Electrodynamics, the Neglected Parameter in the Processing and Properties of Metals with Focus on Aluminum

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Abstract

Application of a DC electric field during the solution heat treatment (SHT) of AA6XXX Al alloys enhanced the solubility of pertinent solutes. Thermodynamic analysis gave that the field reduced both the entropy and enthalpy of solution, and gave a decrease in the Gibbs free energy ΔG_s. This in turn resulted in an increase in solubility, which was proportional to the difference in valence between the excess solute addition and the host. It is proposed that the decrease in ΔG_s by the field results from a reduction in its electronic component, which corresponds to the charge on solute atom-vacancy pairs or complexes.

The increase in solubility during SHT gave a significant increase in the subsequent naturally-aged tensile properties, This provides the potential of reducing the energy requirements and costs in industrial practice.

1. Introduction

The external parameters generally considered in materials science are the temperature, pressure or stress, time and the gas or liquid environment. Usually neglected are electric and magnetic fields. However, in many cases such fields can have a significant influence. In the present paper we review some effects of an electric field applied during the solution heat treatment of the AA6XXX (Mg_2Si) series Al alloys.

The manner in which an electric field can be applied is shown in Fig.1.

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Method (c) if applied to metals would lead with even moderate fields to a high electric current and appreciable Joule heating. Hence, Methods (a) and (b) with vacuum, inert gas or air as the medium are generally employed for applying an electric field to metals. The corresponding electric currents are generally only of the order of 0.1~10 μA/ cm^2.

2. Experimental Findings

Three AA6XXX (Mg_2Si) series Al alloys in the form of 1.8 mm thick sheet were employed in the present tests, namely 6061, 6022 and 6111. Their pertinent alloying constituents are given in Table 1. To be noted are the differences in Mg_2Si, the excess Si in 6022 and the addition of Cu in 6111.

Table1. Pertinent alloying constituents in wt.% in the three 6XXX Al-Mg-Si alloys

Alloy	Mg_2Si	Excess Si	Cu
6061	1.51	0.07	0.01
6022	0.92	0.40	0.06
6111	1.23	0.19	0.79

Figure 2 gives an example of the influence of electric field strength E = 0.1 – 5 *k*V/cm applied during the solution heat treatment (SHT) at 475° – 550 °C of the 6111 alloy on the as –quenched resistivity ρ_w. To be noted is that the as-quenched resistivity increases with field strength up to ~1 *k*V/ cm and then only slightly thereafter, if at all.

The increase in the naturally-aged (T4) tensile properties which resulted following the application of the electric field during SHT is shown in Fig.3. Clearly, the electric field treatment gave a significant increase in the tensile properties. The dashed line shows that the increase in the yield and tensile strength is equivalent to ~ 20 °C decrease in SHT temperature. This reduction in SHT temperature has the potential for an appreciable saving in energy and related costs in industrial practice. The magnitude of the effect of the field however depends on the specific alloy, increasing in the order 6061, 6022, 6111 with little if any effect on 6061. The reason for the differences between the alloys is considered below.

3. Mechanisms

Thermodynamic considerations give that the equilibrium concentration of solute in a metal host is given by [3]

$$C_s = \exp(-\Delta G_s/RT) = \exp[(\Delta H_s - T\Delta S_s)/RT] \quad (1)$$

where ΔG_s is the Gibbs free energy of solution, ΔH_s the corresponding enthalpy and ΔS_s the entropy. RT has its usual meaning. Theoretical considerations and experimental data give that the electric resistivity in metals is related to the solute concentration by [4]

$$\rho_s = (\rho_w - \rho_o) = \alpha C_s^n = \alpha \exp(n\Delta S_s/R)\exp(n\Delta H_s/RT) \quad (2)$$

