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Date September 02, 2003
ABSTRACT

In recent years there has been a renewal of interest in fundamental studies on 6000 series aluminum alloys due to new applications in the automotive and aerospace industries. The work of this thesis focuses on two new approaches to investigating the behaviour of the Al-Mg-Si-Cu alloy, AA6111. First, the temporal evolution of electrical resistivity was measured over a wide range of annealing temperatures (i.e. 200°C to 560°C). From the resistivity data, an approach has been established for extracting the fundamental thermodynamic properties of $Q$ precipitate and, in addition, an estimate of the effect of precipitate spacing on resistivity for a wide range of conditions was developed. Both of these results represent an original approach to relating electrical resistivity measurements to the state of precipitation in the alloy.

The second subject of investigation involved applying thermal spikes (of duration 30 to 300 s) in the temperature range of 220-250°C on material either immediately after the solution treatment or following a period of natural aging. It was found that a 60-second spike at 220°C applied to the alloy immediately after solution treatment can inhibit the deterioration of the paint bake response due to natural aging. In general, it was observed that utilizing the thermal spikes immediately after solution treatment provides a better paint bake response than applying the spike after the natural aging period. Finally, the precipitation hardening model of Esmaeili et al. was extended to examine the temperature-time histories of the thermal spikes. In general, it was found that there was good agreement between the model predictions and the experimental results except for the shortest thermal spike experiments.
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CHAPTER ONE

Introduction

The use of aluminum in automobiles has been increasing for the past two decades. Aluminum’s usage has increased from 39 kg per automobile (i.e. 3% of total weight) in 1976 to approximately 89 kg (7%) in the mid 90s [1]. This has been achieved despite the preference of steel over aluminum by most automakers. The substitution of aluminum for steel is partly influenced by regulatory pressures to meet fuel efficiency standards by reducing vehicle weight and to meet recycling standards. However, other factors such as an increase in the life of a car and an increase in the ability to carry more safety and electronic equipment also play a role in this transition.

The downside of using aluminum is the high cost of primary aluminum as compared to steel and the added fabrication costs of aluminum panels. In general, aluminum by weight is approximately five times more expensive than steel [2]. So far, most of the aluminum substitution has been on a part-by-part basis largely in the form of castings in transmissions, engine blocks, and wheels. Part-by-part replacement cannot be regarded as a completely successful solution and in long term, major changes in car design and the related manufacturing processes are to be taken into account. Moreover, if significant replacement of steel is to be achieved, aluminum sheets are to be substituted for steel in the body and/or chassis of the car. The automobile industry has already realized the necessity of this type of substitution and it has begun manufacturing vehicles with inner and outer aluminum body panels.

6000 series aluminum alloys have been the material of choice for outer body panels in a number of models, e.g. Audi A8. These Al-Mg-Si(-Cu) alloys benefit from an attractive
combination of properties (i.e. moderate strength, good formability, etc.) and low cost. 6000 series alloys are categorized as heat-treatable alloys meaning that they are strengthened through precipitation hardening. The precipitation hardening in automobile applications is usually achieved during the paint bake cycle of a component. In practice, this process is not carried out immediately after the solution treatment of the component which occurs as the last step of processing by the aluminum supplier; as a result due to shipping and handling a delay between solution treatment and artificial aging, i.e. paint bake cycle, is inevitable. The alloy will naturally age during this delay at room temperature and form clusters of solute atoms. This natural aging period has been shown to have an adverse effect on the hardening response of the alloy during the subsequent artificial aging. This undesirable phenomenon was first reported in the late 1960’s. The recent interest of automobile manufacturers in heat-treatable aluminum alloys, especially Al-Mg-Si(-Cu) alloys, has revived academic interest in this poorly understood phenomenon.

The alloy of study in the present work is AA6111, an Al-Mg-Si-Cu alloy. Much of the work done on AA6111 to date has been focused on establishing the precipitation sequence and precipitate type. Less emphasis has been given to the kinetics and evolution laws governing the precipitation process. It is with the aid of these laws that one can adjust various process parameters in practical situations to achieve optimum product quality. Therefore, the objective of this research has been to develop a better understanding of the precipitation kinetics in this alloy. With this objective, resistivity measurements over a wide range of aging temperatures have been conducted. These results have been interpreted in terms of Matthiessen’s law in resistivity.
The solute clustering that takes place during aging has been known to have a pronounced effect on the electrical resistivity of these alloys, however the effect of well-developed precipitates is yet to be elucidated. In this work, resistivity data coupled with quantitative transmission electron microscopy (TEM) and 3-dimensional atom probe (3DAP) results have been used to clarify this issue. A comprehensive resistivity model is developed that can potentially be used to obtain microstructural and kinetic information from electrical resistivity measurements.

Previous studies done on AA6111 alloy have verified that this system does indeed suffer from the detrimental effect of natural aging when artificially aged. An additional objective of this investigation has been to develop novel processing strategies that would minimize this problem. This work is focused on the effect of short thermal excursions, also known as thermal spike treatments, and their ability to produce stable microstructure at room temperature in the solution treated alloy. Another aspect of the spike treatments that has also been examined in this work is the capability of such treatments to regain the lost hardening potential of naturally aged alloys. The possibility of finding the appropriate spike conditions (temperature and time) has been investigated through a series of tensile tests and electrical resistivity measurements on solution treated and naturally aged alloys.

Finally, the modelling of the thermal spike treatments is another topic that has been tackled in the present study. Process models developed for AA6111 mainly deal with isothermal aging. These models can be used to predict the final strength of the alloy after a particular aging procedure. Due to the fact that thermal spike practice is carried out for relatively short times, the heating rate of a sample to the aging temperature is important. Under these circumstances isothermal models are not suitable. For this reason, the models of
Esmaeili et al. have been formulated in differential form and then applied to non-isothermal conditions, such as thermal excursions.
CHAPTER TWO

Literature Review

In this chapter, a basic review of precipitation hardening will be presented. Next, a summary of the current state of knowledge for precipitation in Al-Mg-Si(-Cu) will be provided. Then, more detailed information on the theories that are relevant to the more specific studies conducted in this work are presented. The latter section includes specific information on the theories of electrical resistivity in metals and followed by a section dealing with the principles of thermal spike treatment.

2.1. Precipitation in Age-Hardening Alloys

Precipitation takes place through thermally activated atomic movements, i.e. diffusional transformation involving nucleation, growth and coarsening. This transformation could be expressed in the following way:

\[ \alpha' \rightarrow \alpha + \beta \]

where \( \alpha' \) is the metastable supersaturated solid solution, \( \beta \) a stable or metastable precipitate, and \( \alpha \) a more stable solid solution with the same crystal structure as \( \alpha' \) but with an equilibrium composition [3].

2.1.1. The Heat Treatment

Typical precipitation hardening processes are comprised of two successive treatments: solution treatment and aging treatment. During the solution heat treatment, the second phase particles available in the microstructure are dissolved above their equilibrium solvus temperature. Rapid cooling of the material, the quenching step, after this procedure
suppresses re-precipitation of the solutes. The aging treatment stabilizes the supersaturated alloy through the precipitation of the second phase. This is done by holding the alloy at an elevated temperature for required period of time. Commonly, two terminologies are used with aging: artificial and natural. The former is used when an alloy is aged at a temperature higher than room temperature and the latter once the alloy is aged at room temperature.

2.1.2. Evolution of Precipitation with Aging Time

Precipitation is comprised of two processes: nucleation and growth. The nucleation of the second phase in the matrix can either be heterogeneous (i.e. on dislocations, grain boundaries etc.) or homogeneous. This depends on the availability of driving force for the process. Following nucleation, the second phase grows in size as a result of diffusion of solute(s) from the surrounding matrix toward the particle. In general, solutes are removed from solid solution either by the growth of the previously formed nuclei or by the formation of new nuclei, i.e. the two processes are concurrent.

As in other transformations involving nucleation and growth, the kinetics of precipitation can be modelled using the Johnson-Mehl, Avrami, Kolomokorov (JMAK) model [3,4]. According to this model the fraction of material transformed, \( f \), is given by

\[
f = \frac{\text{volume fraction of precipitates}}{\text{equilibrium volume fraction of precipitates}} = 1 - \exp(-kt^n) \tag{2.1}
\]

where \( k \) is a function of the nucleation rate and growth rate of the precipitates and hence is sensitive to the temperature of transformation. On the other hand, the exponent \( n \) is commonly known as the JMAK exponent and it varies between 1 to 4. In general, \( n \) is independent of the transformation temperature only if the nucleation mechanism does not change [3].
2.1.3. Development of Precipitates with Aging Time

The first phase to precipitate usually does not appear in its equilibrium state and thus a series of metastable phases are often observed before the final equilibrium precipitate appears. The reason for this is that these metastable or transition phases have a lower activation energy barrier for nucleation than the equilibrium phase despite the lower driving force for their precipitation than the equilibrium phase. Thus, the free energy of the system decreases more rapidly via the transition phases than by direct transformation to the equilibrium phase [3].

2.1.4. Precipitation Behaviour of Al-Mg-Si(-Cu) Alloys

An important characteristic of Al-Mg-Si(-Cu) alloys, as in many other aluminum alloys, is that they form nano-scale precipitates. This characteristic complicates the study of precipitates in these alloys. Conventionally, TEM and differential scanning calorimetry (DSC) methods have been used to characterize the precipitates in such alloy systems. In recent years, atom probe field ion microscopy (APFIM) has also been employed, usually in parallel to the previously mentioned techniques, for studying these alloys [5-13]. The latter method is extensively used for analyzing the phases that form during the early stages of aging at low temperatures.

In the literature, there has been some discrepancies regarding the precipitation sequence for Al-Mg-Si(-Cu) alloys. These discrepancies arise mainly due to the complexity of the precipitation sequence, its dependence on the chemistry of the alloy and also due to the different nomenclature used by various authors [13]. For this reason in this review, as in the work of Esmaeili et al. [13], emphasis is given to the precipitate type itself rather than the specifics of the alloy in which it has been studied.
Figure 2.1. shows a DSC thermogram of AA6111 in its as-quenched condition as measured by Esmaeili et al. [13].

![DSC Trace](image)

**Figure 2.1.** Differential scanning calorimetry trace of as-quenched alloy 6111 [13].

The DSC trace is comprised of different precipitation (exothermic) peaks and dissolution (endothermic) troughs. The order, number, and the corresponding temperatures of peaks are similar to DSC results obtained from other 6000 series alloys [6-8,14]. The important precipitation reactions have been delineated as peaks 1, 2, 3, 4, and 5. In the following, a brief review of the information available in the literature on the precipitates corresponding to these peaks is presented.

i) **Peak 1:** Bright-field and dark-field TEM, as well as selected area diffraction patterns (SADP) of an alloy aged near the end of this peak has shown no evidence of any
precipitate(s) [6]. However, APFIM concentration profile after the same heat treatment has indicated that at this stage clusters and co-clusters of Mg and Si are present [6]. In the literature, there is discussion regarding whether solute clusters form during or after quench. Murayama et al. [9], through atom probe observations conducted on an as-quenched Al-Mg-Si alloy, conclude that clusters of Mg atoms are present in the alloy even before the aging treatment and thus these clusters do not contribute to the first exothermic DSC peak. Murayama et al. did not recognize such clusters for Si atoms. In spite of this, studies on Al-Si alloys by Gupta et al. [15] have shown no exothermic peak in the early stages of precipitation, pointing to the fact that the Si atoms also form clusters during quench. In these alloys Si atoms are thought to accompany vacancies when they condense, causing clustering to occur very soon after quenching [16]. It is likely that this process also occurs in Al-Mg-Si alloys [6]. However, in a 3DAP study of a Cu-free Al-Mg-Si alloy by Vaumousse et al. [17], no solute clusters have been observed in the as-quenched alloy.

Additional APFIM investigations carried out on specimens aged for various times at 70°C by Edwards et al. [6] have revealed that co-clusters of Mg and Si do not exist at shorter times and only separate clusters of the two elements were formed. Nonetheless, after aging for longer times the number of separate clusters of Mg and Si decreased and conversely the number of co-clusters increased [6].

All the aforementioned atom probe investigations have been conducted on alloys that bear less than 0.2 wt% Cu content. Recently, 3DAP studies conducted on AA6111, ~0.7 wt% Cu, have pointed out to the presence of Cu in the so-called clusters at the early stages of aging at moderate temperatures [17,18]. In contrast, Murayama et al. [19] in a 3DAP study
done on an alloy having 0.9wt% Cu have shown that Cu does not partition into the clusters; again showing the inconsistencies present in the literature.

In summary, the best knowledge at present suggests that peak 1 is due to the formation of Mg and Si clusters and co-clusters. Some separate clustering of the solute atoms takes place during the quench. The formation and growth of these separate clusters continues throughout the early stages of aging and after a while the co-clusters start to form. The role of Cu atoms during this stage of aging in Cu-containing alloys is yet to be clarified.

ii) Peak 2: TEM bright-field observations made on specimens heated in DSC to this peak have shown very fine precipitates with no defined crystal structure, which have become visible by their strain field contrast [6,9]. In the works of Edwards et al. and Murayama et al. these precipitates have been referred to as spherical GP zones as they do not produce any extra spots or diffuse scattering on SADPs but show spherical contrast. However, in a recent TEM analysis by Marioara et al. [20], the GP zones have been found to be small coherent needles oriented parallel to the (100) directions in the Al matrix. Thus, the exact shape of these zones is yet to be clarified. Gupta et al. [15] consider GP zones and co-clusters essentially the same with only a difference in their size and density of solute atoms, i.e. GP zones are solute clusters with the size and the solute content high enough to give contrast in the TEM image.

iii) Peak 3: The absence of a trough between GP zones’ peak and this peak is an indication that no dissolution of the zones takes place and very likely the GP zones provide heterogeneous nucleation sites for precipitates corresponding to this peak [6,9,20]. Bright-field micrographs of alloys at this stage of precipitation process, an example given in Figure
2.2, show needle shaped precipitates aligned in the <001> directions that are clearly delineated by strain field contrast [6,10,13,21]. These precipitates are denoted as $\beta''$.

![Figure 2.2](image)

**Figure 2.2.** [001]$_{Al}$ bright-field image of AA6111 aged at 180°C for 7 hours [21].

A number of crystal structures have been proposed for $\beta''$ [6,22,23]; the most recent studies report a monoclinic C-centered crystal structure, space group C2/m, with lattice parameters $a=1.53$ nm, $b=0.405$ nm, $c=0.683$ nm and $\beta =105.5^\circ$. The crystallographic orientation relationship has been found to be [23]: (001)$_{\beta''}$ || (001)$_{Al}$ and [100]$_{\beta''}$ || [310]$_{Al}$. The stoichiometric composition of this phase has been found to be $\text{Mg}_5\text{Si}_6$ [20,23,24] where each $\beta''$ unit cell is comprised of two $\text{Mg}_5\text{Si}_6$ units, i.e. 22-atom unit cell [23,24].

