Base Metal Microstructure Considerations For Aluminum Finishing

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Aluminum components tested and found to be conforming to design specifications may sometimes exhibit finish deficiencies after anodizing in a well controlled process in spite of different lots of conforming material (same alloy and temper) finishing well through the same process. The answer to the problem was found in the overlooked characteristic of microstructure. This paper examines the relationship between temper designations, microstructure, and the precipitation hardening process. Published data and results of a current study will be combined to show that although hardness and chemistry may classify a certain alloy and temper, this data can mask an overaged condition of the aluminum, rendering it not readily processable by standard anodizing. The reactions which occur during aluminum finishing will also be discussed.

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Introduction

Alloy Selection for Light Metal Components

Aluminum, Magnesium, Titanium and Beryllium are classified "light metals" as they are frequently used to reduce the weight of components and structures. The property of "lightness" is related to the relative density of the material, 2.7g/cm³ and 1.7g/cm³, for aluminum and magnesium respectively. Upon comparison to the density of other structural metals; 7.9 g/cm³ for iron and 8.9 g/cm³ for copper, it is easy to see why the "light metals" are the preferred materials in the transportation industry, most especially in the aerospace and defense industries where minimizing payload weight can reduce fuel consumption and decrease flight time, important economic considerations.

In addition to low density, aluminum exhibits a high strength to weight ratio, high corrosion resistance and electrical and thermal conductivities. Aluminum is easy to machine and its by-products are not toxic or pyroforic like those of beryllium and magnesium. It is also not as expensive as titanium. Aluminum, therefore, has become the material of choice for certain applications in the electronics and communications industries, specifically in thermal products: chassis, housings and heat sinks, in which all of the favorable characteristics of aluminum can be put into use.

The source for aluminum's inherent corrosion resistance is in its high surface reactivity. Aluminum oxidizes readily, producing a stable passive film. The thickness and uniformity of the film can vary, depending upon the conditions under which it has formed. Anodizing is one of the most common processes utilized today which imparts and controls a uniform oxide film of sufficient thickness to enhance corrosion resistance and maintain thermal conductivity. Both cast and wrought products can be anodized with variation in film thickness and quality depending upon chemistry and microstructure.

In the electronics and communications industries, cast aluminum is sometimes used for connector bodies and housings; however, most assemblies utilize sheet and/or extruded product. Since the focus of this paper is on the use of aluminum in thermal products (heat sinks), wrought products only will be considered.

Significance of Wrought Aluminum Alloy and Temper Designations

The IADS (International Alloy Designation System) alloy designation numbering system for aluminum assigns each wrought alloy a four digit number. The first digit is assigned on the basis of the major alloying element(s). The 1XXX series alloys are essentially unalloyed aluminum, with a 99% aluminum minimum. The 2XXX series alloys contain copper as their major alloying element. The 3XXX series, manganese; the 4XXX series, silicon; the 5XXX series, magnesium; the 6XXX series, magnesium and silicon; and the 7XXX series, zinc. The remaining digits indicate variations in the trace element constituents, and for the 1XXX series alone, minimum aluminum purity. Each class of alloys behaves differently, with composition and structure dictating the working characteristics and subsequent properties. Copper is normally added for strength, chromium to offset the loss of corrosion resistance because of copper additions. Iron is added as a dispersion hardening agent. Magnesium enhances corrosion resistance and silicon, strength.

As cast, aluminum is a soft metal. The high strength to weight ratio touted earlier as a favorable characteristic is achieved in certain aluminum alloys through its significant response to precipitation which occurs during age hardening. These alloys have 2XXX, 6XXX, and 7XXX series designations followed by the letter T with corresponding digits representing the treatment (tempering) sequence. Characteristic hardnesses are obtained through controlled tempering sequences by virtue of precipitation, making temper a specifiable attribute for engineering design. Other alloys, classified as non-heat treatable, derive their strength through strain hardening (various degrees of cold work). These alloys are designated with 1XXX, 3XXX and 5XXX followed by the letter H with corresponding digits representing the degree of cold work, also a specifiable attribute.

Aluminum Alloy 6061 T6 – Chemistry and Thermodynamics

The following case study deals specifically with aluminum alloy 6061 T6. The 6XXX series alloys are unique in that they incorporate two major alloying constituents, magnesium and silicon. The T6 temper indicates the material has been solution treated and artificially aged to a stable hardness of approximately 73 HB.

