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**Impedance spectroscopy response of aluminum-copper-silicon
alloys**

Griffin, Alfred Joseph, Jr., Ph.D.

Rice University, 1991

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RICE UNIVERSITY

IMPEDANCE SPECTROSCOPY RESPONSE OF ALUMINUM-COPPER-SILICON
ALLOYS

by

ALFRED JOSEPH GRIFFIN, JR.

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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May, 1991

ABSTRACT

Impedance Spectroscopy Response of Aluminum-Copper-Silicon Alloys

by

Alfred J. Griffin, Jr.

The effect of increased Cu and Si additions and heat treatment on the polarization resistance, oxide-layer/double-layer capacitance, open circuit potential and breakdown potential of Al-Cu-Si alloys was evaluated. Electrochemical impedance spectroscopy and DC polarization techniques were combined with mechanical property evaluations to determine the relationship between the microstructure of Al-Cu-Si alloys and the ability of their oxide layer to provide protection against corrosion in an aqueous 5% NH_4Cl solution. Alloys were investigated in both the solution-treated and artificially aged conditions. The solution-treatment procedure involved heating the alloys to 550°C for 30 minutes and subsequently water-quenching. Artificial aging was carried out at 250°C. Increased aging times of 1, 2, 8 and 32 hours at 250°C were employed on Al-Cu(2%), Al-Si(2%) and Al-Cu(2%)-Si(2%) alloys in order to correlate the observed electrochemical behavior with the precipitation strengthening reactions which occur during age-hardening. These precipitation reactions govern the resultant microstructure and determine the mechanical behavior, electrochemical behavior and type of corrosion attack observed in Al-Cu-Si alloys.

In general, an increase in the susceptibility to pitting corrosion was correlated to a decrease in the protective oxide layer thickness brought about as a result of increased Cu and Si additions in solution-treated alloys and the precipitation of Guinier-Preston zones in age-hardened alloys. Cu and Si atoms at the metal/oxide interface inhibit the diffusion

of Al^{+3} ions to the oxide/electrolyte interface thereby limiting the oxide-layer thickness. Increased aging times, leading to the formation of Guinier-Preston zones and a concomitant age-hardening peak, also decrease the total number of Al^{+3} ions available for passivation and thereby decrease the oxide-layer thickness. Consequently, the oxide-layer/double-layer capacitance and the polarization resistance of the alloys are correlated to changes in the oxide-layer thickness and the loss in continuity of the oxide-layer with overaging. In addition, the open-circuit and breakdown potentials and the type of corrosion attack observed during anodic DC polarization scans was related to the type of alloying element and their distribution.

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time and it seems that my path has taken me farther and farther away from all of you, you have never left my thoughts.

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INTRODUCTION

Al-Cu-Si alloys are often used as thin-film interconnects in microelectronic devices, largely because of the improved short-term and long-term reliability that can be achieved through the combination of these three elements. Al is frequently chosen as the base metal because it lends itself well to sputtering, offers good adherence to Si substrates, it responds well to photolithographic patterning and etching techniques and can offer both low resistivity and good corrosion resistance. However, unalloyed Al interconnects are rarely used in actual device applications because of their susceptibility to junction spiking at the Al/Si contact areas and electromigration damage.¹ The addition of both Si and Cu to Al interconnects greatly improves their resistance to both of these aforementioned metallization failure mechanisms.

Junction spiking is a term which describes the diffusion of Al into the Si substrate at elevated temperature excursions experienced during processing. The reason Al and Si interdiffuse into one another is attributed to the increased solubility of Si in Al at elevated temperatures. As a result, the Al grows into the Si substrate at the small window openings that provide contact between signal lines and the semiconductor, penetrating both the doped and undoped regions of the Si substrate. An alloy of approximately Al-Si(1%) eliminates the problem by providing the maximum amount of Si soluble in Al at the maximum processing temperature expected (550°C).²

Electromigration is the diffusion of metal ions along the grain boundaries of thin-film metallic conductors stimulated by large current densities generated during actual device operation.^{3,4} If the rate at which electromigration takes place is not

significantly reduced, failure of the microelectronic device either through void formation or hillock formation is likely. Void formation occurs as a result of vacancy coalescence and can lead to opens on the metal interconnects. Hillocks are regions of accumulation of metal ions which can grow large enough to short-out adjacent signal lines which are only microns apart. Cu has been shown to improve resistance to the electromigration damage of Al just described by reducing the diffusivity of Al along grain boundaries.^{5,6} Because precipitation of Cu atoms at or near the grain boundaries takes place at a much higher rate than within the grain interiors at elevated temperatures, such as those seen during device processing, the Cu atoms provide a much higher activation barrier to Al self-diffusion along grain boundaries thereby minimizing device failure via electromigration mechanisms.

As inferred in the previous paragraphs, high reliability thin-film interconnects, from the standpoint of metal adherence, electromigration resistance and junction spiking, must contain both Cu and Si. However, the reliability of these interconnects also depends upon their ability to withstand the stresses which are encountered during the production and operation of integrated circuits themselves. These stresses include the intrinsic stress present as a result of the deposition of the Al film onto the Si substrate, and the extrinsic thermal stress produced during both the subsequent heat treatment of the metallized wafer and during power cycling in actual device operation.⁷ Fortunately, Al-Cu and Al-Cu-Si alloys are age-hardenable, so the strength of interconnects composed of these alloys can be tailored to provide resistance to failure due to mechanical stresses.

Although Cu and Si appear to solve many problems normally encountered in thin-film metallizations used as microelectronic device interconnects, Cu additions are known to increase the susceptibility of these thin-films to corrosion.^{8,9} During photolithography and patterning of the metallizations, wet-chemical and reactive-ion etching is employed.¹⁰ Wet-chemical etchants contain HF, while reactive-ion etchants

employ gases or 'plasmas' containing either chlorine or fluorine.^{11,12} The presence of halogen ions such as chlorine or fluorine exposes the Al-base metallizations to corrosion both during the etching process and in long-term device operation.^{13,14} The actual mechanism by which the Cl or F ions affect corrosion of Al and its alloys is not fully understood, but has been attributed often to the interaction between the ions and the metal/protective oxide layer interface.^{15,16,17} Consequently, since Cu additions may increase the number of mechanical and/or electronic defect sites in the oxide layer, Al-Cu thin films or bulk alloys will be more susceptible to corrosion due to an increased ability for chloride ions to interact with the metal/oxide interface.¹⁸ Therefore, if Al-Cu-Si alloys are to be used as thin-film metallizations, corrosion resistance should also be included as a prime reliability concern.

Mayumi, Hata, Hujiwara and Ueda have studied the effect of reactive ion etching and post-etching treatments on the susceptibility of Al-Cu(0.5%)-Si(1.0) thin-films to corrosion in an effort to improve short-term and long-term reliability of microelectronic devices.¹⁹ In doing so, several observations were made which are relevant to the present work. In particular, elevated temperature and humidity testing led to open-circuit failures due to corrosion in Al-Cu-Si films much more rapidly than in Al-Si films treated to the same reactive ion etching procedure. Their observation supports the idea that Cu and Cu precipitates increase the susceptibility to corrosion by forming galvanic local-action cells between the cathodic Cu precipitates and Cu-depleted zones. Aluminum films which contained Si alone did not appear to be as susceptible to pitting as the films containing Cu. In addition, removal of residual chlorine with deionized water rinses and oxygen-rich chlorofluorocarbon plasmas significantly reduced the amount of corrosion in Al-Cu-Si films, indicating that the presence of Cl ions greatly enhanced corrosion susceptibility.

Similar results were realized by Lee and Eldridge.²⁰ In their study, Al and Al-Cu thin-film metallizations showed an increased susceptibility to corrosion during accelerated corrosion testing in a 25°C/70%RH (relative humidity) environment. These metallizations were etched with a reactive ion plasma (carbon tetrachloride/argon). Significant weight gains were measured with films containing 2 and 4 weight percent Cu, while Al and Al-Cu(1%) films reveal little, if any weight gain. By taking the weight gain to be proportional to the corrosion rate, they concluded that Cu contents beyond 1 weight percent and the presence of residual chloride ions lead to increased corrosion susceptibility. In addition, interpretation of Auger electron spectroscopy results indicate that the oxide layer may be "thin and/or discontinuous" as a result of the etching process.²¹ Consequently, increased corrosion susceptibility is attributed to the formation of an oxide which is not protective, the presence of chloride ions which accelerate oxide breakdown, and the formation of Cu-rich zones or precipitates. Cu precipitates, as discussed earlier, increase corrosion susceptibility by increasing the number of cathodic sites and, correspondingly, the number of galvanic cells between the precipitates and Cu-depleted zones. By exposing the metallizations to a thermal oxidizing treatment, the resistance to corrosion was improved significantly with the formation of a protective oxide layer.

Scully and his co-workers investigated the effect of wet chemical etching on Al-Cu(0.5%) metallizations in HF solutions using both DC and AC electrochemical techniques.²² Fluorine ion residuals, just as has been shown for chloride ion residuals, increase corrosion susceptibility by causing localized breakdown of the oxide layer.²³ The presence of Cu and CuAl₂ precipitates was shown, through Auger electron spectroscopy and impedance spectroscopy techniques, to decrease the thickness of the oxide layer, increasing both the capacitance and the susceptibility to corrosion. Clearly, the interaction between halide ions and the oxide layer increases susceptibility to

localized oxide breakdown, while the presence of Cu and CuAl_2 precipitates decreases the thickness of the oxide layer. In addition, Cu and CuAl_2 precipitates act as efficient cathodes.

Correlations between Cu content, heat treatment, the precipitation of Cu in Al, age-hardening response and the corresponding interdependence between microstructure and corrosion attack in bulk alloys were made by Muller and Galvele²⁴ and Galvele and de De Micheli.²⁵ Solution-treated aluminum-copper alloys containing 1 to 5 weight percent Cu were studied in a 1M NaCl solution. In addition, the age-hardening response of an Al-Cu(3.5%) alloy as a function of aging time was evaluated. Breakdown potentials became more positive with increasing Cu content. No change in the oxide breakdown potential was observed with aging time until the formation of the equilibrium CuAl_2 phase, at which point the breakdown potential became significantly negative.²⁶ Copper enrichment at the grain boundaries during aging led to the formation of a Cu-depleted region adjacent to the grain boundaries. Anodic polarization of the age-hardened alloys consequently led to intergranular corrosion at the galvanic cells formed between the Cu-enriched grain boundaries and the Cu-depleted zones.²⁷ Overaging led to general pitting corrosion similar to that exhibited by Al and the solution-treated Al-Cu alloys.

The thickness of oxide layers on Al and their effect on oxide-layer capacitance had been investigated around the early 1900's during the development of electrolytic capacitors.²⁸ Aluminum oxide is an insulator and has a dielectric constant of approximately 7, allowing the oxide to be used as a capacitor that can sustain high electric fields without any power losses.²⁹ As a result, Al foils were wound into coils and polarized so as to form an oxide layer on their surface. The combination of a large surface area and a thin, electrolytically formed oxide layer led to capacitance values as large as 2000 μF in packages as small as 10 in³, a significant accomplishment during the

1930's.³⁰ Several theories were put forth in order to explain the unusually high capacitances. These included either the presence of an adsorbed "active" gas film between the oxide and the metal or between an aluminum-hydroxide layer and the metal, or the formation of an oxide layer which contains a solid, inner "active" layer film.³¹ In either case, it is this active film that governs the capacitive effect observed in Al-anode electrolytic capacitors.

Cathodic impurities, such as Cu, were detrimental to the reliability and functionality of electrolytic capacitors, similar to the loss in reliability of thin-film metallizations due to corrosion. Specifically, pitting along the surface of the Al base metal and deposition of corrosion products led to DC current leakage and failure of the rectifying properties of the oxide.³² Halogen ion contaminants in the electrolyte of the electrolytic capacitor, even in minute quantities, also increased the leakage current of the oxide-layer and led to the loss of the rectifying properties of these condensers.^{33,34} Moreover, electrolytic formation of the oxide layer was inhibited or slowed down when impurities such as Cu were present so that the time to form an oxide layer was inhibited or significantly reduced. It was for this reason that the best electrolytic condensers were composed of 99.99% Al.³⁵ Therefore, it should become clear that the best corrosion resistance is obtained by using high-purity Al.