Lloyd et al. [25] and Miao et al [5] have identified $\beta''$ as the main strengthening phase in AA6111. Recent quantitative transmission electron microscopy of AA6111 has also confirmed the central hardening role of this precipitate [13].
iv) **Peak 4:** There is considerable disagreement regarding the number, structure, and composition of the phase(s) corresponding to this peak on the DSC trace. This discrepancy is mainly associated with the differences in the composition of the alloys investigated, i.e. this stage of precipitation is sensitive to alloy chemistry. Dumolt et al. [26] and Edwards et al. [6] report the formation of rod shaped $\beta'$ and lath shaped $B'$ in AA6061, which contains a small amount of Cu. $\beta'$ has a hexagonal crystal structure ($a=0.705$ nm and $c=0.405$ nm) [22] and $B'$ has a crystal structure that may be described as either hexagonal ($a=1.04$ nm and $c=0.405$ nm) or base-centered orthorhombic ($a=1.8$ nm, $b=1.04$ nm, and $c=0.405$ nm) [26]. Other researchers [14,25,27] on the other hand report the observation of a lath shaped phase denoted $Q'$ in Cu-containing Al-Mg-Si alloys. Laughlin et al. [28] and Miao et al. [14] consider the difference between the lath shaped precipitates $B'$ and $Q'$ that of only nomenclature. Thus the presence of $Q'$ is confirmed and depending on the Cu content $\beta'$ may also be present.

The crystal structure of $Q'$ has been determined to be hexagonal, with lattice constants $a=1.035-1.040$ nm, $c=0.402-0.405$ nm, and 21 atoms per unit cell [29,30,31]. The orientation relationship $[0001]_Q || [001]_A$ and $(2\overline{1}0)_{Q'} || (510)_{A1}$ is observed for this precipitate [27].

v) **Peak 5:** Miao et al. [14] relate this exothermic reaction to the precipitation of a quaternary lath shape phase. They further designate the name $Q$ to this precipitate following the work of Chakrabarti et al. [27]. Weatherly et al. [32] report the presence of this quaternary phase in AA6111 alloy lying along $<100>_{A1}$ and having a $(510)_{A1}$ habit plane. $Q$ is an equilibrium precipitate with $Q'$ being its precursor phase, i.e. $Q$ has the same crystallographic relations
as $Q'$ but only with lost coherency [19]. The c lattice parameter of $Q$ is identical to that of Al (0.405 nm) making it coherent along its growth direction [32].

Relatively little is known about the $Q$ phase as compared to precipitates in other alloy systems; even a widely accepted stoichiometric composition has not been established for this precipitate. A spread of compositions ranging from $\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_7$ [29] to $\text{Al}_4\text{CuMg}_5\text{Si}_4$ [33] has been reported. Recently Wolverton [30] has indicated that a stoichiometry of the form $\text{Al}_4\text{Cu}_2\text{Mg}_{12-\delta}\text{Si}_7$ is applicable to the $Q$ phase. He further proposed that this composition is temperature dependent and that the $x=3$ composition represents the lowest energy state.

Murayama et al. [19] report of Cu enrichment in $\beta''$ after 10 hour treatment at 175°C and following the observation of $Q$ phase in the overaged alloy by Miao et al. [14], they further argue that $Q$ phase evolves from $\beta''$ in long term aging.

To summarize, a general precipitation sequence of the following form can be proposed for the 6000 series alloys [5,6,14]:

\[
\text{Supersaturated Solid Solution} \rightarrow \text{Mg and Si clusters} \rightarrow \text{co-clusters of Mg and Si} \rightarrow \text{GP zones} \rightarrow \beta'' + Q' \rightarrow Q + \beta (\text{Mg}_2\text{Si})
\]

### 2.2. Electrical Resistivity Theory

In this section an overview of the electrical resistivity method for studying age-hardening alloys is provided. At first, a few terminologies regularly used in relation with resistivity are presented that are helpful in understanding the theories associated with electron motion and electrical resistivity. The fundamental theories of electrical resistivity in metals and alloys will then be reviewed. It will be assumed that the reader is familiar with
the fundamental concepts of electron waves in solids and the corresponding terminologies, which have been considered in a variety of solid state texts (Kittel 1953; Weiss 1963).

2.2.1. Electrical Resistivity of Metals and Alloys

When an electric field is applied to a metal, its free electrons will begin to accelerate in the direction of the electrostatic force. This motion of electrons results in a flow of current. Under the influence of the applied field, the electrons would accelerate and consequently bring about a net drift velocity in the direction of the field. The velocity of the electrons does not continuously increase due to another mechanism which modifies the electron velocities. This mechanism is known as scattering. Scattering applies to electron waves in the same sense as collision applies to electrons regarded as particles [34]. With the consideration of this mechanism an equilibrium is established with a net drift velocity proportional to the field (Ohm's law). Therefore, it is correct to regard scattering as a resisting mechanism in the metal that tries to bring about equilibrium to the metal. This resisting property of the metal that is triggered by scattering is referred to as resistivity (reciprocal of which is known as conductivity).

In the context of this work, scattering is categorized into two types: Bragg and diffuse. Bragg scattering is an event where the scattered electrons are in phase with each other (i.e. coherent) and as a result interfere constructively with one another. The electrons are diffracted from appropriate lattice planes in the crystal and only in specific angles, which are denoted as Bragg angles. Diffuse scattering on the other hand is a coherent or incoherent scattering event where the electrons are scattered from other centers in the crystal other than the lattice planes; these scattering centers will be discussed in Section 2.2.1.1. In diffuse

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scattering, electrons are scattered over a wide range of angles. Figure 2.3 shows a schematic scattering curve where the intensity of the scattered electrons is plotted versus the scattering angle. In this figure Bragg scattering is depicted by the sharp peaks and diffuse scattering by the background.

![Schematic illustration of electron scattering in crystalline materials](image)

Figure 2.3. Schematic illustration of electron scattering in crystalline materials [35].

Resistivity is determined by the rate at which the electrons are scattered. This scattering rate may approximately be described in terms of a relaxation (mean free) time $\tau$ averaged over the Fermi surface [34,35]. The relaxation time, $\tau$, is the time required for an electron to relax to its equilibrium state; this term is also called mean free time since in this time span the electrons do not experience scattering.

The Drude formula [35-39], Equation (2.2), best illustrates the link between scattering rate and resistivity.

$$\rho = \frac{m}{ne^2\tau}$$  \hspace{1cm} (2.2)

where $\rho$ is the resistivity of a metal containing $n$ electrons of charge $e$ and mass $m$ per unit volume, and $1/\tau$ represents the scattering rate.
2.2.1.1. Scattering Centers

The degree of periodicity of the metal determines the amount of electron scattering and hence resistivity [35]. In a perfectly periodic structure, according to Bloch’s theorem, the probability of scattering and thus scattering rate is very high at only Bragg wavenumbers. Specific lattice planes act as scattering centers. This is schematically shown in Figure 2.4(a). In this figure a scattering curve is depicted where it can be seen that no diffuse scattering has occurred and only very sharp Bragg peaks are present. The same situation is also illustrated in Figure 2.4(b) but in an alternative way. The scattering curve is plotted in a two-dimensional polar form in $k$-space superimposed on a spherical Fermi surface (depicted here by the circle). Noting that Bragg scattering has occurred at points where the Brillouin zone (dashed line) is in contact with the Fermi surface. Since Bragg scattering has only affected a small fraction of the Fermi surface, the scattering rate averaged over the whole surface is almost zero and consequently resistivity would be very low.

In practice, perfect periodicity can never be achieved and in addition to the coherent Bragg scattering from the atomic planes, additional diffuse scattering from anything that upsets the periodicity is inevitable. Chemical impurities; crystal imperfections such as vacancies, dislocations, grain boundaries, etc.; and thermal vibration of the lattice (phonons) all are factors that destroy the ideal periodicity [34,40]. Figures 2.4(c) and 2.4(d) show the outcome of such scattering event. In this situation, the intensity of the Bragg reflections is widened and decreased and diffuse scattering can be sited distributed evenly between the Bragg peaks; scattered intensity is not concentrated in sharp peaks anymore [41]. This random scattering results in a non-zero scattering rate when averaged over the Fermi surface and consequently a finite resistivity.
Figure 2.4. Scattering from perfectly periodic (a and b) and real material (c and d). For each case a normal scattering curve and a scattering curve superimposed on Fermi surface is schematically depicted. The Brillouin zone boundary is shown as dashed line in (b) [35].
2.2.1.2. Matthiessen’s Rule

Alloys encompass many types of scattering centers and solving the resistivity problem would therefore seem to be unfeasible at first glance. However, it has been experimentally discovered that in dilute alloys the total resistivity $\rho_{\text{tot}}(T)$ at any measuring temperature $T$ can be written as the sum of two components:

$$\rho_{\text{tot}}(T) = \rho_0 + \rho_{\text{pure}}(T)$$

(2.3)

where $\rho_0$ is the temperature-independent residual resistivity and $\rho_{\text{pure}}(T)$ is the resistivity of the pure host material contributed by the phonons at temperature $T$ [34,35]. This relationship is known as Matthiessen’s rule. The residual resistivity term generally corresponds to the contribution from solute atoms and the effect of other contributors such as vacancies can be neglected mainly because of their lower concentration relative to the impurities [42]. The theoretical basis of Matthiessen’s rule is that the impurity and phonon resistivities act in series and that their effects can be separated. In terms of the overall relaxation time $\tau$ of the alloy this means that

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{\text{pure}}}$$

(2.4)

where $\tau_0$ and $\tau_{\text{pure}}$ being the relaxation time due to solute atoms and phonons respectively.

Matthiessen’s rule is commonly extrapolated for use in concentrated alloys (alloys with more than 1-2% solute concentration). The same relationship still applies but the $\rho_0$ term will also incorporate all contributions from scattering due to atomic disorder [35], e.g. scatterings caused by clusters of solute atoms.
2.2.1.3. Resistivity Anomaly

Resistivity investigations have been employed for studying the precipitation process in age hardening aluminum alloys [37-39, 43-57]. These alloys demonstrate an interesting resistivity behaviour during the initial stages of their precipitation where solute clusters form. At these early stages the resistivity increases despite the depletion of solute atoms from solid solution. The resistivity continuously increases with further aging until a maximum is reached where it then starts to decline. This phenomenon is known as the resistivity anomaly [42].

The theoretical papers surrounding this phenomenon have been divided into two groups supporting different views. The two groups are the RW (Rossiter and Wells) [58, 59] and the HEW (Hillel, Edwards, and Wilkes) [37, 38, 45, 47, 48]. Each group has introduced a different mechanism explaining the aforementioned resistivity behaviour. Subsequently the two views will be discussed, although it should be mentioned that both the RW and the HEW mechanisms have been found to be complementary to each other [39, 49].

i) Rossiter and Wells (RW): As solute clusters form, the crystalline structure of the alloy becomes disordered. A significant increase in scattering is expected in the presence of this highly disordered structure. The new clusters contribute to the resistivity by inducing additional diffuse scattering. As a result, Fermi electrons experience an increased scattering and accordingly the resistivity increases. This is depicted in Figure 2.5. Comparing this figure to Figure 2.4(b) (which can be assumed to belong to an alloy without clusters) shows that the clusters have caused a noticeable increase to the background / diffuse scattering. More precisely, this comparison shows that the presence of the clusters in the microstructure has caused a higher scattering intensity over the entire Fermi surface. The higher intensity
translates into greater number of Fermi electrons that are scattered and so resistivity would increase. The scattering at this stage is isotropic over the Fermi surface meaning that the probability of scattering is equal for all Fermi electrons. The anisotropy that is caused by Bragg scattering, small peaks in Figure 2.5, is negligible with respect to the diffuse scattering.

![Figure 2.5. Schematic representation of scattering occurring at the early stages of solute clustering. Predominant diffuse scattering is evident.](image)

The increase in resistivity continues in this manner via increasing diffuse scattering until the size of the solute clusters becomes equal to or greater than the mean free path of electrons in the alloy. At this stage multiple scattering will take place in the cluster as the electron wave enters it. Hence, the incident electron wave will be attenuated in the cluster [49]. This causes the scattering from the clusters to be reduced to only surface scattering.
The contribution from individual clusters decreases in this way and accordingly resistivity will start to drop.

**ii) Hillel, Edwards, and Wilkes (HEW):** Similar to the RW theory, HEW considers diffuse scattering from clusters, as discussed above, as the reason for the initial increase in resistivity. Disagreement between the two arises concerning the mechanism for the subsequent decrease in resistivity. According to HEW, the decrease is a result of increasing anisotropy of the scattering, i.e. more Bragg type scattering and less diffuse, as the clusters grow in size. When the clusters grow large in size, diffuse scattering from them ceases to be a major contributing factor to the resistivity because there is virtually no disorder caused by such large zones. These clusters only scatter Fermi electrons according to Bragg’s law. A comparison of Figures 2.4(b) and 2.5 illustrates this mechanism put forth by HEW. Assuming that Figure 2.4(b) belongs to an alloy with large clusters and that Figure 2.5 is that of an alloy at the early stages of clustering, it could be said that: in small cluster size limit diffuse scattering is dominant (Figure 2.5), but as clusters grow scattering becomes more Bragg-like and the diffuse scattering diminishes (Figure 2.4(b)). Scattering continuously becomes more limited to only a small fraction of electrons on the Fermi surface that are near the Brillouin zone boundaries and are Bragg scattered. Hence, fewer numbers of electrons are affected leading to the decrease in resistivity.

### 2.2.2. Resistivity of Age-Hardening Alloys

The industrial importance of precipitation hardening alloys, especially those of aluminum, has prompted several resistivity studies on these alloys. The work done in this field can mainly be categorized into three different groups: first, those investigations using electrical resistivity in parallel with calorimetry as a means for determining the precipitation
sequence and/or the effect of different alloying elements [50,51,53]; second, studies concentrated on understanding the resistivity anomaly [37-39,43-49,58,59]; and finally, works done that relate resistivity measurements to precipitation kinetics [51,52,54-57,60].

A common complication to resistivity studies, especially to those of the third category above, is that the role of precipitates (precipitates other than clusters and zones) on the overall measured resistivity of the alloy is unclear. This is very critical in developing a comprehensive formulation for resistivity, which can be used to characterize the alloy behaviour at any stage of aging. It is generally accepted that once precipitates grow to a certain size, their contribution to resistivity could be neglected. However, there is uncertainty regarding this size limit. Consequently, the majority of investigations have been limited to study of these alloys in the overaged condition or they have simply ignored the effect of the precipitates. In the following, some of these investigations will be briefly reviewed.

Miyake et al. [60] correlate the yield strength after aging with resistivity in the coarsening stage of the precipitates of a Cu-Ni-P alloy. In another work Luo et al. [51] translate the evolution of resistivity with aging time to a JMAK type equation for the mole fraction of GPB zones and metastable phases in an Al-Li-Cu-Mg alloy not considering the effect of precipitates. Guyot et al. [52] adopt the HEW model to describe the resistivity evolution of an Al-Zn-Mg-Cu alloy and conclude that the late decrease in resistivity can be attributed to the coarsening of metastable phase. Dorward [54] on the other hand develops a model that considers the resistivity decrease on overaging due to the reduction in the amount of dissolved atoms resulting from precipitate coarsening. Archambault et al. [55] use resistivity to construct the Time-Temperature-Transformation curves of a 7xxx series
aluminum alloy by correlating resistivity to only solute depletion and not precipitates. In a similar approach, i.e. assuming no contribution from precipitates; Matsumoto et al. [56] have determined the volume fraction of precipitates through resistivity measurements. The single case where the effect of precipitates has been taken into account has been in the work of Starink and Li [57]. They consider an Al-Zn-Mg-Cu alloy and model the resistivity by assuming a solid solution matrix containing a population of conducting precipitates. The only problem of this approach is that the individual resistivity of the precipitates is required in order to determine the overall resistivity of the alloy.

