.2}\) as a \% of \(R_{p0.2(\text{max})}\) vs Measured \(R_{p0.2}\) as a \% of \(R_{p0.2(\text{max})}\) for \(\sigma_{\text{min}}\) = variable - ESD 2.57\%

Figure 5-26 shows the subsequent C-curves obtained using this method. It is observed that there is little variation in the C-curve at property values approaching 90 and 99.5\% (0.90 and 0.995) of \(\sigma_{\text{max}}\) but shows a significant difference at the lower percentages <80\% of \(\sigma_{\text{max}}\).
Figure 5-26  Non-Isokinetic Rp0.2 iso-strength C-curves -7010 Overaged

The Boltzman sigmoidal curve fitting constants for $\sigma_{\text{min}}$ and the C-curve $k_2$-$k_5$ coefficients determined using this method are shown in Table 5-11.

<table>
<thead>
<tr>
<th>$k_2$ (s)</th>
<th>$k_3$ (J.mol$^{-1}$)</th>
<th>$k_4$ (K)</th>
<th>$k_5$ (J.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.58E-20</td>
<td>7375</td>
<td>899.0</td>
<td>181144.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$A_1$ (MPa)</th>
<th>$A_2$ (MPa)</th>
<th>$X_0$ (MPa)</th>
<th>$d\chi$ (MPa.K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>112.3</td>
<td>510.7</td>
<td>324.2</td>
<td>21.27</td>
</tr>
</tbody>
</table>

5.9.3 Non-isokinetic Model - 7010 Overaged – Hardness

The measured equilibrium Hv$_{20}$ data determined for 7010-Overaged is shown in Figure 5-27. The values obtained represent the minimum (Hv$_{20\text{mm}}$) hardness obtainable at temperatures ranging from 450 to $150\pm2$°C after 24h. Precipitate growth was assumed to have ceased after this period.
Using a Boltzmann sigmoidal fit as previously described, values were obtained for $A_1$, $A_2$, $X_0$ and $d\chi$ with a $R^2$ fit of 98.5% as shown in Table 5-12.

**Table 5-12 Boltzmann Sigmoidal constants for 7010-Overaged $Hv_20$**

<table>
<thead>
<tr>
<th>$A_1$ ($Hv_{20}$)</th>
<th>$A_2$ ($Hv_{20}$)</th>
<th>$X_0$ ($Hv_{20}$)</th>
<th>$d\chi$ ($Hv_{20}$ C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.41</td>
<td>189.88</td>
<td>386.08</td>
<td>27.71</td>
</tr>
</tbody>
</table>

Figure 5-28 illustrates the predicted hardness $Hv_{20}$ versus measured $Hv_{20(max)}$ as a % of $Hv_{20(min)}$ for $Hv_{20(min)} = a$ temperature dependant variable. The ESD for this method based on the available data set was 7.16%.
Figure 5-28  Predicted Hv20 as % of Hv20(max) vs Measured Hv20 as a % of Hv20(max) for Hv20(min) = a temperature dependant variable.

Figure 5-29 shows the iso-hardness C-curves obtained using this method.

Figure 5-29 Non-Isokinetic Hv20 Iso-Hardness C-curves - 7010 Overaged
As with the R$_{p0.2}$ C-curves, we see a significant difference at the lower percentages (<80%) of the maximum attainable hardness. The $k_2$-$k_5$ coefficients determined using this method are shown in Table 5-13.

Table 5-13 C-curve and H$_{V_{20\text{min}}}$ constants for H$_{V_{20}}$ 7010-Overaged

<table>
<thead>
<tr>
<th></th>
<th>$k_2$ (s)</th>
<th>$k_3$ (J.mol$^{-1}$)</th>
<th>$k_4$ (K)</th>
<th>$k_5$ (J.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.000E-11</td>
<td>2.147E+03</td>
<td>850</td>
<td>120000</td>
</tr>
</tbody>
</table>

5.9.4 Non-isokinetic Model - 7010 Overaged – Electrical Conductivity

In order to use the current model successfully without changes to the formulae for the determination of the C-curve, resistivity, the reciprocal of conductivity was used. The measured equilibrium electrical conductivity/resistivity data determined for 7010-Overaged is shown in Figure 5-30.

Figure 5-30 Electrical Conductivity/Resistivity vs Isothermal hold temperature for 7010-Overaged

The values obtained represent the maximum electrical conductivity/minimum resistivity obtainable at temperatures ranging from 450 to 150±2°C after isothermally holding for
24h. The alloy again was assumed to have reached equilibrium at this point. Using a Boltzmann sigmoidal fit, coefficients were obtained for $A_1$, $A_2$, $X_0$ and $dx$ with a fit of $R^2 = 0.98$ as shown in Table 5-14.

Table 5-14 Boltzmann sigmoidal fit constants for Electrical Conductivity(max)/Resistivity(min) 7010-Overaged

<table>
<thead>
<tr>
<th></th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$X_0$</th>
<th>$dx$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Conductivity (%)IAACS</td>
<td>45.10</td>
<td>37.64</td>
<td>41.89</td>
<td>32.18</td>
</tr>
<tr>
<td>Resistivity (Ωm)</td>
<td>$3.823 \times 10^{-8}$</td>
<td>$4.564 \times 10^{-8}$</td>
<td>$423.138 \times 10^{-8}$</td>
<td>$31.185 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Figure 5-31 illustrates the predicted EC/$\rho$ vs measured EC/$\rho$ as a % of EC(max)/EC(min) for EC(max)/EC(min) = a temperature dependant variable. The ESD obtained based on the available data set was 2.77%. Figure 5-32 shows the iso-conductivity/resistivity C-curves obtained using this method. A much greater scatter of the data was observed compared to the hardness and tensile data.

![Figure 5-31 Predicted EC/$\rho$ vs Measured EC/$\rho$ as a % of EC(max)/EC(min) for EC(max)/EC(min) = a temperature dependant variable]
Figure 5-32  Multiple Iso-conductivity/iso-resistivity C-curves - 7010 Overaged.

The $k_2$-$k_5$ coefficients obtained for the above C-curves are shown in Table 5-15.

Table 5-15  C-curves and Electrical Conductivity/Resistivity constants for 7010-Overaged

<table>
<thead>
<tr>
<th></th>
<th>$k_2$</th>
<th>$k_3$</th>
<th>$k_4$</th>
<th>$k_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s)</td>
<td>(J.mol$^{-1}$)</td>
<td>(K)</td>
<td>(J.mol$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>5.130E-11</td>
<td>6.862E+02</td>
<td>778</td>
<td>133056</td>
<td></td>
</tr>
</tbody>
</table>

5.9.5 Summary and Property Prediction

In order to compare the quench sensitivity of the various properties, hardness measurements were taken from the mounted and polished section heads of the post-tested tensile specimens. A plot of Vickers hardness vs $R_{p0.2}$ for these specimens is shown in Figure 5-33 giving a ratio of 3.71:1 for $R_{p0.2}$:HV$_{20}$. As the amount of precipitation and remaining solute was identical for each measurement, we can state that 95% of the maximum attainable $R_{p0.2} = 497$MPa which is equivalent to $179.9$HV$_{20}$.
Figure 5-33  Hardness (Hv20 vs Rp0.2 for tensile specimens)

179.9Hv20 = 95.2% of the maximum attainable hardness. Using a similar correlation for electrical conductivity/resistivity and Vickers hardness as shown in Figure 5-34, a hardness of 179.9Hv20 is equivalent to 4.502 Ωm.10^-8 or 97.62% of the maximum attainable resistivity.

Figure 5-34  Hardness (Hv20 vs resistivity from Hardness/EC specimens)
To summarise: A loss of solute as measured by electrical conductivity/resistivity of 2.37% corresponds to a 5% loss in Rp0.2 strength and a 4.8% loss in hardness. If the C-curves for equivalent loss of solute (equal amounts of precipitation) for the three measured properties using the non-isokinetic method are compared as shown in Figure 5-35, no difference is observed between the Rp0.2 curve and the hardness curve and only a slightly elevated nose temperature for the electrical conductivity/resistivity curve. No difference in quench sensitivity is observed. We see that for the Vickers hardness, the nose of the curve is at 335°C while for the electrical conductivity of the nose is shifted to a higher temperature at approximately 350°C.

Figure 5-35  Comparison of electrical conductivity, hardness (HV20) and Rp0.2 for equal levels of precipitation/solute loss

A larger scatter was observed for the electrical conductivity/resistivity data compared to the Rp0.2 and hardness data as shown in Figure 5-31. This may be due to chemical inhomogeneity of the supplied forged block which would affect the electrical conductivity to a greater extent compared to the mechanical properties.
5.9.5.1 Continuous cooling – Rp0.2

In order to verify the position of the C-curves using “real world” examples, continuous cooled quenches using various quenchants were also carried out using the method described in section 4.3. The predicted Rp0.2 using the non-isokinetic model and assuming a Boltzman sigmoidal relationship for $\sigma_{\min}$, the predicted Rp0.2 for a selection of continually cooled specimens using different quench media i.e. different quench rates are shown in Table 5-16. Due to the limited availability of tensile specimens, no error data is presented.

### Table 5-16 Predicted and measured Rp0.2

<table>
<thead>
<tr>
<th>Quench Type</th>
<th>Predicted Rp0.2 (MPa)</th>
<th>Measured Rp0.2 (MPa)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonated water</td>
<td>506</td>
<td>503</td>
<td>0.59</td>
</tr>
<tr>
<td>Oil</td>
<td>503</td>
<td>494</td>
<td>1.78</td>
</tr>
<tr>
<td>Boiling Water</td>
<td>500</td>
<td>490</td>
<td>2.00</td>
</tr>
<tr>
<td>Agitated Air</td>
<td>370</td>
<td>353</td>
<td>4.59</td>
</tr>
</tbody>
</table>

5.9.5.2 Comparison of isokinetic and non-isokinetic models

Table 5-17 shows a comparison between classical QFA model and the non-isokinetic models for a selection of the Rp0.2 isothermal hold data.

### Table 5-17 Comparison of isokinetic (QFA ($\sigma_{\min}=0$)) and non-isokinetic model using isothermal hold Rp0.2 data

<table>
<thead>
<tr>
<th>% of $\sigma_{\max}$</th>
<th>Measured Rp0.2 (MPa)</th>
<th>Predicted Rp0.2 QFA Model (MPa)/% $\sigma_{\max}$</th>
<th>Predicted Rp0.2 Non-Isokinetic Model (MPa)/ % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.7</td>
<td>507</td>
<td>517 (1.93)</td>
<td>509 (0.39)</td>
</tr>
<tr>
<td>93.0</td>
<td>482</td>
<td>488 (1.22)</td>
<td>483 (1.02)</td>
</tr>
<tr>
<td>72.3</td>
<td>379</td>
<td>396 (4.29)</td>
<td>379 (0.00)</td>
</tr>
<tr>
<td>61.0</td>
<td>320</td>
<td>332 (3.61)</td>
<td>318 (0.62)</td>
</tr>
<tr>
<td>32.6</td>
<td>171</td>
<td>141 (17.54)</td>
<td>163 (4.67)</td>
</tr>
</tbody>
</table>
These values represent only a subset of the predicted $R_{p0}$ versus measured $R_{p0}$ values for the two models. As can be seen, at 61% of $\sigma_{max}$, the model is very accurate with a % error of 0.62% though it is still evident that at the higher property loss percentages, the error between the measured $R_{p0}$ and the predicted $R_{p0,2}$ begins to increase. On examination of the Avrami $\ln(\sigma/\sigma_{max})$ versus time plot as shown in Figure 5-36, deviations from linearity begin to emerge at the longer isothermal hold times (>1000s).

**Figure 5-36 Avrami Transformation Plot - $\ln(\sigma/\sigma_{max})$ vs Time 7010-Overaged**

This is possibly due to impingement of precipitates, and hence deviations from the JMAK model begin to take effect. A better fit was also obtained for data at temperatures at the nose of the C-curve (~335°C) and below. This may be due to the fact that the C-curve obtained using all these methods assumes that only one type of quench precipitate occurs thus the C-curve is essentially a combination of all the transformation processes occurring during the isothermal quenching. The model also does not distinguish between inter-granular and intra-granular precipitation which is...
observed in the subsequent metallographic examination. A schematic representation of this assumption is shown in Figure 5-37.

![Schematic Representation of multi-phase precipitation in 7010](image)

**Figure 5-37 Schematic Representation of multi-phase precipitation in 7010**

Heterogeneous precipitation of S and T phases has also been observed for long isothermal hold times at 260°C [Deschamps & Brechet 1998b]. These types of processes may also account for the slight triple peaked curve shape observed in the experimental tensile C-curve data (see Figure 5-38).

![Experimental Rp0.2 - Multiple Precipitate C-curves Rp0.2](image)

**Figure 5-38 Experimental Rp0.2 - Multiple Precipitate C-curves Rp0.2**
In order to compare the various models and their accuracy at property prediction, the ESD (based on Rp0.2 data) for the various methods examined are shown in Table 5-18.

**Table 5-18 Rp0.2 Estimated Standard Deviation (%)**

<table>
<thead>
<tr>
<th>Method</th>
<th>ESD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{min}} = 0$ Regression curve fitting</td>
<td>18.19</td>
</tr>
<tr>
<td>$\sigma_{\text{min}} = 0$</td>
<td>6.81</td>
</tr>
<tr>
<td>$\sigma_{\text{min}} = \text{Constant} = 128\text{MPa}$</td>
<td>3.48</td>
</tr>
<tr>
<td>$\sigma_{\text{min}} = \text{Temperature dependant variable}$</td>
<td>2.57</td>
</tr>
</tbody>
</table>

As can be seen from Table 5-18, the variable $\sigma_{\text{min}}$ method provides the best fit based to the available Rp0.2 data set for 7010 in the averaged condition. Figure 5-39 shows a re-plot of Figure 5-4 showing the measured Rp0.2 vs isothermal hold time at 310°C. Also shown are the three main property prediction models fitted to the curve. As we can see the $\sigma_{\text{min}} = \text{temperature dependant variable}$ model shows the best fit to the measured data.

![Figure 5-39 Rp0.2 vs isothermal hold time for 310°C and prediction models](image)

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On examination of the original test matrix for isothermal hold times (see Table 4-2) it can be seen that the test schedule set is heavily biased towards the faster cooling rates (0-20% loss in properties). This is because the starting temperature versus isothermal hold time matrix was based around the schedule for classic QFA, which is only concerned with modelling property loss at up to 10% loss in properties. As the non-isokinetic model is concerned with the possibility of predicting properties at beyond 10% loss, a better distributed and possibly larger data set is required. Other researchers have suggested that in light of this limitation, caution should be exercised when calibrating models like the current one that also contain a large number of variable coefficients (up to 7 have used for some models), which would also suggest that a larger and more well distributed data set would allow for more accurate determination of the $k$ coefficients.