Unalloyed aluminum exhibits good corrosion resistance in most environments because of the formation of a thin aluminum oxide layer on its surface. This oxide layer protects the aluminum base metal underneath by providing both a barrier to further oxidation and a means of isolation of the metal from the surrounding environment. Even though Al is normally a reactive metal with a highly negative electrode potential, the formation of the aluminum oxide layer greatly increases the corrosion resistance of Al. Formation of the aluminum oxide, or Al_2O_3 , is favored because of the strong electrostatic attraction between the electropositive Al^{3+} and the electronegative O^{2-} . As a consequence

of this strong interaction, the Al_2O_3 is an insulator, that is, it takes much energy to once again ionize either the aluminum or the oxygen.

The process of Al_2O_3 formation is commonly known as passivation, that is, the metal is made more passive or is protected. Once the initial oxide-layer is formed, further growth can only occur if Al^{3+} ions diffuse through the oxide layer so that they can react at the oxide-layer/environment interface and increase oxide-layer thickness. If aluminum oxide was not tenacious, or if aluminum oxide would not form at all, Al base metal would not be protected and would uniformly dissolve.³⁶ In reality, however, Al is susceptible to localized corrosion or pitting, especially in aqueous environments containing chlorine and oxygen.

Pitting is caused by the formation of local-action cells between cathodic impurities, alloying elements, intermetallic compounds, grain boundaries or differential aeration cells present on the metal surface. As a consequence, alloying elements such as Cu, Mg, Zn, Mn, Fe or Si, which are often added in order to increase the strength of Al, can lead to an increased susceptibility to corrosion. If the alloy is age-hardenable, precipitation of cathodic elements or compounds both within grains and at grain boundaries can lead to the formation of solute-depleted zones in areas adjacent to the precipitates and in areas adjacent to the grain boundaries, forming galvanic local action cells. Since protection of Al or Al alloys depends on the formation of an oxide layer, it should become clear that precipitates, second-phase particles, inclusions or lattice defects can interfere with oxide formation or the ability of the oxide-layer to protect the underlying metal or alloy, especially if the precipitates, second-phase particles, etc., are cathodic with respect to the matrix. Other galvanic local action cells can be formed wherever a defect in the oxide layer exists or wherever chloride ions interact with the oxide-layer. As stated earlier, the actual mechanism by which the chloride ions cause a breakdown in passivity is not fully understood, but a review of the various theories is given by Szklarska-Smialowska.³⁷

As we have seen, from a corrosion standpoint, unalloyed Al would be an excellent choice for use as a thin-film metallization. However, unalloyed Al has little resistance to electromigration and, in addition, leads to the formation of junction spikes at Al/Si contact windows in microelectronic devices. Consequently, Cu and Si additions, which increase electromigration resistance and eliminate junction spiking, respectively, are critical requirements in the manufacture of reliable thin-film interconnects. Chloride residuals from patterning and etching processes have an adverse effect on the corrosion resistance of these Al-Cu-Si alloys, thereby introducing another reliability problem. It is precisely this interaction which is being considered in the present work.

Although corrosion studies on bulk and thin-film Al, Al-Cu and Al-Cu-Si alloys have been reported, as has been briefly discussed earlier, comprehensive information on the breakdown potential and impedance-spectroscopy response of Al-Cu-Si alloys is not available. The present work is directed towards a thorough evaluation of the effect of Cu and Si additions, along with heat treatment, on the corrosion resistance of bulk Al-Cu-Si alloys within the concentration range of particular interest to microelectronic device manufacture. Assessments are performed in a chloride-containing environment using both AC electrochemical impedance spectroscopy and DC polarization techniques, and the results are discussed in terms of the ability of an oxide layer to form and provide adequate protection against corrosion even when the composition and heat treatment are varied. As discussed earlier, Al-Cu-Si alloys are age-hardenable so that variations in composition and heat treatment are used to correlate the electrochemical behavior observed with the microstructural changes that occur during age-hardening. Therefore, these evaluations will ultimately determine the effect which thermal history has on the development of the microstructure and, in turn, how the resultant microstructure affects the mechanical properties and corrosion resistance of the alloys. In doing so, it is believed that this work will provide extensive information on how to employ both AC

impedance-spectroscopy and DC polarization experiments successfully to the study of corrosion resistance of Al-Cu-Si alloys and evaluation of their oxide-layer properties. Specifically, the polarization resistance, oxide-layer/double-layer capacitance and oxide-breakdown potentials are correlated here to the microstructural changes that occur in Al-Cu-Si alloys during age-hardening.

CHAPTER 1

EXPERIMENTAL PROCEDURE - MECHANICAL BEHAVIOR

Al-Cu alloys are often used as structural materials because of their ability to show an increase in strength with the appropriate heat treatment. The increase in strength is caused by the controlled distribution of fine, hard precipitates within the metal matrix which inhibit the motion of dislocations. This is a process known as precipitation strengthening and it had first been observed by Alfred Wilm in 1911.³⁸ In Al-Cu alloys, strengthening occurs via the segregation of Cu atoms into zones which have the same crystal structure as the metal matrix and are therefore considered to be coherent precipitates. These zones are known as Guinier-Preston zones, named after the men who first determined their existence using x-ray diffraction techniques. Because of the size difference between the solute and solvent atoms, the region within the coherent precipitates is highly distorted, creating a large strain field which acts as a barrier to dislocation motion. If the number of precipitates is large and the distance between each coherent zone is minimized, then the strength of a precipitation-hardened alloy can be maximized. Si can also cause precipitation strengthening, but the loss of coherency with the matrix occurs rapidly so that the age-hardening response is limited.³⁹ Si has also been shown to increase the age-hardening response by increasing the number of dislocation loops in Al-Cu-Si alloys.⁴⁰ Therefore, by studying the precipitation reactions that can occur in Al-Cu-Si alloys during heat treatment and how they affect the microstructure and the resultant change in mechanical properties, then we may be able to consider just how the microstructural changes will affect the corrosion resistance of these alloys.

Consider the partial equilibrium phase diagrams shown in Figure 1. These represent the Al-rich end of the Al-Cu and Al-Si binary phase diagrams. If an alloy containing 1 weight percent solute is heated to a temperature of 550°C, then the alloy is in the single phase α -region. If the alloy is given sufficient time to reach equilibrium so that the solute atoms are completely dissolved in the Al matrix and the alloy is subsequently water-quenched, the alloy will not have sufficient time to form the equilibrium θ -phase. Consequently, a supersaturated solid solution of solute atoms in Al is formed. If we heat the alloy to some intermediate temperature, then the controlled precipitation of solute atoms in Al can take place. This precipitation reaction leading to the eventual formation of the equilibrium θ -phase takes place through the formation of solute-rich zones which are coherent with the matrix, the formation of solute-rich zones which are not coherent with the matrix and the formation of the incoherent equilibrium θ -phase. If we follow the changes in hardness arising from the changes in the microstructure at a given aging temperature, we can develop an age-hardening curve which plots the hardness as a function of aging time at that temperature. These changes in microstructure can be used in explaining the type of corrosion behavior that we observe during our electrochemical experiments. In particular, variations in both Cu and Si contents, as well as thermal treatment, can be used to evaluate their combined effect on the microstructure and the ability of Al, Al-Cu and Al-Cu-Si alloys to resist corrosion.

Sample Preparation:

Samples for the mechanical behavior evaluations were prepared from cast ingots provided by ALCOA Research Laboratories. The composition range of interest was 0 to 2% Cu and 0 to 2% Si, both being covered in 0.5% increments. Nominal and actual analytical compositions for each ingot are listed in Table 1. Samples for Brinell hardness measurements were machined from each ingot 6 cm long, 6 cm wide and 1.8 cm thick.

Figure 1: Al-rich end of equilibrium phase diagrams for (a) Al-Cu^a and (b) Al-Si^b.

^a Reprinted from Murray, *International Metals Review*, **30**, 5, (1984), p. 218.

^b Reprinted from Murray and McAllister, *Bulletin of Alloy Phase Diagrams*, **5**, 1 (1984), p. 75.

TABLE 1: ANALYTICAL COMPOSITION OF Al-Cu-Si ALLOYS

<u>Element</u>	<u>Al</u>	<u>Al-Cu(0.5)</u>	<u>Al-Cu(1.0)</u>	<u>Al-Cu(1.5)</u>	<u>Al-Cu(2.0)</u>
Cu	0.0004	0.47	1.01	1.46	2.02
Si	0.0005	0.00	0.00	0.00	0.00
<u>Al-Si(0.5) Al-Cu(0.5)-Si(0.5) Al-Cu(1.0)-Si(0.5) Al-Cu(1.5)-Si(0.5) Al-Cu(2.0)-Si(0.5)</u>					
Cu	0.017	0.48	0.96	1.46	1.93
Si	0.53	0.53	0.51	0.52	0.51
<u>Al-Si(1.0) Al-Cu(0.5)-Si(1.0) Al-Cu(1.0)-Si(1.0) Al-Cu(1.5)-Si(1.0) Al-Cu(2.0)-Si(1.0)</u>					
Cu	0.008	0.47	0.97	1.48	1.98
Si	1.00	1.00	1.02	1.02	1.03
<u>Al-Si(1.5) Al-Cu(0.5)-Si(1.5) Al-Cu(1.0)-Si(1.5) Al-Cu(1.5)-Si(1.5) Al-Cu(2.0)-Si(1.5)</u>					
Cu	0.005	0.50	0.99	1.52	2.04
Si	1.52	1.57	1.53	1.56	1.57
<u>Al-Si(2.0) Al-Cu(0.5)-Si(2.0) Al-Cu(1.0)-Si(2.0) Al-Cu(1.5)-Si(2.0) Al-Cu(2.0)-Si(2.0)</u>					
Cu	0.00	0.53	1.02	1.51	1.95
Si	2.00	2.02	1.93	1.95	1.97

The solution-treatment temperature was 550°C and the samples were to be held at that temperature for 30 minutes. In order to monitor the time it took for the internal temperature of the samples to reach the solution treatment temperature, a small hole was drilled into a test sample and a thermocouple was placed within. It took approximately 30 minutes for the internal temperature to reach the solution-treatment temperature. Consequently, samples were kept in the furnace for approximately 60 minutes in order for the entire sample block to be considered as being at the solution-treatment temperature for 30 minutes. Each sample was subsequently quenched in a vigorously stirred solution of water which contained a small amount of NaCl in order to accelerate the cooling rate.

The effect of aging treatment on the precipitation of Cu and Si in solution-treated alloys was studied at a temperature of 250°C and an aging time of 30 minutes. In addition, the effect of increased aging time (1, 2, 8 and 32 hours) at 250°C was also investigated for all the Al-Cu, Al-Cu-Si(1%) and Al-Cu-Si(2%) alloys. Each aging time was increased by 40 minutes in order to account for the apparent delay in the equilibration of the entire sample at the aging temperature of 250°C.

Brinell Hardness Measurements:

A 500 kg load and a 10 mm diameter ball indenter were used to make the hardness measurements. Measurements were taken on one side of the samples, which had first been solution-treated. Each sample was then aged and tested on the opposite side. Indentations were spaced no less than three times the diameter of the indentation apart or no closer than three times the diameter of the indentation away from the edge of the sample, as recommended in Metals Handbook, Volume 8.⁴¹ The thickness of the sample was 2 times greater than the minimum recommended. In order to study the effect of aging time, indentations had to be machined off and the sample solution treated prior to further aging. Four indentations were made per sample and the average diameter of the indentations was recorded. Repeatability was excellent and the standard deviations ranged between 0 and 0.13.