Review of the binary phase diagrams for the major alloy constituents for 6061; Al-Mg, Al-Si and Mg-Si, the ternary diagrams for Al-Mg-Si, as well as literature dealing with the 6XXX series alloys indicates the major solute intermetallic phase that forms is Mg₂Si. [1] Balanced amounts of magnesium and silicon are added to form quasi-binary Al – Mg₂Si alloys. [2,3] These alloys comprise the majority of aluminum extrusions and exhibit good weldability, corrosion resistance, typically anodize well and are immune to stress corrosion cracking. Alloy 6061 (Al – 1Mg – 0.6Si) contains 0.25% copper to improve strength and 0.2% chromium to offset any deleterious effects the copper may have on corrosion resistance. Like all of the 6XXX series alloys, the strength of 6061 is developed through precipitation (age) hardening.

Precipitation Hardening

Precipitation can best be described as decomposition of a supersaturated solid solution into its parent phase and excess rejected solute atoms. [4] The rejected solute atoms agglomerate to form a small crystal of their own, perhaps with a few solvent atoms dissolved in it, or react with some of the solvent atoms to form a phase with a crystal structure different from that of either pure metal (i.e. an intermetallic compound). The agglomerate is the precipitate. It enhances the hardness of the soft matrix by increasing local stress within the microstructure by restricting dislocation movement across the crystal.

Precipitation hardenable alloys are characterized by phase diagrams such as figure 1, the quasi-binary phase diagram for Al-Mg₂Si. The precipitation hardening process can be generalized as follows:

- 1. Solution treatment at a relatively high temperature within the single phase region to dissolve the alloying elements into the matrix.
- 2. Rapid cooling or quenching, usually to room temperature, to obtain a supersaturated solid solutin of these elements in the aluminum matrix.

3. Controlled decomposition of the supersaturated solid solution to form a finely dispersed precipitate, by ageing for appropriate times at one and sometimes two intermediate temperatures.



Figure 1: Pseudo-binary phase diagram for Al – Mg₂Si alloys. Precipitation sequence: GPZ(spheres) $\rightarrow \beta''$ (needles) $\rightarrow \beta'$ (rods) $\rightarrow Mg_2Si$ (platelets). [4]

The precipitation sequence involves the nucleation, growth and development of the equilibrium phase. Since precipitation is from a supersaturated solution, the driving force for the formation of the equilibrium phase is large, and is dependant upon the amount of undercooling achieved through quenching (the larger the undercooling, the larger the driving force). Nucleation is heterogeneous within the supersaturated solution because of the presence of quenched-in defects such as vacancies, dislocations and grain boundaries. The driving force for the heterogeneous nucleation of precipitates is therefore presented as the change in volume free energy due to strain, plus the surface free energy of the developing precipitates less the free energy of the defects which lower the free energy by providing surfaces for nucleation.

$$G_{het} = -V(\Delta G_v - \Delta G_s) + \gamma_A - \Delta G_d \qquad (1)$$

The process involves the transition through intermediate phases originating with the nucleation of Guinier-Preston (GP) zones. GP zones are ordered, solute-rich clusters of atoms which retain the structure of the matrix and are coherent with it. Because of the coherent nature, they have a lower interfacial energy that the equilibrium phase. Mondolfo [2] indicated for the 6XXX series alloys that the GP zones are spherical, which also reduces the lattice misfit strain. The reduced strain reduces the barrier to nucleation for the GP zones and they form prior to the intermediate phases which simultaneously:

- a) have higher interfacial energy, and
- b) require additional energy for solute interdiffusion.

This latter requirement is more prevalent in the 6XXX series alloys than in any other aluminum alloy as they require the activation energy to form the equilibrium intermetallic phase Mg₂Si.

After the formation of the spherical GP zones, the intermediate phases precipitate. For the 6XXX series alloys, the precipitation sequence leading to the equilibrium phase, $AI - Mg_2Si$, is preceded by the formation of intermediate phases β'' and β' . In describing the precipitation sequence, Mondolfo indicated that the GP zones elongate in the [100] direction. The intermediate phase, β'' , has a monoclinic structure and a needle-like shape. The structure contains a large number of vacancies and exerts a compressive force on the matrix. The corresponding stress developed through this force increases the hardness of the alloy.

The β'' needles grow to become the next intermediate phase, β' , which have a rod-like shape. β' is semicoherent with the matrix and has a cubic or hexagonal lattice. The departure from coherency increases the compressive force on the matrix, further increasing the hardness of the alloy. Peak hardness is reached just before the Mg₂Si platelets (equilibrium phase) form. The equilibrium phase nucleates at the β' - matrix interface and grows at the expense of the intermediate phase.