The ratio of isothermal data to continuously cooled data also needs to be addressed as suggestions have been made that precipitation mechanisms may be different for isothermal and continuous cooling. Cahn's method holds true for the times evaluated by Staley [Staley 1987] and by this work at isothermal hold times <1000 seconds, providing the loss in ability to develop strength after continuous cooling is the same as the mechanism for the loss of holding at isothermal temperatures, i.e. incoherent precipitation of solute. One group of investigators has shown that loss in strength obtained by slowly quenching aluminium alloys is not a direct function of the solute precipitated during the quench [Berg et al. 2003; Thomson et al. 1971]. Opposed to this is research carried out by a range of researchers who showed by resistively measurements that the loss in strength is directly proportional to the amount of solute lost during the quench. The following sections attempts to address this issue by using Jominy end quench as a source of continuous cooled data.
5.9.5.3 Data set and solver method

All the non-isokinetic models used throughout the course of this work used the Microsoft EXCEL® solver function from Frontline Systems. The solver function uses the Generalized Reduced Gradient (GRG2) Algorithm for optimising non-linear problems and was developed by Leon Lasdon, of the University of Texas at Austin, and Allan Waren, of Cleveland State University [Fylstra, Lasdon, Watson, & Waren 1998]. In the early part of this work on the interrupted quench data models, the solver was used for the determination of all 4 \( k \) coefficients (\( k_1-k_4 \)). For the Jominy specimens in section 5.10.1, just the \( k_2 \) and \( k_3 \) coefficients were varied with independently determined fixed values being used for \( k_4 \) and \( k_5 \). Questions have been raised by several authors with respect to the legitimacy of curves based on multiple variable parameters (4 variables with up to 6 in some cases where \( \sigma_{min} \) and \( \sigma_{max} \) are included) [Tiryakioglu & Shuey 2003]. Depending on the initial solver starting values, similar “best fit” results can be obtained with different values of \( k_2 \) and \( k_3 \) even with independently determined fixed values being used for \( k_4 \) and \( k_5 \).

5.9.5.4 Limitations of EXCEL® solver

The inherent problem with C-curve analysis is that the fitting of C-curve coefficients is a highly non-linear problem irrespective of the method used to solve it. The solver add-on for EXCEL® was used extensively for the iterative determination of the C-curve parameters within the current work, but the program is limited in its ability to recognise global minima. The resultant C-curve \( k \) coefficients are therefore heavily dependent on the initial candidate values selected and have the effect that there may be a more optimised solution than that observed. In order to overcome this limitation several other solvers were evaluated, namely “Whats Best”! and a Premium EXCEL® solver trial version. These solvers were used to try to obtain a global minima but without success.
as they required greater computational facilities than were available. Other researchers have suggested that the use of a Levenburg-Marquardt type algorithm may perform better than the quasi-Newton techniques used by EXCEL\textsuperscript{\textregistered} solver \citep{Shuey, Tiryakioglu, & Lippert 2003}.

5.9.5.5 \textit{k} coefficients

In order to reach the most optimised solution using the limited capability of the EXCEL\textsuperscript{\textregistered} solver, several starting coefficients were evaluated in order to try to optimise the solution. Initial coefficients were based on the values obtained using the curve fitting method. The literature has shown widely different C-curve coefficients obtained using classical QFA for 7000 series alloys though compositional similarities would suggest that they should be very similar (see Table 3-6). This makes it more difficult to relate the coefficients to the composition of the alloys under evaluation and use any trends which might be apparent to adapt the \textit{k} coefficients to account for changes in processing conditions such as different aging regimes or post-quench mechanical processing such as cold compression or stretching for residual stress relief.

In the non-isokinetic models, the \textit{k}_4 coefficient which is related to the solvus was set to a value approximating the solution heat treatment (475°C). Other researchers have used a temperature approximating the \textit{n} solvus temperature. Recent work by Tiryakioglu and Shuey \citep{Tiryakioglu & Shuey 2010a} has recommended that the lesser of the heat treatment temperature or solvus temperature should be used for the value for \textit{k}_4 for alloys such as 2024. \textit{k}_5 which is generally accepted as the activation energy for solute diffusion was set to 133,493 J.mol\textsuperscript{-1} \citep{Sewarzendruber et al. 1980} but this value is only based on the activation energy for diffusion of copper in aluminium (the slowest diffusing element). Some researchers have indicated that this approximation is not a very accurate approach to take as 7010 is essentially a quaternary alloy, so the
activation energy for diffusion will be a combination of the activation energies for diffusion of Zn, Mg and Cu in aluminium [Tundal, Reiso, & Ryum 1994]. To date very little work has been done on inter diffusion in Al-Zn-Mg-Cu alloys [Takahashi, Minamino, & Yamane 2002].

This fixing of $k_4$ and $k_5$ was attempted using the $R_{p0.2}$ data as it provided for a quicker solution as only $k_2$ and $k_3$ were set as variables within the model. This should have provided a better fit to the data but produced a higher ESD than expected. This misfit could is due to several factors: 1) The precipitation of multiple phases during the quench and 2), that the currently determined $k$ coefficients are essentially local minima, with different starting $k$ values producing similar shaped and positioned C-curves but significantly varying final $k$ coefficients, resulting in a non-optimised solution to the problem. Also on fixing $k_4$ and $k_5$ and varying $k_2$, the problem would often become unbounded necessitating the requirement to select alternative starting $k$ values. The introduction of accurate thermodynamically obtained data for the C-curve coefficients constants into the model as opposed to the best fit values determined by the EXCEL$^*$ solver, and also the use of an alternative to the limited abilities of the very basic EXCEL$^*$ solver, should provide more thermodynamically realistic solutions than those achieved to date. The consideration of a standard method regardless of the C-curve coefficients obtained has merit with respect to allowing comparison of various alloys and tempers though the value of the coefficients where all the coefficients are allowed to vary should not be regarded as their true thermodynamic values. One of the objectives of this work has been to predict the properties of an overaged aluminium alloy 7010 under various quenching conditions, to this aim the non-isokinetic models work quite successfully though the strive to use realistic values for the $k$ coefficients should be pursued.
5.10 Jominy End Quench Method

One of the issues in relation to the limited widespread applicability of Quench Factor analysis is the limited amount of C-curve data available in the public domain. This is due to the time consuming effort involved in producing C-curves based on isothermal quench methods. The Jominy end quench test has been suggested as a method for rapidly providing data for a specific set of processing conditions and allows the determination of quench factors for multiple cooling rates \[\text{Mackenzie & Newkirk 2001}\]. The Jominy end quench data also provides a source of continuous cooled data for C-curve construction as opposed to the isothermal data used for classical C-curve construction. The use of isothermal data for modelling essentially a continuous cooling process has been highlighted by previous researchers as one of the major issues regarding the validity of the classical C-curve model. This approach has already been used by Dolan for property prediction in 7050 \[\text{Dolan et al. 2005}\].

5.10.1 Determination of Jominy Cooling Curves using FEA Analysis

In order to use property data generated by the Jominy end quench technique for Quench Factor Analysis it was necessary to predict the different cooling rates along the length of the Jominy test specimen. A heat transfer model of the Jominy end quench specimens developed and constructed by Tanner using the Finite Element Technique (ABAQUS) was used to provide the required cooling curves \[\text{Tanner et al. 2000}\]. One quarter of the test specific specimen was modelled because of the geometric symmetry using heat diffusion elements of Type D3D4 (four node linear tetrahedron) for the head of the test specimen and DC3D8 (eight node quadratic brick) elements for the main shaft of the sample. Properties for thermal conductivity, density and specific heat capacity were taken from the literature \[\text{Tanner et al. 2000}\]. Cooling curves measured
at 3mm from the end of the specimen were used as the main boundary condition to determine the rate of cooling of the remainder of the test pieces.

![Diagram showing Jominy Cooling Curves determined using FEA Analysis.](image)

**Figure 5-40** Jominy Cooling Curves determined using FEA Analysis [Tanner et al. 2000].

Radial heat transfer from the unquenched side of the specimen was ignored as previous researchers had indicated that any heat transfer that may occur to the surrounding air has a minimal effect on the hardness measured [Newkirk & Mackenzie 2000]. Figure 5-40 shows the cooling curves determined by Tanner and Robinson using Finite Element Analysis and an instrumented Jominy end quench sample for aluminium alloy 7010 [Tanner et al. 2000]. These 43 FE modelled cooling curves for 0 to 99mm from the quenched end were used for all the Jominy property prediction calculations.
Figure 5-41  Distance from quenched end versus cooling rate as determined from both experimental and finite element analysis-7010 [Tanner et al. 2000]

Figure 5-41 shows both the instrumented Jominy sample results and the FE predicted average cooling rate between 400 and 250°C along the length of the Jominy end quench specimen. At 3mm. close to the specimen edge, a cooling rate of over 200°C.sec$^{-1}$ is observed with a steady decrease in the cooling rate to approximately 12°C.sec$^{-1}$ after 20mm. Towards the end of the specimen a cooling rate of less than 5°C.sec$^{-1}$ was observed.

### 5.10.2 Vickers Hardness-Hv

Figure 5-42, Figure 5-43 and Figure 5-44 shows the effect of the decreasing cooling rate (i.e. distance from quenched end.) on the Vickers hardness of 7010 in the peak aged, overaged and cold compressed+overaged conditions respectively obtained using the Jominy end quench technique. The term “peak aged” in the context of this work going forward refers to specimens that have undergone an aging process which under normal commercial quenching and aging procedures would result in the maximum tensile
strength for the alloy (T6). In this case, “peak aged” refers to alloy specimens which were subjected to a single stage heat treatment of 120±2°C for 24h. The “overaging” aging treatment is as previously described in section 4.2.

Figure 5-42  Hardness (Hv0.5) vs Distance from quenched end - 7010-Peak Aged

Figure 5-43  Hardness (Hv0.5) vs Distance from quenched end - 7010-Overaged
Figure 5-44  Hardness (Hv₀.₅) vs Distance from quenched end - 7010-Cold Compressed+Overaged

For all three cases there is steady decrease in the hardness of the alloy as the distance from the quench end increases due to the decreasing cooling rate causing precipitation of the coarse non-hardening η phase. For the peak aged (Figure 5-42) specimen the maximum loss of hardness, is reached after approx. 40mm and maintains a hardness of approximately 168Hv₀.₅ while for the overaged and cold compressed+overaged specimens, the attainment of the maximum loss is observed over a greater distance with a steady state not being reached until approximately 75 and 70mm from the quenched end respectively. A hardness of approximately 165 and 160Hv₀.₅ was observed for the overaged and cold compressed respectively at these locations. A comparison of the change in hardness with respect to distance from the quenched end for 7010 in the peak aged, overaged and cold compressed+overaged condition is shown in Figure 5-45. The peak aged sample was observed to have the highest measured hardness of 193Hv₀.₅ at the quenched end (3mm). A hardness of 187Hv₀.₅ was recorded for the overaged sample and the cold compressed+overaged specimen recorded a hardness of 183Hv₀.₅.
the slightly lower hardness being due to the plastic deformation and subsequent accelerated precipitation kinetics though this declines rapidly as the quench rate decreases.

Figure 5-45 Hardness (Hv0.5) vs Distance from quenched end for 7010 in Peak Aged, Overaged and Cold Compressed+Overaged conditions

Figure 5-46 Hardness vs Average quench cooling rate for 7010 in the Peak Aged, Overaged and Cold Compressed+Overaged conditions
Figure 5-46 compares the measured average cooling rates vs Vickers hardness for the three specimens. The cold compressed+overaged specimen demonstrates a much more rapid loss in property as the cooling rate decreases. Though all samples at equivalent quench rates (i.e. distance from the quenched end) have the same level of non-hardening precipitation following the quench, differences in final hardness are observed as expected due to the different post-quench processing and aging regimes. At the most rapid quench rates (>200°C.min⁻¹) which occurs at the quenched end of the Jominy specimen, the peak aged heat treatment provides the highest hardness of 192.5HV₀.₅ followed by the cold compressed+overaged specimen at 187HV₀.₅ and the overaged specimen at 183.5HV₀.₅. The hardness of the cold compressed+overaged sample is lower compared to the overaged sample due to the accelerated GP zone formation and subsequent aging response brought on by the high density of dislocations introduced by the cold compression stage though both specimens were subjected to the same overaging heat treatment.

5.10.3 Isothermal HV₂₀(min) for Peak Aged Specimen

Figure 5-47 shows the minimum hardness - HV₂₀(min), obtained for the peak aged samples prepared as described in section 4.6.7 at again isothermal hold temperatures from 450 to 150°C±2°C for 24h. As in previous experiments, a Boltzmann sigmoidal fit was applied to the experimental data to accurately determine the minimum Vickers hardness (HV(min)) attainable at temperatures from 475 to 150°C±2°C. At 475°C±2°C a hardness of 192±2HV₂₀ was observed with a steady decrease in hardness to approximately 250°C±2°C where a final minimum hardness of 49HV₂₀ was observed. A R² of 0.99 was achieved providing a good fit to the available data.
The Boltzmann sigmoidal fit constants for the peak aged data are shown in Table 5-19.

Table 5-19 Boltzmann Sigmoidal Constants for HV$_{20\text{(min)}}$ 7010-Peak aged

<table>
<thead>
<tr>
<th>$A_1$ (HV$_{20}$)</th>
<th>$A_2$ (HV$_{20}$)</th>
<th>$x_0$ (HV$_{20}$)</th>
<th>$dx$ (HV$_{20}$,°C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.4</td>
<td>199.66</td>
<td>380.41</td>
<td>17.38</td>
</tr>
</tbody>
</table>

5.10.4 Isothermal HV$_{20\text{(min)}}$ for Overaged and Cold Compressed+Overaged Specimens

The HV$_{20\text{(min)}}$-overaged data previously determined was used for the Jominy overaged hardness prediction. Figure 5-48 shows the minimum hardness - HV$_{20\text{(min)}}$ obtained for the cold compressed+overaged samples prepared as described in section 4.6.7 at isothermal hold temperatures from 450 to 150°±2°C for 24h. As in previous experiments, a Boltzmann sigmoidal equation was fitted to the curve to determine the minimum HV$_{20}$ at any temperature from 475°±2°C to room temperature for subsequent use in the quench factor model. At 475°±2°C a hardness of 183±2HV$_{20}$ was observed.
with a steady decrease in hardness to approximately $250^\circ\pm2^\circ$C where a final steady state hardness of $47\pm2$Hv20 was observed. The A1, A2, X0 and $d_\chi$ coefficients for the curve are shown in Table 5-20. A fit of $R^2=0.99$ was obtained for the available data.

