

QUENCHING FUNDAMENTALS

QUENCHING OF ALUMINUM ALLOYS: COOLING RATE, STRENGTH, AND INTERGRANULAR CORROSION

Cooling time-temperature data are not routinely shown, and correlations of cooling rate data, strength, and intergranular corrosion with either residual stress or distortion are rarely reported together. This article addresses this issue.

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Aluminum is solution treated at temperatures generally in the range of 400 to 540°C (750 to 1000°F). During solution treatment, some alloying elements are re-dissolved to produce a solute-rich solid solution. The objective of this process is to maximize the concentration of hardening elements including copper, zinc, magnesium, and (or) silicon in the solid solution. The concentration and rate of dissolution of these elements increases with temperature. Therefore, solutionizing temperatures are usually near the liquidus temperature of the alloy^{1,2}.

If an aluminum alloy is slowly cooled from an elevated temperature, alloying elements precipitate and diffuse from solid solution to concentrate at the grain boundaries, small voids, on undissolved particles, at dislocations, and other imperfections in the aluminum lattice as shown in Fig. 1². For optimal properties, it is desirable to retard this diffusion process and maintain the alloying elements in solid solution. This is done by quenching from the solution temperature. For

quench-hardenable wrought alloys (2xxx, 6xxx, and 7xxx) and casting alloys such as 356, this is accomplished by the quenching process. The objective is to quench sufficiently fast to avoid undesirable concentration of the alloying elements in the defect and grain boundary structure while at the same time not quenching faster than necessary to minimize residual stresses, which may lead to excessive distortion or cracking. After quenching, aluminum alloys are aged, and during this process, a fine dispersion of elements and compounds are precipitated that significantly increase material strength. The diffusion process and precipitation kinetics vary with the alloy chemistry.

The cooling process of age-hardenable aluminum alloys not only affects properties such as strength and ductility, but it also affects thermal stresses. Thermal stresses are typically minimized by reducing the cooling rate from the solutionizing temperature. However, if the cooling rate is too slow, undesirable grain boundary precipitation will result. If the cooling rate is too

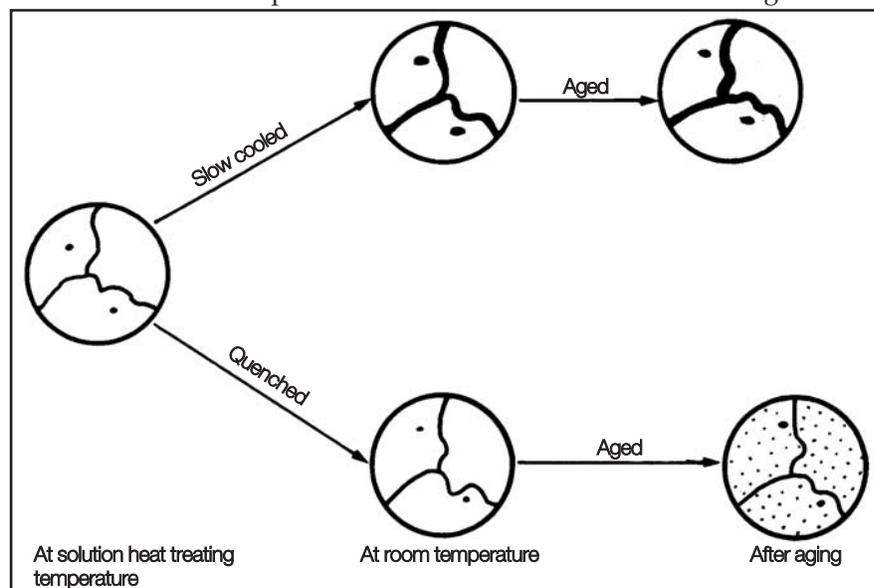


Fig. 1 — Schematic illustration of the solid diffusion processes that may occur during solution heat treatment of aluminum.