The activation energy for the formation of GP zones is reported as 0.37eV; for precipitation, 0.9eV. Heat evolution corresponding to the formation of the various intermediate phases is also reported [2]. These trends show the intermediate transitions that occur during precipitation rather than direct transformation to the equilibrium phase are the result of the lower activation energy barriers for each step. Transformation stops when the minimum free energy equilibrium state of Mg₂Si is reached. See Figure 2.



Figure 2: a) The activation energy barrier to the formation of each transition phase $(\beta \rightarrow \beta'')$ is very small in comparison to the barrier against the direct precipitation of the equilibrium phase (Mg₂Si). b) Schematic diagram showing the total free energy of the alloy vs. time. [4]

A definite increase in hardness can be related to the nucleation of GP zones and the progressive precipitation of the needles to rods, and rods to platelets. A decrease in hardness is noted after the formation of the equilibrium phase. Since the increase in hardness is related to the growth of the precipitate phase into the equilibrium phase, and since transformation ceases upon formation of the equilibrium phase. Some the related to the continued growth, not transformation, of the equilibrium phase.

Precipitate Coarsening

Although completion of the precipitation to the equilibrium phase achieves the minimum free energy of the transformation, instability within the matrix persists because the total interfacial free energy is not at a minimum. Therefore, the high density of smaller equilibrium precipitates from the initial transformation will continue to coarsen into a lower density of larger equilibrium precipitates to minimize the total interfacial area. [4] The precipitate coarsening produces the decrease in hardness. Dislocation pinning effectiveness (the resistance of the crystal to deformation because of the presence of dislocations within the crystal structure) decreases with the decrease in precipitate population. For the precipitation hardenable aluminum alloys, precipitate coarsening will decrease the corrosion resistance and therefore increase the alloy's susceptibility to chemical attack because of increased capillarity at the precipitate-matrix interface. See figure 3.



Figure 3: Schematic of property changes during aging of aluminum-magnesium silicide alloys. [2]

Because of differences in the time of nucleation and rate of growth of the precipitates, a tempered specimen will exhibit a range of particle sizes. Although precipitates within the tempered specimen are at the same temperature and have identical structures and compositions, they have different chemical potentials because of their different sizes. The solute concentration gradient in the matrix adjacent to a precipitate will increase as the radius of precipitate curvature decreases. This is expressed in Thomson's equation and the effect is known as Ostwald Ripening.[4]

$$(\mu_i)_{r'} - (\mu_i)_{r''} = V_i 2 \nu (1/r' - 1/r'') \qquad (2)$$

The higher chemical potential in the smaller precipitates causes diffusion in the direction of the largest precipitates, away from the smaller precipitates. Therefore, the smaller precipitates shrink and disappear while the larger precipitates grow or "ripen". The inverse relationship between the surface energy and the precipitate radius shows the relative instability of the smaller precipitates and therefore the driving force for particle coarsening. Because the reaction is diffusion controlled, the rate of coarsening will increase with increasing temperature.

Excessive coarsening occurs during heat treatment when the material is allowed to "over-age" or spends too much time at temperature during the precipitation hardening process. In addition to coarsening, the precipitates tend to move by way of solid state transport, through the matrix material to the grain boundaries, where the intrinsic energy of the crystal is lower. This further reduces the corrosion resistance of the alloy by creating tiny galvanic cells between the grain boundaries and the matrix material, a condition known as "sensitization" (see figure 4).



Figure 4: Optical photomicrograph of a sensitized 6061-T6 microstructure (X400 - etchant: Tucker's reagent).

Anodizing Aluminum

Under typical atmospheric conditions, a native oxide or passive film naturally forms on aluminum. The native oxide layer is nonuniform, thin and noncoherent. Nevertheless, the native oxide film imparts a certain level of corrosion protection, provided the environment contains no unusual contaminants. Exfoliation, the formation of a network of oxide flakes or "leaves" on the aluminum surface is an example of how corrosion of the surface can be changed through the introduction of sulfur to the environment. In fact, removing sulfur from the atmosphere can control the exfoliation of aluminum [5-7].

Anodizing can be viewed as the deliberate, controlled corrosion of the aluminum surface in sulfuric acid to yield a uniform, continuous protective oxide film. By adjusting the electrolyte chemistry and the oxidation parameters of time and temperature, various types of anodic finishes are achieved. Type I, or chromic acid anodizing has a distinctly different microstructure than Type II, or technical anodizing, than Type III, or hard anodizing. Its unique columnar structure has been extensively studied, and a mechanism for the anodic oxidation of aluminum is presented herein based on intensive microstructural and chemical analyses of various types of anodized aluminum coatings. The results provided increased insight regarding the mechanism for anodic film formation as well as its resultant chemistry.

