External electric field applied during solution heat treatment of the Al-Mg-Si alloy AA6022

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The application of an external dc electric field $E = 5$ kV/cm during the solution heat treatment (SHT) of AA6022 at 475–552°C increased the as-quenched resistivity. An increase continued throughout subsequent natural aging, and there occurred an increase in the tensile properties for the T4 temper. The increase in yield and tensile strength produced by the electric field applied during the SHT is equivalent to a reduction of 10–25°C in the SHT temperature. A thermodynamic analysis of the results indicated that the field reduced both the enthalpy ΔH_s and entropy ΔS_s of solution, giving a reduction in Gibbs free energy ΔG_s, and in turn an increase in solubility of the alloying constituents.

1. Introduction

Prior studies [1–4] have reported that the application of an external dc electric field during the solution heat treatment (SHT) of Al-Cu-Mg and Al-Li alloys gave an increase in the *apparent* solubility of the alloying constituents as measured by resistivity. As a corollary the field thereby reduced the temperature for a given resistivity (i.e., for a fixed amount of solute in solution), the reduction being as much as 60°C [1]. Similar effects of an electric field were obtained by the present authors [5] for the Al-Mg-Si-Cu AA6111 alloy employing both resistivity and hardness measurements. The results indicated that an electric field of 5 kV/cm applied during the SHT of this alloy at 500 to 550°C reduced both the enthalpy ΔH_s and entropy ΔS_s of solution, giving a reduction in the Gibbs free energy ΔG_s and in turn an increase in solubility of the alloying constituents.

The objective of the present study was to investigate further the influence of an electric field applied during the SHT of commercial Al-Mg-Si alloys, which are of interest to the automotive and aerospace industries. The alloy employed in this investigation was a AA6022, which has a significantly lower Cu and Mg content, and a higher excess Si content compared to AA6111. Also considered here is the influence of the field applied during SHT on the tensile properties obtained upon subsequent room temperature (RT) aging to the T4 temper. For purposes of comparison, pertinent results on the AA6111 alloy are included in the present paper.

2. Experimental

The starting material was 0.9 mm thick AA6022 alloy sheet in the T4 temper (room temperature aged) provided by Alcoa Research Center with the following *nominal* composition in wt%. Included for comparison is the composition of AA6111.

Alloy	Si	Fe	Cu	Mn	Mg	Other (Max.)	Mg_2Si	Excess[a]
AA6022	0.8–1.5	0.05–0.20	0.01–0.11	0.02–0.10	0.45–0.70	0.25 Ti 0.25 Zn 0.10 Cr	0.71–1.0	0.54–1.10 Si
AA6111	0.54	–	0.67	0.22	0.89	N.A.	1.40	0.03Si

[a]Excess over that required to form Mg_2Si.

ASTM standard tensile specimens with a 1.2 cm wide × 5.1 cm long gage section had been machined from the sheet with the tensile axis in the rolling direction. The specimens were SHT in air for 10 min at 475–552°C without and with a nominal external dc electric field $E = 5$ kV/cm and then quenched in still water. A schematic of the electrical arrangement for applying the field is shown in Fig. 1. The specimen in all cases was connected to the positive terminal of the power supply. This is indicated in the manuscript by a (+) sign following the magnitude of the field strength. The nominal electric field was taken to be the applied voltage $V = 3.5$ kV divided by the distance $x = 0.7$ cm between each parallel stainless steel electrode and the specimen. The measured electric current ranged between 1.5 and 3.0 mA, increasing with increase in SHT temperature.

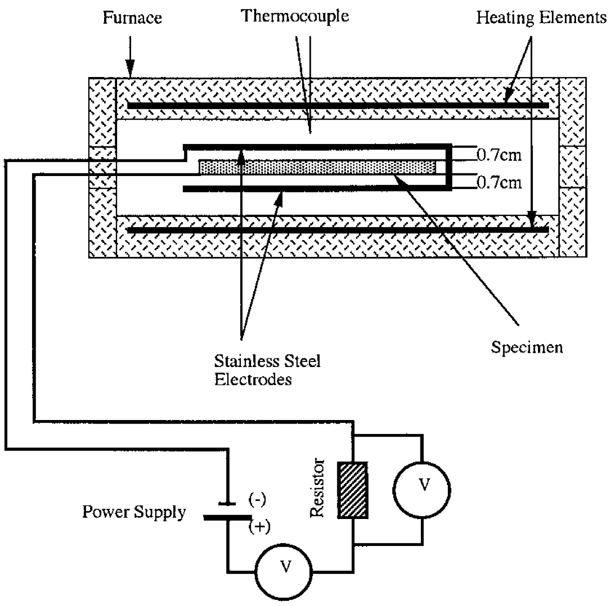

Figure 1 Schematic of the electrical arrangement.