![Graph](image)

**Figure 5-48**  
Hv$_{20\ (\text{min})}$ 7010 Cold Compressed+Overaged Determination

<table>
<thead>
<tr>
<th>Table 5-20</th>
<th>Boltzmann Sigmoidal Fit Constants</th>
<th>Hv$_{20\ (\text{min})}$ 7010 Cold Compressed+Overaged</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (Hv$_{20}$)</td>
<td>A2 (Hv$_{20}$)</td>
<td>X0 (Hv$_{20}$)</td>
</tr>
<tr>
<td>47.44</td>
<td>197.608</td>
<td>390.874</td>
</tr>
</tbody>
</table>

5.10.5 Hv Prediction - Peak Aged, Overaged and Cold Compressed + Overaged

Using the non-isokinetic method described previously (section 5.9.2), hardness for continuous cooled Jominy specimens was determined for the peak aged, overaged and cold compressed+overaged samples. In order to improve the fit based on observations by previous researchers [Tiryakioglu & Shuey 2010a], the values of $k_2$ and $k_3$ were fixed at 748K (475°C) and 133,592 J.mol$^{-1}$ respectively. As discussed in section 5.9.5.5
this value is only based on the activation energy for diffusion of copper in aluminium (the slowest diffusing element). Tiryakioğlu and Shuey suggest that it would be more accurate to use the stochiometrically weighted average of reciprocal diffusivities of the alloying elements [Tiryakioğlu & Shuey 2010a; Tundal et al. 1994]. The value for $k_a$ used was the solution heat treatment temperature. For alloys such as 2024, where complete solubility is not possible, Tiryakioğlu and Shuey have used the solution heat treatment temperature otherwise the solvus temperature should be used [Tiryakioğlu & Shuey 2010a]. It was decided to continue to use the solution heat treatment temperature for $k_a$ as evidence of some solute loss was observed at 440°C (the $\eta$ solvus temperature reported in the literature [Godard et al. 2002]) during the isothermal hold temperature experiments.

Due to a large portion of the data obtained being measured over a region of the sample where the rate of hardness loss is close to zero and has essentially reached a steady state ($\sim 50$mm), optimisation of the $k$ values was carried over a sub-set of the data (0 to $\sim 50$mm) in order to avoid skewing of the “best fit” towards the low-cooling rate end of the specimen.

5.10.5.1 Peak aged

Figure 5-49 shows the measured vs predicted hardness for the peak aged data with an Estimated Standard Deviation of 1.41%. In this case, the measured maximum loss in property over the length of the Jominy test specimen did not exceed 10%. A plot of the predicted and measured hardness vs the distance from the quenched end of the Jominy test specimen is shown Figure 5-50.
Figure 5-49 Measured vs Predicted hardness - $H_{V0.5}$ for Jominy specimen-Peak Aged - ESD= 1.41%

Figure 5-50 Measured and Predicted hardness $H_{V0.5}$ vs Distance from quenched end-Peak Aged

The determined $k_2$ and $k_3$ coefficients for the data set are shown in Table 5-21.
Table 5-21  
$k$ coefficients for $H_{v0.5}$ for Jominy Specimen Peak Aged

<table>
<thead>
<tr>
<th>$k_2$</th>
<th>$k_3$</th>
<th>$k_4$</th>
<th>$k_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s)</td>
<td>(J.mol$^{-1}$)</td>
<td>(K)</td>
<td>(J.mol$^{-1}$)</td>
</tr>
<tr>
<td>8.992E-13</td>
<td>1201</td>
<td>748</td>
<td>133952</td>
</tr>
</tbody>
</table>

5.10.5.2 Overaged

Figure 5-51 shows the measured vs predicted hardness following optimisation of the $k$ coefficients using the EXCEL® solver method for the overaged data with an Estimated Standard Deviation of 1.00%. As with the peak aged specimen, the measured maximum loss in property over the length of the Jominy test specimen did not exceed 10%. An ESD of 1.00% was achieved. The determined $k_2$ and $k_3$ coefficients for the data set are shown in Table 5-22.

![Graph showing measured vs predicted hardness for Jominy Specimen Overaged](image)

Figure 5-51  
Measured vs Predicted hardness- $H_{v0.5}$ for Jominy Specimen Overaged - ESD=1.00%

Table 5-22  
$k$ coefficients for $H_{v0.5}$ for Jominy Specimen Overaged

<table>
<thead>
<tr>
<th>$k_2$</th>
<th>$k_3$</th>
<th>$k_4$</th>
<th>$k_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s)</td>
<td>(J.mol$^{-1}$)</td>
<td>(K)</td>
<td>(J.mol$^{-1}$)</td>
</tr>
<tr>
<td>8.922E-13</td>
<td>1215</td>
<td>748</td>
<td>133952</td>
</tr>
</tbody>
</table>
A plot of the predicted and measured data vs the distance from the quenched end of the Jominy test specimen is shown in Figure 5-52.

Figure 5-52  Measured and predicted $H_v_{0.5}$ vs Distance from quenched end-
Overaged

5.10.5.3 Cold compressed+overaged

Figure 5-53  Measured vs Predicted Hardness-$H_v_{0.5}$-Jominy Specimen - Cold Compressed+Overaged - ESD=0.72%
Figure 5-53 shows the measured vs predicted hardness for the cold compressed+overaged data with an Estimated Standard Deviation of 0.72%.

Figure 5-54 Measured and predicted Hv₀.₅ vs Distance from quenched end - Cold Compressed+Overaged

As with the peak aged and overaged data sets, a similar loss in property was observed with a maximum of 12%. A plot of the measured and predicted hardness vs the distance from the quenched end of the Jominy test specimen is shown in Figure 5-54. The determined $k_2$ and $k_3$ coefficients are shown in Table 5-23.

Table 5-23 $k$ coefficients for Hv₀.₅-Jominy Specimen Cold Compressed+Overaged

<table>
<thead>
<tr>
<th>$k_2$ (s)</th>
<th>$k_3$ (J·mol⁻¹)</th>
<th>$k_4$ (K)</th>
<th>$k_5$ (J·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.9×10⁻¹³</td>
<td>1269</td>
<td>748</td>
<td>133952</td>
</tr>
</tbody>
</table>

5.10.5.4 Jominy C-curves

C-curves were constructed for the specimens using the method outlined in section 5.9.2. Figure 5-55, Figure 5-56 and Figure 5-57 show the iso-hardness C-curves obtained for Jominy specimens in the peak aged, overaged and cold compressed+overaged conditions.
Figure 5-55  Peak Aged multiple iso-hardness C-curves-Jominy test specimens

Figure 5-56  Overaged multiple iso-hardness C-curves-Jominy test specimen
Figure 5-57 Cold Compressed+Overaged multiple iso-hardness C-curves-Jominy test specimen

Figure 5-58 shows a comparison between the 99.5% of maximum property iso-hardness C-curves for 7010 in the peak aged, overaged and cold compressed+overaged conditions.

Figure 5-58 Comparison of 99.5% Hv20 C-curves for Peak Aged, Overaged and Cold Compressed+Overaged 7010 Jominy specimens
This would suggest that the cold compression results in more of the strengthening $\eta'$ being transformed to the equilibrium $\eta$ phase during the overaging aging process as the proportion of $\eta$ in all three cases is the same prior to the post-quench heat treatment. This is due to the cold compression resulting in accelerated precipitation kinetics during the first stage of the overaging heat treatment. Figure 5-59 shows a comparison between the C-curves derived using the interrupted quench and the Jominy end quench techniques for 7010 overaged respectively. As can be seen, there is a shift in the nose of the peak of the curve from 335°C for the interrupted quench C-curve to 315°C for the Jominy derived C-curve.

![Figure 5-59 Comparison of 99.5% Vickers hardness C-curves for 7010 Overaged determined using interrupted quench technique and Jominy end quench specimens.](image)

A slight increase in the apparent quench sensitivity for the Jominy derived C-curve is also observed. A large discrepancy is observed at the temperatures above the nose of the curve at approximately 350°C. This is partly due to the Jominy method providing a much smaller data set for prediction purposes than the isothermal hold methods though
this comparison also raises the legitimacy of using the Jominy end quench method for property prediction. The observed discrepancy is possibly more related to the multiple phases which are identified using the interrupted quench technique but which are not observed when the continuous cooled Jominy quench end method is employed. This may undermine the use of the Jominy end quench technique for alloys where multiple precipitates are produced during the quench.

5.10.6 Isothermal EC /Resistivity - Cold Compressed+Overaged

Figure 5-60 shows the maximum electrical conductivity $\text{EC}_{\text{max}}$ and minimum resistivity $\text{r}_{\text{min}}$ for the cold compressed+overaged samples prepared as described in section 4.6.7 at isothermal hold temperatures from 450 to 150±2°C for 24h.

As in previous experiments, a Boltzmann sigmoidal fit was applied to the experimental data to accurately determine both the $\text{EC}_{\text{max}}$ and/or resistivity $\text{r}_{\text{min}}$ at any temperature from 475°C to room temperature. At 475±2°C, an electrical conductivity of 40.2%IACS (resistivity $4.288 \times 10^{-8} \Omega\text{m}$) was observed with an increase in conductivity.
as the isothermal hold temperature decreases resulting in an electrical conductivity of 46.6 %IACS and 3.699x10^{-8}\Omega m at 210±2°C. The Boltzmann Sigmoidal fit constants for the cold compressed+overaged electrical conductivity/resistivity data is shown in Table 5-24. A fit of $R^2 = 0.99$ was achieved for the data.

Table 5-24  Boltzmann Sigmoidal Fit Constants - Electrical Conductivity - 7010 - Cold Compressed+Overaged

<table>
<thead>
<tr>
<th>Conductivity</th>
<th>$A_1$ (%IACS)</th>
<th>$A_2$ (%IACS)</th>
<th>$X_0$ (%IACS)</th>
<th>$d\chi$ (%IACS °C^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity</td>
<td>3.69 (Ωm.10^{-8})</td>
<td>4.38 (Ωm.10^{-8})</td>
<td>418.94 (Ωm.10^{-8})</td>
<td>31.56 (Ωm.10^{-8} °C^{-1})</td>
</tr>
</tbody>
</table>

Figure 5-61 compares the electrical conductivity/resistivity results for 7010 in the overaged and the 2.5% cold compressed+overaged conditions over the temperature range 220-475±2°C.

The overaged specimen held for 24h at the solution heat treatment temperature (475°±2C) shows an electrical conductivity of 38.8%IACS which indicates that nearly
all the solute has remained in solution, as the isothermal hold temperature is decreased, a steady drop in the alloys ability to keep the solute in solution is observed and the increase in the level of precipitation results in an increase to 45%IACS for the specimen held at 220±2°C for 24h. As can be seen, the cold compressed samples show approximately a 2%IACS higher electrical conductivity compared to the overaged specimen. This is due to the increased number of dislocations in the lattice of the cold compressed specimens causing accelerated aging and an eventual higher level of precipitation compared to the uncompressed overaged samples. A higher level of precipitation results in a higher measured electrical conductivity. Prior to artificial aging, plastic deformation usually results in a lower electrical conductivity compared to non-deformed alloys due to the greater level of electron scattering. This effect is negated by the increased level of precipitation during the artificial aging step. The effect of isothermal hold time was observed to have a relatively negligible effect on the degree of change in the post-aged electrical conductivity between the compressed and uncompressed samples. At 475±2°C the conductivity difference was 1.3%IACS compared to 1.8% and 1.5% IACS at 335±2°C and 210±2°C respectively.

5.10.6.1 Peak-aged

In order to determine the electrical conductivity/resistivity c-curves a similar method used for the determination of the hardness C-curves was applied. Figure 5-62 shows the change in electrical conductivity/resistivity with respect to the distance from the quenched end for the peak aged specimen. A progressive increase in electrical conductivity from 30.4%IACS (5.67Ωmx10⁻⁸) at the quenched end to 31.6%IACS (5.46Ωmx10⁻⁸) at 75mm from the quenched end was observed. This is due to the decreased solute content/increased level of precipitation brought on by the reduced cooling rate as the distance from the quenched end increases.
Figure 5-62 Electrical Conductivity Jominy End Quench specimen – 7010-Peak Aged

On optimisation of the $\kappa$ coefficients using EXCEL*. Figure 5-63 shows the measured electrical conductivity vs the predicted electrical conductivity for 7010 after a peak aged aging schedule.

Figure 5-63 Measured Electrical Conductivity vs Predicted Electrical Conductivity for 7010-Peak Aged-ESD=0.30%
An extremely good fit to the data (ESD=0.3%) is achieved thought though this is mainly due to the small data set (12 samples) and only a <5% change in electrical conductivity over the length of the sample. The optimised $k$ coefficients are shown in Table 5-25. The resulting electrical conductivity C-curve for the 7010-Peak aged specimen is shown Figure 5-64.

<table>
<thead>
<tr>
<th>$k_2$ (s)</th>
<th>$k_3$ (J.mol$^{-1}$)</th>
<th>$k_4$ (K)</th>
<th>$k_5$ (J.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9E-13</td>
<td>1275.323</td>
<td>7.48</td>
<td>133982</td>
</tr>
</tbody>
</table>

Again, the electrical conductivity is shown to be a less quench sensitive property compared to hardness.

![Figure 5-64 Peak Aged Electrical Conductivity C-curve](image)

**Figure 5-64 Peak Aged Electrical Conductivity C-curve**

### 5.10.6.2 Overaged

Figure 5-65 shows the change in electrical conductivity/resistivity with respect to the distance from the quenched end.
Figure 5-65   Electrical Conductivity - Jominy End Quench - Overaged

A rapid increase is observed in the electrical conductivity in the first 20mm of the Jominy specimen where the cooling rates are at their highest from 36%IACS to a final value of approximately 37%IACS at 50mm from the quenched end.

Figure 5-66   Measured Electrical Conductivity vs Predicted Electrical Conductivity for 7010-Overaged ESD=1.71%
Figure 5-66 shows the measured conductivity vs the predicted conductivity following optimisation of the $k$ coefficients using the EXCEL® solver method with a fit of 1.71% achieved. The resulting $k$ coefficients and C-curves are shown in Table 5-26 and Figure 5-67 respectively.

Table 5-26 $k$-coefficients for Jominy electrical conductivity for overaged

<table>
<thead>
<tr>
<th>$k_2$ (s)</th>
<th>$k_3$ (J.mol$^{-1}$)</th>
<th>$k_4$ (K)</th>
<th>$k_5$ (J.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.95E-13</td>
<td>1087.454</td>
<td>748</td>
<td>133952</td>
</tr>
</tbody>
</table>

Figure 5-67 Overaged Electrical Conductivity C-curve

5.10.6.3 Cold compressed+overaged

Figure 5-68 shows the change in electrical conductivity/resistivity with respect to the distance from the quenched end for the cold compressed+overaged Jominy specimen. At the quenched end of the specimen, where the quench rate is at its maximum, an electrical conductivity of 39.3%IACS is measured. This decreases to 40.6%IACS at 63mm from the quenched end as the quench rate decreases and precipitation occurs. A
higher electrical conductivity is observed along the specimen at all points compared to the peak aged and overaged specimens.