2.3. Thermal Spike Treatment

As mentioned in Chapter One, the automobile industry is facing a number of challenging complications in its route to replacing steel with aluminum in vehicles. One of such problems was said to be the fact that natural aging in solution treated Al-Mg-Si(-Cu) alloys deteriorates the hardening kinetics of the material during subsequent age hardening practices. Before discussing the cause of this problem and how it can be avoided, it is beneficial to look briefly at the processing path of the alloy from the beginning and lay out the desired properties at the crucial stages of this path.

2.3.1. Processing Route of Heat Treatable Aluminum Alloy Sheets

Aluminum alloys for sheet production are either direct cast as ingots or continuous cast in the form of thick strips. They are then hot rolled to a preliminary thickness followed by cold rolling to the final thickness and finally winding into a coil. The coil is then solution treated producing a supersaturated solid solution. In automobile applications, before delivering the metal to the vehicle manufacturer, the alloy is aged at room temperature (or
sometimes at a higher temperature to accelerate the effect) for a period of time to promote the formation of fine clusters [61].

At the manufacturer, the metal is deformed to the desired shape and then painted and baked. Along this processing line, it is beneficial for the alloy to show certain properties: it should have sufficient strength for ease of handling, good formability so that it can easily be stamped into the required shape, and significant hardening once subjected to the paint bake cycle. The latter is commonly referred to as the paint bake response of the alloy.

2.3.2. Shortcoming of Conventional Procedure

What was discussed above was the conventional processing route of aluminum sheets for automobile applications. Unfortunately, 6xxx series alloys processed in the conventional manner do not develop their highest potential paint bake response. The reason for this has been found to be the natural aging step that it undergoes after solution treatment [7,9,11,13,62-67]. Figure 2.6 clearly depicts this argument for AA6111.

As shown in Figure 2.6, the naturally aged material yields to a lower strength for aging times shorter than 7 hours as compared to a freshly solutionized alloy. Noting that the industrial paint bake cycle of AA6111 is simulated by a 30-minute heat treatment at 180°C [5,8]. Subsequently, microstructural observations of this problem will be reviewed.

2.3.3. Natural Aging Prior to Artificial Aging in 6xxx Alloys

The deleterious effect of natural aging has been identified and thoroughly reviewed by Pashley et al. [62] in an Al-Mg-Si alloy. This negative effect is in contrast to what had been reported in other alloys, e.g. Al-Zn-Mg alloys [68] where room temperature aging is beneficial to subsequent artificial agings.
Figure 2.6. Aging curves of solution treated and naturally aged AA6111 at 180°C. The window represents the paint bake cycle [67].
During natural aging of the 6xxx series alloys only clusters and co-clusters are formed and no evidence of the formation of GP zones has been reported [7,9,11]. In addition, aging of freshly solutionized alloy at 180°C (paint bake temperature) results in a microstructure consisting of dominantly $\beta''$ precipitates [7,9,11,13,21]. Therefore in the industrial setting, a microstructure containing $\beta''$ precipitates is expected once the paint bake cycle is over.

To confirm this, TEM observations on samples artificially aged after natural aging and also samples artificially aged directly after solution treatment have been conducted [9,11,63]. These observations confirmed the presence of $\beta''$ but they also revealed that natural aging produced a significantly coarser microstructure and it also reduced the number density of the $\beta''$ precipitates developed at 180°C, Figure 2.7.

![Figure 2.7.](image)

*Figure 2.7. [001]$_H$ bright-field image of (a) as-quenched and (b) naturally aged AA6111 aged at 180°C for 7 hours [21].*
This type of behaviour is generally an indication that room temperature aging has decreased the number density of nuclei and thereby reduced the kinetics of precipitation.

2.3.3.1. Justification of the Coarse Precipitation

After solution treatment, the concentration of quenched-in vacancies is high. These vacancies enhance the clustering of solute atoms [3,68,69]. The clusters and co-clusters of Mg and Si gradually form during natural aging. This clustering will lead to a decrease in solute supersaturation of the matrix. A material with a microstructure consisting of homogeneously distributed solute clusters will be heated to the artificial aging temperature. The clusters have a fine dispersion and if the precipitates were to nucleate on them, they would also have had produced a fine structure. This fine structure is not observed and as a result the clusters are most probably not available for the nucleation of the β' phase; clusters would have had acted as heterogeneous nucleation sites for the β' precipitates if they had been stable at this temperature [63]. It was indicated earlier that GP zones most likely provide heterogeneous nucleation sites for β'. So it can be said that the stability of the clusters is a significant problem. However, the fact that a naturally aged microstructure has a lower driving force for β' transformation as compared to a supersaturated solid solution should not be overlooked. The lower driving force stems from the decreased solute supersaturation of the naturally aged alloy. As a result, the reduced kinetics of β' transformation due to natural aging has to also be regarded as a source of this problem.

By assuming a situation where the rate of arrival of fresh solute exceeds the rate of evaporation of solute from the cluster, Pashley et al. [63] have established a general condition for the stability of a cluster formed at T1 when it is heated to a higher temperature T2. In the present review, the two temperatures correspond to room temperature and artificial
aging temperature respectively. They further define a critical size for clusters where clusters larger than the critical size would be stable at $T_2$. Bearing in mind the concept of critical cluster size, it can be said that when a naturally aged alloy is artificially aged, most of the clusters formed at room temperature will dissolve since they are smaller than the critical size [11,63]. As a result, the solute atoms are released into solid solution. In this way the solute supersaturation level of the system will increase. The solute supersaturation continues to increase with dissolution of small clusters to a point where the larger clusters will stabilize and proceed to grow, developing into GP zones and providing nucleation sites for the $\beta''$ precipitates. The formation of a few new clusters might also occur [63]. The fine scale precipitation that would have resulted from aging of the as-quenched material will never occur because the solute supersaturation is always lower and consequently the density of the GP zones available for nucleation of $\beta''$ is much lower. The dissolution of the room temperature clusters is commonly referred to as reversion and it has been reported as the main reason accountable for the negative effect of natural aging [7,9,11,63,64].

2.3.3.2. Solutions to the Problem

Pashley et al. [63] have proposed various possible methods for reducing or eliminating the deleterious effects of delayed aging. They suggest that by addition of copper or by lowering the natural aging temperature (e.g. storing the solutionized material in a cool place), the natural aging slows down and as a consequence the detrimental effect of room temperature aging is reduced. Lowering the storage temperature is not appealing to the industry and it is impractical in most cases. The addition of copper is not always an option either since the destructive effect of natural aging has also been reported in Al-Mg-Si-Cu alloys [13,65-67]. Moreover, addition of copper has a negative effect on the corrosion
resistance of the alloys [70,71]. Pashley et al. also offer two other alternatives for solving this problem. These alternative solutions are in a sense more practical since they can readily be implemented without any radical changes made to the conventional processing route. These solutions are subsequently reviewed.

**i) Pre-aging:** A method that can potentially solve the natural aging problem is to give the alloy a pre-age at a temperature under the cluster/zone solvus immediately after the solution treatment [5,11,63,64]. The duration of this treatment depends on the chosen temperature for the pre-age and it is longer for lower temperatures. The clusters that form during this pre-age treatment have a larger size compared to the ones formed at room temperature since the kinetics of nucleation and growth are faster than room temperature. This microstructure will not be influenced by the storage at room temperature and it will remain unchanged. Now if this structure is taken to the final aging temperature the majority of these clusters will not be reverted. This is because many of the clusters have a size larger than the critical size for stable cluster. Figure 2.8 illustrates this point very well.

At the artificial aging temperature the remaining clusters will develop into GP zones and further provide nucleation sites for $\beta''$. The structure will not be as fine as for the as-quenched material but it will be finer than the naturally aged material and it will provide the required strength.

In an early patent by Hornus [72], an industrial pre-aging or stabilizing treatment is introduced for Al-Mg-Si alloys with the aim of improving their mechanical properties by up to 25%. The process consists of an intermediate heat treatment carried out at a temperature from approximately 100 to 250°C no later than 10 minutes after quenching. In a more recent patent [73], Jin et al. use a more sophisticated approach for implementing the pre-aging
treatment. They use a quenching process that involves four uninterrupted cooling sequences and through this procedure the solution treated alloy experiences pre-aging.

![Figure 2.8](image.png)

**Figure 2.8.** Schematic size distribution of clusters just before the artificial aging treatment (a) without and (b) with implementing pre-aging. \( r_c \) is the critical size of stable cluster at the artificial aging temperature.

**ii) Thermal Spike Treatment:** The detrimental effect of natural aging could also be removed by dissolving the clusters formed during holding at room temperature. This could be achieved by means of a short intermediate heat treatment at a sufficiently high temperature just before the artificial aging cycle [63,74]. This type of treatment where the dwell time at a
specific temperature is kept very short is referred to as thermal spike treatment and it has been the subject of a number of industry-based investigations and patents [75,76].

As a result of this treatment the naturally aged clusters dissolve, releasing the solutes into the solution. The temperature is well above the cluster/zone solvus and thus, they will not form homogeneously in the matrix. At this temperature, heterogeneous precipitation of $\beta''$ will take place to some extent on dislocations. When the time is kept short (e.g. 90 sec), the precipitates will nucleate on dislocations but they will not have time to deplete the region well between the dislocations and the solute supersaturation remains high in these regions. The subsequent final artificial aging treatment will then produce fine scale precipitation since the solute supersaturation has been sufficiently raised. If the holding time at the high temperature is longer, the $\beta''$ precipitates nucleated on the dislocations will grow and deplete the matrix from the solutes, again a coarse structure will result [63]. Hence the time to acquire fine scale precipitation is an upper limit on the time at this temperature and the time required to re-dissolve would be the lower limit.

Thermal spike treatment has not been limited to naturally aged alloys, in an industrial patent by Gupta et al. [61], such spikes have been employed immediately after solution treatment in order to create a stable structure at room temperature. This procedure essentially serves the same function as the long pre-aging treatment that was discussed earlier; the two differ from each other in the way that the spike treatment is carried out at a significantly higher temperature, therefore reducing the dwell time. As before, an upper and lower time limit is introduced; the time should be controlled within these limits so that enough precipitation takes place to stabilize the microstructure at room temperature but does not deplete all solutes from solution in order to obtain good paint bake response.
2.4. Summary

In this chapter, the fundamental aspects of the precipitates in 6000 series aluminum alloys were reviewed. The application of electrical resistivity in the study of precipitation process was examined next. Finally, the use of thermal spikes in removing the detrimental effect of natural aging was explored. In the next chapter, the experimental procedure will be described.
CHAPTER THREE

Experimental Procedures

3.1. Material

The aluminum alloy AA6111 which was used in this study was provided by Alcan International in the form of cold rolled sheets of ~1mm thickness. The chemical composition of the alloy is given in Table 3.1.

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.8</td>
<td>0.6</td>
<td>0.7</td>
<td>0.25</td>
<td>0.2</td>
<td>0.05</td>
<td>0.06</td>
</tr>
</tbody>
</table>

3.2. Thermal Processing

Details of the thermal treatments exercised in this study are covered in this section. To start, the apparatus utilized for the heat treatments is described, followed by two sections explaining the preliminary and secondary heat treatments of the samples.

3.2.1. Heat Treatment Apparatus

Thermal processing of the samples was conducted in either a salt bath or an oil bath. The salt bath was used for treatments where the temperature was greater than 200°C and accordingly the oil bath was used for heat treatments requiring temperatures below 200°C. A salt mixture of 60% potassium nitrate and 40% sodium nitrite was used in the salt bath. The oil bath on the other hand contained silicon oil with a viscosity of 500 cst. An Omega
CN9000A auto-tune controller controlled the temperature of both baths. Independent temperature measurements showed that the bath temperature differed from that of the set temperature by ±3°C. The heating rate of the salt bath at 220°C and 250°C bath temperatures has been measured by collecting temperature-time data in real time. A K-type thermocouple was spot-welded to a 20 × 10 × 1 mm AA6111 coupon and the coupon was immersed into the salt bath for data collection.

3.2.2. Preliminary Heat Treatments

The treatments described in this section were carried out with the purpose of providing the starting heat treatment condition of the alloy. After having prepared the geometry of the test samples, details of which will be provided for each individual test later on, the thermal processing of all samples was initiated by a solution treatment at 560°C for 10 minutes. This was followed by a water quench. Samples processed in the preceding manner are referred to as solution treated or solutionized samples in this work. A number of the solutionized samples were left at room temperature (20-25°C) for 1 day or 2 weeks to naturally age, providing the 1-day and 2-week naturally aged samples. To summarize, the starting condition of the samples before any experiment was set as either solutionized or naturally aged (1-day or 2-week).

3.2.3. Secondary Treatments

Following the preliminary heat treatment exercises, some of the solutionized/naturally-aged samples were annealed again. The secondary treatments used in this work were divided into two groups: (a) single step agings and (b) thermal spike treatments.
a) **Single Step Aging**

For this procedure, solution treated/naturally aged samples were artificially aged at a particular temperature for desired time and subsequently quenched in water. The aging temperatures used for solution treated samples varied from 180°C to 560°C and for naturally aged samples varied from 200°C to 250°C.

b) **Thermal Spike**

Figure 3.1 schematically shows two different schedules, denoted A and B, that have been used for thermal spike treatment. The two schedules have been designed to depict the industrial heat treatment cycle of AA6111 with the minor difference that the thermal excursions have been added to the cycle. The natural aging that occurs after solution treatment in industrial settings has been simulated by a 1-day and 2-week hold at room temperature in Schedules A and B respectively. The main difference between the two schedules is in the heat treatment condition of the material that is subjected to the spike. In Schedule A the thermal spike is applied to a solutionized alloy but in the other instance in Schedule B, the spike is applied to a 2-week naturally aged material. The details of both heat treatment cycles are subsequently reviewed. Noting that the preliminary heat treatments discussed earlier have been incorporated into both cycles.

For cycle A, the samples first went through the 10-minute solution treatment at 560°C. Immediately after water quench, the thermal spike was applied by immersing the samples into the salt bath for the period of the spike, again followed by water quench. The samples were then naturally aged for 1 day and finally artificially aged for 30 minutes at 180°C and quenched in water.
Temperature solution treatment

(a) Schedule A

Temperature solution treatment

(b) Schedule B

Figure 3.1. Investigated thermal spike scenarios: a) thermal spike 1 applied immediately after solution treatment b) thermal spike 2 applied after natural aging. The schematic time scale shown in (a) is different from that of (b).
In cycle B, the samples were allowed to naturally age for 2 weeks after the solution treatment and water quench. Subsequently, the thermal spike was applied in a manner explained previously. The samples were then left at room temperature for 1 day of natural aging and in the end, aged at 180°C for 30 minutes followed by water quench. The details of the different thermal spikes that have been implemented in the aforementioned cycles are tabulated in Table 3.2. Noting that the reported spike times are measured by stopwatch and they include the time to heat up the sample.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>220°C</td>
<td>0.5, 1, and 5</td>
</tr>
<tr>
<td>250°C</td>
<td>0.5, 1, and 5</td>
</tr>
</tbody>
</table>

The six spikes and the two schedules give rise to 12 individual cases that have been examined in this work.

3.3. Testing Methods

This section will cover the specifics of the different testing techniques that have been employed.

3.3.1. Tensile Tests

The mechanical behaviour of the alloy as it underwent different thermal treatments was examined using the results from tensile tests. Tensile samples of the geometry shown in
Figure 3.2 were used. These samples were punched out of the as-received cold rolled sheets parallel to the rolling direction.

Figure 3.2. Tensile sample geometry.