Electrical conductivity (Σ) measurements using an AutoSigma Model 3000 DL meter were made every 4 cm along length of the tensile specimens (6 measurements) within 2 min following the quench and after aging for various times at RT. Reported is the average resistivity $\rho = (\Sigma)^{-1}$ for the measurements, with a scatter of $\pm 1.5\%$. After the specimens had aged at RT for one week (T4 temper), they were tested in tension using an Instron machine at an initial strain rate $\dot{\varepsilon}_o = 3.3 \times 10^{-4}\ \text{s}^{-1}$.

3. Results

The effect of the field applied during SHT on the resistivity ρ_w of the as-quenched specimens is shown in Fig. 2. An increase in ρ_w with application of the field occurred for each SHT temperature T_{SHT}. As shown, the increase in ρ_w with field is equivalent to a decrease ΔT_{SHT} of $\sim$12°C for a constant resistivity. This value of ΔT_{SHT} is only about one-half that which occurred for AA6111 (20–25°C) with regard to ρ_w [5].

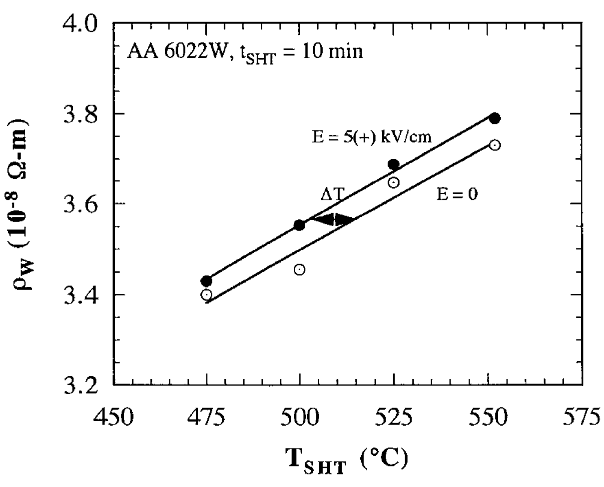

Figure 2 As-quenched resistivity ρ_w vs. solution heat treatment temperature T_{SHT} for tests without and with electric field.

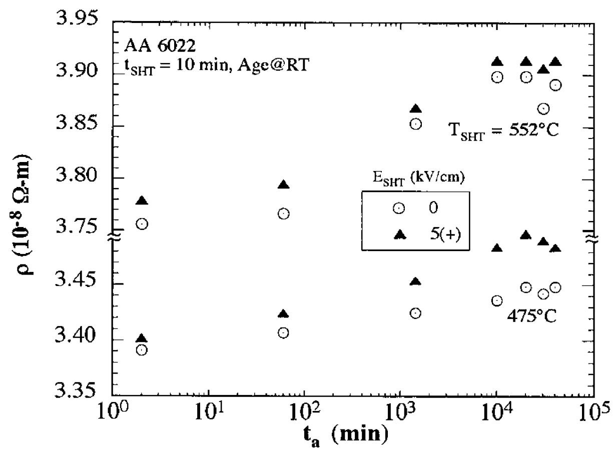

Figure 3 Resistivity ρ vs. log aging time t_a for solution heat treatments at 475 and 552°C without and with electric field.

Fig. 3 plots resistivity ρ vs. log aging time at *RT* for SHTs at 475 and 552°C without and with electric field. To be noted is that an increase in resistivity produced by application of the field during SHT occurs throughout the aging process. The prior field treatment does not appear to have a significant influence on the kinetics of the aging process given by the time to reach the maximum resistivity ρ_{max}. However, the increase in ρ_{max} due to the field for the SHT at 475°C is larger than that at 552°C.