Figure 5-68 Electrical Conductivity/Resistivity-Jominy End Quench-Cold Compressed+Overaged

Figure 5-69 Measured Electrical Conductivity vs predicted Electrical Conductivity for 7010-cold compressed+overaged ESD=1.61%
A plateau is observed from approximately 20 to 50mm from the quenched end. This is probably due to non-uniform compression along the length of the sample which would affect the localised dislocation density along the length of the bar resulting in different precipitation kinetics during aging. Figure 5-69 shows the measured electrical conductivity vs the predicted electrical conductivity following optimisation of the data using EXCEL. The resulting $k$ coefficients are shown in Table 5-27. An ESD of 1.61% was achieved which is a good fit to the data thought again this is mainly due to the small data set and only a small change in electrical conductivity over the length of the sample.

Table 5-27  $k$-coefficients for Jominy electrical conductivity-C-curve-cold compressed+overaged

<table>
<thead>
<tr>
<th>$k_2$ (s)</th>
<th>$k_3$ (J.mol$^{-1}$)</th>
<th>$k_4$ (K)</th>
<th>$k_5$ (J.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.95E-13</td>
<td>920.1251</td>
<td>748</td>
<td>133952</td>
</tr>
</tbody>
</table>

The resulting electrical conductivity C-curve for the 7010 cold compressed+overaged specimen is shown Figure 5-70.

![Electrical Conductivity C-curve - Cold Compressed+Overaged](image-url)
Table 5-28 shows a comparison of the $k_2$-$k_5$ coefficients for the electrical conductivity C-curves (as shown in Figure 5-71) for the three different tempers derived using the Jominy end quench method. $k_4$ and $k_5$ are fixed values.

Table 5-28  Comparison of the $k_2$-$k_5$ coefficients for the electrical conductivity C-curves for the three different tempers

<table>
<thead>
<tr>
<th></th>
<th>$k_2$</th>
<th>$k_3$ (J.mol$^{-1}$)</th>
<th>$k_4$</th>
<th>$k_5$ (J.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Aged</td>
<td>9.1E-13</td>
<td>1275.323</td>
<td>7.18</td>
<td>1.35E+05</td>
</tr>
<tr>
<td>Overaged</td>
<td>8.95E-13</td>
<td>1087.454</td>
<td>7.18</td>
<td>1.35E+05</td>
</tr>
<tr>
<td>CC+Overaged</td>
<td>8.95E-13</td>
<td>920.1251</td>
<td>7.18</td>
<td>1.35E+05</td>
</tr>
</tbody>
</table>

Figure 5-71  Electrical Conductivity C-curves for peak aged, overaged and cold compressed+overaged from Jominy specimens

$k_2$ shows a slightly decreased value for the overaged and cold compressed+overaged samples. This would be consistent with an increased number of dislocations and hence increased availability of nucleation sites in the cold compressed specimen. $k_4$ shows a clearly decreasing trend and is related to the energy required to form a nucleus. This is due to the energy requirement to form a nucleus is lower for heterogeneous precipitation compared to homogenous nucleation. The amount of heterogeneous
nucleated precipitation is greater in both the overaged and higher again in the cold compressed+overaged specimens. The apparent shift in the nose of the curve to a shorter time for the cold-compressed+overaged specimen is due to a greater depletion of solute in the specimen and not a difference in quench sensitivity.

5.11 Microstructural Analysis

5.11.1 Microstructural Analysis-Isothermally Quenched Samples

Examination of the resulting microstructures was carried out in order to relate the resulting microstructure to the C-curves. Figure 5-72 show the optical microstructure at various points on and off the non-isokinetic 99.5 % C-curve for 7010 in the overaged condition. The microstructure at two points on the C-curve show similar microstructures. A point on the curve represents, in this case, points of the same Rp0.2. For comparison, a sample held for a period of over 100 seconds at 335±2°C where the precipitation rate is at its maximum shows large amounts of both coarse grain boundary and intra-granular precipitation non-hardening η phase.

![Figure 5-72 99.5% C-curve optical microstructures.](image)
5.11.2 Microstructural Analysis - Jominy End Quench Samples

The Jominy end quench overaged and peak aged samples which used for the Jominy C-curve construction was cut into 3mm sections for optical microscopy. These samples were polished and etched using the regime describe in section 4.10. Figures 5-73 to 5-76 show the optical micrographs for the peak aged sample at distances of 1.5, 8, 28 and 38mm from the quenched end. Figures 5-77 to 5-81 shows the equivalent change in microstructure for the overaged specimens as the distance from the quenched end (DFQE) increases. As can be seen, there is a marked increase in the amount of both grain boundary and intergranular precipitation for both specimens as the DFQE increases/quench rate decreases with precipitation occurring in the order of grain boundary followed by intergranular precipitation. This is important as the property prediction models under examination in this work do not distinguish between the occurrence of inter and intra granular precipitation. Though the sections of both Jominy specimens were initially quenched at the same rate, the overaged alloy shows much more precipitation as expected at equivalent distances from the quenched end.

5.11.2.1 Jominy end quench peak aged microstructures

Figure 5-73 shows the microstructure for the peak aged specimen 1.5mm from the quenched end. The finite element (FE) predicted cooling curve and the Jominy technique derived peak aged C-curve are also shown. This is a typical microstructure for 7075 close to the peak aged condition. The structure shows the beginning of grain boundary precipitation due to the less than optimum cooling rate as highlighted in the cooling curve (see insert-Figure 5-73). The hardness of the sample was measured at 192.5HV0.5 with an electrical conductivity of 30.4%IACS.
Figure 5-73  Peak Aged-DFQE=1.5mm

Figure 5-74 shows the microstructure, for the peak aged specimen 8mm from the quenched end.

Figure 5-74  Peak Aged-DFQE=8mm

The microstructure shows very clear evidence of grain boundary η phase precipitation.

This is reflected in the less than optimum hardness of the sample 184Hv0.5 with a
corresponding electrical conductivity of 30.6% IACS. The corresponding FE predicted cooling curve is also shown.

Figure 5-75 Peak Aged-DFQE=28mm

Figure 5-76 shows the microstructure of the peak aged specimen alloy at 38mm from the quenched end. Complete saturation of the grain and sub-grain boundaries with precipitation can be observed. This level of grain boundary precipitation is responsible for the drastically reduced mechanical properties of the alloy, \(171HV_{0.5}\) when subjected to cooling rates below the critical quench rate identified by the C-curve. (This microstructure also shows the presence of small amounts Al\(_7\)Cu\(_2\)Fe impurities in the rolling direction as described earlier in section 3.2.4.)
5.11.2.2 Jominy end quench overaged microstructures

At 1.5mm from the quenched end as shown in Figure 5-77, where the cooling rate is close to optimal a typical microstructure for aluminium alloy 7010 in the overaged condition is observed.

Figure 5-77 Overaged-DFQE=1.5mm
This particular microstructure shows very early signs of grain boundary precipitation as the $\eta'$ phase is converted to $\eta$ during the overaging heat treatment with no quench induced intra granular precipitation. The sample recorded a hardness of 187HV$_{0.5}$ and an electrical conductivity of 36.0%IACS which is close to the maximum value achieved for an optimally cold water quenched sample. At 8mm from the quench end as shown in Figure 5-78, the appearance of quench induced precipitation is observed at the grain and sub-grain boundaries. This is reflected in the slight drop in hardness to 184HV$_{0.5}$ and an increase in electrical conductivity to 37.3%IACS as the amount of remaining solute decreases.

![Figure 5-78 Overaged-DFQE=8mm](image)

Figure 5-79 shows the microstructure of the Jominy sample at 28mm from the quenched end showing severe quench induced sub-grain and grain boundary precipitation with the initial appearance of intra-granular precipitates. At 28mm, a significant drop in hardness is recorded to 175HV$_{0.5}$ with a corresponding increase in electrical conductivity to 36.9%IACS.
Figure 5-79  Overaged—DFQE=28mm

At 38mm from the quenched end as shown in Figure 5-80 where the cooling rate is a slow 8°C.sec⁻¹, the sample is saturated with both inter and intra granular quench induced precipitation.

Figure 5-80  Overaged—DFQE=38mm
This is reflected in the substantial drop in hardness to $166H_v0.5$ (12.5%) and the increase in electrical conductivity to $37.0\%IACS$.

5.11.3 Transmission Electron Microscopy

In order to examine the effects of the isothermal hold time on the various precipitation reactions that can occur in 7010, transmission electron microscopy was carried out on a range of samples. The literature has shown that at long isothermal times, the presence of both T and S phases has been identified. Figure 5-8 shows a precipitate free zone (PFZ) and a broken network of coarse grain boundary precipitates.

![Brightfield TEM image of 7010-Overaged showing possible grain boundary η phases and a Precipitate Free Zone (PFZ)](image)

Figure 5-81  Brightfield TEM image of 7010-Overaged showing possible grain boundary η phases and a Precipitate Free Zone (PFZ)

The figure also shows the presence of a large precipitate free zone due to areas surrounding the grain boundary being devoid of solute and quenched in vacancies as well as smaller approx. 30nm possible η type precipitates in the grain boundary, the width of the PFZ being directly related to the quench rate. [Mackenzie 2003]
These equilibrium phase particles are precipitated by heterogeneous nucleation during the quench as homogenous nucleation occurs only when the holding temperature is below 200°C. These heterogeneous nucleating sites primarily consist of grain boundaries such as in this case and Al₃Zr₂ dispersoids. Intragranular fine-scale precipitates are also observed. These are more likely to be of the η' type which is associated with providing the highest level of hardening in 7000 series alloys. Figure 5-82 shows the presence of possible S-Phase in an isothermally held sample at 260±2°C for 1500s followed by overaging. The micrograph also shows the presence of possible large coalesced η phase precipitation at the grain boundary.

![Figure 5-82 Brightfield TEM image of 7010 isothermally held at 260°C for 1500 followed by overaging showing presence of possible S'-phase and large coalesced grain boundary η phases and a PFZ.](image)

260±2°C is lower than the critical temperature for precipitation but the long duration has resulted in the formation of grain boundary precipitates. The long duration of the isothermal hold has resulted in both the apparent precipitation of the equilibrium η type (MgZn₂) type phases as well at the lath shaped S-phase. These large (~200nm) precipitates have nucleated during the isothermal hold and have continued to grow.
during the aging treatment. In Figure 5-82, we also see the presence of a precipitate free zone. The presence of both \(\eta\)-phases and \(S'^{-}\)-phases has previously been observed by Godard et al. in 7010 following long duration holds below the critical temperature [Godard et al. 2002]. Figure 5-83 shows a section taken 35mm from the quenched end of the overaged Jominy end quench specimen.

![Figure 5-83](image)

Figure 5-83  Brightfield TEM Image of 7010 from section of Jominy end quench 35mm from the quenched end showing precipitation of an \(\eta\) precipitate on a dispersoid.

A \(~250\text{nm}\) long quench induced \(\eta\)-type precipitate which has heterogeneous nucleated on an \(\text{Al}_2\text{Zr}_3\) dispersoid is clearly visible (as marked-red arrow). The quench rate at 35mm from the quenched end according to the work carried out previously is \(~10^\circ\text{C/min}\).

5.11.4 Scanning Electron Microscopy

5.11.4.1 Fracture surfaces

Scanning electron microscopy was carried out on the fracture surfaces of a sub-set of the isothermal hold tensile samples. Tensile samples had been tested in the I. direction.
Figure 5-84 to Figure 5-87 show the ST-LT fracture surfaces for interrupted quench samples held at 335°C for period ranging from 2 to 200s. As can be seen, there is definite change in the failure mode as the sample become more ductile as the isothermal hold time increases. At the shorter isothermal hold times the mode of fracture is both transgranular and intergranular fracture. As the amount of precipitation increases, the failure mode moves more primarily towards an intergranular microvoid coalescence type failure.
5.12 The effect of increasing natural aging time (post-quench delay) prior to cold compression on the residual stress magnitudes

The aim of this section of work is to examine the effect of post-quench delay prior to cold compression on the residual stress magnitude. Following quenching, aluminium alloy 7010 will begin to age naturally. Previous work by Robinson and Tanner has shown that the effect of natural aging on residual stress magnitudes are negligible though to date very little publicly available research has examined the effect on the residual stress magnitude of post-quench delay (natural aging) prior to the plastic deformation stage (stretching or compression) which is often used commercial to reduce residual stress [Tanner et al. 2006].

Following the quench, the resulting stress pattern always produces compressive residual stresses on the sample's surface and tensile stresses in the core. In thick aerospace components surface compressive stresses are usually in the order of $\approx 200$ MPa. Plastic deformation by either stretching or compression has been shown to relieve this stress.

5.12.1 Strain Hardening and Natural Aging

A typical compressive engineering stress-strain curve for 7010 as quenched (CWQ) and naturally aged is shown in Figure 5-88.
Figure 5-88  Example compressive engineering stress vs engineering strain

Figure 5-89 shows the 0.2% proof stress vs natural aging time for increasing natural aging time of between 10 and 37560 mins. (~26 days) before cold compression of 2.5±0.1%.

Figure 5-89  Compressive 0.2% proof stress (MPa) vs natural aging time (mins.)
As expected, an increase is observed for the compressive 0.2% proof stress of the alloy due to strain hardening of the alloy as the natural aging time is increased. A 0.2% compressive proof stress of over 400MPa was observed for samples naturally aged for periods over 20000mins. (~14 days). Figure 5-90 shows the change in residual stress with respect to post quench delay on both the L-LT and L-ST surfaces. On the L-ST plane which was parallel to the cold compression direction, no statically significant change in the residual stress magnitude over increasing natural aging time prior to the cold compression was observed. All samples showed a final measured residual stress after cold compression of between 0 and -120MPa.