Tests were carried out at a strain rate of $2 \times 10^{-3}$ s$^{-1}$ using an MTS hydraulic tensile machine with an INSTRON 8500R controller. All tests were conducted at room temperature. Sample elongation during deformation was measured using a 40 mm gauge length INSTRON extensometer. The recorded load and displacement were converted to engineering stress-strain curves and the yield stress was determined according to the 0.2% offset method. The reproducibility of the yield stress measurements was within ±5 MPa.

3.3.2. Electrical Resistivity Measurements

Electrical resistivity testing has been used as another tool for monitoring the changes occurring during thermal processing of the alloy. Strips of 100 × 10 mm were cut from the as-received cold rolled AA6111 sheets and used as resistivity samples. The samples have the same thickness as the original sheet, i.e. approximately 1 mm. To minimize the effect of temperature on the measured resistivity, all tests have been conducted at liquid nitrogen temperature (77K).
The apparatus used for this experiment consists of a custom built rig and a digital data acquisition system equipped with LABVIEW software. The rig, schematically shown in Figure 3.3, operates based on the conventional four-point probe method.

![Schematic illustration of electrical resistivity measurement apparatus.](image)

**Figure 3.3. Schematic illustration of electrical resistivity measurement apparatus.**

The four-point probe setup consists of four stainless steel probes with finite radius. A 5-20 mA adjustable current source is used to supply current through the outer two probes. The volt drop across the sample is measured. This volt drop is then compared with the volt drop across an internal standard resistance (0.1 Ω). From the ratio of these two volt drops the resistance of the sample is calculated and displayed on the system. Having measured the cross-sectional area for each test sample, the reported resistance $R$ was converted manually to resistivity $\rho$ using the following equation:

$$\rho = \frac{RA}{L} \quad (3.1)$$
where $A$ is the cross-sectional area of the sample and $L$ is the spacing between the inner two probes.

A standard AA1100 aluminum alloy sample with known and constant resistivity was used to calibrate the rig. More precisely, at the beginning of each test day a correction was made for the spacing $L$. The resistance of the standard sample was measured and using Equation (3.1) with the known resistivity, the length $L$ was calculated. This spacing was then used for all tests carried out on that day. Moreover, the resistivities were all normalized so that all samples gave the same resistivity value of 18.5 nΩm for the as-quenched condition. Equation (3.2) describes the normalization formula.

$$\rho = \frac{18.5}{\rho_{\text{as-quenched}}} \times \rho_{\text{calculated}}$$

(3.2)

Following this procedure, the reproducibility of the experiments was found to be within ±3%.

It is important to note that the resistivity evolution during multi-step heat treatments of this study, such as thermal spike treatments, has been determined using a single resistivity sample for each cycle that is investigated. In other words, once a sample is thermally treated for a particular stage in a heat treatment cycle and tested for its resistivity, the same sample is once more heat treated for the next stage in that cycle and retested. This quasi-continuous treatment and testing is continued until the end of the cycle.
CHAPTER FOUR

Experimental Results

The evolution of microstructure that occurred during the heat treatments used in this study have been examined indirectly by yield strength and/or electrical resistivity measurements. The results of such investigations are given in this chapter. Also included are the results of experiments aimed at characterizing the heating cycle of the samples in the salt bath.

4.1. Evolution of Electrical Resistivity During Aging

Electrical resistivity has been utilized as a sensitive tool for monitoring the aging behaviour of the material. The resistivity evolution of solution treated AA6111 during aging at different temperatures ranging from 180°C to 560°C is shown in Figure 4.1. Note that for each aging temperature only one sample has been used.

All curves start at a resistivity value of 18.5 nΩm, which corresponds to the resistivity of the as-quenched alloy. The 180°C, 200°C, and 220°C resistivity curves show an initial increase in resistivity followed by a subsequent decrease resulting in a maxima. For other aging temperatures, excluding 560°C, the resistivity starts with a sharp drop and then it levels off. Aging at 560°C initially generates a small decrease in resistivity but the resistivity stays more or less constant throughout the rest of the process.

The magnitude of the plateau-like portion of the curves decreases with increasing the aging temperature from 180°C to 350°C. However, this behaviour is reversed for aging temperatures above 350°C; i.e. an increase in the aging temperature increases the level of the plateau to higher resistivity values.
**Figure 4.1.** Evolution of electrical resistivity of as-quenched AA6111 during aging at different temperatures. Curve at 180°C developed by Esmaeili [65].
4.2. Thermal Spike Treatments

Six thermal spikes incorporated in two different heat treatment schedules A and B, twelve scenarios in total, have been examined in this work. Details of the spikes and the schedules are given in Chapter 3. In order to identify these details about the spikes a number of preliminary experiments have been conducted. The results of these preliminary experiments and the procedure used for choosing the spike conditions are summarized in Appendix A.

For evaluating the effectiveness of the thermal spike treatments, the yield strength of the material was monitored throughout both heat treatment schedules. Yield stress measurements were taken at three points in the heat treatment cycles so that a comprehensive and continuous view of alloy’s evolution was obtained. In order to have a point of reference for comparison, the yield stress was also measured during the two schedules in the absence of the spikes. Electrical resistivity method was also used in parallel with yield stress measurements and the results are given in Appendix B.

4.2.1. Schedule A

As depicted in Figure 3.1, for this cycle the thermal spike was applied immediately after the solution treatment. Thereafter, the material was left at room temperature for one day. Once this period was over, the material underwent a 30-minute treatment at 180°C simulating the paint bake cycle. Yield stress measurements are taken at three stages in this cycle: i) after execution of the spike, ii) after the 1 day hold at room temperature, and iii) after completing the paint bake simulation. The results are shown in Figures 4.2 and 4.3. Included in these Figures are sets of bar charts labelled “No Spike” which correspond to
experiments where Schedule A has been examined without the presence of any spike. Hence, “after thermal spike” refers to the as-quenched yield values in this group of charts.

Examination of Figure 4.2 shows that the 220°C spikes induce an increase in the yield strength of the alloy from 57 MPa in the as-quenched state to 95 MPa, 154 MPa, and 290 MPa after 30-second, 1-minute, and 5-minute spikes, respectively. During the hold period at room temperature, the yield stress increases for the samples with no thermal spike and a 30-second thermal spike while the samples spiked for 1 and 5 minutes showed no change in yield stress. Finally, holding for 30 minutes at 180°C causes an increase in the strength of all the samples, but this increase is much larger for the 30-second and 1-minute treatments. It is important to emphasize that the yield strength obtained at the end of this schedule in the absence of the spike (190 MPa) is at least 60 MPa lower than what has been achieved once the thermal excursions have been included in the schedule.

Figure 4.3 shows the effect of the three 250°C thermal spikes. As in the previous case, the “after thermal spike” yield strength increases with increasing the duration of the spike. The yield stresses that are obtained for 30 seconds and 1 minute durations at this temperature are higher than those of 220°C. One day of natural aging has a notable effect in all cases causing strengthening in the samples. Treatment at 180°C has resulted in an increase in strength of the alloy except for 5-minute spike where the yield stress has remained almost constant at ~270 MPa. On the whole, the final paint bake simulation has a smaller impact on the strengthening of the alloy as compared to what was seen for 220°C spikes.
220°C Spike (Schedule A)

Figure 4.2. The effect of 30-second, 1-minute, and 5-minute 220°C thermal spikes (applied immediately after solution treatment) on the yield strength of AA6111 at different stages of the heat treatment schedule. RT in the legend stands for room temperature.
Figure 4.3. The effect of 30-second, 1-minute, and 5-minute 250°C thermal spikes (applied immediately after solution treatment) on the yield strength of AA6111 at different stages of the heat treatment schedule. RT in the legend stands for room temperature.
4.2.2. Schedule B

In this schedule, as shown in Figure 3.1, the alloy is first solution treated followed by a 2 weeks of holding at room temperature. Upon completion of this holding period the thermal spike is applied. After this thermal excursion, there is another room temperature hold for 1 day. Finally, the heat treatment at 180°C for 30 minutes is carried out. The yield stress evolutions during this heat treatment cycle are shown in Figures 4.4. and 4.5. Yield measurements are made at the same points in the cycle as noted for Schedule A. The same principles used for Schedule A have also been applied to the plotting of these data with the only exception that this time for “No Spike” bar charts, “after thermal spike” refers to the yield strength of a solutionized sample at the end of a 2-week natural aging period.

Figure 4.4 shows that the yield stress drops from 155 MPa, i.e. yield stress of a 2-week naturally aged alloy, to 127 MPa after the 30-second spike is implemented. Increasing the spike dwell time from 30 seconds to 1 minute does not affect the magnitude of this yield drop and the same value is obtained. However, a 5-minute excursion produces strengthening in the alloy, yield stress increases from an initial value of 155 MPa after 2 weeks of natural aging to 195 MPa after this thermal spike. The 1-day hold at room temperature has not affected any of the samples and their strength level has remained the same as that obtained immediately after spike. The heat treatment at 180°C has caused strengthening in all cases; 30-second and 1-minute both have developed same yield stress of ~225 MPa and 5-minute has resulted in an approximately 270 MPa yield strength. Comparing the “No Spike” final yield stress (185 MPa) with that of the others reveals that the presence of the spikes in the heat treatment cycle does lead to higher strengthening during the treatment at 180°C.
**220°C Spike (Schedule B)**

![Bar chart showing the effect of thermal spikes]

**Figure 4.4.** The effect of 30-second, 1-minute, and 5-minute 220°C thermal spikes on the yield strength of 2-week naturally aged AA6111 at different stages of the heat treatment schedule. RT stands for room temperature.
When the thermal excursion temperature is raised to 250°C as shown in Figure 4.5, similar results are observed as for the case of 220°C, i.e. there is an initial reduction in strength. More precisely, the yield decreases from 155 MPa to 111 MPa once a 30-second dwell time is exercised. An increase in holding time from 30 seconds to 1 minute has lead to a yield stress of 149 MPa, which in contrast to 220°C is higher than the stress achieved after 30-second spike. The alloy is significantly strengthened to close to 300 MPa after the 5-minute excursion. The 1 day period at room temperature has not affected any of the investigated cases except for 1-minute spike where an increase in yield stress is observed. After 30 minutes at 180°C, there is a considerable strengthening increment in samples treated with both 30-second (137 MPa increase) and 1-minute (118 MPa increase) spikes but it has not affected the 5-minute excursion. The yield levels obtained at the end of the cycle in samples treated with spikes are higher than the yield stress (185 MPa) observed when no spike treatment is exercised. Finally, a comparison of the two spike temperatures investigated in this specific cycle shows that in general, 250°C spikes yield to higher final strengths in the alloy.

4.3. Temperature-Time Profile of Salt Bath

The dwell times used in the thermal spike treatments are relatively short, thus it has been necessary to find out the real time that each sample spends at a given temperature. Consequently, the temperature-time profile of the salt bath at the two spike temperatures has been examined. These profiles are shown in Figure 4.6.

Despite the initial higher heating rate at 250°C, there is no obvious difference in the time to reach the two temperatures. It takes about 3 to 4 seconds to heat-up a sample to either of the temperatures.
Figure 4.5. The effect of 30-second, 1-minute, and 5-minute 250°C thermal spikes on the yield strength of 2-week naturally aged AA6111 at different stages of the heat treatment schedule. RT stands for room temperature.
Figure 4.6. Temperature-time profile of salt bath at 220°C and 250°C.
CHAPTER FIVE

Discussion and Modelling

The analysis and modelling of the experimental results are provided in the present chapter. This chapter is divided into two main sections where the resistivity and thermal spike studies are considered.

5.1. Electrical Resistivity

In this section, first two simple models are devised for explaining the evolutions of resistivity and precipitate volume fraction during aging in AA6111 system. Using these models the experimentally determined high temperature resistivity data are translated into thermodynamic parameters, which are then used to predict the equilibrium volume fraction of precipitates as a function of temperature. Next, results from previous low temperature resistivity measurements along with microstructural information from TEM and atom probe are employed to relate the resistivity of precipitates to their spacing. This information is used for transforming the developed resistivity model to a more comprehensive version, providing the initial steps for future microstructural modelling using resistivity. Finally, a resistivity model from the literature is implemented and evaluated.

5.1.1. AA6111 Resistivity Model

It is assumed that resistivity in AA6111 follows a modified version of Matthiessen’s formulation, i.e.

\[ \rho = \rho_{\text{true}}(T) + \sum_i \rho_i C_i + \rho_{\text{ppt}}. \]  

(5.1)
where $\rho_{\text{pure}}(T)$ is the temperature dependent resistivity term, $\sum_i \rho_i C_i$ the resistivity induced by solute atoms in solution, and $\rho_{\text{ppt}}$ the resistivity due to precipitates. The terms, $\rho_i$, referred to as solute resistivity coefficients, are the contribution to resistivity per unit concentration of $i$-th solute where $C_i$ is the concentration of this $i$-th solute.

Before applying Equation (5.1) to AA6111 alloy, the following assumptions are to be considered regarding this alloy:

1) All the solute atoms are dissolved after treatment at 560°C for 10 minutes.
2) The precipitating phases are $Q$ (Al$_4$Cu$_2$Mg$_8$Si$_7$) or $\beta''$ (Mg$_5$Si$_6$).
3) Depletion of solutes from solution occurs in atomic proportion to the composition of the precipitate.
4) There is constant contribution to resistivity at 77K from other alloying elements such as Fe that are not present in $Q$ or $\beta''$.
5) Solute resistivity coefficients reported for binary aluminum solid solutions at 77K (shown in Table 5.1) can be applied to the quaternary alloy Al-Mg-Si-Cu.