CHAPTER 2

RESULTS AND DISCUSSION - MECHANICAL PROPERTIES

Effect of Cu and Si and Short-Term Aging on Solution Treated Alloys:

The effect of Cu and Si additions on the Brinell Hardness Number (BHN) of solution-treated alloys is shown in Figure 2. A considerably large increase in hardness with Cu content was observed as a result of substitutional solid solution strengthening in each of the alloys studied. Silicon had a similar effect on the hardness, but only up to approximately 1% Si. Additions of Si beyond 1% increase the hardness only slightly as a second phase of Si (β -phase) is formed within a solid-solution of Cu in Al (α -phase). This can be discussed in terms of the Al-Cu, Al-Si and Al-Cu-Si phase diagrams. The maximum amount of Cu and Si soluble in Al in their corresponding binary systems at 550°C is 5.55 weight percent and 1.30 weight percent, respectively.⁴² However, in the ternary Al-Cu-Si system, the presence of Cu and Si slightly limits the amount of each soluble in Al. At the solution-treatment temperature of 550°C, approximately 1.1 weight percent Si and 4.9 weight percent Cu are soluble in Al.⁴³ Consequently, solution-treatment at 550°C of the Al-Si and Al-Cu-Si alloys containing 1.5 and 2.0% Si did not solubilize all of the Si present so that a two-phase microstructure of α and β was introduced. Increased amounts of Si beyond 1 weight percent Si will thus only slightly increase the strength and hardness of the solution-treated alloys.

Brinell hardness measurements were also made on the solution-treated alloys artificially aged at 250°C for 30 minutes. As presented in Figure 3, increased Cu and Si additions also increase the hardness of artificially aged Al-Cu, Al-Si and Al-Cu-Si alloys. However, almost all of the artificially aged alloys did not exhibit a significant increase in

Figure 2: Effect of Cu and Si on hardness of solution-treated alloys.

Figure 3: Effect of Cu and Si on hardness of artificially aged alloys.

hardness over their solution-treated values. Only the alloys containing 1.5 weight percent or greater of both Cu and Si showed a significant increase in hardness upon aging for 30 minutes. Alloys containing 0.5 weight percent or less of Cu demonstrate a slight decrease in hardness upon aging, especially in the alloys containing 2% Si. Each of these observations owe their explanation to the interaction between the amount of Cu and Si present and the aging conditions used.

Considering the aging conditions, that is, an aging temperature of 250°C and an aging time of 30 minutes, the Cu contents may be too low to cause a significant increase in hardness in Al-Cu alloys. Since the formation of Guinier-Preston, or GP zones, requires diffusion only over small distances, one would expect a rapid increase in hardness given sufficient temperature and time. On the other hand, if the concentration of Cu in Al is low and not evenly distributed, then a much longer aging time or higher aging temperature may be required to form a large number of coherent, metastable precipitates. In addition, since Si has been shown to increase the age-hardening response of Al-Cu-Si alloys,⁴⁴ short-term aging of alloys containing Si would be expected to show some type of increase in age-hardening. As only the alloys containing either 1.5 weight percent or greater of Cu and Si in Al demonstrated a significant increase in hardness, an aging time of 30 minutes at 250°C can only cause an increase in hardness in Al-Cu-Si alloys when enough Cu is available to form metastable precipitates of Cu in Al and enough Si is present to cause an increase in the number of dislocation loops in the material and increase the age-hardening response.⁴⁵ Each of these conditions should contribute to a rapid rise in the age-hardening response after only 30 minutes at 250°C because as the number of dislocations increases, then their interaction with the precipitates also increases, thereby strengthening the material. These observations were verified by studying the effect of Cu content, Si content and aging time on the age-hardening response of Al-Cu-Si alloys.

Effect of Cu Content and Aging Time:

Figure 4 describes the effect of Cu content and aging time on the age-hardening response of Al-Cu alloys. Both the Al-Cu(0.5%) and Al-Cu(1.0%) alloys show no aging response whatsoever. In contrast, the Al-Cu(1.5%) and Al-Cu(2%) alloys begin to show an aging response after an aging time of 1 hour. Peak hardness is achieved in 2 hours for the 2% Cu alloy and peak hardness occurred between 8 and 32 hours in the Al-Cu(1.5%) alloy. During the initial rise in hardness with aging time, the Cu atoms which were dissolved in the Al matrix begin to diffuse and segregate within the matrix. Segregation of Cu atoms occurs within the crystal lattice of the parent Al-matrix, that is, precipitation of Cu atoms occurs such that the Cu-rich zones are coherent with the matrix. These are the Guinier-Preston zones, and peak hardness corresponds to the maximum number of finely dispersed Guinier-Preston zones. Guinier-Preston zones are also known as metastable, or θ' -phase, coherent precipitates. However, particular attention should be placed on the rate at which these alloys reach peak hardness. The increase in hardness is accelerated with an increase in Cu content simply because there is a larger distribution of Cu atoms in the Al matrix which can now form enough metastable, or θ' -phase, precipitates required to impede the motion of dislocations.

Once the hardness has peaked, a decrease in hardness is observed as the aging time increases corresponding to the formation of the equilibrium θ -phase, or CuAl_2 . The θ -phase is incoherent with the matrix and continues to grow in size as the aging time is increased. The driving force for this reaction is the formation of the θ -phase itself, which is the phase that is at equilibrium at room temperature. A loss in hardness is associated with the formation of this phase because as diffusion continues, these precipitates grow in size and are fewer in number so that the interaction between them and the dislocations is now decreased. In addition, since diffusion at or near the grain boundaries occurs much

Figure 4: Effect of Cu content and aging time on hardness of Al-Cu alloys.

more rapidly than within the grain interior, overaging is also accelerated at the grain boundaries.

Effect of Si on the Age-Hardening Response:

Si additions beyond 1 weight percent were found to accelerate the age-hardening response of Al-Cu alloys. In Figures 5 and 6, the age-hardening response as a function of Cu content and aging time are shown for Al-Cu-Si(1%) and Al-Cu-Si(2%) alloys, respectively. As evidenced by the age-hardening response of the Al-Si(2%), Al-Cu(0.5%)-Si(2%) and Al-Cu(1%)-Si(2%) alloys shown in Figure 6, Si alone does not appear to contribute to any significant precipitation hardening since Al-Si(2%) cannot be completely solution-treated. However, there is a gradual decrease in the hardness of these alloys over the entire aging period, suggesting a rapid overaging process. This overaging process is also attributed to the acceleration of the age-hardening response and refining of the precipitates due to the presence of Si.⁴⁶ For the Al-Cu(2%)-Si(2%) alloy, the increased Cu and Si content shift peak hardness to the 1 hour aging time and help reveal both a pronounced peak and a rapid overaging curve, as expected. Similar behavior is exhibited by the Al-Cu(2%)-Si(1%) alloy, where a pronounced age-hardening peak occurs at 2 hours, and a rapid decrease in hardening with aging time corresponding to overaging also occurs. Comparison of Figures 5 and 6 lead to the conclusion that Si indeed accelerates the age-hardening response and that Cu contents of 1.5% and 2% are required in order to see an aging response at all.

Figure 5: Effect of Cu content on hardness of Al-Cu-Si(1.0%) alloys.

Figure 6: Effect of Cu content on hardness of Al-Cu-Si(2.0%) alloys.

CHAPTER 3

EXPERIMENTAL PROCEDURE - ELECTROCHEMICAL BEHAVIOR

Electrochemical evaluations combined DC polarization and AC impedance spectroscopy techniques in an effort to correlate corrosion susceptibility to a decrease in oxide-layer thickness and/or increase in oxide-layer defects as a function of composition and heat treatment. A brief description of the DC polarization and AC impedance spectroscopy techniques employed in these evaluations follows in order to familiarize the reader with the techniques and data interpretation. Detailed descriptions of DC polarization experiments can be found in Crow,⁴⁷ Fontana,⁴⁸ and Barnartt.⁴⁹ Introductory discussions on the subject of AC impedance spectroscopy response are given by Growcock,⁵⁰ Silverman,⁵¹ Dean,⁵² Hladky et al.,⁵³ Mansfeld⁵⁴ and Fontana.⁵⁵

When a metal is immersed into a solution, and the potential of the metal is measured against a suitable reference electrode with respect to time, an open circuit potential will be achieved corresponding to the equilibrium condition between the metal, the electrolyte and the governing cathodic reaction. If the current between the metal and an appropriate inert electrode is measured, the net current will be zero, also corresponding to the equilibrium condition. The open circuit potential measured is known as the corrosion potential, E_{corr} .

However, if a DC potential E above or below the corrosion potential is applied, a net current will be observed corresponding to oxidation of the metal at the anode or the reduction reaction occurring at the cathode, depending on the polarization direction. The difference between the applied potential, E , and the corrosion potential, E_{corr} , is known as the overpotential, η . An overpotential of zero corresponds to the equilibrium condition,

that is, no potential is applied. If an overpotential which is more positive than the corrosion potential is applied to the sample, the sample is said to have been anodically polarized and a net anodic current is induced. Correspondingly, if the sample is cathodically polarized, or made more negative, a net cathodic current is generated. An idealized plot of the net current density as a function of overpotential for a non-passivating metal is shown in Figure 7.

DC polarization experiments on a passivating metal such as Al, on the other hand, reveal the region where passivity occurs. Linear and semi-logarithmic polarization curves of such a metal resemble those shown in Figure 8. On the linear plot of the corrosion current versus electrode potential, the passive region is given by a straight line; that is, very little, if any, corrosion current is detected. On the semi-logarithmic plot, Figure 8b, the passive region is also given by a straight line, and the transition from a net anodic current to a net cathodic current, which occurs at the corrosion potential, can easily be located. At this point, the slope of the $\text{LOG}(|I|)$ versus E plot tends toward infinity. In the absence of any perturbations of the electrode potential, the equilibrium potential would correspond to the minimum corrosion current possible. As discussed above, if an external perturbation of the electrode potential is used to make the electrode either more negative (cathodic) or more positive (anodic) with respect to the equilibrium potential, a net cathodic or anodic current will be realized. In a passive material, a significant rise in the anodic current density should only occur once the oxide layer breaks down. This occurs at what is termed the 'breakdown potential,' E_b . This breakdown potential is often extrapolated from the linear polarization curve, as shown in Figure 8a.

Although the breakdown potential may give an indication of how much work it takes to cause oxide-layer breakdown and whether or not oxide breakdown is made more

Figure 7: Current density as a function of overpotential for a non-passivating metal.

Figure 8: (a) Linear and (b) semi-logarithmic polarization curves for a passivating metal.

spontaneous, it does not give us an indication of the resistance to charge transfer or the oxide-layer thickness. AC impedance spectroscopy, however, does.

AC impedance spectroscopy is a technique which can be used to determine polarization resistance, or charge-transfer resistance, and oxide-layer/double-layer capacitance. It involves the basic assumption that if the current varies linearly with electrode potential at or near the equilibrium open circuit potential, as is the case for Al, then a small sinusoidal voltage (approximately 10 mV) can be applied about the equilibrium open circuit potential, and the corresponding alternating current measured. Applying Ohm's law, the impedance is given by

$$Z = \frac{V_{ac}}{I_{ac}} = \frac{V_{peak} \sin(\omega t)}{I_{peak} \sin(\omega t + \Phi)} ,$$

where V_{peak} and I_{peak} are the applied peak voltage and measured peak current, respectively, ω is the angular frequency of the signal, t is the time and Φ the phase angle between the applied AC voltage signal and the measured current.⁵⁶

An impedance spectrum of a resistor in series with a parallel combination of a capacitor and a resistor is shown in Figure 9, along with the representative electrical circuit. If it is assumed that a slowly corroding electrode like Al can be modeled by such an electrical circuit, then values for the series resistance (R_s), the polarization resistance (R_p) and the oxide-layer/double-layer capacitance (C) can be determined.

