Full length article

Vacancy-tuned precipitation pathways in Al-1.7 Cu-0.025In-0.025Sb (at.%) alloy

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ABSTRACT

Microalloying is a routine method to optimize precipitation and mechanical properties in light metals. Here we study how In and Sb (0.025 at.%) additions in an Al-1.7 at.% Cu alloy benefit precipitation during ageing and investigate the underlying mechanism using scanning transmission electron microscopy and density functional theory (DFT) calculations. The combined additions accelerate precipitation kinetics and increase peak hardness through two different ways. In samples aged directly at low temperatures ($\leq$200 °C) after solid solution treatment, cubic close-packed InSb nanocrystals form first. The truncated {002} surfaces of InSb particles induce the preferential nucleation of Guinier-Preston (GP) zones, θ'' and θ' successively. However, in samples aged at 250 °C, precipitation of θ' precedes that of InSb particles. Supersaturated vacancies trapped by In and Sb solute atoms/clusters play a critical role in switching the precipitation sequence. By tuning how strong the binding between a vacancy and solute atoms is, we successfully invert the temperature dependence of the precipitation sequence. These findings will contribute to understanding precipitation mechanisms and optimizing precipitate distribution in aluminium precipitation hardenable alloys.

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1. Introduction

Al-Cu alloys are the most typical ageing hardenable aluminium alloys and are used in a wide range of applications such as in the aircraft and automobile industries, tracing back to 100 years ago [1]. Binary Al-Cu supersaturated solid solutions at the Al-riched side can decompose into four kinds of Cu-rich phases depending on the ageing time and temperature. GP zones [2,3] are single layers of copper embedded in the Al matrix, and usually form during natural ageing or low temperature (<160 °C) ageing. θ'' contains Cu-rich layers separated by three {002} layers of Al, which can form directly from the matrix or transform from the GP zones. θ' is the dominant strengthening phase at the peak ageing condition [4]. It has a different crystal structure (tetragonal unit cell, a = 0.404 nm, c = 5.80 nm) compared with the Al matrix (face centred cubic, a = 0.404 nm), which induces a significant penalty in the interfacial

energy as well as strain energy, thus making nucleation difficult [5]. Defects in the Al matrix that can reduce the nucleation energy barrier, e.g., dislocations, interfaces, grain boundaries and vacancies/voids, are therefore the preferred nucleation sites for θ'. A finely dispersed θ' with a large length to thickness aspect ratio is usually desired for superior mechanical properties [6].

Microalloying solutes (usually <0.1 at.%) including Sn, In, Cd and Au have been found effective in accelerating precipitation in Al-Cu alloys [7,8]. Even though the beneficial effects of some of these elements were discovered 60 years ago [9–12], no consensus has been reached about their functional mechanisms. Most of them form immiscible alloys with aluminium and have a low solid solubility (usually <0.1 at. %) in the aluminium matrix. The positive mixing enthalpy of most of these elements with aluminium renders their solute states in solid aluminium matrix unstable. Crystals composed of the above-mentioned microalloying elements precipitate easily from the Al-Cu based alloys during artificial ageing. Al-Cu alloys microalloyed with any of them reach a much higher peak hardness in a much shorter ageing time, which is explained by a finer dispersion of θ'. Since the precipitates of some elements always dock at the semi-coherent interface of θ'/Al, heterogeneous nucleation of θ' on these preformed precipitates has been proposed

[7,13]. However, until now, no direct experimental study has conclusively shown that θ' nucleates after the precipitation of these microalloying elements. Further, in heterogeneous nucleation, one would expect the nucleating crystal to have a well-defined and specific crystallographic relationship with the heterogeneous nucleation site from which nucleation occurs. Here, however, the nucleating crystal θ' has several crystallographic orientations with respect to Sn crystals and θ' modifies the crystallographic orientations of Sn precipitates with respect to Al [14,15]. Therefore, how does the microalloying of Sn, In and Cd affect precipitation in Al-Cu alloys is still controversial.

Another clue suggesting the underlying mechanism is that natural ageing is retarded or suppressed in Al-Cu-Sn/In/Cd/Au alloys [9,16]. During natural ageing at room temperature or even lower temperatures in the absence of microalloying elements, Cu solute atoms in the aluminium matrix tend to cluster and form GP zones subsequently. Electrical resistivity and calorimetric measurements imply that Cu atom clustering (diffusing) becomes sluggish if vacancies annihilate significantly during quenching [17,18]. This is because vacancies can accelerate diffusion by reducing the migration energy barrier. Vacancies are effective only when they are free and unbound by other elements with a high binding energy. Here, Sn, In, Cd and Au all have a high binding energy with a vacancy [19]. Hence, microalloying of Sn, In, Cd and Au retards natural ageing by suppressing diffusion at low temperatures. This additional effect on natural ageing does not have too much practical importance for Al-Cu based alloys but has found an important implication in Al-Mg-Si ageing alloys [20]. The trapped excess vacancies by Sn, In and Cd can be released at high ageing temperatures [21], which can remarkably enhance diffusion and consequently facilitate the nucleation of θ'. Without these traps, the excess vacancies originating from quenching will diffuse to sinks and annihilate during room temperature storage. However, to our best knowledge, there are no solid experimental results correlating the enhanced precipitation of θ' with vacancies instead of solute atoms.