### Table 5.1. Specific elemental resistivities at 77K [56].

<table>
<thead>
<tr>
<th>Element</th>
<th>$\rho$ (nΩm / at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>5.28</td>
</tr>
<tr>
<td>Si</td>
<td>6.56</td>
</tr>
<tr>
<td>Cu</td>
<td>7.98</td>
</tr>
</tbody>
</table>

As a result, Matthiessen's law for AA6111 at 77K can be rewritten in the following form for the cases of $Q$ and $\beta''$ precipitates.
i) only $Q$ precipitated,

$$\rho = \rho_{pure}(T) + \rho_{Mg}C_{Mg} + \rho_{Si}C_{Si} + \rho_{Cu}C_{Cu} + \rho_{ppt.} + \text{contribution of other solutes} \quad (5.2a)$$

ii) only $\beta''$ precipitated,

$$\rho = \rho_{pure}(T) + \rho_{Mg}C_{Mg} + \rho_{Si}C_{Si} + \rho_{ppt.} + \text{contribution of other solutes} \quad (5.2b)$$

The above equations could further be simplified by summing up all the terms that do not change during aging into one term defined as $\rho_{base}$. Thus,

$$\rho = \rho_{base-Q} + \rho_{Mg}C_{Mg} + \rho_{Si}C_{Si} + \rho_{Cu}C_{Cu} + \rho_{ppt.} \quad (5.3a)$$

$$\rho = \rho_{base-\beta''} + \rho_{Mg}C_{Mg} + \rho_{Si}C_{Si} + \rho_{ppt.} \quad (5.3b)$$

the term $\rho_{base}$ can easily be calculated for the alloy when the $Q$ and $\beta''$ phases are not present and all solute atoms are in solution, i.e. in the as-quenched state (concentrations given in Table 3.1 are used):

$$\rho_{base-Q} = \rho_{as-quenched} - \rho_{Mg}C_{Mg} - \rho_{Si}C_{Si} - \rho_{Cu}C_{Cu}$$

$$= 18.5 - 5.28 \times 0.9 - 6.56 \times 0.6 - 7.98 \times 0.3 = 7.42 \ \text{n}\Omega\text{m} \quad (5.4a)$$

similarly,

$$\rho_{base-\beta''} = \rho_{as-quenched} - \rho_{Mg}C_{Mg} - \rho_{Si}C_{Si} = 9.82 \ \text{n}\Omega\text{m} \quad (5.4b)$$

During the precipitation of $Q$-phase, Cu, Mg, and Si atoms are depleted from solution in 2Cu:8Mg:7Si proportions. If the amount of Cu, Mg, and Si, in at%, removed from solid solution are given by $f_{Cu}$, $f_{Mg}$, and $f_{Si}$ respectively, then the amount in at% remaining in solution would be:
where 0.3, 0.9, and 0.6 are the concentrations (in at%) of Cu, Mg, and Si in AA6111. Since the proportions by which these elements are present in Q-phase are known, therefore,

\[
f_{Cu} = \frac{2}{8} f_{Mg} = 0.25 f_{Mg} \tag{5.6}
\]

\[
f_{Si} = \frac{7}{8} f_{Mg} = 0.875 f_{Mg}
\]

accordingly,

\[
C_{Cu} = 0.3 - 0.25 f_{Mg}
\]

\[
C_{Mg} = 0.9 - f_{Mg} \tag{5.7}
\]

\[
C_{Si} = 0.6 - 0.875 f_{Mg}
\]

Substituting Equations (5.4a) and (5.7) into Equation (5.3a) will give:

\[
\rho = 7.42 + 5.28(0.9 - f_{Mg}) + 6.56(0.6 - 0.875 f_{Si}) + 7.98(0.3 - 0.25 f_{Mg}) + \rho_{ppt} \nonumber \\
= 18.5 - 13 f_{Mg} + \rho_{ppt} \tag{5.8a}
\]

Now if the same procedure is repeated for β* precipitation where the Mg and Si atoms are removed from solution in 5Mg:6Si proportions, Equation (5.3b) can be written as:
\[ \rho = 9.82 + 5.28(0.9 - f_{Mg}) + 6.56(0.6 - 1.2f_{Mg}) + \rho_{ppt}. \]

\[ = 18.5 - 13f_{Mg} + \rho_{ppt}. \]  

(5.8b)

Although Equations (5.8a) and (5.8b) have been calculated for different precipitates, interestingly both procedures result in identical expressions for resistivity. The reason for this is that the Cu content of \( Q \) balances the effect of the lower Mg:Si ratio compared to \( \beta'' \).

5.1.2. Volume Fraction of Precipitates in AA6111

In order to devise a relationship for the volume fraction of precipitates in AA6111, it is essential to first consider the following data (tabulated in Table 5.2) regarding the structure of the precipitates and the matrix for this alloy.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>Structure</th>
<th>Atoms</th>
<th>Lattice Parameters (nm)</th>
<th>Atomic Volume ( m^3 ) atom</th>
<th>Molar Volume ( m^3 ) mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Al )</td>
<td>-</td>
<td>FCC</td>
<td>4</td>
<td>( a = 0.404 )</td>
<td>( 1.7 \times 10^{-29} )</td>
<td>( 1 \times 10^{-5} )</td>
</tr>
<tr>
<td>( \beta'' )</td>
<td>Mg(_5)Si(_6)</td>
<td>Monoclinic</td>
<td>22</td>
<td>( a = 1.516 ) ( b = 0.405 ) ( c = 0.674 ) ( \beta = 105.3^\circ )</td>
<td>( 1.8 \times 10^{-29} )</td>
<td>( 1.1 \times 10^{-5} )</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Mg(_2)Si</td>
<td>Antifluorite</td>
<td>12</td>
<td>( a = 0.639 )</td>
<td>( 2.2 \times 10^{-29} )</td>
<td>( 1.3 \times 10^{-5} )</td>
</tr>
<tr>
<td>( Q )</td>
<td>Al(_4)Cu(_2)Mg(_8)Si(_7)</td>
<td>Hexagonal</td>
<td>21</td>
<td>( a = 1.04 ) ( c = 0.405 )</td>
<td>( 1.8 \times 10^{-29} )</td>
<td>( 1.1 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Table 5.2. Various facts regarding the phases available in AA6111 alloy.
The precipitate volume fraction is defined as the overall volume of precipitates at any
given time over the volume of the alloy. To simplify the calculations, it is assumed that only
one type of precipitate is available in the alloy, either \( Q \) or \( \beta'' \), and that the volume of the
precipitates can be neglected when compared to the total volume of the alloy. Therefore,
with the molar volumes of the precipitates and the matrix in hand from above, the volume
fraction (depending on the precipitate type) would be:

\[
\begin{align*}
  f_Q &= \frac{V_{\text{mol}}^{\text{ppt}} (\text{mol}_{\text{Mg}}^{\text{ppt}} + \text{mol}_{\text{Si}}^{\text{ppt}} + \text{mol}_{\text{Cu}}^{\text{ppt}} + \text{mol}_{\text{Al}}^{\text{ppt}})}{V_{\text{mol}}^{\text{matrix}} (\text{mol}_{\text{Al}}^{\text{matrix}})} \\
  f_{\beta''} &= \frac{V_{\text{mol}}^{\text{ppt}} (\text{mol}_{\text{Mg}}^{\text{ppt}} + \text{mol}_{\text{Si}}^{\text{ppt}})}{V_{\text{mol}}^{\text{matrix}} (\text{mol}_{\text{Al}}^{\text{matrix}})} 
\end{align*}
\]

where \( V_{\text{mol}}^{\text{ppt}} \) and \( V_{\text{mol}}^{\text{matrix}} \) are the molar volumes of the precipitate and the matrix, respectively;
\( \text{mol}_{\text{Mg}}^{\text{ppt}} \), \( \text{mol}_{\text{Si}}^{\text{ppt}} \), \( \text{mol}_{\text{Cu}}^{\text{ppt}} \), and \( \text{mol}_{\text{Al}}^{\text{ppt}} \) are the total moles of Mg, Si, Cu, and Al in the
precipitates; and \( \text{mol}_{\text{Al}}^{\text{matrix}} \) represents the total mole of Al in the matrix. Substituting for
proper values using the alloy chemistry and data provided at the beginning of this section,

\[
\begin{align*}
  f_Q &= 1.1 \left( f_{\text{Mg}} + f_{\text{Si}} + f_{\text{Cu}} + f_{\text{Al}} \right) \\
  f_{\beta''} &= 1.1 \left( f_{\text{Mg}} + f_{\text{Si}} \right) 
\end{align*}
\]

where as before \( f_{\text{Mg}}, f_{\text{Si}}, f_{\text{Cu}}, \) and \( f_{\text{Al}} \) represent concentrations of each element in the
precipitates. Since the stoichiometry of both precipitates is known, Equations (5.10a) and
(5.10b) can further be simplified:

\[
\begin{align*}
  f_Q &= 1.1 \times 2.6 f_{\text{Mg}} 
\end{align*}
\]

57
Thus, two expressions have been developed that relate the Mg content of \( Q \) and \( \beta'' \) precipitates to their volume fraction.

### 5.1.3. Analysis of Experimental Results

The resistivity results in Figure 4.1 can be reversed to illustrate resistivity as a function of temperature for specific holding times. This is shown in Figure 5.1 where holding times of 2, 4, 40, and 60 minutes are depicted. The resistivity values have been normalized by the as-quenched resistivity of 18.5 nΩm.

![Resistivity graph](image)

**Figure 5.1.** Resistivity of as-quenched alloy aged at different temperatures for the holding times shown.
The first noticeable point in all four curves is that the resistivity initially decreases with increase in aging temperature but at 350°C it starts to behave the opposite way. Another point that can be observed is that the 40 and 60-minute curves are overlapping. This may be a sign that after 40 minutes of treatment the alloy reaches equilibrium at the investigated temperatures and further aging does not have any effect on this equilibrium. Nonetheless, to rationalize this type of behaviour it is necessary to have a closer look at the contributions from solutes in solid solution and precipitates to resistivity, i.e. Equations (5.3a) and (5.3b).

The equilibrium concentration of solute atoms in solution increases with aging temperature. It is therefore expected that the solid solution term in both equations to increase with aging temperature. The magnitude $\rho_{ppt}$. does not have such a straightforward relationship with the heat treatment temperature. But, it is generally accepted that precipitates become less effective scatters as their mean spacing increases. With these two considerations, it is apparent that the initial decrease in resistivity with increase in temperature cannot be explained by the equilibrium solute content of the solid solution. In other words, the alloy does not reach equilibrium for the durations investigated at aging temperatures below 350°C. Scattering from precipitates could be a possible explanation for this decrease. It could be that with an increase in aging temperature the precipitates become coarser both in size and distribution and consequently the precipitate resistivity term slowly diminishes. The resistivity reduction due to this phenomenon is dominant over the increase in resistivity due to solute concentration increase and hence the overall resistivity decreases. It should be noted that in this argument the influence of precipitate type, nucleation, and growth, which vary with aging temperature, have not been considered.
Another possible explanation for the initial decrease in resistivity could be that the solute concentration in solution has yet to reach its equilibrium value. This non-equilibrium situation results in a higher solute concentration in solution at lower temperatures due to the slower kinetics and consequently, higher contribution to resistivity is resulted. The nucleation and growth kinetics of the precipitates play a significant role in this hypothesis and in order to confirm it these processes are to be considered in detail.

For temperatures above 350°C, resistivity does change in accordance to the solid solution content of the alloy. Since the alloy is kept for a relatively long time (40-60 minutes) at these elevated temperatures it may be assumed that the precipitates have grown and/or coarsened to such extent that they do not have a considerable contribution to resistivity (this assumption will be revisited in Section 5.1.3.2.). It can also be assumed that due to the faster kinetics the solute concentration has reached its equilibrium value at this stage. Thus, the resistivity increase with aging temperature is only related to the equilibrium solute concentration in solution. This is useful since with this assumption one can deduce some thermodynamic aspects of the precipitation process in AA6111 system.

5.1.3.1. Thermodynamics of the \(Q\)-Phase

The first step in this process involves converting the resistivity values to the solid solution contents for Mg, Si, and Cu. Following the previous considerations, for holding time of 60 minutes and aging temperatures above 350°C, it can be assumed that solid solution concentration is at equilibrium and the precipitates do not affect the resistivity. Transmission electron microscopy of AA6111 aged at temperatures above 300°C has identified \(Q\) as the predominant precipitate [77,78], thus it is assumed that only \(Q\)
precipitates are present at this stage. Thus for temperatures above 350°C, Equation (5.8a) reduces to:

\[ \rho = 18.5 - 13 f_{\text{Mg}} \]  

(5.12)

It is possible to find the atomic fraction of Mg, Si, and Cu in the precipitates through Equations (5.12) and (5.6) and subsequently obtain the solid solution concentration with the aid of Equation (5.7). This concentration will be the equilibrium concentration at that temperature. The results of this calculation are listed in Table 5.3.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \rho ) (n( \Omega )m)</th>
<th>\text{Q-Phase Concentration (at%)}</th>
<th>\text{Solid Solution Concentration (at%)}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( f_{\text{Cu}} )</td>
<td>( f_{\text{Mg}} )</td>
<td>( f_{\text{Si}} )</td>
</tr>
<tr>
<td>350*</td>
<td>0.153</td>
<td>0.511</td>
<td>0.534</td>
</tr>
<tr>
<td>400</td>
<td>0.104</td>
<td>0.416</td>
<td>0.364</td>
</tr>
<tr>
<td>450</td>
<td>0.083</td>
<td>0.332</td>
<td>0.290</td>
</tr>
<tr>
<td>500</td>
<td>0.048</td>
<td>0.192</td>
<td>0.168</td>
</tr>
<tr>
<td>560</td>
<td>0.006</td>
<td>0.024</td>
<td>0.021</td>
</tr>
</tbody>
</table>

*aging for more than 1 month, independent measurement

After having obtained the solid solution values for Mg, Si, and Cu as a function of temperature, it is now possible to calculate the solubility product for different temperatures. Following the approach of Starink and Li [57], the solubility product for the Q-phase within the aluminum-rich corner of the quaternary Al-Mg-Si-Cu phase diagram can be expressed as:

\[ [C_{\text{Mg}}]^{n}[C_{\text{Si}}]^{y}[C_{\text{Cu}}]^{z} = K_{1} \exp(-\frac{\Delta H_{0}}{RT}) \]  

(5.13)
where $K_1$ is a constant dependent on the choice of standard states, $|\Delta H_0|$ is the magnitude of
the standard enthalpy of the $Q$-phase dissolution / precipitation reaction, and $R$ is the
universal gas constant. In Equation (5.13), Henrian standard states have been assumed for
the solute atoms where the concentration has been expressed in atomic percent.

Using the $C_{Mg}$, $C_{Si}$, and $C_{Cu}$ concentrations given in Table 5.3, it is possible to
determine the constant $K_1$ and the enthalpy $\Delta H_0$ for the $Q$-phase, i.e. a plot of
$\ln\{[C_{Mg}]^8[C_{Si}]^7[C_{Cu}]^2\}$ versus $1/T$ results in a line with a slope of $\Delta H_0/R$ and a $y$-intercept of
$\ln K_1$. Figure 5.2 illustrates this plot with the calculated enthalpy and $K_1$.

![Plot of $\ln\{[C_{Mg}]^8[C_{Si}]^7[C_{Cu}]^2\}$ vs. $1/T$](image)

**Figure 5.2.** Plot of $\ln\{[C_{Mg}]^8[C_{Si}]^7[C_{Cu}]^2\}$ vs. $T^{-1}$. $\Delta H_0 = 495$ kJ/mol $K_1 = 2.8 \times 10^{28}$
Using Equation (5.7), Equation (5.13) can be rewritten in terms of the concentration of Mg in the precipitates, i.e. \( f_{Mg} \). Thus,

\[
(0.9 - f_{Mg})^8 (0.6 - 0.875 f_{Mg})^7 (0.3 - 0.25 f_{Mg})^2 = K_1 \exp(-\frac{\Delta H_0}{RT})
\]  

(5.14)

The terms \( \Delta H_0 \) and \( K_1 \) calculated above can now be inserted into Equation (5.14) in order to determine \( f_{Mg} \) as a function of the aging temperature. This functionality of \( f_{Mg} \) can then be translated into the evolution of equilibrium volume fraction of \( Q \)-phase with aging temperature by means of Equation (5.11a). The outcome of such practice is illustrated in Figure 5.3. Also depicted in this figure are individual data points that represent experimentally determined volume fractions of AA6111 aged at 180°C (for 1 and 7 hours) [13] and 250°C (for 30 minutes) [21].

Using a similar approach with the enthalpy and \( K_1 \) values reported by Grong [79] for the formation of \( \beta - Mg_2 Si \) precipitate, the volume fraction of \( \beta \)-phase can be plotted for comparison with that of \( Q \) as shown in Figure 5.3.

First looking at the two curves, it can be realized that \( Q \) develops to a higher volume fraction as compared to \( \beta \). This is not surprising since a greater number of solute atoms are incorporated into \( Q \). Both volume fraction curves show similar temperature dependence; up to approximately 250°C the volume fractions remain almost constant and thereafter they start to decrease. Finally, it is evident that there is a significant difference between the experimental data points and the curves; this issue will subsequently be discussed.