The capacitive reactance of the circuit shown in Figure 9 is given by

$$X_C = \frac{1}{2\pi f C} ,$$

where X_C is in ohm-cm², f is the frequency in Hz and C is the capacitance in Farads/cm². At high frequencies, X_C approaches 0 so that the impedance measured is equal to the solution resistance. As f goes to 0, X_C approaches infinity so that the total resistance, R_T is equal to the solution resistance plus the polarization resistance. R_s and R_T

Figure 9: Impedance spectrum for a resistor in series with a parallel combination of a capacitor and a resistor.

are clearly indicated in Figure 9. Since R_s is much smaller than R_T , R_T is approximately equal to R_p .

The polarization resistance represents the charge transfer resistance, or corrosion resistance. Consequently, the bigger the polarization resistance or resistance to charge transfer, the higher the corrosion resistance. The relationship between the corrosion current and R_p is derived in Appendix A. By viewing the oxide-layer as the primary resistor under DC conditions, the higher the corrosion resistance, the thicker the oxide-layer.

At intermediate frequencies, the capacitive reactance of the oxide-layer/double-layer provides for a large change in the phase angle between the voltage signal in and the current signal out, allowing us with a means of determining the oxide-layer/double-layer capacitance. When the phase shift between the voltage in and the current out is at a maximum, the capacitance is determined by

$$C = \frac{1}{2\pi f_{\max \phi} R_p} ,$$

where $f_{\max \phi}$ is the frequency at which the phase shift is at a maximum. It should be emphasized that the oxide layer is quite different than that of the double-layer, as the latter is due to the buildup of ionic species in the electrolyte at the metal-electrolyte interface. Consequently, the two are differentiated where appropriate. However, if most of the capacitance is assumed to be due to the oxide layer, then the thickness of the oxide can be determined, provided the dielectric constant of the oxide layer is known, by the following equation:

$$t_{\text{oxide}} = \frac{\kappa \epsilon_0}{C_{\text{oxide}}} .^{57}$$

Here, κ represents the dielectric constant of the oxide layer and ϵ_0 the permittivity of free space, $8.85(10)^{-15}$ Farads/cm.

As the reader may verify, AC impedance spectroscopy offers a substantial amount of information regarding the ability of the oxide layer to provide enough corrosion resistance in terms of its thickness and charge transfer resistance. By correlating the observed electrochemical behavior to the results obtained in Chapter 2, the corrosion resistance can be determined as a function of Cu and Si content and heat treatment. Additionally, the electrochemical behavior and type of corrosion attack can be linked to the microstructural changes that occur during age-hardening. These changes are reflected in the impedance spectroscopy response and DC polarization experiments of Al-Cu-Si alloys and are discussed in terms of oxide film continuity, thickness and resistance to charge transfer.

Sample Preparation:

Samples for electrochemical behavior evaluations were prepared from cast ingots provided by ALCOA Research Laboratories. The composition range of interest was 0 to 2% Cu and 0 to 2% Si, both being covered in 0.5% increments, just as in the mechanical property evaluations. Nominal and actual analytical compositions for each ingot were listed in Table 1. Samples were machined 2 cm long, with a square cross-section of 0.5 by 0.5 cm. Each sample was threaded at each end so as to provide for a sound, mechanical means of electrical contact between the sample and the electrochemical equipment. Two samples from each alloy were prepared, one for evaluation of the alloy in the solution-treated condition and one for evaluation in the short-term, artificially aged condition. Solution-treatment was carried out at 550°C for 30 minutes in air and each sample was subsequently water-quenched. A small amount of NaCl was added to the vigorously stirred quenching bath in order to accelerate the cooling rate. Short-term artificial aging of the solution-treated alloys to be evaluated in this condition was carried out at a temperature of 250°C for 30 minutes. In addition, four samples from the Al-Cu(2%), Al-Si(2%) and Al-Cu(2%)-Si(2%) alloys were prepared in order to study the

effect of increased aging time (1, 2, 8 and 32 hours at 250°C) on the electrochemical behavior of these alloys and correlate the results to the mechanical behavior observed in Chapter 2.

In preparing samples for electrochemical evaluation, the small hole that was tapped on the side of each specimen prior to heat-treatment was used to mechanically attach a threaded brass rod onto each sample, providing both stability and electrical contact. The sample and the attached rod were placed in a Teflon fixture that acted as an epoxy casting mold. The sample was laid flat against the mold bottom with the Teflon fixture providing a means for supporting a glass tube. A glass tube was slipped over the brass attachment rod and secured onto the fixture. Epoxy was then poured into the mold and allowed to fill the glass tube, encasing both rod and sample so that only the square cross-section on the mold bottom was exposed to the electrolyte. The arrangement provided a rigid means of support, isolation of the sample and the attachment rod from the electrolyte, and an easy, readily repeatable method for surface preparation. Figure 10 is a schematic drawing of the Teflon fixture and a finished sample.

Samples were first ground on wet 600 grit SiC paper, rinsed in running tap water, ultrasonically cleaned and dried with acetone. Rough polishing was done with 15, 6 and 1 μm diamond paste taking special care to polish only on aluminum wheels with new Nylon polishing cloths being replaced every 5 samples. In addition, the set of 5 samples were always polished in order of increasing Cu content. These precautions were taken in order to eliminate pitting of the Al matrix during polishing (which may occur when brass polishing wheels are used), to avoid deposition of the Cu from the polishing cloths onto the Al matrix, and minimize the amount of scratches on the surface. In order to minimize the amount of oxide formed in air, each sample was again polished using colloidal silica just prior to immersion in the electrolyte. The colloidal silica, with a pH of approximately 10, helps polish the sample both mechanically and chemically by

Figure 10: Teflon fixture and finished sample.

removing the oxide layer. Samples were polished with the colloidal silica suspension for 2 minutes, rinsed in tap water for 15 seconds, ultrasonically cleaned in deionized water for another 15 seconds, inserted onto the beaker stopper and immersed in the electrolyte. Total time of exposure of the polished surface to air and water was kept constant at 60 +/- 10 seconds.

Electrolyte Preparation:

An aqueous solution of 5% NH_4Cl by weight was prepared with reagent-grade NH_4Cl and chromatography-grade water. A total of 100 grams NH_4Cl was weighed-out and placed in a 2 liter volumetric flask. Water was added until the solution level reached 2 liters and the solution agitated and warmed slightly for 5 minutes in order to dissolve the NH_4Cl .

Electrochemical Methods:

All of the electrochemical experiments were conducted in a 300 ml beaker that had a stopper specially machined so as to ensure accurate placement of a fritted tube, a thermometer and the counter as well as the reference and working electrodes. A Pt wire-mesh cylinder and a saturated calomel electrode were used as the counter and reference electrode, respectively. Each sample was immersed in 200 cm^3 of solution which was kept at $3.5 \pm 2^\circ\text{C}$ by placing the test beaker in an ice bath. Oxygen was blown through the fritted tube for 30 minutes while the solution was agitated using a magnetic stirrer. A constant open-circuit potential was usually obtained within 15 minutes after sample immersion, but an additional 15 minutes was allowed in order to ensure stability. Once the oxygen was shut off, measurements were conducted within approximately 3 minutes, after the sample had been immersed for a total of 35 minutes in the electrolyte. Stability and reproducibility in open-circuit potentials were achieved only when temperature, stirring, immersion time and oxygenation time were tightly controlled. All potentials were measured with respect to a saturated calomel electrode.

Impedance-spectroscopy data were taken using a Solartron Model 1250 Frequency-Response Analyzer together with an EG&G Model 273 Potentiostat. A ± 10 mV amplitude bias was applied about the open-circuit potential at frequencies ranging from 20 kHz to 50 mHz using a sweep rate of between 6 and 8 steps per decade. Data acquisition and analysis were performed on an IBM Model 30 computer using the EG&G M388 software package in conjunction with the EG&G Option 92 AC Interface. Anodic DC polarization experiments were controlled using the EG&G M342 software package and the EG&G Model 273 Potentiostat. All polarization scans had a set scan rate of 3 mV per second, and each scan began upon completion of the impedance-spectroscopy measurements. Total immersion time prior to DC polarization was kept constant at 45 minutes. The presence of surface roughness, voids and cavities in the alloys tended to affect the accuracy of the impedance-spectroscopy measurements. In addition, the fact that each of the castings had varying grain sizes tended to mask the effect of incremental Cu and Si additions and short-term aging response.

CHAPTER 4

RESULTS AND DISCUSSION - ELECTROCHEMICAL BEHAVIOR

Effect of Cu Content:

The polarization resistance, R_p , was marked in the low-frequency region of the Nyquist plot as the real component of the impedance at which the imaginary component vanishes.⁷⁸ The impedance spectroscopy response of solution-treated Al is shown in Figure 11 in order to demonstrate the similarity between it and the impedance spectroscopy response of the electrical circuit shown in Figure 9. Figure 12 demonstrates the effect of Cu content on R_p for the solution-treated and artificially aged Al-Cu alloys. As the copper content increases from 0 to 1%, the polarization resistance decreases, but remains constant for higher Cu concentrations. Artificial aging at 250°C for 30 minutes lowers the polarization resistance with respect to that of the solution-treated alloys, so that the aged alloys would have a higher corrosion current (i_{corr}) than the solution treated alloys.

The capacitance of the oxide and/or double-layer can be determined by either plotting the imaginary component of the measured capacitance versus the real component or by calculating the capacitance according to

$$C = \frac{1}{2\pi f_{\max} \phi R_p} .$$

The capacitance as a function of Cu content is shown in Figure 13 for the solution-treated and artificially aged alloys. Although capacitance measurements of the

Figure 11: AC Impedance-spectroscopy response of solution-treated Al.

Figure 12: Polarization resistance of Al and Al-Cu alloys as a function of Cu content.

Figure 13: Capacitance of Al and Al-Cu alloys as a function of Cu content.

artificially aged alloys contain some scatter, it appears that they remain virtually constant between 0 and 1% Cu. As Cu contents are raised further, the capacitance of the solution-treated alloys increases slightly. The increase in capacitance for Cu concentrations greater than 1% Cu is considerably more pronounced in the aged alloys than in the solution-treated ones. This point will be discussed later.

The results in Figures 12 and 13 point to the role that the protective oxide layer plays in the corrosion of Al-Cu alloys. Earlier investigations showed that the addition of Cu increased the susceptibility of Al to corrosion by the formation of defects or weak spots in the oxide layer.^{59,60,61} Specifically, Auger depth profiling⁶² had revealed that the oxide layer on unalloyed Al was thicker than that on Al-Cu(0.5%) which had Cu present in the Al matrix in the form of CuAl_2 . Such a reduction in oxide-layer thickness and/or the promotion of a flawed layer associated with the presence of Cu can be the cause of the observed drop in R_p and the rise in capacitance for solution-treated as well as artificially aged alloys. As the Cu content is increased beyond 1%, the polarization resistance essentially remains constant. Therefore, as long as the oxide layer is considered to be continuous, double-layer effects can be neglected and the oxide layer can be viewed as the primary resistor and as the dielectric of the condenser.

Metallographic inspection revealed that, in both the solution-treated and aged conditions, the pitting attack on unalloyed Al was evenly distributed throughout the sample surface. As shown in Figure 14, the pit morphology in Al is clearly crystallographic with pit densities and orientations changing from grain to grain. Similar observations have been made not only for Al, but also for Al alloyed with Cu, Zn and Mg.^{63,64} An example of a solution-treated Al-Cu(2%) alloy exhibiting general pitting corrosion, similar to that of the unalloyed Al, is given in Figure 15. This is in sharp contrast to the intergranular attack demonstrated in Figure 16 by the artificially aged Al-Cu(2%) alloy. This attack is also shown in Figure 17 at higher magnification in an

Figure 14: Photomicrograph of Al artificially aged 30 minutes [500X].

Figure 15: Photomicrograph of solution-treated Al-Cu(2%) [500X].