where ρ_w is the as-quenched resistivity and ρ_o the contribution of the insoluble constituents. A plot of $ln\rho_s$ vs $1/T$ thus gives a line with intercept $\beta = \alpha\exp n\Delta S_s/R$ and slope $Q = n\Delta H_s/R$. Knowing ΔH_s and ΔS_s without field, we can then obtain n and α in Eq.2 and in turn the effect of field on entropy and enthalpy. Employing the values of ΔH_s and ΔS_s reported by Grong [5] for the solubility of Mg_2Si in 6XXX Al alloys without field we obtained from the combined effects of the temperature and electric field on ρ_s the effect of the field on the magnitudes of ΔS_s, ΔH_s and ΔG_s. This gave that the field decreased both ΔS_s and ΔH_s, but still gave a decrease in $\Delta G_s = \Delta H_s - T\Delta S_s$. Fig.4 shows that the reduction in these thermodynamic parameters increases with field strength to ~1 *k*V/ cm, following which little if any further decrease occurs. Also to be noted is that the field gives essentially no reduction in ΔG_s for 6061, and a slightly greater reduction for 6111 compared to 6022.

The increase in C_s (employing Eqn.1) which resulted from the reduction in ΔG_s by the field is shown in Fig.5. In keeping with its effect on ΔG_s the field had no effect on C_s in 6061 but increased the solubility C_s in 6022 and 6111, the effect on the latter alloy being larger than on the former. The slight decrease in the effect of the field on C_s with increase in temperature shown in Fig.5 results from the fact that the field reduces the entropy of as well as the enthalpy of solution and thereby ΔG_s is reduced with temperature by quantity $\Delta S_s T$.

Of further interest is the physical mechanism responsible for the effect of the field on solubility. Fig.6 shows that the normalized increase in C_s by the field ($\delta C_{Mg2Si}/\Delta C$) is proportional to the difference in valence ΔZ between the pertinent solute (excess Si in 6022 or the Cu addition in 6111) and the host. ΔC is the atomic fraction of either the excess Si or the Cu addition. The results in Figs 4-6 thus give that ΔG_s contains a significant electronic component in addition to the elastic component due to size misfit. The magnitude of the electronic component is taken to be the reduction in ΔG_s which occurs at $E \approx 1$ *k*V/ cm in Fig.4.

The physical mechanisms responsible for the decrease in ΔG_s by an electric field are considered to include the following: (a) these exists a binding energy between the "excess" solutes (e.g. the excess Si and the Cu addition) and vacancies, which forms solute atom-vacancy pairs or complexes [4,8], (b) the excess solutes modify the electronic charge that is normally associated with a single vacancy in metals[8] and (c) the magnitude of modification of the charge is characterized by the difference in valence $|\Delta Z|$ between the solute and the host [9-12].

4. Summary

The effect of a DC electric field E = 0.1- 5 *k*V/ cm applied during the solution heat treatment at 475°– 550 °C of three 6XXX Al alloys on the solubility of pertinent solutes was determined employing conductivity (resistivity) measurements. Thermodynamic analysis of the results gave that the field enhanced the solubility by reducing both the enthalpy and entropy of solution, which still however gave a reduction in the Gibbs free energy ΔG_s. The decrease in ΔG_s is attributed to a decrease in it's electronic component by the field. The corresponding increase in solubility was proportional to the difference in valence between the pertinent solute and the Al host. It is proposed that the major physical mechanism governing the increased solubility by the field is a reduction in the electronic component of the Gibbs free energy corresponding to solute-vacancy pairs or complexes.

5. Future Work

Evaluating the validity and magnitude of the above listed physical mechanisms is a major objective of our grant from the Forging Industry Educational and Research Foundation and Forging Industry Association.

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Illustrations

Fig.1. Methods by which an electric field may be applied to materials.

