

## INFLUENCE OF TRACES ADDITION OF TIN ON THE GROWTH AND ON THE COARSENING OF THE GUINIER-PRESTON ZONES IN Al-10% at.Ag ALLOY

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### Abstract

The formation of the Guinier-Preston zones in aluminium alloys is closely linked with the excess vacancies. Traces of tin added to an Al-Ag alloy exert an influence on the Guinier-Preston zones precipitation. Due to their high binding energy with vacancies, tin atoms trap some of these available to promote the diffusion of silver atoms for the formation of the Guinier-Preston zones. At 125°C, tin microalloying slows down the reaction of the Guinier-Preston zones precipitation. The diffusion coefficient of the solute atoms in the Sn free alloy and in the Sn added alloy are determined during the coarsening regime which obeys to the Lifshitz, Slyosov and Wagner theory.

**Keywords:** Guinier-Preston zones; precipitation; coarsening; diffusion; vacancies; hardening

### 1 Introduction

Al-Ag supersaturated solid solution evolves towards the equilibrium state following the sequence [1-4]: Supersaturated solid solution → Guinier-Preston (GP) zones → metastable  $\gamma'$  phase → equilibrium  $\gamma$  phase.

The Guinier-Preston zones (GP), consisting of silver atom clusters, are coherent with the matrix. The metastable phase  $\gamma'$ (Ag<sub>2</sub>Al) is semi-coherent with the matrix and the equilibrium phase  $\gamma$ (Ag<sub>2</sub>Al), is incoherent with the matrix.

Precipitation starts from the formation of GP zones, which are isomorphous with the matrix and, therefore, have a lower interfacial energy than intermediate or equilibrium precipitate phases that possess a distinct crystal structure. As a result, the nucleation barrier for GP zones is significantly smaller.

The effect of microalloying elements on the behaviour of age-hardenable alloys such as Al-Ag is an interesting physical problem addressing the mechanisms of transport and aggregation of the solute. Trace elements have been found to exert a disproportionate influence on the structure and properties of Al alloys compared with the amounts added which may be less than 0,1 molar fraction. Most trace element effects arise because they modify the nucleation and the growth characteristics of the phases which form during precipitation [5-9]. It is well known that the formation of the GP zones in aluminium alloys is closely linked with the excess vacancies. A number of models of GP zones precipitation assisted by vacancies has been developed by several authors [10-12].

GP zones formation is governed by a transport mechanism of solute atoms by solute atom-vacancy complexes. The high binding energy between tin atoms and vacancies leads to the formation of vacancy-tin atom pairs and silver atom-vacancy-tin atom complexes.

Our purpose is to study the effect of the addition of traces of tin on the precipitation kinetics of the GP zones in Al-10%at.Ag (39% wt.) alloy using a method based on hardness measurements.

## 2 Experimental methods

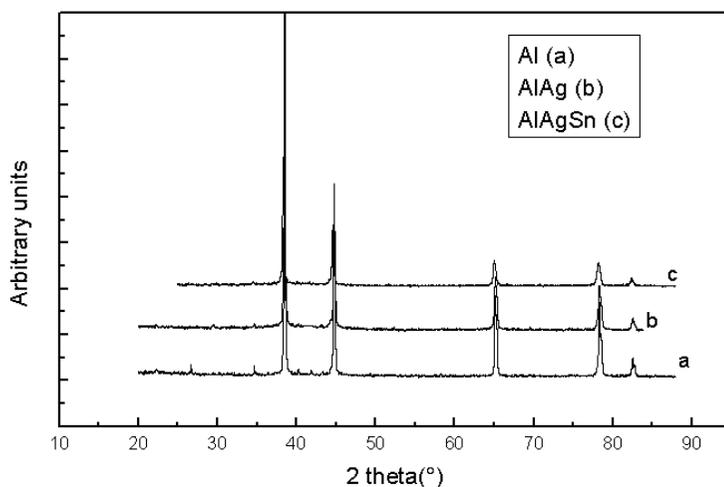
Al10%at.Ag(39% wt.) and Al10%at.Ag0,05%at.Sn (2% wt.) alloys were prepared by melting 99.99%, 99.99% and 99.99% pure aluminum, silver and tin, respectively, under argon protection. After an homogenization at 540°C and quenching, the alloys were cut into platelets specimen were mechanically polished, homogenized at 540°C and quenched into water.

A P1710 Phillips X-ray ray powder diffractometer, utilizing the monochromatic  $\text{CuK}_{\alpha 1}$  radiation, was used for the characterization of our alloys. The microhardness measurements were carried out under a load of 100 g on specimen treated for different times at ageing temperature and quenched into water. The ageing temperature of 125°C, is chosen below the temperature of the GP solvus in the Al rich Ag alloy.