Figure 16: Photomicrograph of Al-Cu(2%) artificially aged 30 minutes [50X].

Figure 17: Photomicrograph of Al-Cu(2%) artificially aged 30 minutes [500X].

area adjacent to a grain-boundary triple point. Here, corrosion at or near the grain boundaries is clearly visible, as pits form within the Cu-depleted zones and in the grain boundaries.

General pitting corrosion prevails in the solution-treated alloy but is replaced by localized attack at or near grain boundaries when the alloy is aged. The solution-treated alloy is in a supersaturated condition and has a fairly non-uniform distribution of Cu throughout the grains. At the aging temperature of 250°C, Cu diffusion becomes effective even during short aging times. As equilibrium is approached, regions of high Cu content form at low energy sites, that is, grain boundaries. These create galvanic local-action cells with the adjacent Cu-depleted areas, accounting for the observed grain-boundary corrosion.

Open circuit potentials for the solution-treated alloys, as shown in Figure 18, are not significantly different from those of artificially aged ones. In both of these, the potential becomes more positive as the Cu content increases. Although a difference between the open-circuit potentials of solution-treated and artificially aged alloys was expected due to the difference in Cu distribution, the combination of low copper content and short aging time may have led to the lack of a significant resolution in the solution-treated and artificially aged potentials. Indeed, as discussed in Chapter 2, an aging response for many of the alloys was not observed until after the alloys had been aged beyond 1 or 2 hours.

Breakdown potentials were determined graphically as the points at which the slope of the current-density versus potential curve undergoes a drastic increase. The breakdown potential is plotted in Figure 19 as a function of Cu content for solution-treated and artificially aged alloys. In both the solution-treated and artificially aged conditions, this potential was virtually identical for Al and Al-Cu(0.5%). Higher Cu content led to a more positive breakdown potential in both the solution-treated

Figure 18: Open-circuit potential as a function of Cu content.

Figure 19: Breakdown potential as a function of Cu content.

and artificially aged conditions. It is plausible that thickness and structural soundness of the oxide layer enhance the breakdown potential. A less resistant breakdown potential can therefore be expected when the effective layer thickness is reduced with increasing Cu content. This corroborates the indication given by capacitance and polarization-resistance measurements concerning the effect of Cu on the layer structure.

Effect of Aging Time on Al-Cu(2%):

Al-Cu alloys are age-hardenable, so that their metallurgical structure and concomitant mechanical properties can be modified by heat treatment. Studying simultaneously the hardness and the electrochemical behavior of an Al-Cu(2%) alloy subjected to aging treatment at 250°C permitted some correlation between corrosion and microstructure in this alloy. The age-hardening curve for the Al-Cu(2%) alloy giving the Brinell hardness number as a function of aging time was shown in Figure 4, Chapter 2. In the solution-treated condition, the Al matrix is supersaturated with Cu atoms. As the solution-treated Al-Cu(2%) alloy was aged, coherent precipitates of Cu formed within the grains and helped strengthen the alloy. A well-defined peak in hardness was observed after 2 hours at 250°C. This peak is caused by the formation of a large number of finely dispersed metastable coherent precipitates, or Guinier-Preston zones. Continued aging favored the formation of the equilibrium CuAl_2 θ -phase which is a non-coherent precipitate with its own crystal structure. The local strain relaxation through the creation of the relatively small number of large non-coherent precipitates is associated with the decrease in hardness, or overaged condition. The differences between solution-treated, peak and overaged hardness values was not as large as those reported for structural Al-Cu alloys because the copper content here was too low to observe the full age-hardening reaction.

Effect of aging time on the polarization resistance of Al-Cu(2%) is shown in Figure 20. An increase in aging time led to an overall decrease in the polarization resistance and a corresponding increase in the corrosion current. The continued precipitation of Cu-rich phases, such as the equilibrium θ -phase, that occurs during prolonged aging promotes this increase in corrosion current and a concurrent decrease in R_p . Copper precipitates act as sites where the cathodic reaction can occur, increasing the efficiency of the overall corrosion reaction by enlarging the cathodic surface area. With the oxide layer being viewed as the primary resistor, the continued formation of these cathodic sites may lead to a reduction in the effective oxide-layer thickness and a corresponding decrease in R_p . It should be noted that, as the aging time was increased, the Nyquist plots demonstrated a drastic change in impedance response, particularly after an aging time of 8 hours.

Aging for 8 and 32 hours led to resolution of two superimposed impedance spectra, as shown in Figure 21. Therefore, the electrical circuit model being used to describe the impedance spectroscopy response (Figure 9) was no longer applicable. Consequently, the electrical circuit model was modified in order to account for the two capacitive reactances observed. After 8 hours, much of the Cu is present in either coherent or incoherent precipitates in the matrix or as incoherent precipitates at the grain boundaries, leading to a second electrode/electrolyte interface distinguishable from that in the Cu-depleted zones and grain interiors. If this indeed is the case, the electrical circuit model shown in Figure 22 can better describe the measured impedance response. The actual impedance response for the Al-Cu(2%) alloy aged for 32 hours is shown in Figure 23.

Figures 22 and 23 can be used to describe physically the changes occurring microstructurally as an Al-Cu alloy is aged and, in turn, how the oxide layer is affected. The first small impedance response in the spectrum represents the formation of Cu-rich

Figure 20: Polarization resistance of Al-Cu(2%) as a function of aging time.

Figure 21: AC Impedance-spectroscopy response of Al-Cu(2%) artificially aged 8 hours.

Figure 22: Circuit model describing impedance response shown in Figure 21.

Figure 23: Impedance-spectroscopy response of Al-Cu(2%) artificially aged 32 hours.

zones which are now in sufficient numbers so as to be resolved in the spectrum. These Cu-rich zones have an oxide layer which is much thinner or not structurally as sound as the oxide layer which would otherwise form on pure Al or solution-treated Al-Cu. The second impedance response represents the Cu-depleted and/or Al matrix oxide-layer. Depletion of Cu in areas adjacent to grain boundaries or solute-rich zones leads to an increase in oxide-layer thickness within these Cu-depleted zones. Consequently, the resistance of the Cu-depleted region is greater than that of the Cu-rich areas. The Cu-rich areas do not passivate like Al or the Cu-depleted Al matrix; in addition, the Cu-rich zones act as efficient cathodes. Therefore, as aging continues, the formation of either coherent or incoherent precipitates leads to some regions where the oxide layer is discontinuous or weak and other regions where the oxide layer is thick, thereby exposing two different interfaces to the electrolyte. As a result, two electrochemical responses are resolved in the impedance spectra.

Figure 24 demonstrates the effect of aging time on the capacitance of Al-Cu(2%). A capacitance peak was observed reproducibly between aging times of 2 and 8 hours corresponding to the hardness peak shown in Figure 4. At this point, the alloy contains the greatest concentration of finely dispersed coherent precipitates. It appears, therefore, that coherent precipitates interfere with the formation of the oxide-layer, thereby decreasing the effective thickness of the oxide layer and forming the capacitance peak. The cause for the steep rise in capacitance with increasing Cu content in alloys aged for 30 minutes (Figure 13) must also be sought in the formation of coherent precipitates. Continued aging beyond 2 hours led to a rapid decrease in the capacitance during the period in which the equilibrium θ -phase forms. CuAl_2 , having its own crystal structure, should inhibit the formation of a continuous oxide layer on the surface of the alloy at or near the precipitate. As discussed earlier, CuAl_2 acts as an efficient cathodic site, increasing i_{corr} . Since an increase in the corrosion current indicates an increase in

Figure 24: Capacitance of Al-Cu(2%) as a function of aging time.

metal-ion activity at the electrolyte/metal interface, a decrease in capacitance with overaging can be attributed to an increased thickness in the capacitive double-layer. Alternatively, an increase in oxide-layer thickness within Cu-depleted zones can also lead to the decrease in capacitance observed.

The effect of aging time on the open-circuit and breakdown potentials of Al-Cu(2%) is shown in Figure 25. Continued aging at 250°C leads to slightly more negative potentials. The decrease in open-circuit and breakdown potentials is linked to the increasing Cu depletion of the matrix during aging, thereby creating a large surface area of low potential. At prolonged aging times, the decrease in pitting potential is small principally because of the low Cu concentrations used. The observed decrease in the pitting potential with aging agrees well with that reported by Muller and Galvele⁶⁴ and Galvele and de De Micheli.⁶⁶

Because the distribution of Cu in Al has been shown to have a strong effect on the age-hardening curve of Al-Cu alloys, the type of corrosion attack during prolonged aging should also reflect the distribution of Cu in Al. Figure 15 was an example of general pitting corrosion observed in solution-treated Al-Cu(2%). Upon aging at 250°C for 30 minutes, Al-Cu(2%) became susceptible to intergranular corrosion, Figure 16. As shown in Figure 26, beyond the peak hardness value, that is, after 2 hours aging time, an overaged condition is created wherein the CuAl_2 precipitates grow throughout the grains, depleting much of the Al matrix of Cu. The precipitates are cathodic with respect to the matrix, so that the alloy begins to exhibit general pitting corrosion similar to that observed for the solution-treated Al-Cu(2%) alloy (see Figure 15). This observation corroborates results reported by Muller and Galvele.⁶

Figure 25: Open-circuit and breakdown potentials of Al-Cu(2%) as a function of aging time.

Figure 26: Photomicrograph of Al-Cu(2%) artificially aged 32 hours [50X].

In conclusion, the effect of Cu and heat treatment on the corrosion resistance of Al-Cu alloys in terms of oxide layer thickness can be summarized as follows. In the solution-treated condition an increase in Cu content leads to a gradual thinning of the oxide-layer and a corresponding increase in capacitance and concomitant decrease in corrosion resistance. Short-term artificial aging leads to the formation of Cu precipitates which are coherent with the Al matrix. Formation of these precipitates interferes with the structural soundness of the oxide layer and causes both a further decrease in corrosion resistance and an increase in oxide-layer capacitance. As aging continues, a peak in both the hardness and capacitance of Al-Cu(2%) is observed. These peaks correspond to the maximum number of small coherent precipitates in the Al matrix. Although this means that the hardness is at a maximum, the corrosion resistance is at a minimum, a result of the overall thinning of the oxide layer. During the aging process, the segregation of Cu at the grain boundaries leads to intergranular corrosion, a result of the formation of galvanic cells between the Cu-enriched boundaries and the Cu-depleted zones. Once overaged, the formation of incoherent precipitates leads to a Cu-depleted Al matrix with a thicker oxide layer, a lower capacitance and a much lower Brinell hardness number. In addition, the type of corrosion attack is similar to the uniformly distributed pitting corrosion observed in unalloyed Al.

Effect of Si Content:

The effect of Si content on the polarization resistance of solution-treated and artificially aged Al-Si alloys is shown in Figure 27. Upon addition of 0.5 weight percent Si, R_p drops to about $4000 \Omega\text{-cm}^2$, remaining there as the Si content increases to 2% in the solution-treated condition. Similar behavior is exhibited by the artificially aged Al-Si alloys, except that the steady-state value of R_p for Si contents between 0.5 and 2.0 weight percent is approximately $200 \Omega\text{-cm}^2$. Much of the initial drop in R_p was attributed to the decrease in grain size caused by the addition of Si. Artificial aging of the Al-Si alloys

Figure 27: Polarization resistance of Al and Al-Si alloys as a function of Si content.

for 30 minutes lowered the polarization resistance with respect to the solution treated values. Consequently, the corrosion resistance of solution-treated Al-Si alloys is greater than that of the artificially aged alloys. Although Si is inert in most environments⁶⁸, the decrease in R_p with aging is ascribed to a loss in structural soundness of the oxide layer as Si precipitates form, allowing them to act as cathodic reduction sites.

