Study of microstructure, microhardness and phases of precipitation during ageing of Cu-Sn and Al-Ag alloys

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Abstract: Ageing study of supersaturated solid solutions Cu-13 wt. % Sn and Al-20 wt. % Ag has shown that the two types of precipitation (continuous and discontinuous) would occur for various temperatures and plastic deformation rates (thickness reduction by cold rolling following rapid quenching in iced water). The precipitated phases take place generally on the grain boundaries (discontinuous precipitation DP) and inside the grains (continuous precipitation CP). A detailed study of phases' development conditions and the growth controlling mechanisms has been carried out, for several ageing temperatures with and without plastic deformation of the supersaturated solid solution using various experimental techniques (optical microscopy, X-ray diffraction and microhardness measurements).

Keywords: Discontinuous Precipitation, Microstructure, Cu-Sn, Al-Ag

1. Introduction

The discontinuous precipitation shows a solid state reaction where a supersaturated solid solution $\alpha 0$ is replaced by a cellular structure composed of two $(\alpha + \beta)$ phases. From scientific and commercial perspective, this reaction was considered of great interest for a long time; this interest is not only the mechanism of the reaction itself, but also the tremendous properties changes of materials that it induces. Since the discovery of the discontinuous precipitation by Agreew et al [1] in 1930 of Ag - Cu alloys, the understanding of this reaction has enormously changed [2-7]. Nevertheless, ambiguities still remain on many important issues related to it. For example, it is still impossible to predict which binary systems, precipitation may occur intermittently, or what are the actual reaction driving forces, or what is the nucleation and growth mechanism that is the most likely for each alloy system.

The continuous precipitation has a large influence on the progress of the decomposition process of some discontinuous supersaturated solutions [8-10]. The discontinuous precipitation is generally controlled by the grain boundary diffusion while the continuous precipitation is controlled by volume diffusion. The grain boundaries constitute an area full of structural defects where the diffusion will always be important, but the appearance of continuous precipitation reaction stops the discontinuous reaction happening there by reducing the migration of solute atoms from the matrix to the grain boundary [11, 12]. On the other hand reciprocal effect, that is, any influence of the discontinuous decomposition reaction on the continuous precipitation, has not hitherto been observed. We know pertinently that this cannot take place for two reasons that we think are important:

- Discontinuous precipitation starts only at grain boundaries and therefore cannot prevent the appearance of a continuous precipitate nucleation within the grain on any defect (dislocation for instance).

- Outside the cell containing the precipitates lamellae, the matrix remains still supersaturated during the discontinuous precipitation and therefore "does not know" that the latter is happening.

In the Cu-13 wt. % Sn alloy used as the matrix of super-conducting Nb/Cu-Sn composites, intensive discontinuous decomposition was discovered after 10% cold deformation followed by prolonged ageing at 553K [13]. The decomposition of Cu3Sn from a supersaturated solid solution of tin in copper during ageing is initiated by discontinuous precipitation and followed by continuous precipitation. The cell growth rate decreases with ageing time after linear growth rate of the cells. This was attributed to the influence of continuous precipitation on the cell growth. The mass transport of tin during the linear cell growth occurs by grain boundary diffusion of tin in a copper-tin solid solution and prior cold work increases the rate of continuous precipitation but has no effect on discontinuous precipitation [11].

The basic sequence of decomposition in Al-Ag alloys has been found to be as follows [14]:

α(fcc) phase $\rightarrow$ spherical GP zones $\rightarrow$ metastable γ'-phase (hcp) $\rightarrow$ equilibrium γ- phase (hcp). The interfacial structure and growth kinetics of γ' and γ (Ag2Al) precipitate plates in Al-Ag alloys have been studied by conventional and in-situ transmission electron microscopy (TEM) technique because these precipitates represent one of the simplest diffusion transformations involving a distinct change in crystal structure, i.e. from fcc to hcp [15].