## 3 Results and discussion

### 3.1 Characterization of the solid solutions

The as quenched solids solutions, Al-Ag and Al-Ag-Sn, are 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 solids solutions, the X-ray ray powder diffraction spectra give peaks diffraction at the analogous positions of those given by the aluminium. The Al, Al-Ag and Al-Ag-Sn powder diffraction spectra show that the successive peaks are at analogous positions (**Figs. 1a, b, c**) and their integrated intensities vary in the same ratio (**Table 1**). The lattice parameters of Al, Al-Ag and Al-Ag-Sn, determined using the Nelson-Riley [13] extrapolation function, are respectively 4,0462 Å, 4,0478 Å and 4,0467 Å with an error estimated at 0,05%. In such a case, there is practically no difference between these lattice parameters. This is due to the fact that there is a little difference between the Al and the Ag atomic radius and the Sn, which has a larger atomic radius, is added in traces proportion.



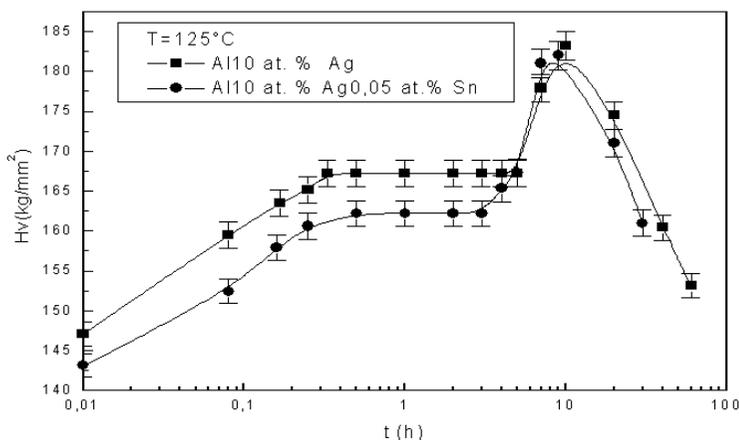
**Fig. 1** X-ray powder diffraction spectra of Al, Al-Ag and Al-Ag-Sn as quenched solid solutions

**Table 1** Integrated intensities ratios

hkl	Al( $I_{hkl}/I_{111}$ )	AlAg( $I_{hkl}/I_{111}$ )	AlAgSn( $I_{hkl}/I_{111}$ )
111	100	100	100
200	50	51	53
220	21	30	29
311	20	21	21
222	6	6	6

### 3.2 Hardening evolution

The isotherm curves of hardness, established at 125°C show a first step of hardening due to the GP zones precipitation and a second step due to the precipitation of the metastable  $\gamma'$  phase (**Fig. 2**). The obtained degree of hardening depends on the volume fraction, the structure of the precipitates and the nature of the interface between the metastable phases and the aluminum matrix [14-19].

**Fig. 2** Isotherm hardness curves at 125°C

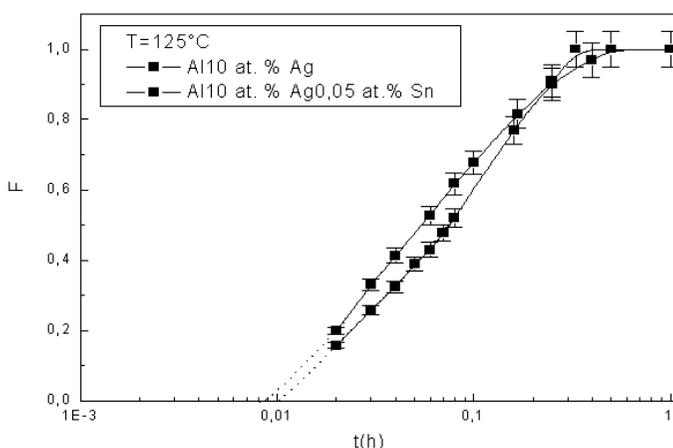
The intermediate bearing corresponds to the metastable equilibrium state of the precipitation of the GP zones during which their volume fraction is maximum. The softening is due to the coarsening of the particles of the  $\gamma'$  phase and to the precipitation of the equilibrium  $\gamma$  phase. These isotherm curves of hardness show that tin atoms retard the establishment of the metastable equilibrium state of the GP zones precipitation by trapping some of quenched-in vacancies. Due to the high binding energy between tin atoms and vacancies, tin atom-vacancy pairs and silver atom-vacancy-tin atom complexes are formed, thus reducing the number of free vacancies available to promote the diffusion of Ag atoms for the formation of the GP zones. These curves show also that tin addition stimulates the precipitation of the metastable  $\gamma'$  phase. This is due to the fact that tin atoms are absorbed at the interface  $\gamma'$  with matrix and reduce the interfacial energy required for precipitate nucleation [20, 21]. An alternative explanation is that the clustering of tin elements, which have a larger atomic volume than matrix aluminium, would create a compressive volume strain in the matrix, thus attracting a high concentration of vacancies and silver atoms to the interfacial region, providing an excellent condition for the nucleation of the metastable  $\gamma'$  phase [22].