In Figure 28, the measured capacitance as a function of Si content is presented for both the solution-treated and artificially aged alloys. Interestingly, no variations in capacitance were observed with increased Si additions for the artificially aged alloys. The capacitance value is approximately $7\mu\text{F}/\text{cm}^2$, similar to the capacitance of unalloyed Al. The measured capacitance can therefore be attributed to the protective oxide layer of the Al matrix. However, this does not necessarily mean that the thickness of the oxide layer on Al-Si alloys is the same as in unalloyed Al because both the dielectric constant and the number of defects introduced with the addition of Si may contribute to the measured capacitance.

Also of interest in Figure 28 is the measured capacitance of the solution-treated alloys which, although they contain a considerable amount of scatter relative to the artificially aged values, indicate that the capacitance increases slightly with increasing Si content. As Si is only soluble up to approximately 1.25% at 550°C, Si contents between 0 and 1.0% were expected to yield results different from those which contain 1.5 and 2.0 weight percent Si. In the solution-treated condition, the latter will contain two phases since Si is present in excess of the amount soluble at 550°C. Consequently, Al-Si alloys containing less than 1.25% Si would be expected to have a capacitance value similar to that of unalloyed Al. However, increased Si contents may cause a slight increase in capacitance if dissolved Si either interferes with the formation of the oxide layer or alters the dielectric constant of the active inner layer. Amounts of Si in excess of 1.25% would be expected to cause an increase in the capacitance if the presence of both dissolved and

Figure 28: Capacitance of Al and Al-Si alloys as a function of Si content.

undissolved Si in the solution-treated condition also interferes with the structural soundness and integrity of the oxide-layer. This would help explain the apparent decrease in capacitance with short-term aging as this may relieve interphase stresses and improve the capacitive response. It should be reemphasized that although the measured capacitance in the Al-Si alloys may at first glance indicate that the oxide layer in these alloys may be thinner or not as structurally sound in the solution-treated condition as in the artificially aged condition, the polarization resistance of the former is indeed slightly greater than the latter. This may be a result of the lack of resolution of impedance spectra for both the Si and the Al matrix which would be expected in a two-phase alloy.

Metallographic inspection of the Al-Si alloys revealed that Si in the solution-treated condition leads to uniformly distributed pitting corrosion. In fact, it appeared that solution-treated Al-Si alloys are 'etched' so as to reveal grain orientations as shown in Figures 29 and 30, which represent the type of corrosion observed near a grain boundary triple-point in solution-treated Al-Si(1%) at magnifications of 200 and 500X, respectively. Figure 31 is also a high magnification micrograph of solution-treated Al-Si(1%) revealing the crystallographic attack on Al-Si(1%). The type of attack is the same as that observed in unalloyed Al and solution-treated Al-Cu alloys (see, for example Figures 14 and 15).

As discussed earlier, Al-Si(1.5%) and Al-Si(2.0%) cannot be solution-treated because at 550°C, approximately only 1.25% Si is soluble in Al. Consequently, two phases would be expected in the solution-treated condition. Figure 32 is a 500X magnification micrograph revealing the second-phase Si in Al-Si(2%); the Si appears as dark gray nodules within grains and as elongated globules at the grain boundaries. Although the second-phase is present, the type of corrosion in solution-treated Al-Si(1.5%) and Al-Si(2.0%) is the same as in the Al-Si alloys containing less than

Figure 29: Photomicrograph of solution-treated Al-Si(1%) [200X].

Figure 30: Photomicrograph of solution-treated Al-Si(1%) [500X].

Figure 31: Photomicrograph of solution-treated Al-Si(1%) [500X].

Figure 32: Photomicrograph of solution-treated Al-Si(2%) [500X].

1.25%Si. The type of corrosion attack on solution-treated Al-Si(2%) shown in Figure 33 is similar to that shown in Figure 32 even though the presence of Si at a grain boundary triple point is visible.

Artificial aging at 250°C for 30 minutes did not lead to any significant changes in the type of corrosion attack observed in Al-Si alloys. This was not surprising since the presence of second-phase Si in the solution-treated Al-Si(1.5%) and Al-Si(2.0%) alloys did not induce any type of corrosion attack distinguishable from alloys containing less than 1.25% Si. Consequently, short-term artificial aging and the resulting precipitation of Si in previously solution-treated Al-Si alloys containing less than 1.25% Si should not alter the type of corrosion attack observed. This behavior is shown in Figures 34 and 35 for Al-Si(1%) artificially aged for 30 minutes. In Figure 35, crystallographically oriented pitting corrosion near a grain boundary triple point is clearly visible. Here, one grain has practically been removed due to uniform pitting corrosion while the onset of pit 'tunneling' in the other two grains is present.

As discussed in the previous paragraph, short-term artificial aging of Al-Si(2%) did not affect the type of corrosion attack in Al-Si (2%); however, Si appeared to have coalesced into nodules within the grains. Figures 36 and 37 demonstrate both the presence of Si at the grain boundaries and the Si nodules in the grain interiors. The formation of Si nodules upon aging may be the reason a stable capacitance was measured for all the Al-Si alloys that were artificially aged whereas in the solution-treated condition, the capacitance slightly increased with increasing Si content. If Al-Si alloys are solution-treated, formation of a protective oxide layer which is in a highly stressed condition may occur, but the measured capacitance is slightly higher than would be expected due to the presence of dissolved Si.

Open-circuit potentials for the solution-treated Al-Si alloys are not significantly different than those of artificially aged ones, as shown in Figure 38. Furthermore, the

Figure 33: Photomicrograph of solution-treated Al-Si(2%) [500X].

Figure 34: Photomicrograph of Al-Si(1%) artificially aged 30 minutes [200X].

Figure 35: Photomicrograph of Al-Si(1%) artificially aged 30 minutes [500X].

Figure 36: Photomicrograph of Al-Si(2%) artificially aged 30 minutes [500X].

Figure 37: Photomicrograph of Al-Si(2%) artificially aged 30 minutes [500X].

Figure 38: Open-circuit potential of Al and Al-Si alloys as function of Si content.

potential became only slightly more positive upon the addition of 0.5% Si, remaining essentially constant for higher Si contents. With Si being considered inert in an aqueous chloride environment relative to Al,⁶⁹ increased Si additions would not be expected to cause a significant change in the open-circuit potential either in the solution-treated or artificially aged condition. Therefore, open-circuit potentials and metallographic inspection indicate that Si additions and short-term aging have little effect on the electrochemical behavior of Al-Si alloys.

Breakdown potential as a function of Si content is plotted in Figure 39 for solution-treated and artificially aged Al-Si alloys. In the solution-treated condition, Al, Al-Si(0.5%) and Al-Si(1.0%) have approximately the same breakdown potential. Al-Si(1.5%) and Al-Si(2.0%) have slightly more negative breakdown potentials indicating that dissolved Si may lower the breakdown potential because of the formation of a mechanically weak oxide layer (a result of the solution-treatment procedure), in agreement with the impedance spectroscopy results. This indicates that dissolved Si may increase the work required to cause oxide breakdown, while the presence of second-phase Si decreases the amount of work required to cause oxide breakdown. There was no significant difference between the breakdown potentials of artificially aged and solution-treated Al-Si alloys. Increased Si additions tend to make the breakdown potential of artificially aged alloys slightly more negative.

Effect of Aging Time on Al-Si(2%):

Figure 6 in Chapter 2 demonstrated that Al-Si(2%) does not exhibit an age-hardening response. As aging times increased, a gradual decrease in hardness was observed and was attributed to the coalescence of the Si-rich phase into nodules and the loss of coherency between Si precipitates and the Al matrix.

Figure 39: Breakdown potential of Al and Al-Si alloys as function of Si content.

The effect of aging time on the polarization resistance of Al-Si(2%) is shown in Figure 40. A rapid decrease in R_p was observed upon aging for 30 minutes at 250°C; between aging times of 1 and 32 hours, R_p remained constant. Although Al-Si(2%) cannot be fully solution-treated, the decrease in polarization resistance with aging must be due to weakening of the oxide layer as a result of either Si coalescence and disregistry between Si and the Al matrix, or the precipitation of the maximum amount of Si soluble in Al. Solution-treated Al-Si(2%) has a higher polarization resistance than artificially aged Al-Si(2%) as a result of the apparent formation of a structurally sound oxide-layer. Aging must therefore cause a loss in oxide-layer integrity because of the rapid precipitation of Si. Although this indicates an overall drop in charge-transfer resistance, one would expect little, if any, direct contribution of the Si-rich phase to the total corrosion current as Si is inert in most environments.

Emphasis should be placed on the fact that only one impedance spectrum was observed in all of the Al-Si(2%) alloys aged from 0.5 to 32 hours. Therefore, the electrical circuit model shown in Figure 9 was used to describe the observed spectrum.

Figure 41 is a plot of the capacitance of Al-Si(2%) as a function of aging time at 250°C. As in the case of unalloyed Al and the artificially aged Al-Si alloys, there is little or no significant change in capacitance with aging time. Since it appears that Si is relatively inert, the measured capacitance must be due to the oxide layer of the Al matrix, while the observed drop in polarization resistance (see Figure 41) is attributed to a loss in oxide-layer integrity as Si is precipitated and/or the formation of cathodic reduction sites. As the mechanical defects in the oxide layer may be extremely small and the Si relatively inert, a second capacitive reactance corresponding to the presence of second-phase Si or Si precipitates may not have been detected.

Open circuit and breakdown potentials as a function of aging time at 250°C are given in Figure 42. No change in open-circuit potential with aging time is observed. An

Figure 40: Polarization resistance of Al-Si(2%) as a function of aging time.

Figure 41: Capacitance of Al-Si(2%) as a function of aging time.

Figure 42: Open-circuit and breakdown potentials of Al-Si(2%) as a function of aging time.

increase in breakdown potential upon aging for 8 and 32 hours is apparent. Si is present in Al-Si(2%) alloys in a distinct second phase in the solution-treated and artificially aged condition, so no change in open-circuit potential with aging time is to be expected. The positive shift in breakdown potential can be explained with the continuous formation of mechanical defects, as discussed earlier. However, it is possible that a Si-bearing oxide may have a higher breakdown voltage or an interface which is of a chemical nature quite different from that found within the Al matrix.

Figures 43 and 44 are 500X photomicrographs of Al-Si(2%) aged for 8 and 32 hours, respectively. Pitting corrosion occurs in areas adjacent to the second-phase Si. This is the same type of corrosion attack exhibited by Al, solution-treated Al-Cu, solution-treated Al-Si and artificially aged Al-Si alloys. Increased aging times on Al-Si(2%) can thus be concluded to have little effect on the type of corrosion attack observed. It does appear, however, that regions which contain, or are adjacent to, the Si-rich phase are cathodically protected so that these areas are not attacked.

Although data on the effect of Si additions and heat treatment on Al-Si alloys contain some scatter, an overall review of the results indicate that Si, whether present as a second-phase or as a substitutional alloying element, has little effect on the electrochemical behavior of Al-Si alloys. All of the artificially aged Al-Si alloys and the Al-Si(2%) alloy aged for extended times had approximately the same capacitance value. Consequently, the measured capacitance is ascribed to that of the Al matrix oxide layer. The polarization resistance appeared to increase slightly as the Si content was raised between 0.5 and 2.0%, but grain size effects may have masked a significant difference. Aging decreases polarization resistance as a result of the precipitation of a Si-rich phase. Si-rich precipitates may act as sites for cathodic reduction and disturb oxide layer integrity. The only significant difference in electrochemical behavior was the shift in

Figure 43: Photomicrograph of Al-Si(2%) artificially aged 8 hours [500X].

Figure 44: Photomicrograph of Al-Si(2%) artificially aged 32 hours [500X].

breakdown potential in Al-Si(2%) aged for 8 and 32 hours. This was attributed to the formation of Si nodules and continued precipitation of Si.

Effect of Cu and Si:

Investigations into the effect of Cu and Si content on the electrochemical behavior of Al-Cu-Si alloys proved to be troublesome. Two governing factors which were not taken into account during the beginning of this research project were variations in both grain size and casting defects. Bookmold ingots of each alloy composition were ordered from ALCOA. The only requirement placed on the casting procedure employed was that all ingots be processed in the same manner.