![Figure 5-90 Residual stress (L-LT Surface and L-ST) and 0.2% compressive proof stress (MPa) vs Natural aging time (minutes) (1)](image)

On the L-LT plane, a similar response was observed albeit with a reduced overall reduction in the observed residual stress compared to the L-ST plane. A greater overall reduction in the compressive residual stress on L-LT plane was expected, though friction at the sample platen interface may have reduced the effect. Other researchers
have reported that frictional effects between the sample and the steel compression platens can result in a complicated stress distribution on the surfaces in contact with the platens [Altschuler et al. 1988]. Though a lubricant was used during the cold compression step, imperfections in the surface flatness of both the sample and the platens may have resulted in the lubricant being "squeezed out" from between the surfaces thus increasing the level of friction at the sample/platen interface. A detailed finite analysis of the stress magnitudes during cold compression with variations in the coefficient of friction has been carried out by Tanner et al. who showed that high coefficients of friction (>1) can lead to high surface tensile stresses and high compressive core stresses [Tanner et al. 2003]. The sample size used for these experiments was 25(ST) x 25(LT) x 35mm(L). This was due to practical issues with respect to the limited load capacity of the Dartec 500kN universal testing machine used for compression as the alloy became stronger with natural aging. These are relatively small samples compared to the usual size samples recommended for residual stress analysis by x-ray diffraction. Sample geometry effects in general have been shown to have a significant effect on the measured residual stress as discussed in section 3.7.1.1.3 [Withers et al. 2001]. Peak broadening was also observed which in some cases required manual intervention to determine the best peak fit to the data. These inconsistencies and geometry issues would suggest that neutron diffraction would be a more suitable method for the evaluation of residual stress for these types of experiments.
5.12.2 The Effect of Varying % Cold Compression on Residual Stress Magnitudes

Figure 5-91  L-LT and L-ST Plane - Residual Stress vs %Cold Compression

Figure 5-91 shows the results of measurement of residual stresses on both the L-LT and L-ST planes vs % cold compression in the ST direction. As can be seen, there is a progressive decrease in the residual stress on both the L-LT and L-ST as the level of cold compression is increased from 0 to 4.75%. This is due to the yield stress of the alloy exceeding the residual stress thus causing a reduction in the residual stress magnitude within the specimen. Figure 5-91 indicates that 2% is sufficient to remove the majority (>100%) of the residual stress on the L-ST plane when compressed in the ST direction.
6 Conclusions

1) Rp_{0.2}: Vickers hardness and electrical conductivity C-curves based on classical Quench Factor Analysis and modifications to the classical Quench Factor Analysis model were constructed, evaluated and compared for 7010 in a an overaged temper. The limitations of the curve fitting method and classical QFA were demonstrated. A decrease was observed for the Estimated Standard Error for Rp_{0.2} from 18.19% for the curve fitting model where \sigma_{mm}=0 to 2.57% for the non-isokinetic where \sigma_{mm} is a temperature dependant variable.

2) The non-isokinetic model was shown to be more accurate than the isokinetic model when the loss in mechanical property is greater than 90% of the maximum achievable property value. The non-isokinetic model compared to the Classical QFA model provided a better fit to the data under 90% of the maximum attainable Rp_{0.2} with an error of 4.67% at 32.6% of the maximum attainable Rp_{0.2} compared to 17.54% at 32.6% using classical QFA.

3) A comparison of Rp_{0.2}, Vickers hardness and electrical conductive/resistivity C-curves for 7010 in the overaged showed no difference in quench sensitivity. A slightly higher nose temperature was observed at 350°C compared to the Vickers hardness and Rp_{0.2} at 335°C.

4) Hardness and electrical conductivity C-curves were constructed for 7010 in the peak aged, overaged and cold compression+overaged tempers using the Jominy end quench techniques as a source of continuously cooled data.
5) The effect of the introduction of a post-quench delay prior to cold compression on the final residual stress was examined and found to be inconclusive. No statistically relevant change in residual stress magnitude was observed for periods of between 10 and 37560 minutes (~26 days).

6) 2% cold compression in the ST direction is sufficient to remove 90% of the quench induced residual stress in 7010 alloy on the L-ST plane. There is no benefit of cold compressing to 4% when compared to 2.25%.
7 Future Work

1) The variable $\sigma_{\text{min}}$ non-isokinetic model is only valid where the precipitation of one phase is assumed. The current work has identified that the model has limitations at long temperature and times where the precipitation of $S$ has been observed. In order to identify the valid range of the current model the boundaries of the $\eta, \eta'$ and $S$ phase forming region need to be determined using electron microscopy. Recent work by Tiryakioglu has demonstrated a model for multiple quench precipitates and should be compared to existing models [Tiryakioglu & Shuey 2010a].

2) Conduct experiments to determine the solvus temperature and evaluate the influence of using this temperature in preference to the solution heat treatment temperature when determining $\sigma_{\text{min}}$.

3) Validation of the 7010 cold compressed+overaged C-curve using real world cold compressed forgings.

4) The usefulness of the Jominy end quench method could be extended by the use of alternative quenchants and insulation of the Jominy end piece in order to slow down the cooling rate thus extending the property prediction capability of the Jominy technique.

5) The determination of independently derived $k$ coefficients from physical data would provide for more realistic c-curves.
6) The effect of a post-quench delay in the application of cold compression and its effect on residual stress magnitudes were investigated. The results achieved were inconclusive. Further studies using neutron diffraction of larger sample sizes for residual stress measurement should be undertaken.
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APPENDIX 1 — Theoretical basis for relationship between quench factor and strength prediction [Staley et al. 1993]

 Interruption to the quench by the introduction of an isothermal hold step decreases the ability of the alloy to become stronger [Staley 1987]. This reduction is due to the precipitation of heterogeneous nucleated precipitates which are of a size and distribution where they make no contribution to the strength of the alloy. The remaining solute is assumed to precipitate in a form which improves the strength of the alloy during the subsequent artificial aging stage. The effects of the isothermal hold on the attainable strength can be described by:

\[ \sigma_e = \sigma_{\text{max}} \exp \left[ - (kt)^p \right] \]  

Equation A1- 1

Where: 
- \( k \) = Constant
- \( \sigma_e \) = Yield strength
- \( \sigma_{\text{max}} \) = Maximum attainable yield strength

When the equation is valid, the relationship between time and the \( \ln \left( \frac{\sigma_e}{\sigma_{\text{max}}} \right) \) at the isothermal hold temperature is linear, with a slope of 1 on a log-log axis. If we consider the Avarami equation for growth, which describes the isothermal transformation kinetics at a particular temperature, the equation can be modified to relate the attainable strength to isothermal hold time and temperature as follows:

\[ V_c = V_{c,\text{max}} \left[ 1 - \exp(-kt)^q \right] \]  

Equation A1- 2

Where: 
- \( V_c \) = Volume fraction of coarse precipitates which do not contribute to strengthening
\( V_{c,\text{max}} = \text{Equilibrium vol. fraction of coarse precipitates at hold temperature (T)} \)

Following precipitation of the strengthening phases during aging:

\[ V_a = V_{a,\text{max}} - V_c \quad \text{Equation A1-3} \]

Where: 
- \( V_a = \text{Volume fraction of hardening precipitates after aging} \)
- \( V_{a,\text{max}} = \text{Maximum volume fraction of hardening precipitates after aging} \)
- \( T = \text{temperature} \)

Substituting for \( V = V_c \) in Equation A1-2 and rearranging gives:

\[ \frac{1 - \frac{V_{c,\text{max}}}{V_{c,\text{max}}} + \frac{V_a}{V_c}}{1 - \exp(-kt)} = \left[ 1 - \exp(-kt) \right] \quad \text{Equation A1-4} \]

The value of \( V_{a,\text{max}} \) would appear to be much greater than the value for \( V_{c,\text{max}} \) due to the decreasing solubility with decreasing temperature of most of the solute in aluminium. The solvus temperatures for GP zones and transition participates produced during the aging process, however, are considerably lower than those for the equilibrium precipitate. Consequently not all the solute precipitates in underaged and peak aged tempers, and maximum volume fractions of fine precipitates produced during aging are less than predicted from equilibrium diagrams. Therefore, values for \( V_{a,\text{max}} \) are about the same as those for \( V_{c,\text{max}} \), so that the value of \( V_a \) term \( \frac{V_{a,\text{max}}}{V_{c,\text{max}}} \) approaches unity. Also, small deviations from unity in the value of \( \frac{V_{a,\text{max}}}{V_{c,\text{max}}} \) are not critical when the value of
\( \frac{V_{\alpha}}{V_{\alpha, \text{max}}} \) is close to unity. This would be the case if only a small fraction of the solute was precipitated as coarse particles. For such cases Equation A1-4 above can be rewritten:

\[
\frac{V_{\alpha}}{V_{\alpha, \text{max}}} = \left[ 1 - \exp(-kt) \right]^n
\]

Equation A1-5

\( \sigma_{\text{mm}} \) Yield strength is introduced by assuming that it is to consist of a contribution by the matrix \( \sigma_{\text{mm}} \) plus a contribution from the fine precipitates produced during the aging treatment \( \sigma_i - \sigma_{\text{mm}} \). The maximum strength possible when there is no hold at an intermediate temperature is \( \sigma_{\text{max}} - \sigma_{\text{mm}} \). The term \( \sigma_i - \sigma_{\text{mm}} \) is proportional to the volume fraction of the strengthening precipitate raised to a power, \( V_i^m \), and the term \( \sigma_{\text{max}} - \sigma_{\text{mm}} \) is proportional the maximum volume fraction of the strengthening precipitate possible at the aging temperatures, raised to the same power. \( V_{i, \text{max}} \). The exponent \( m \) is a constant related to the hardening mechanism. As discussed above, \( V_{\alpha, \text{max}} \) is approximately equal to \( V_{\alpha, \text{max}} \):

\[
\left[ \frac{\sigma_i - \sigma_{\text{mm}}}{\sigma_{\text{max}} - \sigma_{\text{mm}}} \right]^{\text{max}} = \frac{V_{\alpha}^m}{V_{i, \text{max}}^m}
\]

Equation A1-6

Therefore equation A1-5 can be rewritten as:
\[
\left( \frac{\sigma_x - \sigma_{\text{min}}}{\sigma_{\text{max}} - \sigma_{\text{min}}} \right)^m = \exp\left[1 - (kt)^n\right]
\]  \hspace{1cm} \text{Equation A1-7}

Where \( m' = \frac{1}{m} \)

For alloys where \( \sigma_{\text{min}} = \sigma_{\text{max}} \), Equation A1-7 can be approximated by:

\[
\left( \frac{\sigma_x}{\sigma_{\text{max}}} \right)^m = \exp\left[1 - (kt)^n\right]
\]  \hspace{1cm} \text{Equation A1-8}

Taking logs both sides twice and rearranging

\[\ln \left[ \ln \left( \frac{\sigma_x}{\sigma_{\text{max}}} \right) \right] = \ln \left( \frac{k^n}{m'} \right) n \ln t \]  \hspace{1cm} \text{Equation A1-9}

Replacing the term \( k^n/m' \) with a constant \( k \), equation A1-9 can be rewritten as

\[\frac{\sigma_x}{\sigma_{\text{max}}} = \exp\left[1 - (kt)^n\right] \text{ or } \sigma_x = \sigma_{\text{max}} \exp\left[1 - (kt)^n\right]\]  \hspace{1cm} \text{Equation A1-10}

Which is identical to Equation A1-1 when \( n=1 \)
APPENDIX 2 - Methodology for substitution of $1/C_t(T)$
for $k(T)$ [Staley et al. 1993]

![Figure A2-1 Three step cooling curve](image-url)

By assuming a three step cooling curve as shown in figure A2-1 where the material is quenched instantaneously to and from each isothermal hold. Using notations from section 3 and Equation 3-29, the following can be written:

$$\sigma_1 = \sigma_{\text{min}}(T_1) + \left(\sigma_{\text{max}} - \sigma_{\text{min}}(T_1)\right)\exp\left(-\frac{\Delta t_1}{C_1(T_1)}\right)$$  \hspace{1cm} \text{Equation A2-1}

After the first isothermal hold, the material is quenched to temperature $T_2$. Thus,

$$\sigma_1 = \sigma_{\text{min}}(T_2) + \left(\sigma_{\text{max}} - \sigma_{\text{min}}(T_2)\right)\exp\left(-\frac{\Delta t_2}{C_1(T_2)}\right)$$  \hspace{1cm} \text{Equation A2-2}
Where \( \tau_i \) = "equivalent time" for temperature \( T_2 \), i.e. the time necessary to attain a value of \( \sigma_i \) at temperature \( T_2 \) instead of \( T_1 \). Now the following expression for \( \sigma_i \) can be written:

\[
\sigma_i = \sigma_{\text{min}}(T_i) + \left[ (\sigma_{\text{max}} - \sigma_{\text{min}}(T_i)) \exp \left( -\frac{\tau_i}{C_i(T_i)} \right) \exp \left( -\frac{\Delta T_i}{C_i(T_i)} \right) \right]
\]

Equation A2-3

Comparing Equations \([\text{A2-2}]\) and \([\text{A2-3}]\) we can obtain:

\[
\sigma_i = \sigma_{\text{min}}(T_i) + (\sigma_i - \sigma_{\text{min}}(T_i)) \exp \left( -\frac{\Delta T_i}{C_i(T_i)} \right)
\]

Equation A2-4

This equation is identical to equation A2-1 if we shift time by one segment to the right on the cooling curve. Using an identical argument:

\[
\sigma_i = \sigma_{\text{min}}(T_i) + (\sigma_i - \sigma_{\text{min}}(T_i)) \exp \left( -\frac{\Delta T_i}{C_i(T_i)} \right)
\]

Equation A2-5

And it follows that:

\[
\sigma_i - \sigma_{\text{min}}(T_i) + (\sigma_{i-1} - \sigma_{\text{min}}(T_i)) \exp \left( -\frac{\Delta T_i}{C_i(T_i)} \right)
\]

Equation A2-6

Equation A2-6 indicates that the property loss for a given isothermal segment of the cooling curve depends only on the current driving force \( \sigma_{i-1} - \sigma_{\text{min}}(T_i) \), and not on the path which was used to get to the current point. After subtracting \( \sigma_{i-1} \) from both sides of Equation A2-6 and rearranging, we obtain:

\[
\Delta \sigma_i = \sigma_{i-1} - \sigma_{\text{min}}(T_i) \left( \exp \left( -\frac{\Delta T_i}{C_i(T_i)} \right) - 1 \right)
\]

Equation A2-7

Where: \( \Delta \sigma_i = \sigma_i - \sigma_{i-1} \).
Now the exponential function can be expanded in the Taylor expansion:

\[ \exp(-x) = 1 - x + o(x) \]

where the function \( o(x) \) has the following property:

\[ \lim_{x \to 0} \left( \frac{o(x)}{x} \right) = 0 \]

Using this expansion in equation A2-7, we get

\[ \frac{\Delta \sigma}{\Delta t} = \sigma_{r,\infty} - \sigma_{\text{min}} (T) \left( - \frac{1}{C_i(T)} + \frac{o(\Delta t)}{\Delta t} \right) \]

Equation A2-8

And passing to the limit as \( \Delta t \to 0 \) produces:

\[ \frac{d\sigma}{dt} = - \frac{1}{C_i(T)} \left( \sigma - \sigma_{\text{min}} (T) \right) \]

Equation A2-9

Which is Equation 3-28 and is identical to Equation 3-26 with

\[ k(T) = \left( \frac{1}{C_i(T)} \right) \]
APPENDIX 3 - Methodologies for C-Curve Construction

In order to carry out the complex data manipulation and calculations required for the generation of C-curves using the different methods outlined in the main body of this work, Microsoft EXCEL\textsuperscript{x} in conjunction with the regression analysis tools and the EXCEL\textsuperscript{x} Solver add-on from Frontline Systems are used. Origin 8 Professional from OriginLab\textsuperscript{x} was used for the determination of the minimum property values with respect to the isothermal hold temperatures required for the non-isokinetic methods.