In a sample of Al-4.5 at. % Ag alloy aged at temperatures up to 498K where coarser GP zones exist, reversion into a plate-like metastable γ'-precipitates takes place [16]. The study of the growth effect of GP zones near the surface and grain boundaries as vacancy sites of the stress-strain parameters of Al-Ag alloys has been carried out [17].

A study of ageing in cold‑worked Al-Ag alloys during the first stage of precipitation was performed, by means of small‑angle x‑ray scattering. The deformation of precipitated particles by cold‑work is a new and powerful means of investigating the mechanism of plastic deformation inside the material [18].

2. Experimental Methods

These materials were prepared in our laboratory by fusion in a device at a high vacuum (10^{-5} Torr) using pure materials. After the melting the ingots have undergone plastic deformation by cold rolling before the homogenization treatment in order to accelerate the structure homogenization kinetics. The homogenization temperature and ageing were chosen from the equilibrium diagrams [13].

After mechanical polishing with diamond paste, the samples are attacked in the following chemical baths after cleaning with alcohol and ultrasounds: concentrated nitric acid (53%) for Cu-13 wt. % Sn alloy during one second

and Keller's reagent for the Al – 20 wt. % Ag alloy at room temperature for (1-20) s. The microstructure evolution has been followed mainly by optical microscopy and X-ray diffraction. The X-ray diffraction analysis is performed by a "PAN Alytical X' Pert PRO" diffractometer using CuKα radiation; to prevent oxidation of the samples during different analysis a protective atmosphere of nitrogen was used. The Vickers microhardness was measured with an AFFRI hardness testing machine.

The chemical analysis of the Al-20 wt. % Ag and Cu- 13 wt. % Sn alloys is presented in Table 1:

Table 1. *Chemical composition of Al-20 wt. % Ag and Cu- 13 wt. % Sn alloys.*

Element	Al	Zn	Fe	Cu	Si	Mg
wt.	%	79.92	19.95	0.05	0.02	0.05	0.01
Element	Cu	Sn	Al	Ni	Si	Mg
wt.	%	86.95	12.89	0.07	0.03	0.04	0.02

3. Results and Discussions

3.1. Cu – 13 wt. % Sn Alloy

A 40 minutes homogenization performed after plastic deformation is normally insufficient to trigger the recrystallization reaction. If it is followed by quenching and ageing at lower temperature, it must therefore have an influence on the precipitation phenomenon, because of structural defects it introduces into the matrix, we took three samples which were subjected to deformation by cold rolling 20, 40 and 60 % respectively, followed by homogenization annealing 40 minutes at 873K, quenching in water and ageing at 553K. For the first sample (= 20 %) the precipitation takes place only on the grain boundaries (in a form of cells which tend to stretch and become rods of well defined direction with regards to the position of grain boundary) (Fig. 1a, b). We note that the precipitation kinetics is very slow and it is the phase ε (Cu3Sn) that is observed according to equilibrium diagram and literature data [9-11].
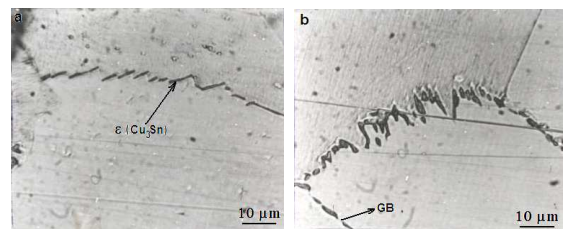

Fig. 1. *Cu-13 wt. % Sn alloy deformed of 20 %, homogenized at 873K for 40 min, quenched in iced water and ageing at 553K for 350 hours (a) and 1700 hours (b), (GB-grain boundary).*

For the second sample (ε = 40 %), we observed two types of precipitation: inter-granular and intra-granular (Fig. 2). The latter is stimulated by the presence of sliding lines and shows to be more abundant after a long ageing (Fig. 2a). In some areas of the grain it forms a structure similar to that of Widmanstätten (Fig. 2b). In all cases it is always
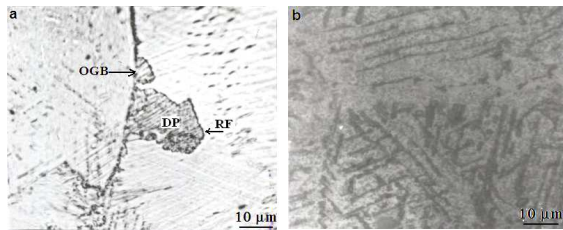
the ε (Cu3Sn) that arises.