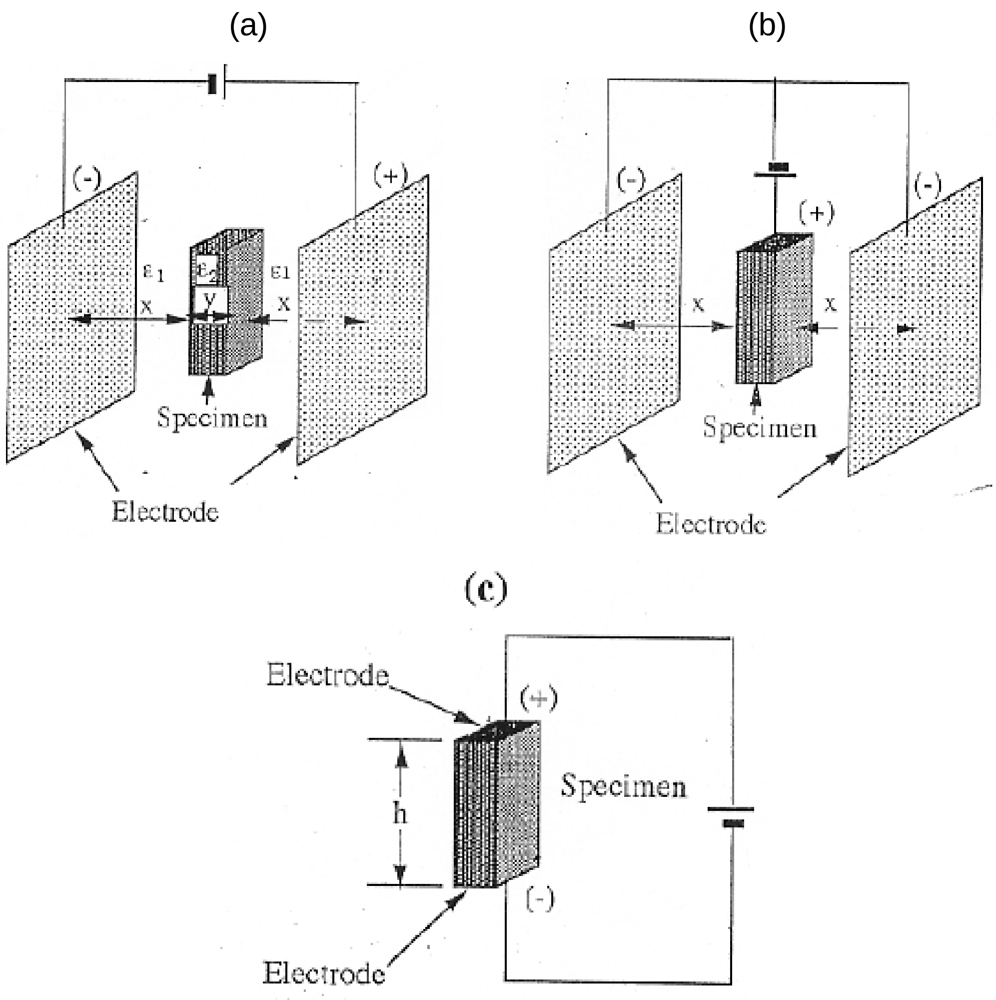
Fig.2. The as-quenched resistivity ρ_w vs electric field strength E applied during the solution heat treatment of the AA6111 Al alloy at 475° – 550 °C. From Jung and Conrad [1].

Fig.3. Tensile properties of naturally- aged AA6111 following solution heat treatment at 475° – 550 °C without and with electric field E_{SHT} = 0, 2 and 5 *k*V/ cm. ΔT_{SHT} indicates the reduction in the SHT temperature by the field and still meets specified tensile properties. From Jung and Conrad [2].

Fig.4. Effect of electric field strength applied during the solution heat treatment of the three 6XXX alloys on the entropy ΔS_s, enthalpy ΔH_s and Gibbs free energy ΔG_s of solution. Data from Refs.1, 6, 7.

Fig.5. Calculated effect of an electric field E = 5 *k*V/ cm on the solubility (phase diagram) of Mg_2Si in Al for the three 6XXX alloys. Data from Refs.1, 6, 7.