Curve fitting method as developed by Richard Cudd - HDA Forgings (Mettis Aerospace)

This example uses the experimental determined tensile data set for 7010 in the overaged condition. The equation of the C-curve as defined by Staley is written as follows:

\[
C_i(T) = -k_1 k_2 \exp\left(\frac{k_3 k_4^2}{RT(k_4 - T)^2}\right) \exp\left(\frac{k_5}{RT}\right)
\]

Equation A3- 1

Where:

- \( C_i \) = Critical time required to precipitate a constant amount of solute (s)
- \( k_1 \) = Constant that equals the natural log of the fraction untransformed during quenching (no units)
- \( k_2 \) = Constant related to the reciprocal of the number of nucleation sites (s)
- \( k_3 \) = Constant proportional to the energy required to form a nucleus (J.mol\textsuperscript{-1})
- \( k_4 \) = Constant related to the solvus temperature (K)
- \( k_5 \) = Activation energy for diffusion, \( Q_0 \) (J.mol\textsuperscript{-1})
In order to use the acquired data in a manner suitable for use with Microsoft EXCEL®,
the C-curve equation was rewritten as follows where Log₁₀ is utilised to simplify the
classical Staley C-curve equation. A correction factor 0.43429 is introduced in the course of
this derivation as a result of using \( \ln(x) = \frac{\log(x)}{0.43429} \)

\[
\log C(T) = \log(k_1k_2) + k_1k_2 \left( \frac{1}{RT(k_3 - T)} \right) + k_3 \left( \frac{k_4}{RT} \right)
\]

Equation A3-2

This equation can then be simplified by the amalgamation of constants to:

\[
\log C(T) = C_1 + C_2 \left( \frac{1}{RT(k_3 - T)} \right) + C_3 \left( \frac{1}{RT} \right)
\]

Equation A3-3

Where \( C_1 = \log(k_1k_2) \), \( C_2 = k_1k_2 \) and \( C_3 = k_3 \) \( k_4 \)

Where \( C_1, C_2, \) and \( C_3 \) are constants:

Using this form of the equation, the isothermal data set was entered into the EXCEL®
worksheet for regression analysis as shown in Table A3-1. The value of \( k_4 \) was then
manually altered with each iteration in order to minimise the misfit between the
experimentally determined C-curve data and the calculated C-curves.
Table A3-1 demonstrates this process for two values of \( k_4 \). \( k_4 \) is the constant related to the solvus temperature of the alloy and analysis of other published C-curve data has shown this value to be between 700 and 1000 in methods where no restrictions are placed on the value of the \( k \) coefficients. The \( k_4 \) value in the \( \frac{1}{(k_4-T)^2} \) column in the above EXCEL worksheet was initially calculated with arbitrary values from 700 to 1000. The \( C_i \) values highlighted are \( C_i \) values calculated for \( k_4 = 700 \) (highlighted in red), these calculated \( C_i \) values will obviously change as we increment the value of \( k_4 \). Using the results of this table the \( \log C_i \) and \( \frac{1}{T} \) were copied and pasted to a new position on the worksheet in order to facilitate the use of the regression analysis tool. The \( \frac{1}{(k_4-T)^2} \) data for one of the \( k_4 \) values was copied and pasted adjacent to the \( \frac{1}{T} \) column (Table A3-2) and regression analysis carried out using the EXCEL regression analysis tool.
Table A3-2

<table>
<thead>
<tr>
<th>Log $C_t$</th>
<th>$1/T \text{K}$</th>
<th>$1/T(k_4-T)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.79934</td>
<td>0.002070</td>
<td>4.3968E-08</td>
</tr>
<tr>
<td>2.02119</td>
<td>0.001969</td>
<td>5.3399E-08</td>
</tr>
<tr>
<td>1.20412</td>
<td>0.001876</td>
<td>6.7273E-08</td>
</tr>
<tr>
<td>1.25527</td>
<td>0.001792</td>
<td>8.8877E-08</td>
</tr>
<tr>
<td>0.69897</td>
<td>0.001715</td>
<td>1.2530E-07</td>
</tr>
<tr>
<td>0.90309</td>
<td>0.001645</td>
<td>1.9432E-07</td>
</tr>
<tr>
<td>0.69897</td>
<td>0.001580</td>
<td>3.5192E-07</td>
</tr>
<tr>
<td>1.07918</td>
<td>0.001520</td>
<td>8.6154E-07</td>
</tr>
<tr>
<td>1.69897</td>
<td>0.001464</td>
<td>5.0652E-06</td>
</tr>
<tr>
<td>3.58378</td>
<td>0.001403</td>
<td>8.2990E-06</td>
</tr>
</tbody>
</table>

On initiating the regression analysis option, the $Y$ range and $X$ range data in the dialogue box is input as follows: The $Log C_t$ data was assigned to the $Y$-range and the $X$ range was selected by highlighting both the $1/T$ and $1/T(k_4-T)^2$ data columns. In the output options the "new worksheet" option was selected and renamed with the chosen $k_4$ value chosen (in this case 700). This resulted in the creation of a new worksheet (named "700") (See Figure A3-1) which contained the completed regression analysis for $k_4=700$. This process was repeated for the range of values of $k_4$ as described earlier.
The result of primary interest from the regression analysis worksheet was the $R^2$ value (see Figure A3-1). In order to determine the “best” fit to the experimental data, the $k_4$ values were plotted against the $R^2$ values determined from the regression analysis for each individual $k_4$. The regression analysis was then repeated to “narrow down” the highest $R^2$ value using refined $k_4$ value and hence the best fit to the available data. A subset of the plotted $R^2$ for $k_4=840$ to 870 is shown in Figure A3-2. The optimum $k_4$ value determined for this set of data was 855 with a corresponding regression analysis $R^2$ value of 0.975142.
Figure A3-2  \( R^2 \) Values vs \( k_4 \) values from EXCEL* regression analysis worksheet

Following optimization of the \( k_4 \) value, the remaining constants were derived using the following set of equations (see Figure A3-3). Data for the constants A, B and C for the table are copied from the "intercept", "X variable 1" and "X-variable 2" cells respectively for the optimum \( k_4 \) value.

![Figure A3-2](image)

<table>
<thead>
<tr>
<th>( k_4 )</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>( R^2 )</th>
<th>( k_5 )</th>
<th>( k_6 )</th>
<th>( k_7 )</th>
<th>( k_8 )</th>
<th>( k_9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>855</td>
<td>-15.33278</td>
<td>7889.566189</td>
<td>112485847</td>
<td>0.975172</td>
<td>151040.9072</td>
<td>2945.826151</td>
<td>-5.1293E-02</td>
<td>4.6475E-16</td>
<td>9.06064E-16</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
  k_5 &= B \\
  k_3 &= \frac{C(8.314)}{k_2^2(0.43429)} \\
  k_1 &= \ln(0.95) \\
  k_2 &= 10^{-1} \\
  k_2 &= \frac{k_1 k_2}{k_3}
\end{align*}
\]

Figure A3-3  Table and formulae used to determine \( k_2, k_1 \) and \( k_4 \).

Where: \( R = \text{Universal Gas Constant} = 8.314 \ (\text{JK}^{-1} \text{mol}^{-1}) \)

0.43429 is a correction factor that is included during the simplification of the C-curve equation as a result of using the Log of the C-curve equation.

\[
\ln(x) = \frac{\log(x)}{0.43429}
\]
The value \( k_1 = \ln(0.95) \), this is the natural log of the percentage of the attained property on which the experimental C-curve was based. Using the obtained values of \( k_2 \) to \( k_5 \) from the relationships described above, using \( k_1 = \ln(0.95) \) and substituting into the original C-curve formula for temperatures from 190-470°C. The \( C_r \) values for the 95% C-curve can be determined as shown in Table A3-3 by multiplication of the various C-curve equation components.

\[
C_r = k_1 k_2 \exp \left[ \frac{k_3 k_4^2}{RT(k_4 - T)} \right] \exp \left[ \frac{k_5}{RT} \right]
\]

**Equation A3-4**

<table>
<thead>
<tr>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
<th>( k_4 )</th>
<th>( k_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0512833</td>
<td>9.061E-15</td>
<td>2946</td>
<td>855</td>
<td>151040.9</td>
</tr>
</tbody>
</table>

**Table A3-3**  
C-curve construction worksheet (determination of \( C_r \) values)

<table>
<thead>
<tr>
<th>Temp.(°C)</th>
<th>Temp.(K)</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( k_3 )</th>
<th>( k_4 )</th>
<th>( C_r )(99.5%)</th>
<th>Temp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>470</td>
<td>743</td>
<td>-0.051293</td>
<td>9.06064E-15</td>
<td>4.87E+12</td>
<td>226359944253</td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>460</td>
<td>733</td>
<td>-0.051293</td>
<td>9.06064E-15</td>
<td>1.19E+21</td>
<td>5507865239</td>
<td>460</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>723</td>
<td>-0.051293</td>
<td>9.06064E-15</td>
<td>6.94E+19</td>
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For other % C-curves, \( k_1 \) was substituted with the \( \ln \) of for example, 0.95 or 0.90 to construct the 95 or 90% C-curves respectively.
For the determination of the mechanical properties such as hardness and $R_{p0.2}$, the measured maximum property value is much greater than the minimum property ($\sigma_{\text{max}} > \sigma_{\text{min}}$). Staley stated that the process can be simplified by assuming that the value of $\sigma_{\text{min}} = 0$. For electrical conductivity C-curves where there is a requirement to determine a percentage variation in the electrical conductivity, the electrical conductivity values %IACS values were converted to electrical resistivity using the equation in the main text where 

$$ \text{Resistivity (}\Omega \text{m } 10^{-8}) = \frac{172.41}{\% \text{IACS}} $$

**Quench Factor analysis and property determination**

To determine the quench factor of the alloy, the C-curve $k$ coefficients are used in conjunction with the process cooling curve. Figure A3-4 below shows the calculation of the Quench Factor ($Q$) and the predicted $R_{p0.2}$ for alloy 7010 subjected to a boiling water quench and subsequently overaged.

**Figure A3-4  Quench Factor Analysis (QFA) worksheet**
The t (see column A) represents the time intervals in seconds generated by the data recorded by the data acquisition system during the quenching of the sample. The temp column (column B) corresponds to the temperature recorded at each time interval. The “Avg. Temp °C” column – (column c) is the average temperature between the time intervals and “Avg. Temp K” (column d) is the corresponding average temperature converted into Kelvin. The C; column calculates the critical time using the previously calculated k constants.

The incremental quench factor (q) is determined by the division of the time increment (see cell A11) by the C; value and is shown in column “q”. The Quench Factor “τ” is then calculated by the summing of the values of the incremental quench factors over the critical range 450-150°C. The EXCEL" formulas for identifying the critical range automatically from the worksheet are shown for clarity. This process was repeated for different quench media.

The mechanical property of the alloy (in this case the Rp02 can be determined using the equation A3-5 below. (this is also shown in Figure A3-4) along with the corresponding EXCEL" formula).

\[ \sigma = \sigma_{\text{max}} \exp(-k \tau) \]  

Equation A3-5

In this case the alloy was predicted to have an Rp02 of 499 MPa with a corresponding quench factor of 9.4. The term \( \sigma \) is used interchangeably throughout the body of this appendix to describe the mechanical property under evaluation as opposed to the normal convention of using \( \sigma \) to represent nominal stress.
C-curve Non-isokinetic method (Jominy)

In order to use the non-isokinetic method where \( \sigma_{\text{min}} \) is a variable as opposed to a fixed value (zero or non-zero), a new data set to account for the variation of the minimum achievable property value (e.g. hardness or proof stress) with respect to isothermal hold temperature was required. This example is for the Jominy method but applies equally to the non-Jominy method where “distance from the quenched” end” hardness is replaced by hardness/Rp0.2 data generated from the isothermal step quench data at the various temperatures and hold times.

Variable \( \sigma_{\text{min}} \) values for use in the EXCEL\(^x\) property prediction were determined by fitting a Boltzmann sigmoidal curve to the experimental >24h equilibrium isothermal hold data thus providing a set of values for \( \sigma_{\text{min}} \) over the full quenching temperature range. Curve fitting was carried using Origin 8 Pro Software. Figure A3-5 and A3-6 shows this process for hardness data obtained for 7010 in an overaged condition.

Figure A3-5 Curve fitting of isothermal hardness data.
In order to fit a Boltzman sigmoidal fit to the experimental data, using OriginPRo8 select tools > analysis > fitting > non-linear curve fit from the Origin menu bar. Under category, chose polynomial and under function select Poly4 as shown in Figure A3-5 and Figure A3-6.

Figure A3-6 Boltzman Sigmoidal fit obtained using OriginLab Pro 8

Origin then creates a table with values for A1, A2, xo and dx which describes the curve and can be used to determine a value for σmin mathematically. Figure A3-7 shows the “initial data” worksheet. The experimentally determined average Vickers hardness results, the Boltzman sigmoidal fit coefficients for the isothermally held samples and the previously determined maximum attainable property value Hv20(max) (in this case Vickers hardness 189.7 Hv0.5) for 7010 in the overaged condition were entered into the worksheet.
Figure A3-7 Initial Data Worksheet

Figure A3-8 shows the analysis sheet used for the minimising of the Estimated Standard Deviation. Data from beyond 50mm from the quenched end was ignored for the process of the fit for the Jominy to avoid skewing of the data. The ESD value is then minimised using the EXCEL solver function as described below. The solver function was initiated by selecting the solver function from the Tools pull down menu as shown in Figure A3-9
Figure A3-8  Analysis Worksheet

Figure A3-9  Solver Pull-down menu - selection
This displays the Solver Parameter Dialogue box as shown in Figure A3-10. The Set Target Cell box is the ESD cell $C2$ and is minimised by changing cells $B4:B5$ i.e. $k_2$ and $k_3$

![Solver Parameters Dialogue Box](image)

**Figure A3-10 Solver Parameters Dialogue box**

Several other options are available for modification as shown in the Solver Options dialogue box below (Figure A3-11). The figure shows the options chosen for this particular exercise. A full description of the various selectable options and their effect on the final solution are available at [http://www.frontsys.com](http://www.frontsys.com).

![Solver Options Dialogue Box](image)

**Figure A3-11 Solver Option Dialogue Box**
Figure A3-12 show the worksheet used to determine the hardness at increasing assistance from the quenched end. This example shows a predicted hardness of 187.6 HV at 3 mm from the quenched end. The worksheet also included an error checking mechanism whereby C values which exceeded the maximum allowable number in EXCEL (i.e. >E+100) resulting in "errors of magnitude" were capped at E+10.

