

Precipitation Kinetics of the GP Zones in Al4,65at.% Ag(15%Wt.)

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Abstract The precipitation of the Guinier-Preston zones in Al4,65at.% Ag(15% wt.), studied using an electrical resistivity measurements technique during an isothermal aging, follows a nucleation, growth and coarsening stages. The particles growth obeys the JMAK law while their coarsening, the LSW theory. The diffusion coefficient of the solute atoms, during the GP zones formation at 125°C, is in the order of $(8,69 \pm 2,17).10^{-21}$ m²/s. The electrical resistivity of the alloy results from the contribution of the Guinier-Preston zones and that of the matrix. Due to the weak Guinier-Preston volume fraction, the electrical resistivity of the alloy is essentially due to the matrix contribution.

Keywords: precipitation, GP zones, electrical resistivity, diffusion

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1. Introduction

An Al-Ag supersaturated solid solution evolves towards the equilibrium state following the sequence [1,2,3,4]:

Supersaturated solid solution \rightarrow Guinier-Preston (GP) zones \rightarrow metastable γ '-phase \rightarrow equilibrium γ -phase

The Guinier-Preston zones, consisting of silver atom clusters, are coherent with the matrix. The metastable phase $\gamma'(Ag_2AI)$, is semi-coherent with the matrix and the equilibrium phase $\gamma(Ag_2AI)$, is incoherent with the matrix. The electrical resistivity results from the interaction between the free electrons and the lattice defects in the alloy. In a non deformed supersaturated solid solution, during an isothermal aging treatment, we can assume that the contribution of the dislocations and that of the grain boundaries to the electrical resistivity remain constants. Thus, the electrical resistivity variations are essentially attributed to the interactions of the free electrons with the solute atoms and the particles precipitate phase [5,6]. During an isothermal aging treatment, due to the migration of the solute atoms to the precipitate particles, the contributions of the matrix to the electrical resistivity of the solid solution decrease whereas that of the precipitate phase increase. Our purpose is to study the precipitation kinetics the of GP zones in Al4,65at.%Ag(15%wt.) during an isothermal aging using a method based on an electrical resistivity measurements.

2. Experimental Methods

Al4,65at.% Ag(15% wt.) alloy was prepared by melting 99.99% and 99.99% pure aluminum, and silver,

respectively, under an argon protection. After an homogenization at 540°C and a quenching, the alloys are cut into platelets specimen which are mechanically polished, homogenized at 540°C and quenched into water

A P1710 Phillips X-ray ray powder diffractometer, utilizing the monochromatic $CuK_{\alpha l}$ radiation, is used for the characterization of our alloys. Electrical resistivity measurements were carried-out using the four points method at room temperature.

3. Results and Discussion

3.1. Characterization of the Solid Solution

The as quenched solid solution, Al4,65at.% Ag(15% wt.) is characterized by X-ray diffraction on powder specimen. It is well known that an as quenched substitutional solid solution is in a disordered state. In the case of aluminium based solid solutions, the X-ray powder diffraction spectra give peaks diffraction at the analogous positions of those given by the aluminium. The Al and Al-Ag powder diffraction spectra show that the successive peaks are at analogous positions (Figures 1a,b) and their integrated intensities vary in the same ratio (Table 1). The lattice parameters of Al and Al-Ag, determined using the Nelson-Riley [7] extrapolation function, are respectively 4,0462 Å and 4,0478Å.

Table 1. Integrated intensities ratios

hkl	Al (I_{hkl}/I_{111})	$Al-Ag(I_{hkl}/I_{111})$
111	100	100
200	50	51
220	21	30
311	20	21
222	6	6



Figures 1. X-ray diffractograms of Al(a) and Al-Ag (b) as quenched solid solution

3.2. Electrical Resistivity Curve

During the GP zones formation, the electrical resistivity of the alloy decreases and reaches a constant value at the metastable equilibrium state (Figure 2) during which the volume fraction of the GP zones is maximum [8,9,10].



Figure 2. Electrical resistivity variation during the GP zones precipitation at $125^\circ\mathrm{C}$

3.3. Precipitation Kinetics

During the precipitation of the GP zones, the transformed fraction, F, which represents the ratio between the volume occupied by the GP zones at a time t and their volume at the metastable equilibrium state, is given by the relation:

$$\mathbf{F} = \left(\rho(\mathbf{t}) - \rho(\mathbf{o})\right) / \left(\rho_{\text{metastable equilibrium state}} - \rho(\mathbf{0})\right)$$

where $\rho(0)$ is the as quenched electrical resistivity, $\rho(t)$, the electrical resistivity of the alloy at the time t during the precipitation of the GP zones, and $\rho_{(metastable equilibrium)}$, the electrical resistivity of the alloy at the metastable equilibrium state of the GP zones precipitation.