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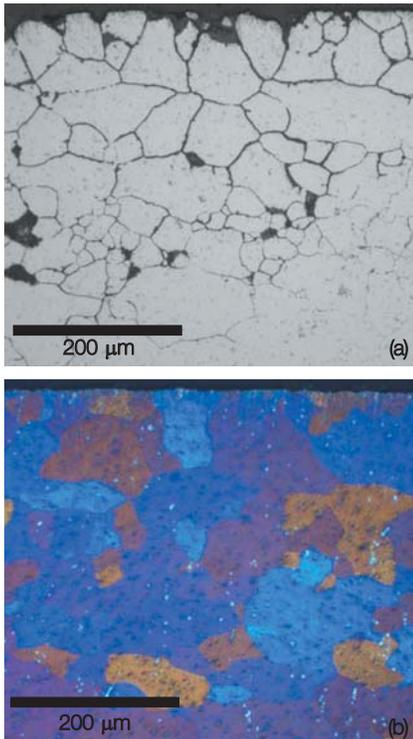


Fig. 2 — Sample cross section after corrosion test illustrating intermetallic deposition in the grain boundaries in the surface region (a); Microstructure of sample cross section (b). Corrosion testing according to BS ISO 11846:1995 method B. Sample material is a model AlMgSi aluminium alloy (6000 series) extruded using a research extrusion press with a reduction ratio of 34:1. Sample dimensions = 78 × 2.7 mm. Source: G. Svenningsen, Norwegian University of Science and Technology, Trondheim, Norway.

fast, there is an increased propensity for distortion. Therefore, one of the primary challenges in quench-process design is to select quenching conditions that optimize strength while minimizing distortion, and at the same time ensure that other undesirable properties are not obtained, such as intergranular corrosion, which is also cooling rate dependent.

Bates and Totten have addressed the selection of quenchant and quenching conditions that will optimize material strength and minimize the potential for distortion^[3]. However, although it is well-known that properties such as corrosion resistance are also cooling rate dependent, the problem of quenching system evaluation with respect to strength, distortion, and corrosion are rarely evaluated together. The objective of this article is to provide an overview of intergranular corrosion (IGC) of aluminum alloys and to illustrate the effect of cooling rate on both strength and IGC.

Pitting and Intergranular Corrosion

Pitting is the most common corrosion process encountered with aluminum alloys, and is a major cause in variations in the grain structure between adjacent areas on the metal surfaces in contact with a corrosive environment. Pitting results in the formation of very small holes (pits) in the surface, which are covered by white or gray powder-like deposits appearing as blotches on the surface^[4].

Intergranular (intercrystalline) corrosion occurs most commonly in the following aluminum alloys: Al-Cu-Mg (2xxx); Al-Mg (5xxx), which is similar to the Al-Cu-Mg alloys; Al-Mg-Si (6xxx); and Al-Zn-Mg-Cu (7xxx)^[5,6].

(The 2xxx, 6xxx, and 7xxx series are heat treatable). IGC refers to a selective dissolution of the surface grain-boundary zone, and typically, the grains below the surface zone are not attacked (Fig. 2). As discussed above, upon cooling from the solutionizing temperature, alloying elements may concentrate at the grain boundaries to form intermetallic compounds that differ electrochemically from the adjacent matrix and the metal adjacent to the grain boundaries^[7,8].

The critical temperature range and time (s) for the transition of pitting to intergranular corrosion is shown by the so-called TTP (time-temperature-property) or C-curve illustrated in Fig. 3^[9]. The C-curve for 2024-T4 shows the change in corrosion behavior by correlating the critical temperature range where precipitation was fastest. Increased intergranular corrosion for 2024-T4 will be favored if cooling rates are excessively slow during quenching. Similar behavior can be shown for other aluminum alloys. Therefore, it is important that cooling rates during quenching be sufficiently fast to avoid this undesirable behavior.

As the IGC process continues, exfoliation will result, which refers to the lifting of the surface grains caused by expansion due to increasing volume of the corrosion products accumulating in the subsurface grain boundaries^[10]. It has been reported that exfoliation results in severely reduced structural strength, plasticity, and fatigue. Exfoliation in aircraft aluminum alloy structural materials is most often observed with extrusions, where the grain thicknesses are often less than the rolled forms^[4].