The binding between vacancies and solute atoms is, in most cases, achieved through size compensation in the aluminium crystal lattice. It is still an open question how direct interatomic binding between solute atoms affects the role of vacancies. Similarly to In, Sb has a high binding energy with a vacancy and a negligible solid solubility in aluminium at room temperature, which makes it a candidate for trapping vacancies on demand in Al-Cu based alloys. Due to strong interatomic binding, In and Sb can form a semi-conductor material, InSb ($\mathrm{F\bar{4}\ 3\ m}$, a covalent crystal). This is in contrast to the well-studied elements, Sn, In, Cd and Au, whose ground states are metallic crystals. Therefore, it will be interesting to investigate how the combined additions of In and Sb work in Al-Cu alloys.

Here using an Al-Cu-In-Sb alloy as an example, we explored the typical mechanisms of microalloying additions on enhancing precipitation. We found direct experimental evidence of both a vacancy-controlled mechanism and a heterogeneous nucleation of θ' from preformed InSb nanocrystals. There are two precipitation pathways depending on the stability of binding between solute atoms and a vacancy. Normally, ageing temperature is a critical parameter and determines which mechanism is dominant. A high ageing temperature generally releases the majority of vacancies from solute atoms, thus giving a vacancy-dominated mechanism where θ' nucleates before InSb precipitates. When most vacancies are trapped by In and Sb solute atoms at low ageing temperatures, diffusion of Cu is sluggish, and θ' nucleates after InSb precipitates. Since the switching between the two mechanisms is essentially dependent on how strongly a vacancy binds with In and Sb atoms, by tuning the quenching process and pre-ageing conditions, we also succeeded in controlling how the solute atoms work independent of the ageing temperature.

2. Experimental and computational procedures

Alloys with nominal compositions of Al-1.7 at.% Cu-0.025 at.% In-0.025 at.% Sb and Al-1.7 at.%Cu were prepared from pure Al (5N), Cu (5N) and InSb semi-conductor wafer ($\mathrm{F\bar{4}\ 3\ m}$, >6N). Homogenization was carried out in a salt bath at 520 °C for 24 h followed by rolling with a thickness reduction of 50%. Disks of 3 mm in diameter and 0.5 mm in thickness were cut out from the rolled ingots, which were used for the following heat treatments and transmission electron microscopy characterization. The prepared disks underwent a further solution treatment at 520 °C for 1 h and were quenched in room temperature water and then aged at 160 °C, 200 °C and 250 °C for different times. We used two heat treatment procedures that differed from the conventional process. In the first one, disks were quenched in an oil bath at 160 °C for 60 s after solution treatment and then to water, followed by normal ageing at 200 °C. In the second one, disks with normal quenching were aged at room temperature for 10 days before artificial ageing at 250 °C. The aged disks were mechanically thinned to ~0.15 mm by hand grinding and then twin-jet electropolished in a nitric acid and methanol solution at −25 °C with a voltage of 13 V. Hardness measurements were performed on bulk samples prepared with similar heat treatment procedures. The applied load was 500 g and indentation time was 10 s. The reported values below are averages over 10 measurements.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was performed on a JEOL JEM 2100F operated at 200 kV. A convergence semi-angle of 13 mrad and a collection inner semi-angle of 65 mrad were used. No image processing was performed except minor contrast and brightness adjustments. Elemental mapping was carried out using a JEOL Si(Li) X-ray energy dispersive spectroscopy (EDS) detector. The sample thickness was measured by comparing convergent beam electron diffraction (CBED) patterns with simulated patterns using the JEMS software. The number density and length histograms of precipitates were measured by hand from low magnification HAADF-STEM images (100k).

The binding energies between solute atoms and a vacancy were calculated using the plane wave density functional theory method, as implemented in the Vienna ab initio Simulation Package (VASP). We used the generalized gradient approximation (GGA) method and the Projector Augmented Wave potentials supplied with the code. Geometry relaxations were performed with an energy cut-off of 500 eV, allowing a full relaxation with respect to supercell vectors as well as ionic positions. We used 64-atom to 500-atom supercells to obtain the binding energies between a vacancy and different configurations of solute atoms. Here only first and second nearest neighbour separation between solute atoms and a vacancy were considered. In addition, a solute atom was always put at the first nearest neighbour positions of a vacancy, but it could be at the second nearest neighbour positions of another solute atom. The binding energy is the energy gain or penalty of putting solute atoms and a vacancy together and is calculated by the following expression:

$$E_b = E(Al_{N-x-y-1}In_xSb_yV_1) + (x+y)*E(Al_N) - xE(Al_{N-1}In_1)$$
$$- yE(Al_{N-1}Sb_1) - E(Al_{N-1}V_1)$$

(1)

where E is the ground state energy of a supercell and the subscripts in parenthesis indicate the numbers of vacancies and atoms. For