Fig. 2. *Cu-13 wt. % Sn alloy, deformed of 40%, homogenized at 873K for 40 min, quenched in iced water and ageing at 553K for 400 hours (a, b). OGB-location original grain boundary, RF-reaction front of DP.*

For the third sample ($\varepsilon = 60$ %), the precipitation is more homogeneous and takes place within the grains; it is comparable to a continuous precipitation of ε phase (Fig. 3). Figure 4 sums up the results of this study and shows clearly that the precipitation is stimulated by a prior deformation of the sample (it does not practically appear for these same maintaining times at 553K) if the sample was not submitted to a prior deformation (case of an alloy studied by Sudareva et al [12]).
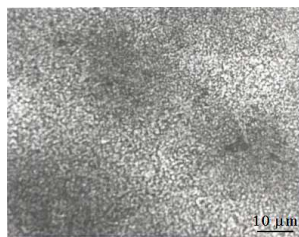

Fig. 3. *Cu-13 wt. % Sn alloy deformed of 60 %, homogenized at 873K for 40 min, quenched in iced water and ageing at 553K for 1400 hours.*
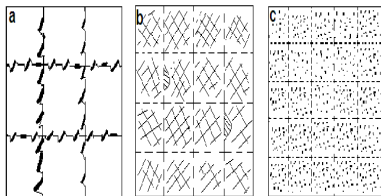

Fig. 4. *Types of precipitation observed for a Cu-13 wt. % Sn alloy, deformed $\varepsilon = 20$ % (a), 40 % (b) and 60 % (c), homogenized for 40 mn at 873K quenched and aged at 553K.*

The microhardness variation curves of Cu-13 wt. % Sn alloy during ageing at 553K are presented in Fig. 5. The alloy becomes soft with ageing time extension and its mechanical properties are reduced by the appearance of equilibrium precipitate ε (Cu3Sn). As expected, it has been found that when discontinuous precipitation leads to the formation of lamellae, the coarsening did not lead to a globalization but only to an increase in the lamellae spacing. It is then always possible to distinguish between continuous and discontinuous precipitation [19].
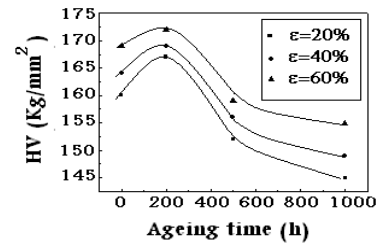

Fig. 5. *Vickers microhardness variation HV for Cu-13 wt. % Sn alloy, homogenized for 40 mn at 873K quenched and aged at 553K.*

3.2. Al – 20 wt. % Ag Alloy

In the Al-Ag system, optical metallographic is therefore a straightforward method to study the precipitation morphology. Typical microstructures of aged specimen at higher temperature (623K) are shown in Fig. 6. Contrary to most alloys that exhibit discontinuous precipitation, the aspect of precipitate particles at grain boundaries is quite different.

The third sample has been aged at 623K. Two types of precipitation were observed:

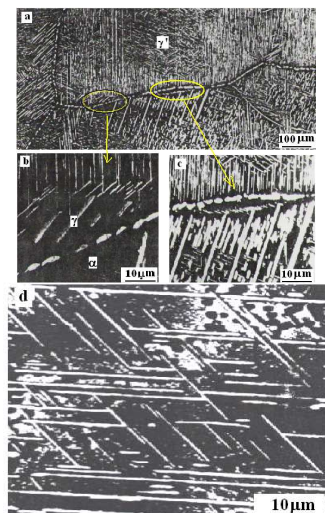1. Discontinuous precipitation at grain boundaries (Fig. 6 a-c).