Note that the approach presented in this section represents the first attempt known by the author to quantify a temperature dependent solubility product for the \( Q \)-phase.
5.1.3.2. Contribution of Precipitates to Resistivity

The goal of this section is to estimate the contribution of precipitates to resistivity over a wide range of aging conditions. The curve in Figure 5.3 is an estimate for the equilibrium volume fraction of $Q$ precipitate. However, the heat treatments corresponding to the experimental points in this figure dominantly produce non-equilibrium phases (i.e. $\beta''$). Thus, these data points are non-equilibrium volume fractions which will approach the equilibrium volume fractions for long annealing times (times that may be totally impractical).
Different precipitates co-exist in the non-equilibrium microstructure. To allow for the co-existence of $\beta''$ and $Q$ precipitates, as a first approximation, Equations (5.11a) and (5.11b) are averaged so that the volume fraction precipitated is represented by:

$$f_{Q+\beta''} = 1.1 \times 2.4 f_{Mg}$$

(5.15)

The term $f_{Mg}$ from the above equation can be extracted and inserted into Equation (5.8) to develop a resistivity relationship in terms of the volume fraction of precipitates. Thus,

$$\rho = 18.5 - 4.9 f_{Q+\beta''} + \rho_{pp.}$$

(5.16)

The difference between the curve in Figure 5.3 and that of the TEM experiments represent the amount of solute atoms still in solution; i.e. given enough time these solutes will develop into stable precipitates increasing the volume fraction to the curve. The concentration still in solution can be calculated using first Equation (5.15) to determine $f_{Mg}$ and then inserting this calculated value into Equation (5.7) for the final concentration. This concentration can then be used to calculate the solid solution contribution to resistivity. The overall resistivity for these aging treatments has also been determined experimentally; hence it is possible to determine if the precipitates have any effect on the overall resistivity. For this purpose, the overall resistivity and the experimental volume fractions in Figure 5.3 are inserted into Equation (5.16) and $\rho_{pp.}$ is calculated. The result of this exercise is that the precipitates do have an effect on the resistivity. Table 5.4 summarizes the different resistivity terms for each of the heat treatments investigated. Also included in this table are three other heat treatments [77], which have been conducted at higher temperatures. These data are treated in the same way described above in order to identify the precipitate
contribution. The volume fractions for these treatments however have not been measured through TEM studies and their equilibrium values from Figure 5.3 are assumed for the calculations.

In addition to TEM, 3-D atom probe experiments have also been conducted on AA6111 for various aging treatments [18]. Through these studies the composition of the matrix is directly determined and via Equation (5.3a) \( \rho_{\text{ppt.}} \) is calculated. These results are tabulated in Table 5.5. It is important to point out that Equation (5.3a) has been used in this calculation not because \( Q \) phase is precipitated through these heat treatments but because this equation includes a solid solution term for Cu atoms, which is necessary for analyzing the atom probe results.

From Table 5.5 it can be seen that the precipitates have a considerable contribution to the resistivity; approximately 15-25% of the overall resistivity is due to the precipitates. This can be compared with what was seen in Table 5.4 where at maximum ~12% of the total resistivity came from precipitates.

The calculated precipitate spacings in Tables 5.4 and 5.5 are three-dimensional spacings and depending on the type of data acquired from the experimental techniques either of the following equations can be employed:

\[
L_{3D} = N^{-1/3} \tag{5.17a}
\]

where \( N \), the number density of precipitates, is experimentally determined or

\[
L_{3D} = \left( \frac{\pi^2 l}{f} \right)^{1/3} \tag{5.17b}
\]

where \( r \) radius, \( l \) length, and \( f \) volume fraction of precipitates are verified by experiment.
### Table 5.4. Different resistivity terms for treatments corresponding to TEM experiments.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Volume Fraction (%)</th>
<th>Calculated Precipitate Spacing (nm)</th>
<th>$f_{Mg}$ (at%)</th>
<th>Total Resistivity ($\Omega_m$)</th>
<th>$\rho_{ss}$ ($\Omega_m$)</th>
<th>$\rho_{ppt.}$ ($\Omega_m$)</th>
<th>$\frac{\rho_{ppt.}}{\rho_{total}} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1hr@180°C</td>
<td>0.63</td>
<td>17.30 $\dagger$</td>
<td>0.24</td>
<td>17.6</td>
<td>6.8</td>
<td>2.2</td>
<td>12.4</td>
</tr>
<tr>
<td>7hr@180°C</td>
<td>0.74</td>
<td>22.42 $\dagger$</td>
<td>0.28</td>
<td>16.8</td>
<td>6.3</td>
<td>1.9</td>
<td>11.6</td>
</tr>
<tr>
<td>30min@250°C</td>
<td>1.20</td>
<td>53.86 $\dagger$</td>
<td>0.45</td>
<td>14.4</td>
<td>4.0</td>
<td>1.8</td>
<td>12.4</td>
</tr>
<tr>
<td>150min@300°C</td>
<td>1.60*</td>
<td>242 $\dagger$</td>
<td>0.56</td>
<td>12.0</td>
<td>3.8</td>
<td>0.8</td>
<td>6.4</td>
</tr>
<tr>
<td>900min@300°C</td>
<td>1.60*</td>
<td>440 $\dagger$</td>
<td>0.56</td>
<td>11.5</td>
<td>3.8</td>
<td>0.3</td>
<td>2.4</td>
</tr>
<tr>
<td>12min@450°C</td>
<td>0.91*</td>
<td>902 $\dagger$</td>
<td>0.32</td>
<td>14.5</td>
<td>7.0</td>
<td>0.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* estimates assuming that the volume fraction is close to the equilibrium values from Figure 5.3

$\dagger$ calculated using Equation (5.17a)

### Table 5.5. Different resistivity terms for treatments corresponding to the 3-D atom probe experiments.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Matrix Composition (at%)</th>
<th>Calculated Precipitate Spacing (nm)</th>
<th>Total Resistivity ($\Omega_m$)</th>
<th>$\rho_{ss}$ ($\Omega_m$)</th>
<th>$\rho_{ppt.}$ ($\Omega_m$)</th>
<th>$\frac{\rho_{ppt.}}{\rho_{total}} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75h@60°C</td>
<td>0.73±0.01Mg</td>
<td>5.31*</td>
<td>20.3</td>
<td>9.3</td>
<td>3.6</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>0.52±0.01Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25±0.01Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24h@90°C</td>
<td>0.71±0.01Mg</td>
<td>5.85*</td>
<td>20.0</td>
<td>7.9</td>
<td>4.7</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>0.36±0.01Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.22±0.01Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2h@120°C</td>
<td>0.65±0.01Mg</td>
<td>5.41*</td>
<td>19.5</td>
<td>8.4</td>
<td>3.7</td>
<td>19.1</td>
</tr>
<tr>
<td></td>
<td>0.41±0.01Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.28±0.01Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4min@180°C</td>
<td>0.59±0.01Mg</td>
<td>7.94*</td>
<td>18.9</td>
<td>7.1</td>
<td>4.3</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>0.31±0.01Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25±0.01Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* calculated using Equation (5.17a)
An existing hypothesis indicates that $\rho_{ppt}$ is inversely proportional to the precipitate spacing. To examine this theory $\rho_{ppt}$ has been plotted against the precipitate spacing for each of the reported aging treatments, Figure 5.4. Figure 5.4 illustrates that the inverse relationship between the resistivity and the precipitate spacing does hold. As the spacing between precipitates increases, their contribution to resistivity also diminishes. It is possible to explain this type of behaviour in terms of multiple scattering of electrons by the precipitates. When the precipitates are widely spaced, an electron scattered by one particle will have a good chance of not encountering another particle throughout its path and thus avoiding the scattering. In contrast when the precipitates are in close vicinity of one another, an electron may encounter several of these secondary phases in its path and consequently suffer multiple scatterings. As a result in the latter case an increased resistivity is experienced.

An important fact that should not be overlooked at this stage is the role of the solid solution matrix in this whole scattering process. Nonetheless, an electron scattered from a precipitate will travel in the matrix before reaching another particle and during this period of time scattering in the matrix is very likely to take place. So to investigate the contribution of precipitates more rigorously one has to see whether scattering from the matrix and the precipitates can be separated from each other or not; in other words, can Matthiessen’s rule be applied to these alloys or not. The answer to this fundamental issue is yet to be clarified but for the time being the validity of Matthiessen’s rule will not be questioned. Having given this caveat, an equation can be fitted to the data points of Figure 5.4 resulting in a relationship for the precipitate resistivity term, i.e.
Figure 5.4. Evolution of precipitate resistivity with precipitate spacing.

\[ \rho_{pp} = \frac{13}{(L_{3D})^{0.5}} \]  \hspace{1cm} (5.18)

Substituting the above Equation for \( \rho_{pp} \) in Equation (5.16) will give

\[ \rho = 18.5 - 4.9f_{Q,p} + \frac{13}{(L_{3D})^{0.6}} \]  \hspace{1cm} (5.19)

which is an all-inclusive expression describing the evolution of resistivity in AA6111 irrespective of the precipitate type. Equation (5.19) is very valuable in two ways: first, it
relates resistivity to the volume fraction of precipitates; second, it can be used for both underaged and overaged alloys. The latter point is very important because most expressions available in literature can only be used for overaged conditions. Having said that, from a practical point of view this relationship is not ideal since it is dependant on quantitative TEM studies for verifying $L_{3D}$. Moreover, TEM studies other than those employed in this work are still required to explore the capabilities of the above equation, e.g. use of Equation (5.19) to determine volume fraction of precipitates.

To summarize, it has been shown that the contribution of precipitates to resistivity is important and that it diminishes as the precipitate spacing increases. This represents a novel approach to examining resistivity measurements in precipitation hardening systems. However, it is an acceptable assumption to disregard this contribution, as it is often seen in the literature, for certain aging treatments where the precipitates do not affect the resistivity significantly (e.g. prolonged treatments at relatively high temperatures). Regarding this point, this assumption was used in Section 5.1.3. of this work for 60-minute treatments at temperatures above 350°C and now its validity is confirmed (Table 5.4).

5.1.4. HEW Resistivity Model for AA6111

Among the proposed resistivity models in the literature, the HEW and RW models are perhaps the most discussed of all and in contrast to the other models, they are partially based on electron mobility calculations. It is thus beneficial to implement such semi-empirical models and compare them with conventional empirical models that are solely based on Matthiessen’s rule. For this purpose, the HEW model has been adopted for AA6111 alloy.
5.1.4.1. The Model

According to HEW model the precipitate resistivity term of a binary alloy that has a total solute concentration $N_a$, $Z$ number of zones per host atoms, and $N$ number of solute atoms within a precipitate, is given by:

$$
\Delta \rho = \left[ \frac{1-g}{\rho_{\text{pure}}(T) + (N_a - NZ)\rho_a + ZF(N)} + \frac{g}{\rho_{\text{pure}}(T) + (N_a - NZ)\rho_a + ZF(N) + ZB(N)} \right]^{-1} - (\rho_{\text{pure}}(T) + N_a\rho_a) \tag{5.20}
$$

where $B(N) = \beta N^{4/3}$ and $F(N) = \delta N^{2/3}/[1 + (\hat{N} / N^{2/3})]^2$. In this equation $\rho_{\text{pure}}(T)$ is the resistivity of pure host metal, $\rho_a$ specific resistivity of solute atoms; $g$, $\beta$, $\delta$, and $\hat{N}$ free parameters, $F(N)$ and $B(N)$ functions representing small angle scattering and Bragg scattering respectively. The separation of the expression in brackets into two terms, one with and the other without the Bragg scattering function $B(N)$, follows the fundamental assumption in HEW theory where anisotropy in scattering due to Bragg scattering is identified as the main cause of resistivity decrease.

Equation (5.20) can be extrapolated for use in systems with more than one alloying elements. The outcome of such extrapolation for AA6111 at the early stages of aging where Mg and Si atoms mainly develop into precipitates is shown below:

$$
\Delta \rho = \left[ \frac{1-g}{18.5 - Z(N_{Mg}\rho_{Mg} + N_{Si}\rho_{Si}) + ZF(N)} + \frac{g}{18.5 - Z(N_{Mg}\rho_{Mg} - N_{Si}\rho_{Si}) + ZF(N) + ZB(N)} \right]^{-1} - 18.5 \tag{5.21}
$$
the terms $N_{\text{Mg}}$ and $N_{\text{Si}}$ are the number of Mg and Si atoms in a precipitate, $\rho_{\text{Mg}}$ and $\rho_{\text{Si}}$ are Mg and Si resistivity coefficients, and the other terms/parameters are as before. In this equation, $Z$ and $N$ (including $N_{\text{Mg}}$ and $N_{\text{Si}}$) are the only terms that are functions of aging time; subsequently these evolution functions will be defined.

Assuming a distribution of needle-shaped $\beta''$ precipitates with average radius $r$ and length $l$, $N$ would be:

$$N = \frac{\text{vol. of one precipitate}}{\text{vol. of precipitate per atom}} = \frac{\pi r^2 l \ (m^3)}{1.8 \times 10^{-29} \ (m^3/\text{atom})}$$  \hspace{1cm} (5.22)$$

In the expression above, the volume of precipitate per atom (referred to as $V_{\text{ppl.}}$ in Section 5.1.2) is calculated for $\beta''$ unit cell containing 22 atoms (10 Mg and 12 Si). In a similar way if this volume is calculated based on the individual number of Mg and Si atoms in the unit cell, one would get

$$N_{\text{Mg}} = \frac{\pi r^2 l \ (m^3)}{4 \times 10^{-29} \ (m^3/\text{atom})} \quad \text{and} \quad N_{\text{Si}} = \frac{\pi r^2 l \ (m^3)}{3.3 \times 10^{-29} \ (m^3/\text{atom})}$$  \hspace{1cm} (5.23)$$

Again in accordance to definition of $Z$,

$$Z = \frac{\text{no. of precipitates}}{\text{tot. no. of host atoms}} = \frac{f}{(6.1 \times 10^{28})(\pi r^2 l)}$$  \hspace{1cm} (5.24)$$

where $f$ is the volume fraction of precipitates and $6.1 \times 10^{28}$ is the number of Al atoms per $m^3$ of material. By knowing the variation of $f$, $r$, and $l$ with aging time $Z$ and $N$ (including
\( N_{Mg} \) and \( N_{Si} \) are defined and accordingly the residual resistivity \( \Delta \rho \) can be determined. Finally, Matthiessen's law is employed to give the overall resistivity of the alloy:

\[
\rho = \rho_{\text{pure}}(T) + \sum_i (N_{a}^i - N_i Z) \rho_i + \Delta \rho = 18.5 - Z(N_{Mg} \rho_{Mg} + N_{Si} \rho_{Si}) + \Delta \rho \quad (5.25)
\]

where \( N_{a}^i \) is the total concentration of solute atom \( i \) in the alloy.

### 5.1.4.2. Model Implementation

The fundamental relationships that are essential to this model, more precisely the evolution of \( f, r, \) and \( l \) during aging, have been adopted from the work of Esmaeili et al. [67,80]. However, these relationships are only available for aging at 180°C and as a result the model can only implemented for this temperature.

Esmaeili et al. use a JMAK type expression to describe the precipitate volume fraction kinetics:

\[
f = 0.74 \cdot (1 - \exp(-kt)) \quad (5.26)
\]

The term \( f \) is the volume fraction in percentage, \( k = 6.73 \times 10^{-4} \text{ s}^{-1} \), and \( t \) is the aging time. A growth law of the form depicted below is utilized for describing the evolution of \( r \) at the early stages of aging.

\[
r = \sqrt{(r_0^2 + k't)} \quad (5.27)
\]

where \( r_0 = 1 \times 10^{-3} \text{ m}, k' = 7 \times 10^{-23} \text{ m}^2\text{s}^{-1} \), and \( t \) is the aging time in seconds. It is further shown that the radius \( r \) is linearly related to length \( l \) via equation

\[
r = 0.09l + 0.83 \quad (5.28)
\]
In this expression both \( r \) and \( l \) are in \( nm \). With all the necessary kinetic information in hand and assuming that the same solute resistivity coefficients as those reported for binary aluminum alloys can be used, the model is implemented. The result is illustrated in Figure 5.5, noting that the best values for the free parameters \( g, \beta, \delta, \) and \( \hat{N} \) are 0.26, 7, 42, and 4.2 respectively.