Electrochemical Behavior of IGC Processes

IGC is caused by the formation of a microgalvanic cell between the intermetallic compounds formed in the grain boundary during cooling and the adjacent metal. These intermetallic compounds may be either anodic or cathodic, with respect to the adjacent metal, depending on their composition. Figure 4 illustrates these two situations^[11]. In one case, noble (inactive) alloying elements may precipitate in the grain boundaries leaving a depleted zone adjacent to the grain boundary, which is electrochemically active (Fig. 4a). Conversely, electrochemically active alloying elements may precipitate at the grain boundary, and then the metal adjacent to the

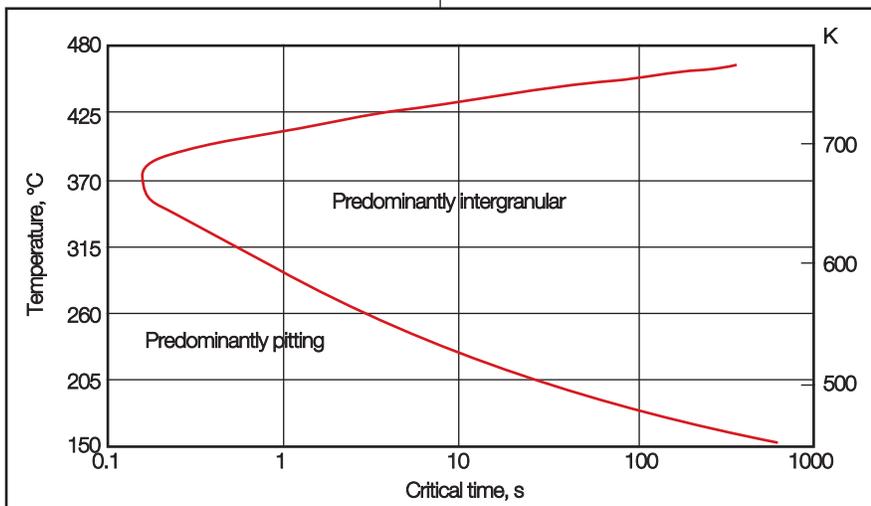


Fig. 3 — Curve indicating cooling rate dependent mechanism of corrosion attack on aluminum alloy 2024-T4 sheet.

grain boundary will be noble (Fig. 4b). Note that corrosion behavior has also been shown to be due to microstructural changes from the heat treatment process, which will not be discussed here. The reader is referred to Reference 12 for more detailed discussion.

To illustrate this process, consider IGC occurring in 2xxx or 7xxx alloys that would be caused by the loss of copper or sufficient magnesium in areas near the grain boundaries to create an anodic electrochemical potential. The electrochemical potential (referred to as electromotive force, or EMF) for various aluminum alloys provided in Table 1 shows that the presence of copper in solid solution with aluminum makes it more cathodic^[13]. The cathode is the positive electrode in an electrochemical circuit, and, therefore, it is the electrode that gains electrons or electrons flow from the anode (which possesses the more negative potential) to the cathode (more positive potential). An aluminum alloy containing 4% copper in solid solution has an EMF of -0.69 V. However, copper concentrations in the grain boundaries may reduce the EMF to -0.84 V, making it more anodic. Grain boundary corrosion may also occur when the grain boundary precipitates are more anodic than the adjacent solid solution. For example, Mg₂Al₃, MgZn₂ and Al_xZn_xMg are more cathodic than CuAl₂ and Al_xCu_xMg^[14]. When two dissimilar metal compounds with different electron affinities (EMF values) are connected, there is a potential for electrons to pass from the material with the smaller affinity for electrons (anode – the more negative pole) to the material with the greater affinity for electrons (cathode – the more positive pole). A potential difference between the materials will increase until equilibrium is achieved. This equilibrium potential is defined as the potential that balances the difference between the propensity of the two metals to gain or lose electrons.

