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Mechanisms of precipitation induced by large strains in the Al-Cu system

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ABSTRACT

The strain induced decomposition of super saturated solid solutions of Cu in Al has been experimentally investigated. A solutionized Al-Cu alloy has been severely deformed by high pressure torsion at room temperature at different strain levels. The resulting microstructures have been systematically characterized using transmission electron microscopy and atom probe tomography. It is established that Cu rich particles nucleate and quickly grow along boundaries during deformation, leading to a full decomposition of the solid solution. Besides, a significant and systematic Cu segregation along grain boundaries has been revealed. Based on these experimental data, the contribution of deformation induced vacancies, dislocations and boundaries were considered to account for the strain induced precipitation. It is concluded that the collection of solutes by moving boundaries might be considered as an important mechanism leading to strain induced precipitation.

1. Introduction

Solute atoms play a critical role in the microstructure evolution of Al alloys during deformation due to their interaction with crystalline defects. This is the typical case of Mg in solid solution that gives rise to a strong strain hardening due to a reduced dynamic recovery as compared to pure Al. At higher level of deformations, using severe plastic deformation (SPD) processes like High Pressure Torsion (HPT) or Equal Channel Angular Pressing (ECAP) for example [1] small amount of impurities or solute atoms also lead to a more intensive grain refinement as they promote a higher dislocation density and pin boundaries [2–4]. In the case of precipitate hardening Al alloys, if it is necessary or desired to combine deformation processes with the age hardening treatment, a solution treatment is typically performed at first, then it follows the processing and finally the precipitation hardening treatment. This last step could be affected by the defects created during the deformation since they act as heterogeneous nucleation sites but also because solutes may segregate along defects like dislocations or boundaries. Recently, a special emphasis has been given to the combination of UltraFine Grained (UFG) structure obtained by SPD combined with precipitate hardening [5–10]. The motivation is often to reach a significantly higher yield stress but also to improve the ductility. However, to optimize the properties, the main challenges are to avoid grain growth during the precipitation treatment and the heterogeneous precipitation along boundaries. There is another issue on the top of this: the redistribution of solute elements during the plastic deformation. It has been shown indeed by a number of authors that a significant redistribution of solutes during SPD may occur under large level of deformation even at ambient temperature [3,11–13]. For example, Straumal et al. [12] have demonstrated that Zn-rich supersaturated solid solutions in fcc Al decompose completely and reach the equilibrium state at room temperature. They also found that this process is less pronounced for Mg-rich super saturated solid solutions, because of the high nucleation barrier of Al_3Mg_2 phases. In more complex alloys, G. Sha and co-authors have reported that HPT or ECAP processing may also give rise to a fastest precipitation kinetic and significant grain boundary (GB) segregation or depletion of solutes [14,15]. In a

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more systematic way, the influence of the deformation level on the SPD induced nucleation of θ phase along GBs at ambient temperature in a binary Al-Cu alloy has been investigated by Hohenwarter et al. [11]. On a similar alloy, Mohamed et al. have also reported that such structure exhibits a poor thermal stability with a significant grain growth in few minutes at 353 K only [16]. It is however interesting to note that Huang et al. [17] did not observe precipitates in Al-4 wt.% Cu alloy directly after SPD by ECAP at ambient temperature. They appeared only during natural aging (NA) within 9 months after deformation. The decomposition rate of solid solutions during SPD processing necessary depends on the solute content and on the deformation temperature, and thus might be connected to the nucleation driving force of second phase particles. However, the kinetic seems also affected because of significantly enhanced atomic mobility during SPD [3,6–9,12]. It is often explained by enhanced diffusion, promoted by deformation induced vacancies, however the exact mechanisms of the decomposition of Al solid solutions during large level of deformation is not fully understood yet. The aim of this work was to systematically investigate, at different level of deformation, the microstructure of severely deformed Al-Cu solid solutions. This binary system was chosen because it is a model system for precipitate hardening Al alloys, it has been widely investigated and it is still an important basis for the design of modern Al alloys. In the present work, Transmission Electron Microscopy (TEM) and Atom Probe Tomography (APT) analyses were carried out to follow the redistribution of solute atoms (Cu) within the microstructure down to the atomic scale and to quantitatively evaluate the contribution of defects generated by the plastic deformation.

2. Experimental procedures

A model Al-Cu alloy containing 0.83 at.% Cu was directly cast as 20 mm rods and homogenized at 485 °C for 12 h. Small disc shaped samples (20 mm in diameter and 1 mm thickness) were cut out and subjected to a solution treatment at 500 °C during 1 h followed by water quenching to achieve a homogeneous distribution of Cu atoms in the Al fcc matrix. Then, these samples were deformed by HPT [1] at room temperature under a pressure of 6 GPa and a rotation speed of one turn per minute. To investigate a full range of strain deformation, some samples were deformed with 0.5, 1, 5, 10 and 60 rotations. At a distance of 5 mm from the center, this corresponds to a strain rate of about 0.5 s^{-1} and shear strains of about 15.5, 31, 155, 310 and 1860 respectively.