### 3.3 Precipitation kinetics of the GP zones

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 Merle relation (1) [23]:

$$H_v(t) = F \cdot H_{v(\text{metastable equilibrium})} + (1-F) \cdot H_v(0) \quad (1)$$

where  $H_v(0)$  is the as quenched hardness,  $H_v(t)$ , the hardness of the alloy at the time  $t$  during the precipitation of the GP zones, and  $H_{v(\text{metastable equilibrium})}$ , the hardness of the alloy at the metastable equilibrium state of the GP zones precipitation. The incubation times, which values are determined by extrapolation, are very short in comparison with the necessary times to reach the metastable equilibrium state and are characteristics of rapid nucleation in the two both alloys, Al-Ag and Al-Ag-Sn, because of the high supersaturation of the quenched in vacancies (**Fig. 3**).



**Fig. 3** Transformed fraction during GP zones precipitation in Al-Ag and Al-Ag-Sn alloys at 125°C

#### 3.3.1 Growth regime

The curves of the variations of  $\ln(\ln(1/(1-F)))$  versus  $\ln(t)$ , show that the growth stage obeys to the JMAK (Johnson-Mehl-Avrami-Kolmogorov) law (2),

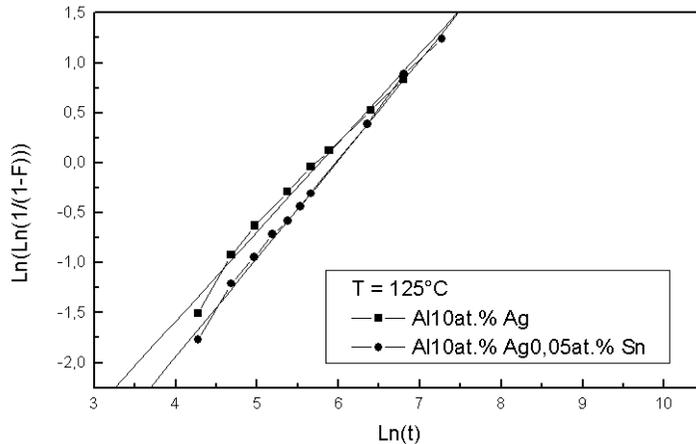
$$F = 1 - \exp(-kt)^n, \quad (2)$$

of the growth controlled by solute atom diffusion, where  $n$  and  $k$  are the growth parameters (**Fig. 4**).

The values of  $n$  are characteristics of a heterogeneous precipitation in the two alloys while the values of  $k$ , which characterizes the transformation kinetic, show a delay of the precipitation of the GP zones in Al-Ag-Sn alloy (**Table 2**).

**Table 2** Values of the growth parameters at 125°C

T (°C)	Al-10at.%Ag		Al10at.%Ag0.05at.%Sn	
	n	k (s <sup>-1</sup> )	n	k (s <sup>-1</sup> )
125°C	0,89	31.10 <sup>-4</sup>	0,98	24.10 <sup>-4</sup>



**Fig. 4** Determination of the growth parameters for Al-Ag and Al-Ag-Sn alloys at 125°C

The parameter  $k$ , which characterizes the precipitation kinetics, is given by the relation (3):

$$k = A \exp(-Q/RT) \quad (3.)$$

where  $A$  is a constant,  $Q$ , the activation energy,  $R$ , the gas constant and  $T$ , the temperature. In first approximation, considering that the constant has the same value in the two alloys, we determine a difference between the apparent activation energies of the solute atom diffusion during the GP zones formation in AlAgSn alloy,  $Q_{AlAgSn}$ , and in AlAg alloy,  $Q_{AlAg}$ ,  $\Delta Q$  in the order of 12 kJ/mol corresponding to 0,125 eV/atom, showing that the precipitation of the GP zones is faster in the Sn free alloy. This difference may be attributed to the binding energy between the Sn atom and the vacancy which is lower than the value of 0,25eV calculated by Wolverson [24].