Fig.6.The increase in solubility of Mg_2Si (δC_{Mg2Si}) normalized with respect to the concentration ΔC of the excess Si in 6022 and the Cu addition in 6111 vs the difference in valence between the designated solute and the Al host.



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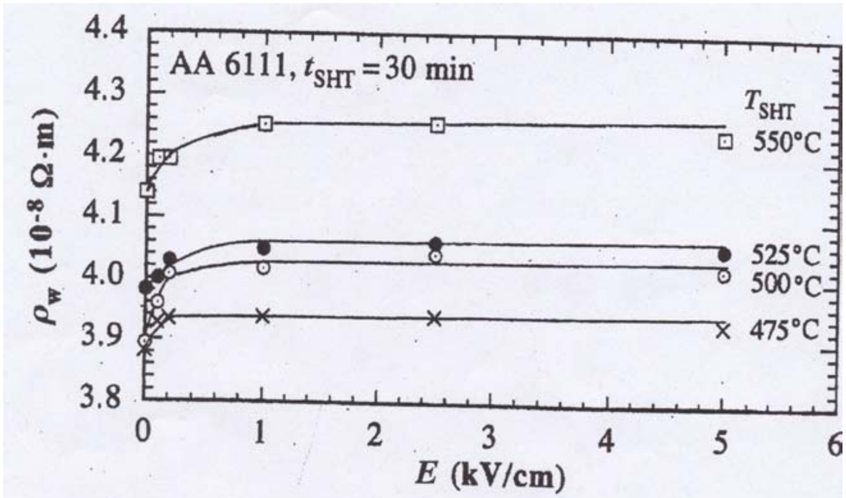
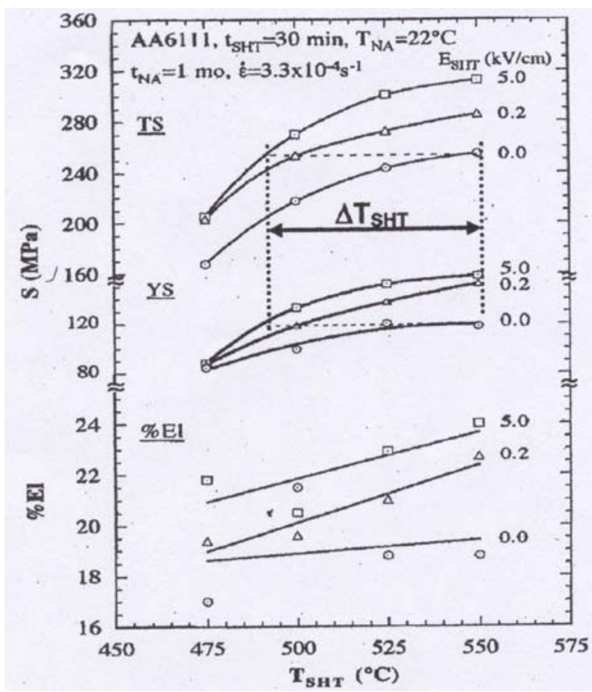


Fig.2. The as-quenched resistivity ρ_w vs electric field strength *E* applied during the solution heat treatment of the AA6111 Al alloy at 475° – 550 °C. From Jung and Conrad [1].