![Figure 5.5. HEW model for AA6111 at 180°C.](image)

The model describes the data well and the values of the free parameters are in good agreement with what has been reported by Edwards and Hillel [38] after the appropriate correction [47] is applied to them. However, the model is quite flexible and is very sensitive to small changes in the fitting parameters. This is indeed the weakness of the model and
furthermore, these parameters do not have a physical basis. Moreover, these parameters are specific to this aging temperature (it was not possible to have a general model over a range of aging temperatures).

In the end, one has to be careful not to sacrifice one of the main purposes of modelling, i.e. better understanding of underlying mechanisms of a phenomenon, for the sake of a good prediction and fit.

5.2. Thermal Spike Treatment

A detailed analysis of the thermal spike results is provided in the following sections to assess the potential of such treatments as a feasible solution to the industrial problem discussed earlier.

5.2.1. Criteria for Spike Selection

Before providing a definition for a successful spike treatment it is necessary to describe the type of properties which are desired for the alloy at the various stages of the treatment. It was briefly mentioned in Section 2.3.1. that the auto manufacturer requires the as-received material to have enough strength to withstand any damage during its handling and it should also show good formability during deformation processes. To satisfy both these contradicting requirements, a yield stress of 90-150 MPa is generally desired [78]. This sets a measure for assessing a spike: after the application of a spike, the yield strength should be within the aforementioned range. It is also preferred that the alloy does not age at room temperature after it has been subjected to a spike. The reason for this criterion is very obvious, natural aging is detrimental to paint bake response. Finally, an alloy subjected to 30-minute treatment at 180°C immediately after the solution treatment develops a yield
strength of 280-300 MPa. Thus, a final strength as close to this value is desired. Fulfillment of this last criterion is a measure of the ability of the thermal spike to revive the deteriorated paint bake response of naturally aged alloys.

5.2.2. Overview of Investigated Thermal Spike Treatments

The results of the two heat treatment Schedules A and B are reviewed in this section. For simplicity, the acceptable yield stress ranges delineated above as criteria for successful thermal spikes have been superimposed on the experimental results.

5.2.2.1. Schedule A

i) 220°C: The results of these spikes are portrayed in Figure 5.6. Focusing on the “after thermal spike” yield stresses, it can be observed that only the 30-second and 1-minute spikes fall within the acceptable window and 5-minute spike has to be discarded. The reason for this behaviour is that as the duration of the spike is increased, the precipitation reaction proceeds further translating into a higher strength value.

Moving to the next stage of treatment, i.e. 1-day hold at room temperature, it can be seen that except for 30-second spike, no change in strength is observed. Since a stable microstructure at room temperature is desired, the 30-second spike can also be eliminated. The duration of this spike is so short that even after the spike is implemented, solute supersaturation remains at a high level to provide sufficient driving force for the formation of clusters at room temperature. Moreover, the resistivity of this sample (Appendix B) also shows an increase with hold at room temperature. This increase can only be due to the clustering of solutes.
Interestingly, in the absence of any spike, even with only 1-day of natural aging the simulated paint bake response of the alloy is reduced to 190 MPa. Introduction of the spikes into the heat treatment cycle however improves the paint bake response. After having considered all the criteria, the only treatment that is left is the 1-minute spike. After 30-minute treatment at 180°C the yield stress of a sample treated by the 1-minute excursion has increased to ~290 MPa which is approximately 100 MPa higher than for the case of no thermal spike. In summary, only 1-minute spike qualifies all the three conditions and has the potential to be used as a solution to the natural aging problem.

**220°C Spike (Schedule A)**

![Graph showing yield strength vs. duration of spike](image)

*Figure 5.6. Results of 220°C spike in Schedule A. Windows representing the acceptable yield stresses for two of the stages in the schedule are superimposed on the results.*

**ii) 250°C:** The acceptable yield limits superimposed on 250°C spike results are plotted in Figure 5.7. Considering the yield stresses developed immediately after the application of the
thermal excursions, it is evident that as the duration of the treatment is increased a higher
yield strength is obtained. Again, this is due to the higher volume fraction of precipitates that
develop for longer holding times. Among the three, only the 30-second spike's strength falls
within the acceptable range.

All samples after spike treatment have an unstable microstructure at room
temperature, which is undesired. The unstable microstructure results from the fact that after
all these treatments there is still sufficient supersaturation and thus driving force for
clustering to occur at room temperature.

![250°C Spike (Schedule A)](image)

**Figure 5.7.** Results of 250°C spike in Schedule A. Windows representing the acceptable yield stresses for two
of the stages in the schedule are superimposed on the results.

The treatment at 180°C has caused an increase in the yield strength of samples treated
with 30-second and 1-minute spikes but no such change is observed for the case of 5-minute
spike. The yield stresses developed at this final leg of the treatment do not reach the desired magnitude. Based on these considerations, it can be concluded that none of the 250°C spikes are suitable since the three criteria are not met for any of them.

Finally, it is worth comparing the difference in results for the two different spike temperatures. It was observed that the 1 and 5-minute treatments at 250°C do not inhibit the clustering of solutes at room temperature while those at 220°C do. This is in contradiction to what had been anticipated. Due to the faster kinetics involved at higher temperatures (250°C in this case), precipitates remove the solute supersaturation to a greater extent as compared to lower temperatures (220°C here). Consequently, the driving force for clustering should also be lower in samples treated at higher temperatures. A possible explanation to this behaviour could be related to differences in nucleation behaviour at the two temperatures. It has been observed that the number density of precipitates at 250°C is very low. As a consequence, the precipitate spacing at 250°C is large [21]. Thus, at 250°C the inter precipitate spacing is sufficiently large that at the region midpoint between the precipitates the supersaturation is sufficiently high to allow for clustering at room temperature.

5.2.2.2. Schedule B

i) 220°C: Figure 5.8 shows the results from the 220°C thermal spikes. An initial decrease in "after thermal spike" stress is observed after the 30-second spike is applied; the yield stress decreases from an initial value of 155 MPa (i.e. strength after 2 weeks of natural aging) to 127 MPa once this spike is implemented. This stress then remains constant with increasing the time to 1 minute but the longer treatment of 5 minutes has caused it to go up to 195 MPa. Before the thermal spike exercise, the samples contain a distribution of naturally aged
clusters and have a yield stress of 155 MPa. Once subjected to the spike temperature, some of the clusters dissolve but concurrently some precipitation occurs. Dissolution of solute clusters is accompanied by a decrease in the strength of the alloy, i.e. the initial drop to 127 MPa. At this stage softening due to cluster dissolution is dominant over precipitation hardening. Upon longer treatment, 1 minute, the softening and hardening reach a balance keeping the yield constant at 127 MPa. Treating the alloy for still longer time, 5 minutes, causes the precipitation hardening factor to become dominant and increase the strength to 195 MPa. All “after thermal spike” yield stresses but the 5-minute, which has a relatively high strength not suited for forming processes, fall within the acceptable range. In all cases 1 day of natural aging has no effect on the yield stress of the samples that have experienced the thermal spikes. Thus, the microstructure has been stabilized.

![220°C Spike (Schedule B)](image)

Figure 5.8. Results of 220°C spike in Schedule B. Windows representing the acceptable yield stresses for two of the stages in the schedule are superimposed on the results.
The paint bake cycle simulation at 180°C increases the yield strength in all cases, but it has the most significant impact where the 30-second and 1-minute spikes have been exercised. Overall, the yield stresses after the paint bake simulation are low considering the maximum hardening potential of the alloy. Despite the fact that these spikes have been successful in improving the “after 30min at 180°C” yield stress from 185 MPa in their absence to above 220 MPa, they do not fulfil the last requirement and are thus not suitable.

**ii) 250°C**: At 250°C, Figure 5.9, dissolution of solute clusters is again observed as an initial drop in the “after thermal spike” stress. However, the magnitude of this drop is greater than that seen at 220°C previously. Due to the faster precipitation kinetics at 250°C, this stress starts to increase just after 1-minute as compared to the 5-minute at 220°C. Yield stresses developed after both 30-second and 1-minute spikes are within the designated range. The 5-minute excursion has induced a pronounced increase in strength which falls within the window of what is desired after paint bake treatment; such a high strength alloy would have poor formability.

Holding at room temperature does not affect the material that has been treated by either 30-second or 5-minute spikes. This is not the case for the 1-minute where a small strengthening has occurred. To explain this type of behaviour, one can speculate that fewer natural aging clusters are dissolved after 30 seconds at 250°C than after 1 minute. As a consequence, the solute concentration that is returned to solution is higher after 1-minute spike. On the other hand, after 5 minute even more clusters are reverted and the solute supersaturation is the highest of all. The extent of precipitation is just the opposite of the cluster reversion; more solutes are depleted from solution by the precipitates as the treatment
Figure 5.9. Results of 250 °C spike in Schedule B. Windows representing the acceptable yield stresses for two of the stages in the schedule are superimposed on the results.

time is increased. Hence after the 30-second spike, less solute is depleted from solution as compared to the longer spikes, but at the same time fewer number of solute atoms are returned to solution through the reversion of the clusters. All this will result in a matrix with low solute supersaturation that is stable at room temperature. At the other extreme, more solutes are returned to solution by cluster dissolution after 5-minute but these solutes are subsequently removed by precipitation which takes place during this period. Again the supersaturation of the matrix remains low and it does not reach the critical value to provoke clustering at room temperature. Finally, treatment for 1-minute produces an intermediate situation where despite higher rate of solute removal from solution as compared to 30-second, the amount of solute in solution will remain sufficiently high that natural aging will occur. The precipitation is not as intensive as 5-minute and the amount of solute atoms
reverted into solution are not as low as 30-second. In other words, the rate at which solutes are put back into solution is higher than the rate they are depleted.

In the scenarios where the thermal spikes are included, yield stresses obtained after the paint bake simulation show an improvement of at least 70 MPa when compared to the “No Spike” case. Only 1 and 5-minute spikes however reach the window that has been set. At the end of the day, none of the spikes satisfy all three criteria. However, if the stability of the microstructure had not been an issue, 1-minute would have been the spike of choice.

5.2.2.3. Comparison of Schedules A and B

The thermal spike treatment of Schedule A is primarily aimed at producing a microstructure that is stable at room temperature and at the same time has a good paint bake response. Since this spike is to be applied to a solution treated alloy, it must be carried out at the aluminum production plant. On the other hand, the spike treatment in Schedule B is mainly responsible for reviving the solute supersaturation that has been lost during natural aging so that a good paint bake response is obtained. This thermal excursion has to be implemented at the vehicle manufacturer where the naturally aged sheets are received. This difference in the site where the spike treatment is to be conducted may or may not offer advantages for either of the schedules but this is beyond the scope of this work. It is also clear that for more precise comparisons of this type, the technique that will be used for implementation of the thermal excursion (e.g. laser, induction, etc.) should also be taken into account.

Now looking at the two schedules from another point of view, at first, Schedule A would be favoured over its counterpart B since no successful spike was identified for the latter. This is true if the criteria that have been introduced are all to be fulfilled. However,
satisfaction of all these conditions might not be mandatory at the same time. For example in Schedule B, the production line may be configured in such a way that once the material is subjected to a spike, it will directly go for the paint bake cycle without any delay at room temperature. In this way the stability of the structure is not an issue and a 1-minute spike at 250°C is acceptable. So, the success of a thermal spike exercise really depends on how a successful spike is defined. This definition is not fixed and it varies from case to case. The definition that has been introduced in this work can be regarded as a limiting ideal case and thus, it is hard to satisfy.

5.2.3. Modelling of Thermal Spikes

In this portion of the work, an attempt has been made to model the yield strength evolution of AA6111 as it experiences a thermal spike. This model if implemented successfully can be used to predict the spike dwell time necessary for producing a desirable strength in the alloy. For this purpose two yield strength models developed by Esmaeili et al., one for isothermal aging of as-quenched AA6111 [80] and the other isothermal aging of naturally aged AA6111 [81], have been modified to be used for thermal spike treatments.

5.2.3.1. Thermal Spikes in Schedule A

Since the spikes in Schedule A are applied to a solution treated alloy, the isothermal aging model for as-quenched AA6111 will be used. The model is based on the so-called internal state variable approach [82]. It has only been calibrated for aging temperatures in the range of 160°C to 220°C. In this model, the overall yield stress of the alloy \( \sigma_{YS} \) is expressed in terms of contributions from precipitates (\( \sigma_{p} \)), solute atoms (\( \sigma_{s} \)), and pure matrix (\( \sigma_{m} \)) added linearly, i.e.
\[ \sigma_{ys} = \sigma_{ppt} + \sigma_{ss} + \sigma_i \]  

(5.29)

A constant contribution of 10 MPa has been assumed from the pure matrix but the other terms are defined as follows:

\[ \sigma_{ppt} = Af_r^{1/2} \]  

(5.30a)

\[ \sigma_{ss} = B(1 - f_r)^{2/3} \]  

(5.30b)

where \( A \) is a constant equal to 325 MPa for 220°C, \( B = 50 \) MPa, and \( f_r \) is the relative volume fraction of precipitates given by:

\[ f_r = 1 - \exp(-kt) \]  

(5.31)

where \( t \) is the aging time and \( k \) is a kinetic parameter which has an Arrhenius relationship with aging temperature, i.e.

\[ k = k_0 \exp\left(-\frac{Q}{RT}\right) \]  

(5.32)

where \( k_0 = 3280 \) s\(^{-1}\) and \( Q = 58 \) kJ/mol for AA6111.

Since in thermal spike treatments the dwell time at a temperature is relatively short, the heat-up of the sample cannot be ignored. Accordingly, a non-isothermal condition has to be considered. To do so, the non-isothermal heating during spike treatment is broken up into \( i \) short intervals of isothermal holds. Thus,

\[ f_r^i = f_r^{i-1} + \left. \frac{df_r}{dt} \right|_i \cdot \Delta t = f_r^{i-1} + k \exp(-kt)|_i \cdot \Delta t \]  

(5.33)
where $f_{r-1}$ and $f_r$ are the relative volume fractions at the $(i-1)$-th and $i$-th interval and $\Delta t$ is the time interval. In this study a time interval of 0.5 seconds has been used. Finally, using the experimentally determined temperature-time profiles at 220°C and 250°C, Figure 4.6, and Equations (5.29), (5.30), (5.32), and (5.33) the yield stress evolution is modelled. Since the model is calibrated for only 160-220°C temperature range, it is important to emphasize that the evolution laws of the model have been extrapolated to be used for 250°C. For this purpose, all the constants in the abovementioned equations are kept at the same value as that of 220°C except for $A$ in Equation (5.30a) where a value of 246 MPa is used at 250°C. The model is implemented and plotted against the “after thermal spike” yield stresses, as shown in Figures 5.10 and 5.11.

At 220°C the model predictions are reasonable. For the 30-second spike, the model prediction is 35% too low. However, for 1 and 5-minute the model is within 10%. The extrapolated model at 250°C over-predicts the 30-second yield stress by approximately 10% but is within 2-3% for the 1 and 5-minute cases. The discrepancy between model predictions and experimental results at short spikes could be due to the fact that the original Esmaeili model was not really intended for such short aging times.