IGC Control

The degree of IGC may be controlled by the selection of the temper and maximizing the cooling rate that will provide minimum distortion. For example, the T4 and T6 temper conditions are typically selected when optimum resistance to IGC is required^[15]. Schuler reported that the critical cooling rates (cooling rates between 750 and 550°F) for the 7xxx series to be <400°F/s and 1000°F/s for the 2xxx se-

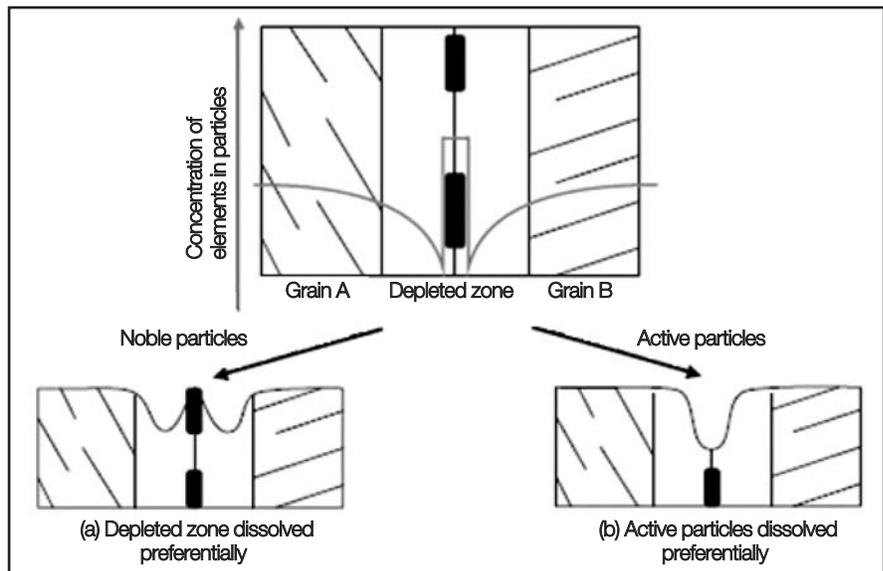


Fig. 4 — Illustration of two potential IGC processes.

Table 1 — Electrode potentials of aluminum solid solutions and constituents

Solid-solution composition	Potential, V (0.1 N Calomel Scale) ¹
α (Ag-Mg) (Mg ₅ Al ₈)	-1.24
Al + Zn+Mg (4% MgZn ₂ Solid Solution)	-1.07
Al+Zn (4% Zn Solid Solution)	-1.05
β (Zn-Mg)(MgZn ₂)	-1.05
Al+Zn (1% Zn Solid Solution)	-0.96
Al+Mg (7% Mg Solid Solution)	-0.89
Al+Mg (5% Mg Solid Solution)	-0.88
Al+Mg (3% Mg Solid Solution)	-0.87
α Al-Mn (Mn-Si ₆)	-0.85
Aluminum (99.95%)	-0.85
Al+Mg+Si (1% MgSi ₂)	-0.83
Al+Si (1% Si Solid Solution)	-0.81
Al+Cu (2% Cu Solid Solution)	-0.75
(Al+Cu) (CuAl ₂)	-0.73
Al+Cu (4% Cu Solid Solution)	-0.69
α (Al-Fe)(FeAl ₃)	-0.56
NiAl ₃	-0.52
Silicon	-0.26

1. Measured in an aqueous solution of 53 g NaCl + 3 g water per liter at 25°C. [The order of the EMF values in the table indicates the ability of a compound to reduce any compound metal below it. The values are reduction potentials. The α (Ag-Mg) (Mg₅Al₈) compound at the top of the list has the most negative number, which indicates that it is the strongest reducing agent in the series shown. The strongest oxidizing agent is silicon with the least negative (most positive) EMF potential.] Source: Ref 1.

ries to achieve optimal resistance to IGC. The data in Table 2 show the effect of cooling rate on IGC for 50 mm AA7075 round bar^[16]. The depth of attack was consistently greater toward the center of the round bar as the cooling rate decreased.

Other factors affecting IGC include transfer rate from the furnace to the quench, air entrainment in the quench, and the ratio of section mass/surface area. However, these factors, in the final analysis, affect cooling rates, and, therefore, IGC.