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</tr>
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<tbody>
<tr>
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<td>=A3*4/3</td>
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</table>

Figure A3-12 Distance from quenched end–3mm worksheet

Using the values determined from the “Distance from quenched end” worksheets. Ct values for the iso-hardness C-curve were calculated in a separate worksheet as shown in Figure A3-13
Figure A3-13 $C_i$ values for Iso-hardness C-curve calculations (90% of Hv$_{\text{max}}$)

The $C_i$ (sec.) values vs Temperature (°C) using the data generated for various percentages of the maximum attainable hardness are then plotted as shown in Figure A3-14 to produce the final iso-hardness C-curves.

Figure A3-14 Iso-Strength Curves for 99.5, 95, 90, 80, 70, 60, 50, 40% of the maximum attainable Vickers hardness (Hv)
APPENDIX 4 - Publications

The application of advances in quench factor analysis property prediction to the heat treatment of 7010 aluminium alloy

Precipitation kinetics and the time temperature property curves of 7010
Precipitation kinetics and the time temperature property curves of 7010
R. J. Flynn  
Materials Ireland Research Centre, National Technological Park, Limerick, Ireland
J. S. Robinson  
Department of Materials Science and Technology, University of Limerick, Ireland

Abstract

Prediction of mechanical property levels in thick section heat-treatable aluminium alloys can be made using quench factor analysis. The utilisation of this technique requires both a description of the quench path and a time-temperature (T-T) curve for the property of interest. Few time temperature property curves for the less common alloys exist in the public domain. 7010 is a forging and plate alloy widely used for strength critical aerospace components. Hardness and electrical conductivity T-T curves produced by standard interrupted quench techniques are presented for 7010-T76. In addition, specimen cut from a 7010-W52 forging have been utilised to produce a tensile 7010-T76 C-curve and the influence of cold compression on the precipitation kinetics determined.

Introduction

Aluminium alloy 7010, 7xxx (Al-Zn-Mg-Cu) series alloys through controlled precipitation of a supersaturated solid solution can achieve the highest strength at room temperature of any of the wrought aluminium alloys with yield strengths in excess of 500MPa. 7010 (D11D5636) is a heat treatable alloy with an excellent strength-to-weight ratio, which was developed by Alcan International and HIDA Forgings Ltd for specific structural applications within the aerospace industry. The composition of 7010 is very similar to Alcoa’s 7050. Both these alloys use zirconium as the main grain-refining agent through the formation of AlZr dispersoids rather than chromium which is used in 7075. A comparison of the elemental composition of 7010, 7050 and 7075 is shown in Table 1.

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Table 1: Elemental composition (wt%) and specification for 7010, 7050 and 7075

The T76 temper is a quenched and overage heat treatment primarily used to prevent exfoliation and improve stress corrosion cracking resistance in sheet components. This temper is now more in demand by aircraft designers due to the decrease in the use of chromium based surface treatments.

C-curves and quench factor analysis. In order to strengthen aluminium alloys, rapid quenching from above the solvsus temperature is required to retain hardening elements and intermetallic compounds in solid solution while avoiding the precipitation of coarse secondary phases. Quenched parts may then be aged through controlled decomposition to produce a precipitation-hardened microstructure. There are several methods available for the prediction of post-quenched physical properties in aluminium alloys, the most noted being that developed by Fink and Willey. This method describes Time-Temperature-Property (TTP) curves or C-curves, which are determined using an interrupted, quench technique. The subsequent development of Quench Factor Analysis by Evancho and Staley gave more accurate predictions for non-linear kinetics and relies on the availability of accurate TTP information. Continuous cooling precipitation kinetics are defined by Eq. 1 and 2.

\[ C = \text{Transformed fraction} \]
\[ \tau = \text{Quench factor} \]

\[ \tau = \int_{t_0}^{t} \frac{dt}{C} \]

where:

- \( t_0 \) = Quench start time (s)
- \( t_f \) = Quench finish time (s)
- \( C_t \) = Critical time as a function of temperature (s)

The C-curve is the loci of the critical times and identifies the critical temperature range where the precipitation rate is at its maximum and hence, the time required to attain the desired physical properties. The \( C_t \) function, which mathematically
describes the curve and consequently the precipitation kinetics, can be estimated by Eq. 3:

\[ C_r = k_1 k_c \exp\left( \frac{k_2 k_4^2}{RT(k_4 - T)} \right) \exp\left( \frac{k_5}{RT} \right) \]  \hspace{1cm} \text{Eq. 3}

where:

- \( C_r \): Critical time required to precipitate a constant amount of solute (s)
- \( k_1 \): Constant that equals the natural log of the fraction untransformed during quenching
- \( k_2 \): Constant related to the reciprocal of the number of nucleation sites (s)
- \( k_4 \): Constant related to the energy required to form a nucleus (J.mol\(^{-1}\) K\(^{-1}\))
- \( k_5 \): Constant related to the solvus temperature (K)
- \( k_6 \): Constant related to the activation energy for diffusion (J.mol\(^{-1}\))
- \( R \): Universal gas constant (J.mol\(^{-1}\) K\(^{-1}\))
- \( T \): Absolute temperature (K)

The required property of the alloy can be predicted from Eq. 1:

\[ \sigma_r = \sigma_{\text{max}} e^{b_1 \beta} \]  \hspace{1cm} \text{Eq. 4}

where:

- \( \sigma_r \): Predicted property value
- \( \sigma_{\text{max}} \): Property after infinite quench
- \( Q \): Cumulative quench factor

The cumulative quench factor \( Q \) is described by Eq. 5:

\[ Q = \Sigma \tau \]  \hspace{1cm} \text{Eq. 5}

\( Q \) is the sum of the incremental quench factors \( \tau \), which is determined from the combination of a cooling curve and C-curve for the alloy under consideration. It is defined as the ratio of the time step length divided by its corresponding \( C_r \) value and can be expressed by Eq. 6:

\[ \tau = \frac{A_t}{C_r} \]  \hspace{1cm} \text{Eq. 6}

where:

- \( \tau \): Incremental quench factor
- \( A_t \): Time step

The complexity of determining C-curve information and their scarcity within the public domain has slowed the widespread use of Quench Factor Analysis for aluminium alloys. It is the purpose of this paper to address this issue.

Using the Fink & Willey\(^1\) interrupted quench technique, a Time-Temperature-Property C-curve has been constructed for 7010-176 tensile specimens followed by multiple regression analysis to determine coefficients \( k_5-k_6 \). Calculation of these constants allows property prediction C-curves to be constructed.

**Experimental**

Sample Preparation. 112 tensile test pieces were machined from a 7010-W52 rectilinear open die forging manufactured on a 20MN draw down hydraulic press supplied by IIDA Forging Ltd., Redditch, UK. These forgings are similar to those, which after aging and machining form part of the wing spar assembly in the Airbus A330/A340. The forgings had dimensions 3045 (1-L-Longitudinal) \( \times \) 160 (L1-Long Transverse) \( \times \) 125 mm (X1-Short Transverse direction). After forging the block was solution heat treated at 475°C for 6h followed by cold compression of 2.4±0.5% on a 120MN hydraulic press. Tensile blanks were cut from the L1 direction as shown in figure 1 and machined to the tensile test piece illustrated.

**Figure 1**: Tensile test piece geometry and location of tensile specimens
Specimens for hardness and electrical conductivity measurements consisted of 6mm x 0.2mm (0.256") thick, 25±0.1mm (0.98") square coupons cut from sections of a similar rectangular forging block. Samples were annealed at 475±1°C and allowed to furnace cool.

**Cooling Curves.** In order to determine the required time for samples to reach equilibrium on quenching, cooling curves for both tensile and hardness-electrical conductivity samples were determined. This was accomplished by using an embedded K-type thermocouple centrally located within the sample and a data acquisition system. Samples were quenched from the solution temperature of 475±1°C to the various interrupt quench temperatures to determine the time required for the sample to reach equilibrium. Data was recorded at a frequency of 4Hz for the duration of the run and the resultant cooling curves constructed.

**C-curve determination.** C-curves were determined using the interrupted quench technique as previously described. A matrix of 10 temperatures and 8 isothermal hold times based on a previously determined 9110±1°C C-curve was constructed using temperatures from 210 to 440±1°C and at periods ranging from 2 to 15000 seconds as shown in table 2.

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<th>220</th>
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<td>700</td>
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<td>900</td>
<td>1000</td>
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Table 2: Time-temperature matrix for isothermal heat treatment

80 samples were solution heat treated at 475±1°C for 2 hours using a circulating water quenching system. Following solution treatment, the specimens were rapidly quenched in a Houghton Durcrite salt bath containing an AG 140 Degussa specification sodium nitrate potassium nitrate eutectic mixture.

Isothermal heat treatment was carried out in accordance with the matrix schedule, taking into consideration the time required for the sample to reach equilibrium. This was followed by a cold water quenching (22°C) and artificial aging to the T76 condition as shown in figure 2 (40h @ 120±1°C and 8h @ 172±1°C).

Post solution heat-treated samples were stored at -20°C while awaiting the T76 heat treatment to delay natural aging.

Samples marked in figure 1 as A9, B10, C3 and D4 were determined to be representative of the forging and used as the 100% tensile property samples. These together with hardness and electrical conductivity samples were prepared by solution treatment at 475±1°C for 2h followed by cold water quenching to room temperature and subsequently aged to the T76 condition. 4 samples, F4, B5, F15 and G16 were also aged using the same artificial aging schedule directly from the W52 condition to the T7652 condition. The "W" temper designation indicating that the alloy has been solution heat treated but that the supersaturated solid solution is in an unstable condition.

Square coupon samples for hardness and electrical conductivity measurements were annealed above the solvsus temperature at 475±1°C and allowed to furnace cool. Solution heat treatment, isothermal heat treatment and artificial aging were carried out in the same manner as the tensile samples.

Tensile properties were determined using a Darve 500KN servo hydraulic universal testing machine in accordance with BS444, using a load piece of 6x0.05mm (0.256") diameter with a gauge length of 30mm (1.18") as previously described in figure 1. An Epsilon Corp. extensometer was used to measure extension.

Hardness testing was performed on the square coupon samples using an Instron Wolpert HVS-Vickers hardness tester, calibrated to the requirements of ASTM E92-02, taking an average of three measurements across the width of the sample.

Conductivity measurements were conducted in accordance with ASTM E1004-91 using a Verimeter M49000 eddy current conductivity meter. Calibration was carried out using a 7010 traceable standard of known conductivity and results are reported as a percentage of the International Annealed Copper Standard (%IACS). In figure 2, it is shown that 2h at 475°C and 8h at 172°C were the critical temperatures for the C-curve.

**Results**

Cooling curves were constructed for both tensile specimens and square hardness-electrical conductivity coupons as previously described, a subset of which, are shown in figures 3 and 4.

The time required for the tensile and hardness-electrical conductivity samples to reach within 5°C of the isothermal hold temperature was determined to be 3 and 6 seconds respectively.

After solution treatment, cold water quenching and aging to the T76 temper, the maximum attainable 0.2% proof stress (Rp0.2), hardness and minimum electrical conductivity
obtained was 524 MPa, 189.7 HV20 and 37.2 %IACS respectively.

Figure 3: Cooling curves for square hardness/electrical conductivity samples

Using this information and the data generated from the interrupted quenching curves, an example of which is shown in figure 5. experimental C-curves were constructed for Rpu.2, hardness and electrical conductivity. The coefficients k2, k3, k4, and k5 for defining the predicted C-curves were determined using multiple regression analysis from the 95% untransformed data. The values obtained for Rpu.2 7010-T76 and for 2 other 7XXX series alloys, with coefficients taken from the literature are shown in table 3. Table 4 shows a comparison in coefficients for Rpu.2, hardness and electrical conductivity C-curves for 7010-T76.

Table 3: Rpu.2 C-curve coefficients for 7010-T76, 7050-T76 and 7075-T6

<table>
<thead>
<tr>
<th>Alloy</th>
<th>k2</th>
<th>k3</th>
<th>k4</th>
<th>k5</th>
</tr>
</thead>
<tbody>
<tr>
<td>7010-T76</td>
<td>4.41E-15</td>
<td>2945</td>
<td>855</td>
<td>1.5E+5</td>
</tr>
<tr>
<td>7050-T76</td>
<td>2.21E-19</td>
<td>5190</td>
<td>850</td>
<td>1.8E+5</td>
</tr>
<tr>
<td>7075-T6</td>
<td>4.11E-13</td>
<td>1050</td>
<td>780</td>
<td>1.4E+5</td>
</tr>
</tbody>
</table>

Table 4: 7010 C-curve coefficients for Rpu.2, hardness and electrical conductivity

Figures 6 and 7 show experimental C-curves and predicted 90, 95, 99 and 99.5% of the total achievable Rpu.2 and hardness values for 7010-T76 calculated using alternative k1 values. The points on the C-curve loci at different time- temperature co-ordinates correspond to equivalent property values and from these curves we see that the most critical range occurs between 400 and 250°C with the nose of the curve at occurring at 340°C.

Figure 9 shows the electrical conductivity C-curve for 7010-T76 with 95, 99 and 99.5% predicted values and experimental 92 and 95% C-curves equivalent to 40.54 and 39.25% IACS.
The correlation between the predicted and experimental C-curves for 90% of predicted property value was low. This is possibly due to several reasons: 1) The maximum property value used was determined experimentally and since it is impossible to quench at an infinite rate some solute was lost. 2) The complete cooling curve to the isothermal hold temperature was not used and quench factors need to be taken into account (figure 9 shows the variation of Rp0.2 with quench factor). 3) Experimental error at the experimental 95% property value determination being compounded in the 90% prediction calculations. Recommendations available in the literature suggest for a 7050 alloy that cooling rates through the critical temperature range should exceed 300°C/sec. This is only possible to obtain for small sheet samples. Using the square coupons and tensile sample specimens it was not possible to achieve cooling rates of greater than 150°C/sec.

Table 5 shows average values for the T7652 temper and T76. T7652 refers to aging directly from the W52 or cold compressed condition without an intermediate re-solution heat treatment. 7000 series alloys are not stable at room temperature and age indefinitely over many years and are seldom used in the “W” temper.

Attainable strengths of 7XXX alloys are directly related to the amount of solute remaining in solid solution after the quench. Natural aging is a process of zone formation, not true precipitation and hence the quantity of final precipitation is lower than the re-solution treated T76.