### 3.3.2 Coarsening regime

According to the Lifshitz, Slyosov and Wagner (LSW) theory [25, 26], 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 (4):

$$x_m - x_e = (kt)^{-1/3} \quad (4.)$$

where  $x_m$  is the solute matrix concentration at a time  $t$ ,  $x_e$ , the solute matrix concentration at the metastable equilibrium state and  $k$  is given by the relation (5):

$$k = D(RT)^2/9\sigma^2x_e^2V_m \quad (5.)$$

where  $D$  is the diffusion coefficient,  $T$ , the temperature,  $\sigma$ , 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 (6):

$$F = (x_0 - x_m)/(x_0 - x_e) \quad (6.)$$

where  $x_0$  is the alloy solute atom concentration and  $x_e$ , the solute atom concentration of the matrix at the metastable equilibrium state. The solute atom concentration of the matrix at the metastable

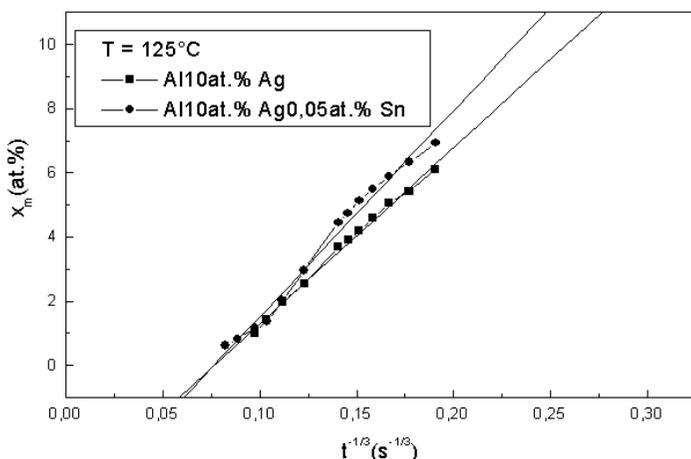
equilibrium state, determined from the metastable equilibrium diagram [27] is taken equal to 0,52 at.% at 125°C.

The curves of the **Fig. 5** show that the supersaturation of solute atoms varies linearly against  $t^{-1/3}$  and is in accordance with the LSW theory of the coarsening. The diffusion coefficients of the solute atoms (7):

$$D = D_0 \exp(-Q/RT) \quad (7.)$$

where  $D_0$  is the pre exponential factor,  $Q$ , the activation energy,  $T$ , the temperature and  $R$ , the gas constant, during the GP zones coarsening are determined using the values of  $k$  obtained from the slopes of these curves, and taking  $\sigma = 0,3 \text{ J/m}^2$  [28] and  $V_m = 10^{-5} \text{ m}^3/\text{mol}$ .

The diffusion coefficient of the solute atoms in the Sn free alloy and in the Sn added alloy are respectively in the order of  $(1,2 \pm 0,4) \cdot 10^{-21} \text{ m}^2/\text{s}$  and  $(7,6 \pm 2,3) \cdot 10^{-22} \text{ m}^2/\text{s}$ . These values are comparable to the value of  $5,56 \cdot 10^{-21} \text{ m}^2/\text{s}$  determined at 125°C by Alexander and Slifkin [29].



**Fig. 5** Variation of the solute atom matrix concentration during the coarsening stage at 125°C

Since the tin is added in a traces proportion, we can assume that the pre exponential factor has the same value in the Sn free alloy and in the Sn added alloy. So, in first approximation, the ratio between the diffusion coefficient of the solute atoms in the Sn free alloy and the diffusion coefficient of the solute atoms in the Sn added alloy gives a difference between the activation energy of the diffusion the apparent activation energies of the solute atom diffusion during the GP zones formation in AlAgSn alloy,  $Q_{\text{AlAgSn}}$ , and in AlAg alloy,  $Q_{\text{AlAg}}$ ,  $\Delta Q$  in the order of 16,1 kJ/mol corresponding to 0,16 eV/atom. In first approximation, this difference may be attributed to the binding energy between the Sn atom and the vacancy. This value is lower than the value of 0,25eV calculated by Wolverton [24].

#### 4 Conclusion

In the Al10%at.Ag 0,05 % at.Sn alloy, tin atoms form tin atom-vacancy pairs and tin atom-vacancy-silver atom complexes which retards the precipitation of the GP zones at 125°C. In both Al-Ag and Al-Ag-Sn alloys, the growth kinetics of the GP zones obeys to the JMAK law and their coarsening, to the LSW theory of the coarsening of precipitates.

The differences between the apparent activation energies of the solute atom diffusion during the GP zones formation in an AlAgSn alloy,  $Q_{\text{AlAgSn}}$ , and in an AlAg alloy,  $Q_{\text{AlAg}}$ , determined during the growth regime and during the coarsening regime, are in the order of 0,125 eV/atom and 0,16 eV/atom respectively may be attributed, in first approximation, to the binding energy between the Sn atom and the vacancy. The diffusion coefficients of the solute atoms in the Sn free alloy and in the Sn added alloy are respectively in the order of  $(1,2 \pm 0,4) \cdot 10^{-21} \text{m}^2/\text{s}$  and  $(7,6 \pm 2,3) \cdot 10^{-22} \text{m}^2/\text{s}$ .

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