At this point, it is important to note

that often in the industry, cooling behavior of various quench media is determined using an Inconel 600 probe

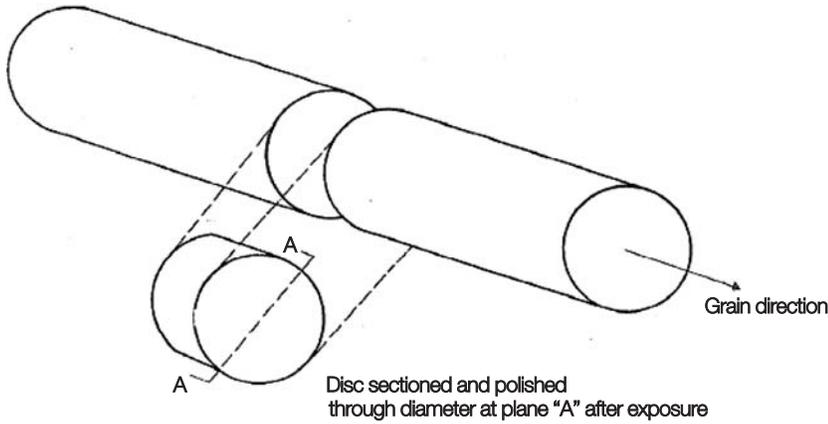


Table 2 — Effect of cooling rate on maximum intergranular penetration of 7075 as a function of cooling rate

Sample ID	Cooling rate, °C/s (50 mm diam bar)	Location(a)	Depth of attack, mm
A	53	Surface	0.46
		Center	0.56
B	50	Surface	0.30
		Center	0.86
C	30	Surface	0.46
		Center	0.61
D	17	Surface	0.74
		Center	1.09

(a) Surface: within 3.2 mm of cylinder surface. Center: within 3.2 mm of centerline of the cylinder. Source: Ref 16.

Table 3 — Thermal conductivity and specific heat capacity for different materials

Material	Thermal conductivity, m ² s ⁻¹	Specific heat, kJ kg ⁻¹ K ⁻¹
Aluminum 99.5	95 × 10 ⁻⁶	0.896
Silver 99.5	174 × 10 ⁻⁶	0.235
Nickel	14 × 10 ⁻⁶	0.448
CrNi Steel(a)	4 × 10 ⁻⁶	0.477
Inconel 600(b)	4 × 10 ⁻⁶	0.465

(a) Austenitic stainless steel SAE 30304. (b) Nickel based alloy.

according to ISO 9950 or ASTM D6200. However, the thermal conductivity of Inconel 600 is much less than that of aluminum as shown in Table 3^[17]. Clearly, the low thermal conductivity of Inconel 600 versus aluminum renders this probe to relatively insensitive to the cooling properties experienced by an aluminum alloy during quenching.

Silver probes are also used to evaluate quench severity exhibited by different quenchants. Because of the similarity of the thermal characteristics of silver and aluminum, and because of the significantly lower oxidation tendency for silver relative to aluminum, the cooling behavior of AlMgSiCu and a silver (99.5%) probe was compared^[17].

Thermal conductivity (λ) and specific heat capacity of various materials are provided in Table 3. Thermal conductivity is a measure of the rate of propagation of temperature change in a body and is related to the specific heat capacity by:

$$\alpha = \frac{\lambda}{\rho \times C_p}$$

where α is thermal diffusivity, C_p is specific heat capacity, λ is thermal conductivity, and ρ is density of the material.

Tensi, et. al., compared cooling curves recorded during quenching of an aluminum (AlMgSiCu) and a silver specimen (Ag 99.5) in a Type I water-soluble polymer quenchant solution. The Type I aqueous polymer quenchant concentration was 10% by volume and the bath temperature was 25°C. The temperature of both probe materials when quenched was 520°C. Both probes were cleaned with 600 grit abrasive paper before each test. The cooling curves obtained are shown in Fig. 5.