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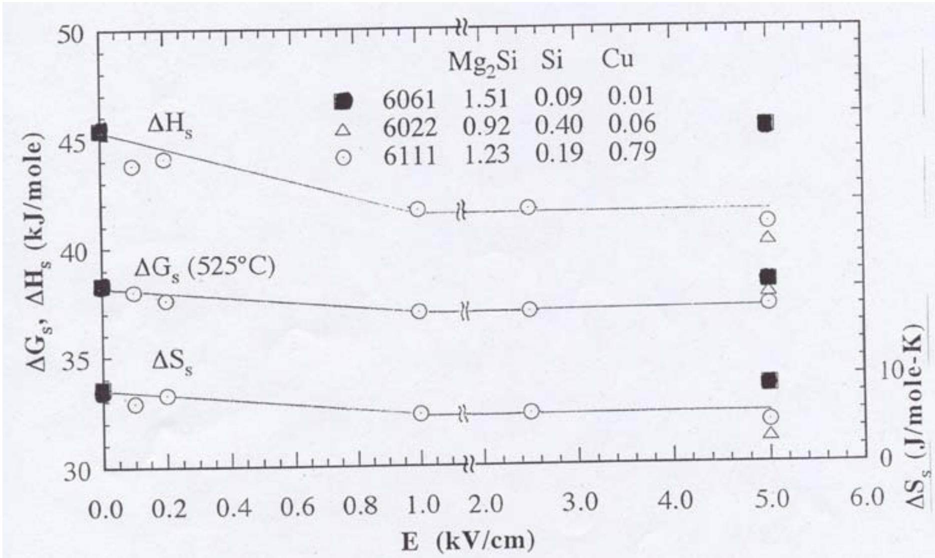

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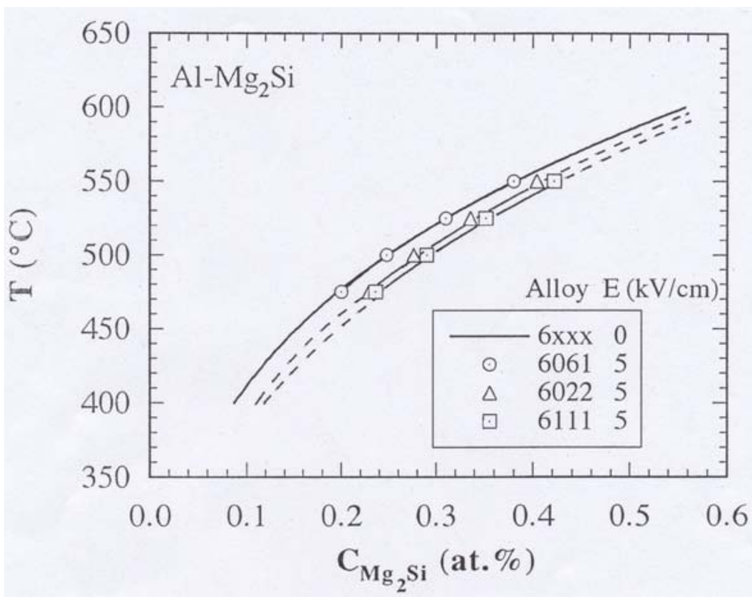

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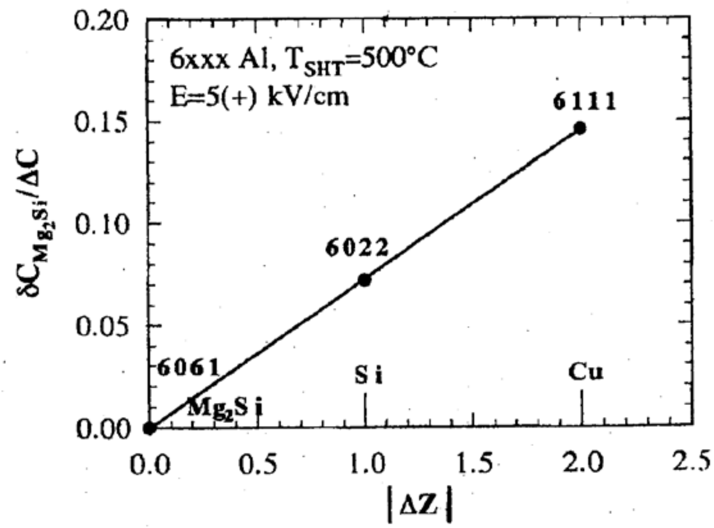

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