Surface Reconstruction

A comprehensive thermodynamic treatment of chemisorption, which precedes surface oxidation, is presented in Murr [8]. It is important to note that the resultant "infant" oxide layer begins at nucleation sites that may have a preference for certain crystallographic surface orientations as well as surface structural features such as dislocations, steps, or ledges. Temperature impacts nucleation such that fewer preferential sites will form at lower temperatures. On the molecular level, it has been shown that grain boundaries, inclusions and other forms of surface contamination will also impact the initiation of the oxidation reaction [9].

It is at this point in the anodizing reaction that the presence of coarse precipitates will interfere with finish formation. The increase in point-to-point surface resistance caused by the difference in chemical potential between the precipitate and the matrix can alter the level of chemical attack by the electrolyte as well as the corrosion mechanism (exfoliation) that normally sustains anodic oxide nucleation and growth. Typically, if the defects are small enough, the reaction will occur around the precipitates and the precipitate will be included in the finish (see figure 5).

If the microstructural defects are coarse enough, as in the case of overaged material, the grain boundaries will exhibit preferential attack during pretreatment. Anodizing heavily etched material will accentuate, rather than mask the condition, often yielding an unacceptable appearance.



Figure 5: TEM photomicrograph of anodic oxide finish on a 6061 T6 substrate. Arrow indicates a cluster of point defects which disrupted uniform formation of the anodic oxide finish.

Case Study

The Effects of Substrate Microstructure on the Anodic Finish

Several samples of black anodized alloy 6061 T6 extruded aluminum heat sinks were submitted to determine the nature and cause for a surface condition identified as "smut". See figures 6 and 7. The heat sinks were anodized following Type II anodizing procedures; from an electrolyte of approximately 14% sulfuric acid (180g/l H_2SO_4), at room temperature (20°C) for 1 hour.

The 6061 T6 substrates were subjected to chemical analysis and hardness testing and found to be in compliance with material specifications. Scrutiny of the anodizing process found all aspects of the process under control. Other material similarly tested and found compliant from different tempering lots reportedly processed well.



Figure 6: Documentary photograph of heat sinks which exhibited unacceptable surface condition.



Figure 7: High magnification (X100, as processed surface) documentary photograph of anodized surface of heat sinks. Note the high level of grain boundary relief evident even through the black anodized surface finish.

Comparative analysis of the surface and bulk microstructures of heat sinks that exhibited the "smut" (bad) and that did not exhibit "smut" (good) was performed. The results determined samples which exhibited smut exhibited a microstructure with coarse, intergranular precipitates. Those which processed well exhibited comparable grain size but exhibited finer, more well dispersed precipitates. See figure nos. 8 - 10.

The measured similarity in base metal hardness for good and bad samples coupled with the distinct differences in microstructure indicated the substrate aluminum supplied to manufacture the heat sinks had been overaged during heat treating to a point where hardness identical to a T6 temper was achieved. Unfortunately, exposure of the coarser microstructure to the anodizing process parameters produced large intergranular pits in the aluminum surface. The columnar microstructure of the anodized film could not properly form across the pits, producing a discontinuous structure. The discontinuous structure retained anodizing solution which wept out as the components dried, producing the observed "smut".



Figure 8: Microstructure of "bad" appearing heat sinks exhibits coarse intergranular precipitates as well as high concentrations of dislocation pits across the matrix surface (X400 – etchant: Tucker's reagent).

Recommendations were made to the metal finisher of the heat sinks to return any unprocessed 6061 T6 material from the overaged lot for re-solution treatment and proper tempering. Unfortunately, all of the material had been processed. However, a routine analysis program was begun to verify the microstructure of incoming extrusions prior to anodizing as well as the chemistry and hardness.



Figure 9: Anodized finish on "bad" appearing heat sink exhibits a lack of continuity across deep scallop-shaped etch pits (X400 – etchant: Keller's reagent)



Figure 10: Anodized finish on "good" appearing heat sink. Note the continuity of the finish. Microstructure exhibits precipitation characteristic for quality aged material. (X400 – etchant: Keller's reagent)

Conclusion

The light metals, especially aluminum, fill an important niche in the transportation, electronics, and communications industries. For the precipitation hardenable alloys, many of the desirable characteristics of the light metals are obtained through heat treatment. As with any material, it is necessary that subsequent processing be well controlled such that the resultant material characteristics derived through that process is what are intended and desired. Understanding the metallurgical aspects of the material history, which for this case study were heat treatment and finishing, can optimize finish product quality and expedite failure analysis in the event of a defect.

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