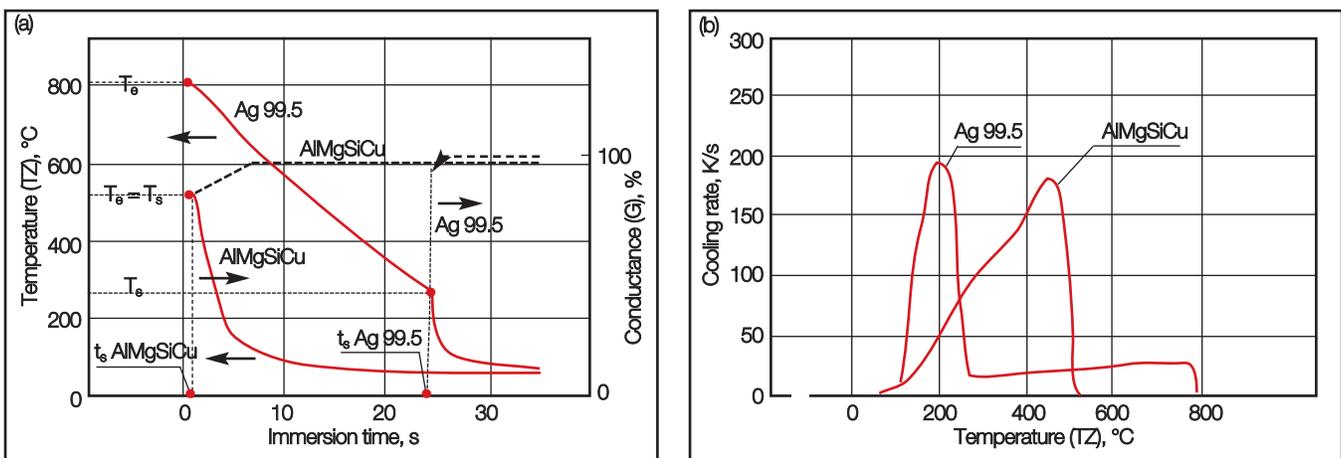


Fig. 5 — Comparison of the cooling processes of a cylindrical AlMgSiCu probe (15 mm diam. × 45 mm) with those of a silver probe; cooled into a 10% solution of a water-soluble polymer at 25°C (temperatures recorded at the geometric center of the probe); solution treating temperature is 520°C for the AlMgSiCu probe; annealing temperature is 800°C for the silver probe; (a) changes in temperature and conductivity as a function of time; (b) cooling rate as a function of temperature.