Fig. 6. *Microstructures of Al – 20 wt. % Ag alloy homogenized 16 hours at 823K, quenched in iced water and aged at 623K during 115 hours (a-c) and 190 hours (d).*

2. Intergranular continuous precipitation which occurs in a form of needles inside the grain, comparable to the Widmanstätten structure (Fig. 6d).

It should be noted that despite a long extension of the ageing time, the lamellar cells do not progress well within the grain because of the occurrence of continuous precipitation in the form of Widmanstätten structure, which hinders the development of the cells.

The spectrum of X diffraction shown in Figure 7 confirms obviously the discontinuity of reaction; during the ageing a halving of the peak of diffraction is observed. We also note a displacement of the diffraction lines in the continuous precipitation and any peak of the phases γ' and γ. To better appreciate this halving of the lines we have still

recourse to the diffraction of the X-rays by using a Debye-Scherrer back plan Fig. 8. For the not deformed samples, the obtained movies presenting spots of diffraction are characteristic of a structure with big grains the nature of which it is difficult to estimate [19]. For the deformed sample 30 %, after 1 hour of ageing in 553K, we observe rings of diffraction, characteristics of a structure with fine grains.
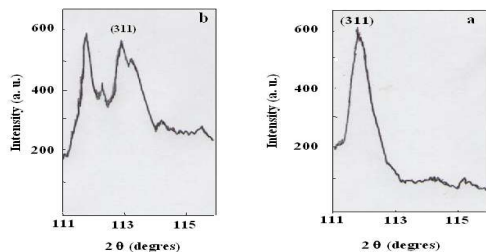

Fig. 7. *X-ray diffraction peak of Al-20 wt. % Ag alloy, homogenized at 823K for 5 h quenched (a) aged at 553K for 5 h (b). CuKα radiation (10 mA, 30 kV).*
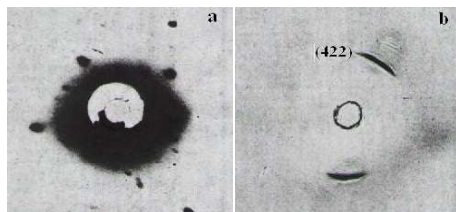

Fig. 8. *Debye-Scherrer back plane films of Al-20 wt. % Ag alloy, homogenized at 823K for 5 h quenched (a), deformed 30% and aged at 553K for 1 h (b). CuKα radiation (10 mA, 30 kV).*

The precipitate grows as a faulted structure, but after long ageing times the faults are removed and the lattice becomes ordered. The transformation occurs by discontinuous precipitation involving a grain growth mechanism.

4. Summary and Conclusion

The study of both Cu-Sn and Al-Ag alloys has enabled us to confirm the multiplicity and complexity of precipitation phenomena and to better appreciate the interaction and mutual influence of two types of precipitation in an alloy.

By means of very simple experimental methods but quite rigorous, we show that:

* The precipitation reaction is very slow in the Cu-13 wt. % Sn alloy and only a preliminary plastic deformation can stimulate appreciably.

* The plastic deformation is important (10 and 30 %), moreover, the grain obtained after homogenization and quenching is fine.

* Two types of precipitation occur in Cu-13 wt. % Sn

alloy. However, the intermittent precipitation is limited to a deformation of the grains boundaries in an attempt of development stopped by plentiful one haste continues intergranular (in the form of structure of Widmansttaten).

* In Al-20 wt. % Ag, the formation of cells with lamellae is observed inside grains as well as on the boundaries.

* Both types of precipitation are observed in both alloys: discontinuous with lamellar form and continuous inside the grains that stop the growth of these blades by depriving them of solute atoms flow towards the reaction front.

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