Fig. 4 shows the influence of the electric field applied during SHT on the tensile properties following aging for 2 weeks at room temperature (T4 temper). It is seen that the electric field treatment increased all three tensile properties, namely the yield strength, tensile strength

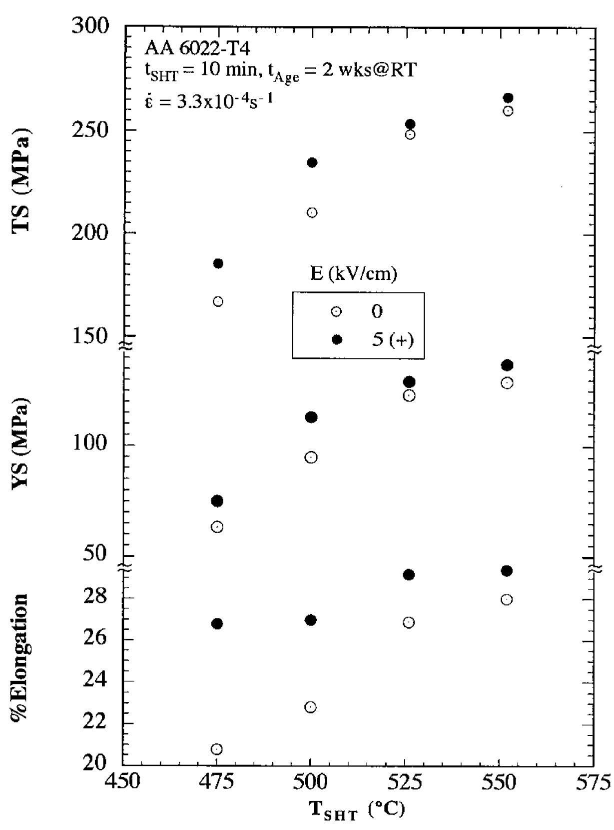

Figure 4 Tensile properties in the T4 temper following solutionizing at 475 to 552°C without and with electric field.

and percent elongation. Again, the magnitude of the effect decreased with increase in T_{SHT}. The parabolic nature of the curves for the yield strength and tensile strength give an equivalent reduction ΔT_{SHT} of $\sim$10°C at 500°C and $\sim$25°C at 550°C for a constant yield or tensile strength.

4. Analysis and discussion

Theoretical and experimental considerations [6–9] give for solute solubility in a random solid solution

$$\rho_s = \alpha_{\rho_s} c_s^{n_{\rho_s}} = \alpha_{\rho_s}[\exp(-\Delta G_s/RT)]^{n_{\rho_s}} \quad (1)$$

where $\rho_s = (\rho_w - \rho_o)$ is the *additional* resistivity due to the concentration c_s of the pertinent solute in solution and $\Delta G_s = \Delta H_s - T\Delta S_s$ is the Gibbs free energy of solution. α_{ρ_s} and n_{ρ_s} are constants relating the resistivity to the concentration. For the present alloy and test conditions we will assume that the dissolved solutes are mainly Mg_2Si (presumably forming Al-Mg-Si-vacancy complexes [9–11]), which are retained in solution during the quench. The value of $\rho_o = 3.25 \times 10^{-8}$ Ω-m for the present alloy is taken to be the resistivity obtained upon heating a specimen for 40 min at 550°C and then furnace-cooling to room temperature. Substituting $\rho_w - \rho_o$ for ρ_s and T_{SHT}(K) for T in Equation 1 gives

$$\rho_s = (\rho_w - \rho_o) = \beta_{\rho_s} \exp\left(-Q_{\rho_s}/RT_{SHT}\right) \quad (2)$$

where $\beta_{\rho_s} = \alpha_{\rho_s} \exp(n_{\rho_s}\Delta S_s/R)$ and $Q_{\rho_s} = n_{\rho_s}\Delta H_s \cdot$ Q_{ρ_s} is thus an *apparent* activation enthalpy of solution. According to Equation 2 a plot of log ρ_s vs. $1/T_{SHT}$ should be a straight line with slope $Q_{\rho_s}/(2.3R)$. Such a plot is presented in Fig. 5 for the present alloy with and without field applied during SHT. The values of Q_{ρ_s} and β_{ρ_s} determined from the slopes and intercepts of the two lines (least squares fit) are listed in Table I. Included are the values of these parameters obtained in the same manner for AA6111 [5], which are significantly smaller than those for AA6022. To be noted is that the field reduced both Q_{ρ_s} and β_{ρ_s}, and for both alloys.