The transformed fraction curves show a short incubation time determined by extrapolation of the curves, due to the high supersaturation of the vacancies obtained at the quenching (Figure 3). The curves show also the steps of the growth and the coarsening of the GP zones.

3.3.1. Growth Regime

The variation curve of LogLog(1/1-F) against Log t suggests that GP zones precipitation kinetics obeys to the JMAK law of the growth controlled by the diffusion of solute atoms: $F = 1 - exp - (kt)^n$, where n and k are the

growth parameters (Figure 4). The slope of the LogLog(1/1-F) curve, gives, for n and k, the respective values 0,91 and $11.10^{-4}s^{-1}$.



Figure 3. Transformed fraction during isothermal aging at 125°C



Figure 4. Determination of the growth parameters

3.3.2. Coarsening Regime

According to the LSW theory [11,12], in a highly diluted alloy and closely to the metastable equilibrium state of the GP zones precipitation, the matrix supersaturation is given by the relation $x_m - x_e = (kt)^{-1/3}$ where x_m is the solute matrix concentration at a time t, x_e , the solute matrix concentration at the metastable equilibrium state and $k = D(RT)^2/9\sigma^2 x_e^2 V_m$, where D is the diffusion coefficient, T, the temperature, σ ,the interfacial energy between the GP zones and the matrix and V_m , the molar fraction of the GP zones.

The solute atom concentration of the matrix during the precipitation of the GP zones is determined from the transformed fraction using the relation $F=(x_0-x_m)/(x_0-x_e)$ where x_0 is the alloy solute atom concentration and x_e , the solute atom concentration of the matrix at the metastable equilibrium state (Figure 5). At 125°C, the value of x_e , determined from the metastable equilibrium diagram [13] is equal to 0,53 at.%.



Figure 5. Matrix solute atom concentration during the GP zones precipitation at $125^\circ\mathrm{C}$

The curve of the Figure 6 shows that the supersaturation in solute atoms vary linearly against t $^{-1/3}$ and is in accordance with the LSW theory of the coarsening (Figure 6). Using the value of k obtained from the slope of this curve, and taking $\sigma = 0.3$ J/m² [14] and $V_m = 10^{-5}$ m³/mol, we determine a diffusion coefficient of the solute atoms, during the GP zones formation at 125°C, in the order of (8,69 \pm 2,17).10⁻²¹m²/s.



Figure 6. Variation of the solute atom matrix concentration during the coarsening stage

4. Contributions of the Matrix and of the GP Zones to the Electrical Resistivity

According to the Matthiessen rule, the electrical resistivity results from the contribution of the phonons and that of all defects in the alloy such the dislocations, the grain boundaries, the solute atoms and the precipitate particles. During an isothermal aging treatment, the contribution of phonons remains constant and, in a non deformed alloy, the contributions of defects such the dislocations and the grain boundaries remain constant while that of the solute atoms and the precipitate particles vary. The electrical resistivity contribution of the matrix is determined from the variation curve of the electrical resistivity of homogenized alloys containing different concentrations of solute atoms (Figure 7) and the matrix solute atom concentration (Figure 4).



Figure 7. Electrical resistivity of homogenized Alxat.% Ag alloys

The electrical resistivity contribution of the GP zones is obtained from the difference between the electrical resistivity of the alloy and the electrical resistivity contribution of the matrix (Figure 8).



Figure 8. Contributions to the alloy electrical resistivity of the matrix, R_m , and of the GP zones, R_{GP} , during the GP zones precipitation at 125°C

The preponderant contribution to the electrical resistivity of the alloy is that of the matrix. This is due to the weak GP zones volume fraction which is given by the relation

$$\mathbf{f}_{\mathbf{V}} = \left(\mathbf{x}_0 - \mathbf{x}_m\right) / \left(\mathbf{x}_p - \mathbf{x}_m\right)$$

where x_0 is the alloy concentration in solute atoms, x_m , that of the matrix and x_p that of the precipitate particles at the equilibrium metastable state, and represented in Figure 9 taking a value of 55% for x_p [13]. The maximum value of the GP zones volume fraction obtained at the metastable equilibrium state is in the order of 7,49 %.



Figure 9. GP zones volume fraction during isothermal aging at 125°C

5. Conclusion

The GP zones precipitation kinetics study, using an electrical resistivity measurements, during an isothermal aging at 125°C shows that the GP zones growth obeys to the JMAK law of the growth controlled by the diffusion of the solute atoms and their coarsening, to the LSW theory of the coarsening of precipitates. The diffusion coefficient of the solute atoms, during the GP zones formation at 125°C, is in the order of $(8,69 \pm 2,17).10^{-21}$ m²/s. The contribution of the matrix and that of the GP zones to the electrical resistivity were determined separately.

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