In the as-received condition, Al had a grain size of approximately 3 mm while Al-Cu(2%)-Si(2%) had a grain size of approximately 0.5 mm. Si is a grain refiner, so increasing Cu and Si content and the fact that ingots were cast at various times within a 6 month span may account for the observed variations in grain size. Conjointly, as the Si and Cu contents were increased, the number of casting defects increased dramatically. These defects include porosity and what appear to be 'tears' or acicular voids. Porosity and voids in the material lead to the formation of pockets where the oxide-layer becomes discontinuous and causes a localized concentration of the electrolyte within. A decrease in grain size increases the amount of cathodic grain boundary area available for the reduction process and thereby increases the corrosion current. Since the electrode surface area was kept constant at 0.25 cm^2 , the smaller grain size alloys will thus have a faster aging response and a larger corrosion current than alloys with a comparatively large grain size. Both defects and grain size were believed to have contributed to scatter in the data. Scatter was not a significant problem in evaluating Al-Cu alloys, which had few casting defects and little variation in grain size. Data on the effect of aging time on Al-Cu(2%), Al-Si(2%) and Al-Cu(2%)-Si(2%) alloys also did not contain a significant

amount of scatter, a result of samples for increased aging times being machined from the same ingot.

Figure 45 represents the effect of Cu and Si additions on the polarization resistance of solution-treated Al-Cu-Si alloys. An increase in Cu content leads to a rapid drop in polarization resistance in Al-Cu alloys, while in Al-Cu-Si alloys, Cu additions lead only to a gradual decrease in R_p . Interestingly, all of the Al-Cu-Si(2%) alloys have a higher polarization resistance in the solution-treated condition than the alloys containing between 0.5 and 1.5% Si. Artificial aging of Al-Cu-Si alloys further decreases R_p , as shown in Figure 46. Al-Cu-Si alloys containing either 0.5 or 1.0% Si have a higher polarization resistance as the Cu content increases between 0.5 and 1.0 %, suggesting a rapid aging response when Si is initially present as a dissolved substitutional element (recall that Si is soluble in Al-Cu-Si alloys only up to about 1.1%).

In Figure 47, capacitance values for solution-treated Al-Cu and Al-Cu-Si alloys containing 1.0 and 2.0% Si are shown. Increasing Cu contents increase the capacitance of Al-Cu and Al-Cu-Si(1.0%) alloys therefore decreasing oxide-layer thickness. For the alloys containing 2.0% Si, no variation in capacitance was observed.

Figure 48 demonstrates the effect of Cu and Si content on the capacitance of short-term artificially aged Al-Cu-Si alloys. Overall, oxide-layer thickness can be interpreted as having decreased with increasing capacitance corresponding to higher Cu and Si content. This was particularly true for the alloys bearing 1.5 and 2.0% Si and 1.5 and 2.0% Cu. The higher Cu and Si-containing alloys reveal a rapid aging response in both the polarization resistance and capacitance measurements much in the same way that high Si and Cu contents accelerate the age-hardening response. As discussed earlier in the mechanical properties section (Chapter 2), Cu contents greater than 1.5% are necessary to see an age-hardening response and Si contents greater than 1.0% are required to accelerate the aging response.

Figure 45: Polarization resistance of solution-treated Al-Cu-Si alloys as a function of Cu and Si content.

Figure 46: Polarization resistance of artificially aged Al-Cu-Si alloys as a function of Cu and Si content.

Figure 47: Capacitance of solution-treated Al-Cu-Si alloys containing 1 and 2% Si as a function of Cu content.

Figure 48: Capacitance of artificially aged Al-Cu-Si alloys as a function of Cu and Si content.

The rapid change in impedance response upon aging of Al-Cu-Si alloys can be linked to an acceleration of the age-hardening process. Age-hardening is governed by precipitation of Cu within the grains and at grain boundaries. Although Si may accelerate the precipitation reaction itself, a reduction in grain size would also accelerate the aging response because the diffusion path to the boundaries is decreased. However, appearance of a second capacitive reactance upon short-term aging of Al-Cu(2.0%)-Si(0.5%), Al-Cu(2.0%)-Si(1.0%), Al-Cu(1.5%)-Si(1.5%), Al-Cu(2.0%)-Si(1.5%), Al-Cu(2.0%)-Si(1.5%) and Al-Cu(2%)-Si(2%) strengthens the argument for an acceleration of the precipitation reactions.

The impedance response for Al-Cu(2%)-Si(1.0%) artificially aged for 30 minutes at 250°C is shown in Figure 49. The first impedance hump is due to the precipitated Cu at the grain boundaries and within the Al matrix and the second hump is due to the Al matrix itself. Consequently, metallographic inspection of anodically polarized Al-Cu-Si alloys should reveal two corroding interfaces in the artificially aged condition as in the Al-Cu alloys discussed earlier.

Photomicrographs of solution-treated and artificially aged Al-Cu(2.0%)-Si(1.5%) are shown in Figures 50 and 51, respectively. Contrast between uniform pitting corrosion in the solution-treated condition and corrosion adjacent to grain boundaries in the artificially aged condition is discernible. Clearly, the grain size is much smaller than in the Al-Cu alloy shown in Figure 15. Higher magnification micrographs of artificially aged Al-Cu(2%)-Si(1.5%) are presented in Figures 52 and 53. Grain boundaries, and the Si-rich phase within the matrix and between grain boundaries were not visibly affected by anodic polarization. As the grain boundaries in the artificially aged condition contain significant amounts of the Si-rich phase and Cu precipitates, grain boundaries may be considerably more noble, or cathodic, than both the Cu-depleted region and the grain interiors.

Figure 49: Impedance response of Al-Cu(2%)-Si(1%) artificially aged 30 minutes.

Figure 50: Photomicrograph of solution-treated Al-Cu(2%)-Si(1.5%) [50X].

Figure 51: Photomicrograph of artificially aged Al-Cu(2%)-Si(1.5%) [50X].

Figure 52: Photomicrograph of artificially aged Al-Cu(2%)-Si(1.5%) [200X].

Figure 53: Photomicrograph of artificially aged Al-Cu(2%)-Si(1.5%) [500X].

As in the Al-Cu alloys, uniform pitting prevails in solution-treated Al-Cu-Si alloys because Cu is dissolved within the matrix. Once the alloys are aged at 250°C for 30 minutes, precipitation of Cu and Si at or near the grain boundaries leads to the formation of galvanic local-action cells between Cu and Si-rich boundaries and the depleted zones adjacent to them. However, Si appears to protect both the grain boundaries and the areas immediately in their vicinity, making both the depleted regions and the entire grain interiors more anodic with respect to the overall cathodic grain boundary area. With the grain size in the Al-Cu-Si alloys being so small, the increase in grain boundary area would therefore be expected to significantly enhance the anodic dissolution of both the grain interiors and the Cu and Si depleted zones. In addition, Si accelerates the aging process itself, as evidenced by the formation of two superimposed impedance spectra and a rapid increase in hardness upon artificial aging for 30 minutes at 250°C.

Open-circuit potentials as a function of both Cu and Si content for solution-treated and artificially aged Al-Cu-Si alloys are presented in Figures 54 and 55, respectively. For solution-treated alloys, additional Cu and Si contents increase the open-circuit potential substantially. Artificial aging for 30 minutes at 250°C caused a decrease in the open-circuit potential for the Al-Cu-Si alloys which contain 1.0, 1.5, and 2.0% Si; no change in the open-circuit potential of the artificially aged Al-Cu and Al-Cu-Si alloys containing 0.5% Si was observed. Since artificial aging of Al-Cu(2%) caused a gradual decrease in open-circuit and breakdown potentials as a result of the formation of Cu-depleted zones, the rapid drop in open-circuit potential of Al-Cu-Si alloys with Si contents greater than 0.5% is attributed to an acceleration of Cu precipitation at the boundaries and the associated Cu-depletion.

The simultaneous effect of Cu and Si additions on the breakdown potential of Al-Cu-Si alloys could not be adequately resolved due to a variation in grain size and the presence of casting defects. Since grain size across the entire matrix was not uniform,

Figure 54: Open-circuit potentials of solution-treated Al-Cu-Si alloys as a function of Cu and Si content.

Figure 55: Open-circuit potentials of artificially aged Al-Cu-Si alloys as a function of Cu and Si content.

variations in the amount of cathodic grain-boundary area available for reduction processes can play a significant role in altering the breakdown potential and impedance spectroscopy response. In addition, casting defects such as those illustrated in Figure 56 can also lead to problems in resolving breakdown potentials due to localized variations in electric field, electrolyte concentration and oxide-layer formation near or within these defects.

Effect of surface preparation and surface defects had been investigated during the initial stages of this research and it was concluded that the best results could only be obtained on very smooth, defect-free surfaces. This would explain why unalloyed Al, Al-Si and the Al-Cu alloys yielded such good results as these were relatively defect-free compared to the Al-Cu-Si alloys. In addition, investigations into the effect of aging time on Al-Cu(2%), Al-Si(2%) and Al-Cu(2%)-Si(2%) also produced good results since alloy samples for each aging time were taken from their parent ingot, minimizing variations in casting defects and grain size which would otherwise occur if the samples were machined from different ingots.

Effect of Aging Time on Al-Cu(2.0%)-Si(2.0%):

In Chapter 2, the effect of aging time at 250°C on the age-hardening response of Al-Cu(2.0%)-Si(1.0%) and Al-Cu(2.0%)-Si(2.0%) was shown in Figures 5 and 6. In the solution-treated condition, these alloys are supersaturated with Cu. During the aging treatment, coherent precipitates of Cu begin to form and strengthen the Al matrix. At peak hardness, a large distribution of small coherent precipitates maximize the impediment to dislocation motion. However, as precipitation occurs much more rapidly at the grain boundaries, a Cu-depleted zone adjacent to the boundaries is developed. This promotes the formation of galvanic local-action cells between Cu-depleted zones and Cu-enriched grain boundaries. Si was found to accelerate the age-hardening response resulting in a decrease in the time required to reach both peak hardness and the overaged

Figure 56: Example of casting defects present in some of the Al-Si and Al-Cu-Si alloys.

condition. Consequently, Cu-depletion near the grain boundaries and Cu-enrichment within grain boundaries would also be expected to be accelerated. However, Si is already present in the grain boundaries as a second-phase in Al-Cu(2%)-Si(2%), and since Si does not limit the solubility of Cu in Al, precipitation of both Si and Cu will occur rapidly at the grain boundaries and in the areas adjacent to them. This leads to Cu and Si enrichment of the grain boundaries and the areas adjacent to them, and probably the formation of a depletion region; however, the thickness of this depletion region and its distance from the grain boundaries was not determined.

Artificial aging of Al-Cu(2%)-Si(2%) for 30 minutes promoted the appearance of two capacitive reactances in the impedance spectrum. The high-frequency response corresponds to the Cu-enriched regions such as grain boundaries and the low-frequency response corresponds to that due to the Al matrix. Figures 57 and 58 contrast the impedance response of solution-treated and short-term aged Al-Cu(2%)-Si(2%), respectively. The electrical circuit model switches from that shown in Figure 9 to the one shown in Figure 21. Previously in Al-Cu(2%), two impedance responses were detected after aging for 8 hours at 250°C, whereas in Al-Cu(2%)-Si(2%), the second response occurred after only 30 minutes. The accelerated response is due to the presence of Si. Therefore, the resolution of two impedance spectra as aging time increased can help explain both the drop in polarization resistance and the peak in the capacitance response in both Al-Cu(2%) and Al-Cu(2%)-Si(2%).

Figure 59 illustrates the effect of aging time on the overall polarization resistance. As the alloy is aged, the precipitation of Cu governs the resistance to charge transfer so that the Cu precipitates, having a low resistance to charge transfer, lower the polarization resistance. Since Cu precipitates increase in size and number as the aging process proceeds, the increase in precipitate area lowers the overall corrosion resistance of the alloy.