A more comprehensive approach to modelling of this process would involve recalibration of the original model for only short aging exercises. In this way the emphasis of the model will be shifted towards the region where it is important to thermal spike treatments.
Figure 5.10. Comparison of experimental and modelling results for yield strengths developed immediately after spike treatments at 220°C of Schedule A.
Figure 5.11. Comparison of experimental and modelling results for yield strengths developed immediately after spike treatments at 250°C of Schedule A.
5.2.3.2. Thermal Spikes in Schedule B

In Schedule B, a 2-week naturally aged alloy is subjected to thermal spike and therefore, the isothermal aging model developed by Esmaeili et al. specific to the aging of naturally aged AA6111 [81] is adopted. This model, as in the aforementioned model, follows the principals of internal state variable modelling approach. The model describes the kinetics of simultaneous precipitate formation and cluster dissolution during artificial aging at 160-220°C temperature range. The fundamental relationships of the model are summarized below.

Similar to Equation (5.29), a linear addition rule is used for considering the contributions from precipitates, solid solution, and pure matrix. This time an additional contribution from natural aging clusters has also to be considered. Thus,

\[ \sigma_{IS} = \sigma_{ppt}^* + \sigma_{ss} + \sigma_i \quad (5.34) \]

where \( \sigma_{ppt}^* = (\sigma_{ppt}^2 + \sigma_{clusters}^2)^{1/2} \) and it incorporates both contributions from precipitates and clusters. Subsequently, the relationships for each of the four terms defined above will be given.

\[ \sigma_i = 10 \text{ MPa} \quad (5.35a) \]

\[ \sigma_{ss} = C_1 (1 - f_{r(clusters)}^{NA} f_{r(clusters)}^{AA} + f_{r(ppt)}^{NA})^{2/3}, \quad C_1=50 \text{ MPa} \quad (5.35b) \]

\[ \sigma_{ppt} = C_2 f_{r(ppt)}^{1/2}, \quad C_2=315 \text{ MPa} \quad (5.35c) \]

\[ \sigma_{clusters} = C_3 (f_{r(clusters)}^{NA} f_{r(clusters)}^{AA})^{1/2}, \quad C_3=160 \text{ MPa} \quad (5.35d) \]
The parameter $f^{NA}_{r\text{(clusters)}}$ is the relative volume fraction of clusters developed during natural aging, $f^{AA}_{r\text{(clusters)}}$ relative volume fraction of clusters during artificial aging, and $f_{r\text{(ppt)}}$ relative volume fraction of precipitates during artificial aging. The relationships that explain the evolution of each of these terms with aging time are listed in Table 5.6.

Table 5.6. Evolution expressions for different relative volume fractions.

<table>
<thead>
<tr>
<th>Function</th>
<th>Temperature Dependence</th>
<th>Derivative $\frac{df_r}{dt}$</th>
<th>Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f^{NA}<em>{r\text{(clusters)}} = 1 - \exp(-k</em>{NA}t^{0.5})$</td>
<td>$-$</td>
<td>$-$</td>
<td>$k_{NA}=0.02 \text{ hr}^{-1}$</td>
</tr>
<tr>
<td>$f^{AA}_{r\text{(clusters)}} = (1 - Bt^{1/2})^3$</td>
<td>$B = B_0 \exp(-\frac{Q_1}{RT}) - \frac{3B}{2}t^{-1/2} (1 - Bt^{1/2})^2$</td>
<td>$Q_1=88 \text{ kJ/mol}$ $B_0=1.08 \times 10^8 \text{ s}^{-1/2}$</td>
<td></td>
</tr>
<tr>
<td>$f_{r\text{(ppt)}} = 1 - \exp(-kt)$</td>
<td>$k = k_0 \exp(-\frac{Q_2}{RT})$</td>
<td>$k \exp(-kt)$</td>
<td>$Q_2=95 \text{ kJ/mol}$ $k_0=1.04 \times 10^7 \text{ s}^{-1}$</td>
</tr>
</tbody>
</table>

In Table 5.6, $t_{NA}$ is the duration of natural aging. In this work, since all samples are naturally aged for 2 weeks ($t_{NA}=336 \text{ hrs}$) before the spikes are applied, $f^{NA}_{r\text{(clusters)}}$ is fixed. The other two relative volume fractions evolve with aging time. As before, to take care of non-isothermal heating during spike treatment, Equation (5.33) is used for explaining the evolution of $f^{AA}_{r\text{(clusters)}}$ and $f_{r\text{(ppt)}}$ with aging time. Figures 5.12 and 5.13 show the model predictions at 220°C and 250°C. The same temperature-time profiles and time interval employed in the previous modelling exercise have been utilized.
The yield values corresponding to 30-second and 5-minute spikes at 220°C completely coincide with that predicted by the model. A difference of less than 10% is observed between model and experiment for 1-minute 220°C spike, which is satisfactory. The major shortcoming of the model is in predicting the yield stress of the 2-week naturally aged alloy, i.e. the yield strength at aging time zero.

The agreement between model and experiment for the 250°C spikes was less good but in general a difference of approximately 20-30% is observed. The 220°C model is acceptable in the sense that its predictions are in agreement with the experimental results but it falls short of explaining the natural aging and dissolution processes adequately. This is clearly evident in the starting portion of the curve in Figure 5.12 where the model gives low yield strength for the 2-week naturally aged alloy. In addition, the trough corresponding to the initial dissolution of clusters is also small compared to the experiments. Employment of a shorter time interval in Equation (5.33) will cause a reduction in the error that is incurred when non-isothermal heating is broken up into several isothermal holdings. At 250°C, the abovementioned arguments may not be repeated since a more fundamental issue has to be addressed first; the original model by Esmaeili et al. is not calibrated for 250°C. This may indeed be the source of the discrepancy observed between the model and experiments. As in the model discussed in Section 5.3.2.1. it is helpful to have the original model recalibrated for short times and also wider temperature range.
Figure 5.12. Comparison of experimental and modelling results for yield strengths developed immediately after spike treatments at 220 °C of Schedule B.
Figure 5.13. Comparison of experimental and modelling results for yield strengths developed immediately after spike treatments at 250°C of Schedule B.
CHAPTER SIX
Conclusions and Future Work

6.1. Conclusions

The current project has involved two related areas of research. First, electrical resistivity has been used as a tool to study precipitation in AA6111 and second, an examination of the potential for using thermal spike treatments to eliminate the detrimental effect of natural aging on paint bake response has been conducted. The conclusions will be summarized in terms of these two themes.

6.1.1. Electrical Resistivity Studies

First, the use of electrical resistivity has been shown to be a very useful tool for studying precipitation behaviour in 6000 series aluminum alloys although clearly the analysis of this data requires careful considerations. Specifically, the following important points have been deduced from this work:

1) The magnitude of the electrical resistivity reaches a plateau value for solution treated samples aged at temperatures above 350°C when the duration of aging was greater than 40 minutes. It is proposed that this plateau is result of the microstructure approaching equilibrium at these aging temperatures and that at these high temperatures the contribution of precipitates is sufficiently small to be ignored such that resistivity value can be directly related to the solid solution content.

2) In a novel approach, it is shown that by using Matthiessen’s rule and an assumption regarding the composition of the precipitate, it is possible to derive the evolution of equilibrium volume fraction of precipitates with aging temperature. From this analysis,
an estimate of the temperature dependent solubility product for the \( Q \) phase can be obtained. To the best knowledge of the author, this represents the first attempt to quantify this parameter.

3) The contribution of precipitates to the overall resistivity has been assessed over a wide range of temperatures and aging times by considering the resistivity difference between equilibrium and non-equilibrium states at any given aging temperature and through comparison with a unique set of quantitative TEM and atom probe field ion microscopy available from related studies undertaken at UBC. This represents the first attempt, to date, to quantify the effect of precipitates on electrical resistivity in 6000 series aluminum alloys. It was found that the precipitate resistivity term was inversely related to the spacing of the precipitates as might be expected from theoretical considerations.

4) At aging temperatures below 250°C, the contribution to resistivity from precipitates was estimated to be as high as 25% of the total measured resistivity. Therefore, ignoring the effect of precipitates on electrical resistivity for simplification purposes, as it is commonly seen in the literature, must be done with great caution.

5) A modified form of Matthiessen’s law, which includes a contribution from precipitates, has been proposed. This allows for the potential to translate electrical resistivity into precipitate volume fraction if coupled with quantitative transmission electron microscopy measurements.

6.1.2. Thermal Spike Experiments

The following conclusions can be drawn after the thermal spike studies:

1) The detrimental effect of natural aging can be minimized or removed by applying short thermal excursions to the alloy either before natural aging or after natural aging.
2) The optimum heat treatment schedule was determined to be of the form shown below:

3) Utilizing thermal spike immediately after solution treatment in order to produce stable microstructure at room temperature, provides a better paint bake response than having the natural aging clusters removed by spike treatment exercised after the natural aging period.

4) The amount of solute available in solution before the paint bake cycle is the main factor deciding the success of a thermal spike treatment. When treating solutionized alloys with thermal spikes, lower spike temperatures are most likely to be successful since they remove less solutes from solution. By contrast, when naturally aged alloys are treated, higher spike temperatures would probably be more useful because they are better able to revert more natural aging clusters.

5) In the final analysis, the effectiveness of a spike treatment is very much dependent on the property and processing requirements for the alloy in the appropriate industrial process.
6.2. Future Work

There are a number of areas for which further studies could be used to complement and/or advance the present investigation.

6.2.1. Suggestions Regarding the Electrical Resistivity Studies

1) It has been discussed that the precipitation process in AA6111 is complex in the sense that it includes various precipitates, which may be present in the microstructure concurrently. In this work, an equation is derived that correlates the total volume fraction of both $Q$ and $\beta''$ phases to the concentration of Mg in solution. This expression has been derived by simply averaging the individual volume fraction equations of $Q$ and $\beta''$. Instead of averaging, it is proposed to follow a more comprehensive approach that includes development of an equation which varies with the ratio of the different precipitates with respect to one another.

2) The equilibrium concentration of the major alloying elements in solution has been calculated in this investigation. It is beneficial to utilize these concentrations towards the construction of a phase diagram for the equilibrium phase $Q$.

3) More resistivity and quantitative transmission electron microscopy experiments are needed to validate the resistivity model that has been developed in the present work. It would be very useful to quantify the relationship between volume fraction/number density of precipitates and the electrical resistivity for a wider range of aging conditions. Specifically, additional atom probe experiments for low temperature aging conditions would be useful to further examine the dependency of precipitate resistivity on precipitate size.
6.2.2. Suggestions Regarding the Thermal Spike Experiments

1) It is useful to monitor the microstructural evolution during the spike treatments by means of TEM studies. Such studies would help to shed light on the underlying mechanisms which affect the size and distribution of the precipitates.

2) In the present research no deformation process has been included in the two investigated schedules. This is in contrast to what is being practiced in industry. It would therefore be useful to have a more realistic simulation of the industrial settings, i.e. it is of value to integrate a deformation step into the schedules. A 2% stretching of the samples would be sufficient.

3) There is still considerable effort required with respect to the modelling of the thermal spike treatment. Due to the short aging times and high heating rates involved in these experiments, a successful model must include a detailed model for the nucleation, growth and dissolution of the precipitates.

4) Finally, a study on the feasibility of using thermal spike treatments under industrial situations is useful. This would include an investigation into the various techniques that can potentially be employed for carrying out a spike and also the economical issues surrounding this matter.
REFERENCES


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APPENDIX A-Spike Conditions

A series of electrical resistivity and yield stress measurements were carried out in order to verify the temperature and time range where an appropriate spike could be found. Resistivity is used as a primary means for evaluating the potential of a temperature for being used as a spike. Once probable temperatures have been identified, yield stress testing is utilized to further filter them. The time range over which the selected temperatures might be of use is then defined from interpretation of yield measurements. Subsequently the details of the procedure are given.

Samples with different heat treatment histories; namely as-quenched, naturally aged for 1 day, and naturally aged for 2 weeks; have been aged at 200°C, 220°C, 250°C, 270°C, and 300°C. The resistivity evolution during these agings is recorded for holding times as short as 30 seconds up to an hour, Figure A.1. The short time, i.e. less than 10 minutes, region of the curves are examined.

Treatment at a potential spike temperature would have to first of all dissolve the natural aging clusters to some extent to revive the solute supersaturation. Secondly, it should not lead to a microstructure consisting of well-developed precipitates which cannot act as nuclei during subsequent artificial aging; it was mentioned in Chapter Two that GP zones (large clusters) provide nucleation sites for $\beta''$ that is desired to form during subsequent aging. So, these two criteria are to be satisfied. It is hard to assess the fulfillment of the first criterion from the resistivity results since a number of concurrent processes are active at this stage which affect resistivity in opposite ways: i) the dissolution of clusters, due to the release of solutes into solution should be reflected by an

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Figure A.1. Evolution of electrical resistivity of as-quenched, 1-day naturally aged, and 2-weeks naturally aged AA6111 during aging at different temperatures. NA stands for natural aging.
increase in resistivity, ii) once the clusters are dissolved, their contribution to resistivity diminishes and hence resistivity should decrease, and iii) new precipitates are forming by consuming the solutes from solution so resistivity should decrease. Nonetheless, having the second criterion in mind, one can realize that temperatures in the 200°C to 250°C range are appropriate candidates. In this temperature range, the resistivity values of the as-quenched alloy for times shorter than 10 minutes are always lower than that of naturally aged alloys. The higher resistivity of the naturally aged alloys is a consequence of the presence of clusters in the microstructure and hence satisfaction of the second criterion. This type of behaviour is not observed for 270°C and 300°C and these temperatures are eliminated.

Now that the temperatures are narrowed down to 200°C, 220°C, and 250°C, the evolution of yield strength during aging at these temperatures is investigated. As before, three thermal histories are considered: as-quenched, 1 day and 2 weeks of natural aging. The results are depicted in Figure A.2. The first criterion discussed above, i.e. dissolution of clusters, can easily be recognized by a reduction in yield stress during early stages of aging. As illustrated in Figure A.2, at 220°C and 250°C the naturally aged alloys show a trough at the beginning of their aging curves. This yield reduction is more pronounced for the 2-week naturally aged conditions and especially that of 250°C. This decrease is vaguely detected for only 2-week naturally aged condition at 200°C. Taking all these observations into account, 220°C and 250°C are considered as the temperatures of choice for spike treatments. 200°C is discarded since it is not high enough of a temperature that can cause substantial dissolution of the clusters.
Figure A.2. Evolution of yield strength of as-quenched, 1-day naturally aged, and 2-weeks naturally aged AA6111 during aging at different temperatures. NA stands for natural aging.

Another useful fact that can be recognized from the 220°C and 250°C aging curves is that all dissolution troughs occur in less than 6 minutes (0.1 hr) of heat treatment. A proper dwell time for the spikes has to fall within this time limit. Aging for longer times results in significant strengthening of the alloy, reflecting the formation of stable precipitates. Consequently, 30 seconds, 1 minute, and 5 minutes are chosen for spike dwell time.
APPENDIX B-Thermal Spike Resistivity

The microstructure evolution during thermal spike treatments (Schedules A and B) was monitored indirectly by electrical resistivity measurements. These results are shown in Figures A.3 and A.4.

![Graph showing resistivity measurement results for 220°C and 250°C spikes.](image)

**Figure A.3.** Evolution of electrical resistivity during thermal spike treatment, Schedule A.
Figure A.4. Evolution of electrical resistivity during thermal spike treatment, Schedule B.