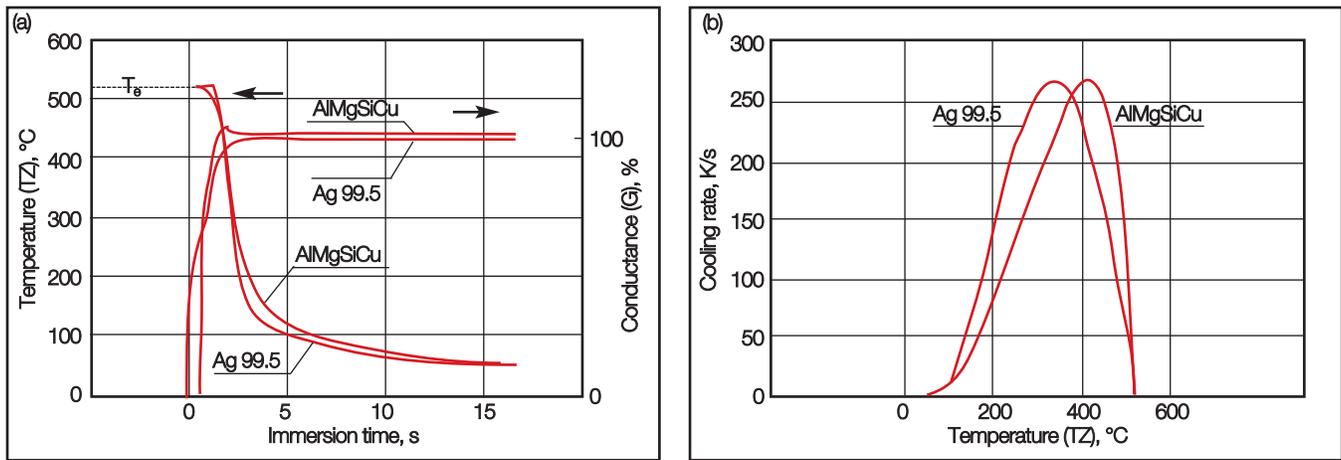


Fig. 6 — Comparison of cooling processes of a cylindrical AlMgSiCu probe (15mm diam x 45mm) with those of a silver probe; probes quenched into distilled water at 25° (probe temperatures recorded at the geometric center); solution treating temperature is 520°C for the AlMgSiCu probe; annealing temperature is 520°C for the silver probe; (a) changes in temperature and conductivity as a function of time; (b) cooling rate as a function of temperature.

The polymer film surrounding the probe surface ruptured simultaneously around the entire surface, also called explosive rewetting, for both probes, and the rewetting times ($t_f - t_s$) were extremely short. However, a stable film-boiling range lasting about 4 s was observed for the silver probe, which was not observed for the aluminum probe. The centerline probe temperature was about 440°C for silver and 500°C for aluminum. The reason that the rewetting of the silver occurs about 4 s later for the silver probe is the greater oxidation resistance of silver. Initially, the presence of surface oxidation will facilitate film rupture, thus enhancing the boiling process. In this case, sufficient oxidation had not yet occurred on the surface of silver relative to aluminum, thus there was a 4s delay in the rewetting process for silver. (The ratio of heats of formation of Ag_2O_2 and Al_3O is 0.05.) When the quenching temperature of the silver probe is increased to 800°C, considerable stabilization of the film-boiling occurs as observed in Fig. 5a. Wetting now starts at about 260°C after 24 s compared with the start of wetting of the AlMgSiCu probe after 1 s at about 500°C.

The main reason for this stabilization of the film-boiling phase of the entire surface of the silver probe is the reduction of the silver oxide at the higher temperature. The high-temperature annealing of the silver probe removes the oxide and leaves a bare metal surface, resulting in stabilization of film boiling during quenching, especially in water-soluble polymers. Accordingly, the maximum cooling rate of the silver probe is not reached until a centerline probe temperature

of 200°C as shown in Fig. 5b.

If distilled water at room temperature is used as the quenchant instead of an aqueous polymer, the silver and the AlMgSiCu probes show almost identical cooling behavior with coinciding rewetting kinematics as shown in Fig. 6. This means that the quenching behavior determined in water with silver probes can be safely compared with those obtained for aluminum probes. However, when polymer solutions are used, there are clear differences, especially with respect to initial wetting.

It is important that whatever probe material is used to evaluate quenching behavior to be expected with the aluminum alloy of interest, it should properly model the actual quenching process occurring, especially if cooling rate dependence of the quenching media and process is being used to determine the potential for IGC. For these reasons, it is recommended that heat treaters request cooling curve data obtained using either an aluminum or silver probe. (The advantage of silver relative to aluminum is its inertness and therefore it may be reused, whereas aluminum alloy probes typically cannot.)

Conclusions

An overview of the IGC process was provided and contrasted to pitting corrosion. It was shown that the propensity for IGC of heat treatable aluminum alloys is cooling rate dependent. It is recommended that in view of IGC processes in many applications such as aerospace and automotive, that IGC should be evaluated along with strength and residual stress/distortion as important and more routine screening parameters

The propensity for IGC of heat treatable aluminum alloys is cooling rate dependent. It is recommended that in view of IGC processes in many applications such as aerospace and automotive, that IGC should be evaluated along with strength and residual stress/distortion as important and more routine screening parameters than is now performed.

than is now performed. Furthermore, cooling time-temperature data is preferably obtained using the aluminum alloy of interest. However, silver probes may, under the appropriate conditions, reasonably model the cooling behavior of the aluminum alloy of interest, but this needs to be demonstrated experimentally. **HTP**

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