Figure 57: AC Impedance-spectroscopy response of solution-treated Al-Cu(2%)-Si(2%).

Figure 58: AC Impedance-spectroscopy response of artificially aged Al-Cu(2%)-Si(2%).

Figure 59: Effect of aging time on polarization resistance of Al-Cu(2%)-Si(2%).

As shown in Figure 60, the capacitance as a function of aging time exhibits a peak after 2 hours of aging at 250°C corresponding to the peak hardness value. The formation of the coherent precipitates interferes with the formation of the oxide layer, thereby simultaneously minimizing the effective thickness of the oxide layer and maximizing the capacitance. Continued aging beyond 2 hours led to a rapid decrease in capacitance during the period in which the equilibrium θ -phase forms. In discussing the drop in capacitance with overaging in Al-Cu(2%), it had been postulated that formation of CuAl_2 , having its own crystal structure, interfered with the formation of the oxide layer. As a result, the drop in capacitance was attributed to the increase in double-layer thickness at or near the precipitates.

The effect of aging time on the open-circuit and breakdown potentials of Al-Cu(2%)-Si(2%) is shown in Figure 61. A rapid decrease in both occur upon aging, reaching a steady-state value after about 2 hours. The steady-state value for the breakdown potential is the same as was determined for unalloyed Al, i.e., -611 mV. Therefore, since the 2-hour steady-state value for the breakdown potential of Al-Cu(2%)-Si(2%) is equal to that of the artificially aged unalloyed Al, the breakdown potential must be due to the formation of Cu-depleted zones. Once again, the rapid decrease in breakdown and open-circuit potentials in aged Al-Cu(2%)-Si(2%) relative to that observed in Al-Cu(2%) can be associated with either a smaller grain size and the corresponding increase in grain boundary area or the acceleration of the aging process due to the presence of Si.

The type of corrosion attack exhibited by Al-Cu(2%)-Si(2%) artificially aged for 32 hours is shown in Figure 62 and it illustrates the uniform pitting corrosion observed in both the solution-treated and overaged conditions. In the Al-Cu(2%)-Si(2%) alloy aged 1 hour, corrosion near the grain boundaries is visible, as depicted in Figure 63. Cu and Si enrichment of the grain boundaries and the areas adjacent to them make them much

Figure 60: Effect of aging time on capacitance of Al-Cu(2%)-Si(2%).

Figure 61; Open-circuit and breakdown potentials of Al-Cu(2%)-Si(2%) as a function of aging time.

Figure 62: Photomicrograph of Al-Cu(2%)-Si(2%) artificially aged 32 hours [500X].

Figure 63: Photomicrograph of Al-Cu(2%)-Si(2%) artificially aged 1 hour [500X].

more cathodic than the depleted regions and/or the grain interiors. As a result, anodic dissolution of the depleted regions and grain interiors is enhanced, particularly since the grain boundary area is so large; the larger the cathodic area, the greater the efficiency for cathodic reduction. This explains why the smaller grain-size material is so susceptible to pitting corrosion in the areas away from the grain boundaries, such as the depleted regions and the grain interiors.

CHAPTER 5

CONCLUSIONS

In solution-treated Al-Cu, Al-Si and Al-Cu-Si alloys, additions of Cu and/or Si led to an increase in hardness due to a significant amount of substitutional solid-solution strengthening. Artificial aging at 250°C for 30 minutes did not alter the hardness of these alloys because of the relatively low amount of Cu and Si contents present. Al-Cu(1.5%) and Al-Cu(2%) alloys aged for 1, 2, 8 and 32 hours exhibited an age-hardening response. A peak in the hardness was obtained when the number of coherent precipitates was maximized and the size of the precipitates was minimized. The strain fields induced by the precipitates and the precipitates themselves act as barriers to dislocation motion. Continued aging led to growth of the coherent Cu precipitates into the larger, incoherent CuAl_2 precipitates at the expense of the fine, coherent precipitates. As large, incoherent precipitates do not maximize the number of obstacles to dislocation motion, an overaged condition was achieved. Si was found to accelerate age-hardening response by acting as heterogeneous nucleation sites, thereby increasing the rate of precipitate formation and decreasing the amount of time required to reach peak hardness.

Solution-treated Al, Al-Cu, Al-Si and Al-Cu-Si alloys form a protective oxide-layer which can be modeled as both a capacitor and a resistor. The impedance of a circuit consisting of an oxide-layer acting as both a capacitor and a resistor in parallel is given by

$$\frac{1}{Z_p} = \frac{1}{R_p} - \omega C_{ox} i$$

where Z_p is the impedance, R_p is the polarization resistance, ω is the frequency, C_{ox} is the oxide-layer capacitance, and i represents the imaginary number, $\sqrt{-1}$. In the limit as ω goes to zero,

$$R_p = \frac{\rho_{ox} t_{ox}}{A_{ox}}$$

where ρ_{ox} is the resistivity of the oxide layer, t_{ox} is the thickness of the oxide layer and A_{ox} is the area of the oxide layer. As the thickness decreases, there is a concomitant decrease in polarization resistance. Increased Cu and Si additions led to a decrease in polarization resistance. Although the resistivity of the oxide layer may have changed, it is believed that the decrease in resistance is due to a decrease in oxide-layer thickness.

Precipitation of Cu during aging caused a drop in the overall resistance. Once a significant number of these precipitates formed, an impedance spectrum composed of two smaller, superimposed impedance spectra was observed. This spectrum can be described by

$$\frac{1}{Z_p} = \frac{1}{R_{Cu}} - \omega C_{dl}i + \frac{1}{R_{matrix}} - \omega C_{matrix}i$$

where R_{Cu} represents the resistance due to Cu precipitates, C_{dl} is the capacitance due to the double-layer formed adjacent to the Cu precipitates, R_{matrix} is the resistance of the oxide layer on the matrix and C_{matrix} is the capacitance of the matrix oxide layer. In the limit as ω goes to zero, the overall resistance is

$$R_p = \frac{1}{A_{Cu} \left(\frac{1}{\rho_{Cu} t_{dl}} - \frac{1}{\rho_{ox} t_{ox}} \right) + \frac{A_{sample}}{\rho_{ox} t_{ox}}}$$

A_{Cu} represents the area of the Cu precipitates, ρ_{Cu} the resistivity of the precipitates, t_{dl} the thickness of the double-layer adjacent to the precipitates, ρ_{ox} the resistivity of the oxide layer in the Cu-depleted matrix, t_{ox} the oxide-layer thickness, and A_{sample} the sample area, which is constant. Since $\rho_{Cu} t_{dl} \ll \rho_{ox} t_{ox}$, as the precipitate area increased, the overall corrosion resistance decreased. Consequently, artificial aging and the concomitant

precipitation of Cu leads to a decrease in corrosion resistance. Just as Si was found to accelerate age-hardening, the appearance of two superimposed impedance spectra was also accelerated. This was attributed to an increase in the rates of both nucleation and growth of Cu precipitates.

Al-Cu(2%) and Al-Cu(2%)-Si(2%) alloys aged for extended periods of time at 250°C exhibited a capacitance peak. This maximum capacitance value corresponds to the age-hardening peak produced by the formation of coherent Cu precipitates. These precipitates interfere with the formation of a thick, protective oxide layer, thereby minimizing oxide-layer thickness and maximizing the overall capacitance. As the alloys were overaged, a drop in capacitance was observed. The drop in capacitance with aging was attributed to the formation of the equilibrium precipitate, a loss in oxide-layer integrity at or near the precipitates, and the corresponding formation of both a double-layer at the precipitate/electrolyte interface and a Cu-depleted zone.

The formation of Cu-depleted zones during aging, especially near grain boundaries, accounted for the observed decrease in open-circuit and breakdown potentials in Al-Cu and Al-Cu-Si alloys. Galvanic local-action cells developed between Cu-enriched grain boundaries and Cu-depleted zones gave rise to localized pitting corrosion at or near the grain boundaries. This was in sharp contrast to the type of corrosion attack observed on solution-treated Al-Cu and Al-Cu-Si alloys, which pitted uniformly across the entire surface. Si-rich areas did not appear to be attacked. In addition, areas adjacent to the Si-rich phase within the grains and along grain boundaries were protected compared to the grain interiors. Si-bearing alloys had a much smaller grain size, so increased cathodic grain boundary area may have caused a significant amount of corrosion farther away from the grain boundaries themselves.

APPENDIX A

When a metal is immersed into an electrolyte and the potential of the metal is measured against a suitable reference electrode with respect to time, an open circuit potential will be achieved corresponding to the equilibrium condition between the metal, the electrolyte and the governing cathodic reaction. If the current between the metal and an inert platinum electrode is measured, the net current will be zero, also corresponding to the equilibrium condition. The open circuit potential measured is known as the corrosion potential, E_{corr} . However, if a potential E above or below the corrosion potential is applied, a net current will be observed corresponding to oxidation of the metal at the anode, or reduction of the hydrogen at the cathode (assuming this is the governing cathodic reaction). If a more noble or cathodic potential with respect to the open circuit potential is applied to the metal, the net current measured would rapidly increase. If the LOG of the measured current is plotted as a function of external potential E , a linear region is obtained away from the equilibrium open circuit potential. The equation describing this behavior is known as the Tafel Equation:

$$E = a + \beta \text{ LOG}(I)$$

where β is the slope of the line describing E as a function of $\text{LOG}(I)$.

The net current is the difference between the cathodic and anodic reaction currents:

$$I = I_c - I_a .$$

At $E = E_{\text{corr}}$, the net current is zero. Therefore, the corrosion current is simply

$$I_{\text{corr}} = I_c = I_a .$$

If the potential described by the Tafel equation is referenced to the corrosion potential, the Tafel equation for a single electrode process becomes

$$E - E_{\text{corr}} = \beta \text{ LOG } \left(\frac{I_{\text{a or c}}}{I_{\text{corr}}} \right) .$$

Solving for the electrode current (either anodic or cathodic),

$$I_{\text{a or c}} = I_{\text{corr}} \exp \left(\frac{2.3(E - E_{\text{corr}})}{\beta} \right) .$$

For the net current, the individual Tafel equations should be added:

$$I = I_{\text{corr}} \left[\exp \left(\frac{2.3(E - E_{\text{corr}})}{\beta_c} \right) - \exp \left(\frac{2.3(E - E_{\text{corr}})}{\beta_a} \right) \right] \quad [1]$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively.

AC electrochemical impedance spectroscopy can be applied about the corrosion potential E_{corr} in order to determine the charge transfer, or polarization resistance

$$R_p = \left(\frac{dE}{dI} \right)_{E = E_{\text{corr}}}$$

where dE/dI represents the slope of the line at, or near, E_{corr} . By applying a sinusoidal voltage about E , and measuring the impedance, we can determine the low-frequency AC (essentially DC) polarization resistance

Dividing-through Equation [1] by I_{corr} and taking the derivative of I with respect to E , the following equation is obtained:

$$\frac{1}{I_{\text{corr}}} \cdot \frac{dI}{dE} = 2.3 \exp(E - E_{\text{corr}}) \left(\frac{1}{\beta_c} - \frac{1}{\beta_a} \right) \quad [2].$$

At $E = E_{\text{corr}}$, Equation [2] becomes

$$\frac{1}{I_{\text{corr}}} \cdot \frac{dI}{dE} = 2.3 \left(\frac{1}{\beta_c} - \frac{1}{\beta_a} \right) \quad [3].$$

By assuming that the right-hand side of Equation [3] is a constant called $1/\Theta$, the corrosion current is

$$I_{\text{corr}} = \Theta \cdot \frac{dI}{dE} .$$

Since $dE/dI = R_p$,

$$I_{\text{corr}} = \frac{\Theta}{R_p}.$$

Therefore, as the polarization resistance increases, the corrosion current decreases.

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