According to Grong [12] the equilibrium solubility c_s without field of Mg_2Si in 6000-series Al alloys is given by

$$c_s = 2.9\exp(-45.4 \text{ kJ/mole}/RT) \quad (3)$$

giving $\Delta H_s = 45.4$ kJ/mole and $\Delta S_s = 8.85$ J/mol-K. The value of the exponent n_{ρ_s} for $E = 0$ can then be obtained by taking $n_{\rho_s} = Q_{\rho_s}/\Delta H_s$. The values of n_{ρ_s} for AA6022 and AA6111 at $E = 0$ (1.83 and 1.12, respectively) determined in this manner are included in Table I. Theoretical considerations for a random solid solution give $n_{\rho_s} \approx 1.0$ [8], which has been found for binary Al alloys [9]. The value $n_{\rho_s} = 1.12$ for AA6111 is thus in reasonable accord with theory and with the behavior of binary Al alloys. In contrast, the value $n_{\rho_s} =$ 1.83 for AA6022 is significantly larger.

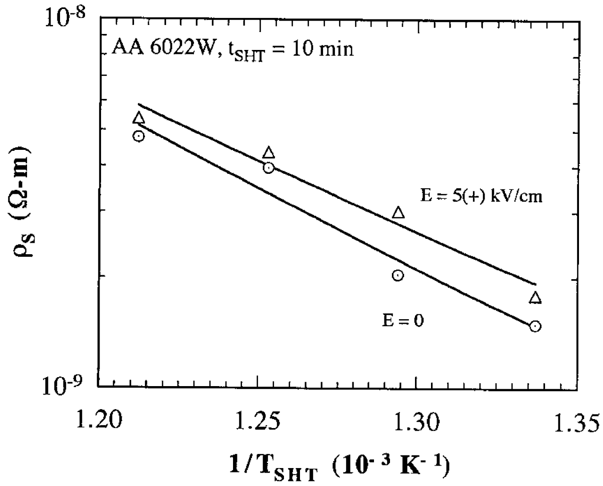

Figure 5 Effective resistivity $\rho_s = \rho_w - \rho_o$ vs. $1/T_{SHT}$ for specimens solutionized without and with electric field.

Equations 1–3 give $\alpha_{\rho_s} = \beta_{\rho_s}/(2.9)^{n_{\rho_s}}$. Taking the values of β_{ρ_s} and n_{ρ_s} for $E = 0$ in Table I, one obtains $\alpha_{\rho_s} = 1.4 \times 10^{-4}$ Ω-m for AA6022 and $\alpha_{\rho_s} = 2.6 \times 10^{-6}$ Ω-m for AA6111. Again, the magnitude of α_{ρ_s} for AA6111 is in accord with that reported for binary Al alloys [9], while that for AA6022 is significantly larger.

To obtain the effect of the electric field on ΔH_s and ΔS_s we will assume that the parameters α_{ρ_s} and n_{ρ_s} are not changed by the field treatment. One then obtains

$$\Delta H_s(E) = Q_{\rho_s}(E)/n_{\rho_s}(E = 0) \quad (4)$$

and

$$\Delta S_s(E) = \frac{R \ln\left[\beta_{\rho_s}(E)/\alpha_{\rho_s}(E = 0)\right]}{n_{\rho_s}(E = 0)} \quad (5)$$

where the symbol (E) refers to the value with the field and $(E = 0)$ without the field. The magnitudes of $\Delta H_s(E)$ and $\Delta S_s(E)$ obtained employing Equations 4 and 5 are listed in Table I. It is seen that the field reduced ΔH_s by $\sim$5 kJ/mole and ΔS_s by $\sim$6 J/mol-K for both alloys. In view of the reduction in both the entropy and

TABLE I Values of the parameters determined from the effects of solution heat treatment temperature without and with electric field on the effective resistivity ρ_s

Alloy	E (kV/cm)	β_{ρ_s} (Ω-m)	Q_{ρ_s} (kJ/mol)	n_{ρ_s}	α_{ρ_s}(Ω-m)	ΔH_s (kJ/mol)	ΔS_s (J/mol-K)	ΔG_s 525°C (kJ/mol)
AA6022	0	9.55×10^{-4}	83.24	1.83	1.4×10^{-4}	45.4[a]	8.85[a]	38.5
(Present)	5 (+)	2.66×10^{-4}	73.62	1.83	1.4×10^{-4}	40.2	3.02	37.8
AA6111 [5]	0	8.63×10^{-6}	50.87	1.12	2.6×10^{-6}	45.4[a]	8.85[a]	38.5
	5 (+)	3.82×10^{-6}	44.33	1.12	2.6×10^{-6}	39.7	2.77	37.5

[a]From data by Grong [12].