<table>
<thead>
<tr>
<th>Temper</th>
<th>T7652</th>
<th>T76</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rp0.2 (MPa)</td>
<td>457.5*</td>
<td>524*</td>
</tr>
</tbody>
</table>

Table 5: Comparison of T7652 and T76 tempers for 7010

Cold compression however, increases the distribution of Guinier-Preston zones and due to the two-step aging 176 temper as shown in figure 4, their transformation to transition precipitates, gives a Rp0.2 of 457.5 MPa for the 17652 condition which is only 10% less than that of the 176 condition.
On examination of the T7652 $R_p$, results, values tended to be slightly higher toward the surface of the block than towards the core. A $R_p$ of 466 MPa was recorded for the corner or the block while a value of 453 MPa was recorded for the core due to faster cooling rates.

This poses an additional difficulty for $C$-curve analysis as most thick products, i.e. plate / forgings are mechanically stress relieved.

**Summary and conclusions**

The experimental $C$-curves exhibit typical property and precipitation kinetics behaviour for 7XXX series aluminium alloys. At temperatures below 210°C the rate of precipitation is low even though the thermodynamic potential for precipitation formation is high, requiring long soakage times. As the temperature increases towards the nose of the $C$-curve at approximately 335°C, the degree of supersaturation increases. The time required to nucleate and grow precipitates is under 10 seconds and is diffusion controlled. At higher temperatures typically above 400°C but below the solvus, soakage times in the order of 1000-15000s or more are required due to the low degree of supersaturation.

On comparing the 99.5% property prediction $C$-curves as shown figure 10, variations in the quench sensitivity for the different properties under consideration were observed. Good correlation exists between the tensile and hardness curves between 440 and 335°C degrees after which the curves diverge with equivalent hardness values being achieved in shorter quench times to that of the $R_p$. This may possibly be due to the higher cooling rates experienced at the sample surface thus allowing for more retained solid solution. While $R_p$ and hardness values depend on the amount of precipitation present, previous work\(^1\) has shown that electrical conductivity gives a good indication of the degree of solute that is removed during quenching from the solid solution. Other work\(^6\) has shown that the degree of supersaturation determines the volume fraction of the final precipitate and explains the good correlation between electrical conductivity and tensile properties. The shape of the $C$-curves and the relationship between $R_p$ and electrical conductivity as shown in figure 11 clearly demonstrates this for 7010-T76.

**Conclusions.**

- $R_p$, hardness and electrical conductivity $C$-curves for 7010-T76 have been determined.
- Coefficients for 7010-T76 have been determined.
- Good correlation between hardness and tensile $C$-curves was observed.
- The rate of cooling during quenching to the isothermal hold temperatures was not rapid enough to prevent some transformation especially at the nose of the $C$-curve.

**Acknowledgments**

The authors would like to thank the technical staff of the Materials Science Department at the University of Limerick and of the Materials Ireland Research Centre in the preparation of this paper.

**References**

THE APPLICATION OF ADVANCES IN QUENCH FACTOR ANALYSIS PROPERTY PREDICTION TO THE HEAT TREATMENT OF 7010 ALUMINIUM ALLOY

R.J. Flynn¹ and J.S. Robinson²
1. Materials Ireland Research Centre, University of Limerick, Ireland; email: bob.flynn@ul.ie
2. Department of Materials Science and Technology, University of Limerick, Ireland; email: jeremy.robinson@ul.ie

ABSTRACT

7010 is an Al-Zn-Mg-Cu forging and plate alloy, used in the aerospace industry for the production of key structural components. The alloy develops its strength through the development of a precipitation-hardened microstructure produced by aging of a quenched super-saturated solid solution. For over 30 years the Evancho and Staley developed Quench Factor Analysis model has been applied successfully to the prediction of post-quenched physical properties, in aged aluminium alloys. In recent years improvements have been made to the initial model incorporating the effect of remaining solute on nucleation rate as a function of temperature. This extends the usefulness of the Quench Factor approach to beyond the 15% loss in properties, allowing the prediction of properties in both fast quenched and slow cooled conditions such as in annealing. Tensile Time-Temperature-Property (TTP) or ‘C’ curves produced by an interrupted quench technique are presented for 7010-T76 including Quench Factor Analysis and subsequent modifications based on an improved non-isokinetic model.

Keywords: Aluminium Alloys, Quench Factor Analysis, 7010, Heat Treatment

1 INTRODUCTION

Quench Factor Analysis (QFA) [1] to date has been shown to be very successful as a property prediction technique in the post – quenched properties of both cast and wrought aluminium alloys where the maximum property loss did not exceeded 10-15%. Recent developments [2] have now shown that it is possible to successfully predict properties beyond this limit using modifications to the original quench factor analysis model.

1.1 Aluminium Alloy 7010

7010 is a zirconium containing 7xxx series Al-Zn-Mg-Cu alloy which attains its strength by rapid quenching from above the solvus to form a metastable supersaturated solid solution which can then be precipitation hardened (aged) to produce the required mechanical properties. These properties are dependent upon the quench-cooling rate from the solution heat treatment temperature as this determines the amount of solute available for the precipitation of the strengthening phases.

1.2 Property Prediction and Quench Factor Analysis

In order to relate the quenching rate with the final alloy strength, Fink et al. [3] developed a technique to determine the temperature range over which the quench rate has the most critical influence over the mechanical properties after aging. This was achieved by construction of Time-Temperature-Property (TTP) or ‘C’ curves using an interrupted quench technique which defines the time required to precipitate sufficient solute to reduce the strength by a specified amount but this method proved unsuitable where variations in the quench rate through the critical range occurred. This led to the subsequent development of Quench Factor Analysis.

The critical time \( C(T) \) function which mathematically describes the C-curve is defined as[1] as:

\[
C_i(T) = -k_5 k_4 \exp\left(-\frac{k_1 k_4^2}{RT(k_1 - T)}\right) \exp\left(\frac{k_4}{RT}\right)
\]

where, \( C_i(T) \)=Critical time required to precipitate a constant amount of solute (s), \( k_5\)=Natural log of the fraction untransformed, \( k_2\)=Reciprocal of the number of nucleation sites (s), \( k_1\)=Energy required to form a nucleus (J.mol\(^{-1}\) K\(^{-1}\)), \( k_3\)=Constant related to the solvus temperature (K), \( k_4\)=Constant related to the activation energy for diffusion (J.mol\(^{-1}\) K\(^{-1}\)), \( R\)=Universal gas constant (J.mol\(^{-1}\) K\(^{-1}\)) and \( T\)=Absolute temperature (K).

QFA is based on the principle of using isothermal transformation kinetics to predict transformations under non-isothermal conditions at temperatures
below the solvus, such as those that occur during continuous cooling. For aluminium alloys this transformation is described by:

$$\zeta = 1 - \exp(k_1 \tau)$$  \hspace{1cm} (2)

where, $\zeta$ = Fraction untransformed, $k_1$ = Constant and $\tau$ = Measure of the amount transformed (Quench Factor). Cahn’s analyses of transformation kinetics during continuous cooling [4] showed that for isokinetic reactions the fraction transformed under non-isothermal conditions is given by:

$$\tau = \int \frac{dt}{C_i(T)}$$  \hspace{1cm} (3)

where, $t_0$ = Quench start time (s), $t_f$ = Quench finish time (s), $C_i(T)$ = Critical time as a function of temperature (s). When $\tau=1$ the fraction transformed equals the fraction represented by the c-curve.

1.3 Property Prediction

The required property of the alloy can be predicted from equation (4)[5]:

$$\frac{\sigma_v - \sigma_{\text{min}}}{\sigma_{\text{max}} - \sigma_{\text{min}}} = \exp(k_2 \tau)$$  \hspace{1cm} (4)

where, $\tau$ = Quench factor, $\sigma_v$ = Rp0.2 (T76), $\sigma_{\text{min}}$ = Min. Rp0.2 (T76) (constant or temperature dependent), $\sigma_{\text{max}}$ = Max. Rp0.2 (T76) after an infinitely fast quench and $k_2$ = Natural log of the fraction untransformed during quenching.

Evancho et al. [1] in their original model set $\sigma_{\text{min}}=0$. In order to utilise Cahn’s model of predicting the extent of transformation under non-isothermal conditions. Based on that assumption:

$$\sigma_v = \sigma_{\text{max}} e^{k_2 \tau}$$  \hspace{1cm} (5)

2 EXPERIMENTAL

6mm diameter tensile test pieces were machined from the LT direction of a cold compressed (2.25 ± 0.5%) AA7010-W52 rectilinear open die forging manufactured by IIDA Forging Ltd., Redditch, UK.

2.1 C-Curve Determination

Samples were solution heat treated (2h@475 ± 5°C) followed by rapid quenching (<3s) into a sodium nitrite/potassium nitrate eutectic mixture at temperatures ranging from 210 to 440 ± 2°C and at isothermal holding periods from 2 to 15000 secs. This was followed by a room temperature quench (RTQ ~ 22°C) and artificial aging to the T76 condition (10h@120 ± 2°C + 8h@172 ± 2°C). Cooling curves were determined using a data acquisition system and an embedded K-type thermocouple centrally located within a representative sample. Time – temperature data was recorded at a frequency of 10Hz. Tensile properties were determined in accordance with BS4A4. The cumulative quench factor ($\tau$) was determined from the combination of a cooling curve and C-curve where $\tau$ is defined as the sum of the incremental quench factors as shown in equation 6.

$$\tau = \sum q_i$$  \hspace{1cm} (6)

$q_i$ is defined as the ratio of the time step length divided by its corresponding $C_i$ value and can be expressed by equation 7.

$$q_i = \frac{\Delta t}{C_i(T)}$$  \hspace{1cm} (7)

where, $q_i$ = Incremental quench factor and $\Delta t$ = Time step.

3 RESULTS AND DISCUSSION

Figure 1 C-Curves predicted from experimental Interrupted Quench data of 95% of Rp0.2 max

Method 1

The isothermal hold time ($t$) required to attain 95% of the maximum Rp0.2 at each isothermal hold temperature was plotted producing an experimental C-curve. Using multiple linear regression analysis, coefficients $k_2$, $k_3$, $k_4$ and $k_5$ in equation 1 were determined as 5.6E-20, 5.78E+3, 8.97E+2 and 1.90E+5 respectively, and the theoretical C-curves constructed for 90, 95 and 99.5% of the maximum Rp0.2 ($\sigma_{\text{max}}$) as shown in figure 1. Using the cooling curves and the constructed C-curves, the resulting quench factors ($\tau$) were determined allowing the prediction of Rp0.2 using equation 5.

Method 2 Quench Factor Analysis

In order to improve the correlation between the measured and the predicted Rp0.2, the measured
R_p0.2 values were plotted against the predicted values. Using EXCEL® solver, the estimated standard deviation (ESD)[6] was minimised for various values of _k_2- _k_5 using the initial multiple regression coefficients as candidate values. _k_2- _k_5 coefficients using this technique were calculated as 5.8E-20, 7.37E+3, 8.99E+2 and 1.81E+5 respectively. R_p0.2 predicted values using this technique and the method 1 are shown in table 1. A comparison of the resultant 99.5% C-curves is shown in figure 2.

### Table 1 Predicted R_p0.2, Method 1 and 2

<table>
<thead>
<tr>
<th>% of actual σ_max</th>
<th>Measured</th>
<th>Method 1</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td>514</td>
<td>517</td>
<td>516</td>
</tr>
<tr>
<td>86</td>
<td>508</td>
<td>506</td>
<td>509</td>
</tr>
<tr>
<td>92</td>
<td>480</td>
<td>496</td>
<td>486</td>
</tr>
</tbody>
</table>

### 3.1 Non-isokinetic Model

In order to use Cahn’s model for isokinetic transformations the value of σ_min was assumed to be equal to 0, which has the result of QFA predicting the properties of alloys, cooled very slowly at temperatures in the upper portion of the curve, approaching zero, as the fraction of the maximum property value decreases. To overcome this limitation, a non-isokinetic model was developed[2] where σ_min is related to the slope of the solvus curve extending the property prediction beyond the 15% loss limit. In order to retain the maximum amount of solute available for precipitation hardening the alloy is quenched at as close to an infinite rate as possible from the solution heat treatment temperature. If an alloy is quenched to a temperature below the solution heat treatment temperature, held isothermally until equilibrium is achieved and subsequently quenched to room temperature, a quantifiable amount of solute will be lost from the alloy. The solute remaining is proportional to the maximum achievable R_p0.2 at that temperature (σ_max(T)) and is equivalent to the strength that would be obtained if the alloy was solution heat treated at that temperature. Therefore an increasing amount of solute is lost as the isothermal hold temperature decreases, until equilibrium is reached which implies a lower σ_min. It follows that the relationship between σ_min and the isothermal hold temperature should follow the same trend as the solvus curve from the equilibrium phase diagram. This model is based on the assumption that strength and solute content follow a linear relationship and that the alloy loses an incremental amount of the capability to develop the property over each individual time interval, thus:

$$\Delta \sigma_j = (\sigma_j - \sigma_{\text{min}(T_j)}) \left[1 - \exp \left(-\frac{\Delta H_0}{C(T)} \right) \right]$$

where, \(\Delta \sigma_j\) = Loss of incremental amount of strengthening capability, \(\Delta t_j\) = Time interval (s), \(C(T)\) = Critical time (s), \(\sigma_{\text{min}(T_j)}\) = Minimum R_p0.2 at temperature (T) (MPa) and

$$\sigma_{j+1} = \sigma_{\text{max}(T_j)} - \sigma_{\text{min}} - \sum_{j=1}^{n} \Delta \sigma_j \text{ (MPa)}$$

The R_p0.2 after quenching is thus defined as the sum of the incremental losses as shown in equation 10:

$$\sigma = \sigma_{\text{max}} - \sum_{j=1}^{n} \Delta \sigma_j$$

If we assume that the R_p0.2 and solute content show a linear relationship, the R_p0.2 of the alloy will be equivalent to the intrinsic annealed R_p0.2 of the alloy plus a strength factor related to the solute content, s, thus:

$$\sigma = \sigma_{\text{min}} + As$$

where, s=Solute content and σ_min=Annealed R_p0.2 (MPa) and A=Constant related to the solute content. If we assume that there exists a temperature T_{int} below which the driving force is insufficient for precipitation and we represent the solute content at this temperature as s_{int} then:

$$\sigma_{\text{min}} = \sigma_{\text{int}} + A(s - s_{\text{int}})$$

Combining with equation 12:

The change in solubility with temperature can be described by the following equation:

$$s = \exp \left(-\frac{\Delta H_0}{RT}\right) \exp \left(\frac{\Delta S}{R}\right)$$

where: \(\Delta H_0\)=Standard enthalpy (J. mol\(^{-1}\)), \(\Delta S\)=Standard entropy (J. mol\(^{-1}\) K\(^{-1}\)). Combining with equation 12:
The non-isokinetic model shows substantial improvement over the original QFA model and demonstrates that the non-isokinetic approach to property prediction for 7010-T76 alloys is valid extending the property prediction to up to 70% loss of property.

REFERENCES