To characterize the evolution of microstructures down to the atomic scale at different levels of deformation, TEM observations and APT analyses were carried out.

TEM samples were prepared from standard 3 mm discs drilled out at a distance of 5 ± 1 mm from the center of the samples processed by HPT. Then they were mechanically polished on both sides to reach a thickness of about 200 μm and finally electropolished using a Struers TENUPOL® device (electrolyte: 30%vol. HNO_3 and 70%vol. methanol, temperature: −30 °C, voltage: 17 V). In a final stage, samples were subjected to low energy ion milling with a GATAN® Precision Ion Polishing System (accelerating voltage: 3 kV, incidence angle of Ar ions: ± 3°, duration: 15 min). TEM and Scanning TEM (STEM) observations were performed on a JEOL®-ARM200F operated at 200 kV. Low magnification STEM images and Energy Dispersive X-ray (EDS) measurements were carried out with a probe size of 0.2 nm and a convergence angle of 34 mrad. EDS analyses were performed with a JEOL® JED-2300 detector. The probe size was reduced down to 0.1 nm for lattice imaging. STEM Dark Field (DF) images were recorded with a collection angle in a range of 20–50 mrad and STEM High Angle Annular Dark Field (HAADF) images with a collection angle in the range of 50–180 mrad. To quantify the number density and the volume fraction of precipitates, the thickness of imaged areas was estimated using Energy Filtered TEM (EFTEM) with a Gatan Imaging Filter (GIF Quantum®). Thickness maps were computed assuming a mean free path of 200 keV electrons in Al of 133 nm [18]. Last, the crystallographic structure of precipitates was identified using conventional electron diffraction with a parallel beam. Grain sizes were estimated from STEM-BF images and precipitate sizes from STEM-HAADF images. If non equi-axed, then an average was calculated between the largest and the smallest dimension. Values provided in the present manuscript were obtained from at least 200 measurements for each state.

APT Samples were prepared by electro-polishing (micro-loop technique at room temperature) starting from small rods (0.3 × 0.3 mm in cross-section) cut at a distance of 5 ± 1 mm of HPT discs center. Sharp tips were obtained with a solution of 2% perchloric acid in monobutylic ether of ethylene glycol under a voltage of 15 V. Samples were field evaporated in an energy compensated wide angle tomographic atom probe (ECOWATAP) at 40 K with a standing voltage in a range of 3.5–11 kV, a pulse fraction of 20% and a pulse repetition rate of 30 kHz. Three dimensional reconstructions and data processing were carried out with the "GPM 3D data software".

3. Results

3.1. Evidence of deformation induced precipitation and influence of the shear strain level

As expected, the large level of deformation gives rise to an UFG structure (Fig. 1(a, c, e, g)). The grain size, as estimated from STEM-DF images, is in a range of 300–500 nm for all states with a slightly higher value for the lowest shear strain but without any measurable variations for a shear strain larger than 31 (Fig. 2(a)). As shown on STEM-HAADF images (Fig. 1(b, d, f, h)), the shear deformation led to the nucleation of Cu rich nanoscaled precipitates (brightly imaged). These precipitates exhibit some complex shapes and are mainly located along GBs and on triple lines. It is important to note that careful observations at higher magnification did not reveal any other precipitates homogeneously nucleated within grains. These observations are rather consistent with the data published by A. Hohenwarter et al. [11] for an Al-3wt.%Cu alloy processed in similar conditions (HPT at room temperature). However, it is interesting to note that the present data demonstrate that the strain induced precipitation starts in the early stage of deformation (γ = 15.5, Fig. 1(b)) and that the mean particle size significantly decreases when the shear deformation increases (from 70 to 40 nm, see Fig. 2(b)). This indicates that the particles that have nucleated and grown in the early stage of deformation are refined later when the plastic deformation is continued.

Using electron diffraction the Cu rich particles were unambiguously identified as θ and θ′ phases (data not shown here) and their composition was measured by APT and EDS. A particle intercepted in a volume analyzed by APT is displayed on Fig. 3(a). The composition profile computed across this particle (Fig. 3(b)) clearly shows that it contains 20 ± 2 at.% Cu which is consistent with values reported by other authors for the θ′ phase [19]. A large number of particles have been probed using EDS (data not shown here), 90% of them exhibited a similar Cu content (in a range of 17–23 at.%) while others had a concentration in a range of 30 to 35 at.%, closer to the expected stoichiometry.

The evolution of the volume fraction of precipitates as a function of the shear deformation exhibits a sharp increase in the early stage of deformation (up to γ ~ 50) and then stabilizes toward the equilibrium volume fraction (Fig. 2(c)). It seems to indicate that for