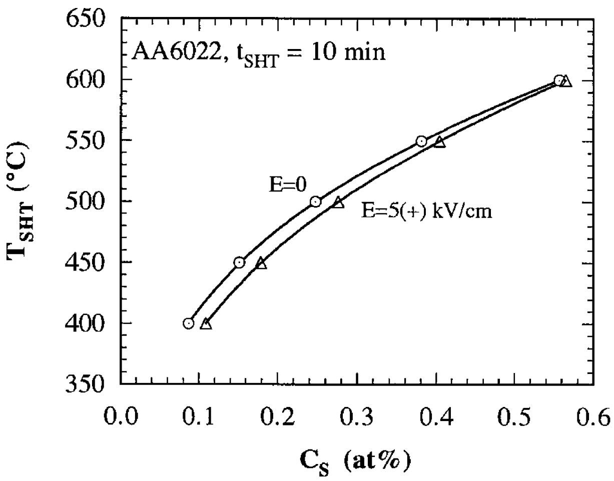

Figure 6 Predicted increase in solubility by application of an electric field $E = 5(+)$ kV/cm during the solution heat treatment of AA6022.

enthalpy by the field, the decrease in Gibbs free energy $\Delta G_s = \Delta H_s - T\Delta S_s$ is only of the order of ∼1 kJ/mol at the SHT temperatures (475–552°C) employed here; see Table I.

The change in solubility with temperature in AA6022 corresponding to the decrease in ΔG_s with field is shown in Fig. 6. The field gives a 26% increase in solubility at 400°C, but only a 1.4% increase at 600°C. The difference results from the reduction in entropy as well as enthalpy by the field. Similar changes in solubility occurred for the AA6111 alloy [5]. The decrease in the effect of E on ρ_{max} in Fig. 3 and on the tensile properties in Fig. 4 with increase in SHT temperature is in keeping with the decreasing difference in solubility indicated in Fig. 6. Again, this results from the fact that the field reduced ΔS_s as well as ΔH_s.

Of interest is the physical significance of the effect of the field on ΔH_s and ΔS_s. Theoretical considerations [6] give that ΔH_s corresponds to the lattice strain and electronic energy resulting from the dissolved solute and ΔS_s reflects the change in vibration frequency. Hence, the reductions in both ΔH_s and ΔS_s by the field indicates that the field reduced both the energy and corresponding lattice frequency pertaining to the soluble constituents.

The parameters α_{ρ_s} and n_{ρ_s} relate to the scattering of electrons by the soluble constituents, presumably Al-Mg-Si-(Cu)-vacancy complexes. Although the magnitudes of these two parameters are appreciably larger for AA6022 than AA6111, the product $\alpha_{\rho_s} c_s^{n_{\rho_s}}$ differs only by a factor of approximately two for the temperature and composition range in Fig. 6. The larger value of this product for AA6022 can be attributed to the excess Si in the alloy compared to AA6111.

5. Summary and conclusions

The effects of an external dc electric field $E = 5(+)$ kV/cm applied during the solution heat treatment (SHT) of the Al-Mg-Si alloy AA6022 at 475–552°C were determined regarding: (a) the as-quenched resistivity, (b) the resistivity during subsequent natural aging, and (c) the tensile properties in the T4 temper. The following are the results obtained and conclusions derived therefrom:

(1) The electric field treatment increased the as-quenched resistivity. Moreover, an increase in resistivity continued throughout the subsequent natural aging. The magnitude of the effects due to the field decreased with increase in SHT temperature.

(2) The electric field treatment increased the tensile properties (i.e., the yield strength, tensile strength and percent elongation) in the T4 temper. Again, the magnitude of the effect decreased with increase in SHT temperature.

(3) For a constant yield or tensile strength, the effect of the electric field treatment at $T_{SHT} \approx 500$–550°C was equivalent to a reduction in solutionizing temperature of 10–25°C.

(4) A thermodynamic analysis of the present results gave that the field decreased both the enthalpy ΔH_s and entropy ΔS_s of solution, giving a reduction in the Gibbs free energy ΔG_s and in turn an increase in solubility over the SHT temperature range.

(5) As a result of the reduction in ΔS_s by the field as well as a reduction in ΔH_s the predicted increase in solubility at 400°C is by a factor of 26%, while that at 600°C is only 1.4%.

(6) The reduction with increase in SHT temperature in the influence of the electric field treatment on the naturally-aged resistivity and tensile properties is in keeping with the smaller increase in solubility due to the field.

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