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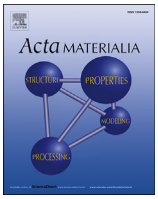

Full length article

The enhanced theta-prime (θ′) precipitation in an Al-Cu alloy with trace Au additions

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ABSTRACT

Linking the atomic level kinetic precipitation pathways induced by elemental additions to the resulting microstructure is fundamentally desirable for the design of new classes of light alloys. Aberration-corrected scanning transmission electron microscopy (AC-STEM) and first principles calculations were used to investigate the influence of trace Au (200 ppm) additions on precipitation in an Al-Cu-Au alloy. These Au additions resulted in a significant enhancement of the low-temperature age hardening, which was demonstrated to be associated with accelerated precipitate nucleation and growth. Atomic-resolution annular dark field (ADF) imaging showed the clearly reduced critical length and thickness of θ′ precipitates with Au additions, therefore accelerating the nucleation of θ′. Agglomerated Au clusters were observed in θ′ precipitates, which were demonstrated to correspond to a localised energetically favourable state. These observations have been explained through first-principles calculations and relevant thermodynamic modelling. This work provides a potential way to refine the alloy microstructure for improving the mechanical behaviour of light alloys.

1. Introduction

In automotive and aerospace applications, aluminium alloys use many elemental additions to produce dense precipitate size distributions (PSDs) for improving mechanical strength [1,2]. Increased precipitate volume fraction through ageing treatment is mainly responsible for the observed materials strength, but the final optimisation requires the control of a number of factors such as size distributions and aspect ratio [3,4], crystallographic orientation [3], and heterophase interfacial structures [5]. These factors are essentially linked to the atomic structures within precipitate and matrix phases, as well as their interplays. However, the present understanding of how the atomic level structure induced by alloying additions controls PSDs remains little known. This lack of understanding results from the difficulties in atomic-scale compositional characterisation [6,7], as well as insufficient accuracy and limited computational capacity in bottom-up multi-scale modelling [7–10].

Al-Cu is a textbook binary model alloy for investigating the effect of atomic level structure on precipitation sequences. At sufficiently low ageing temperatures (for example, ≤160 °C) Guinier-Preston (GP) zones precipitate at the early stage of phase separation followed by the precipitation of the metastable θ″ (Al_3Cu) and θ′ (Al_2Cu) and equilibrium θ (Al_2Cu) phases [2]. The θ′ phase is the most important precipitate strengthener in Al-Cu-based alloys. Unfortunately, it does not nucleate easily at low temperature and as a result, alloying elements used as lattice defects are often introduced in order to enhance θ′ nucleation rates [11]. Copper additions, having a relatively moderate negative mixing enthalpy within Al (−0.155 eV/atom, as given in Table 1 and calculated from

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Table 1
The formation enthalpy of solute atoms in aluminum, calculated from the thermodynamic databases in Refs. [11,12,15].

Formation enthalpy	Cu	Ag	Au
(eV/atom)	−0.15	−0.03	−0.56

Ref. [12]), first precipitate from supersaturated solid solution as metastable GP zones with a single pure Cu layer. As deduced from Gibbs free energy theory [13], negative enthalpy favours a spontaneous mixing and hence a metastable configuration. In contrast, positive enthalpy does not favour the mixing so could result in an absence of such metastable configuration. Therefore, the pathway for phase transformation could be altered. For instance, it has been shown that silver having a small negative mixing enthalpy within Al (−0.03eV/atom [14]), could explain the nearly spherical GP zones in the Al-Ag systems [15]. These observations suggest that alloying elements with relatively small solute mixing enthalpy segregate at the interface to form a metastable configuration. Therefore, the kinetic precipitation pathway in phase transformations varies with mixing enthalpy. Less well understood is how a solute element with strong negative mixing enthalpy with Al affects θ′ precipitation at the atomic level. Given that gold has a much stronger negative formation energy within aluminium (−0.56 eV/atom [16]) compared to silver and copper, its precipitation sequence in binary Al-Au alloys is not expected to include metastable GP zones, and this is indeed what is experimentally observed [17–19]. Moreover, the precipitation sequence in Al-Au involves the formation of the η′ (Al_2Au) phase, which is structurally similar to θ′ [17]. However, how this ternary addition affects the phase transformation, in particular at the atomic level mechanism, has not hitherto been studied.

With the advent of aberration-corrected scanning transmission electron microscopy (AC-STEM), sub-Å resolution STEM imaging now allows for direct observation of atomic site occupations in precipitates [20]. In addition, first-principles calculations can deliver a fundamental understanding of atomistic interactions [21]. Combining these two well-developed techniques, it is now possible to establish a picture linking the atomic-level structure to phase transformations.

Here we report the effect of trace Au additions (200 ppm) to an Al-Cu alloy on the ageing response and microstructures. In particular, we explore how Au alters the nucleation and growth of θ′ at the atomic level using ADF-STEM imaging and first-principles calculations. We find that Au accelerates the ageing response through enhanced nucleation of θ′. We show that this is achieved through dissolution of Au into θ′ and the consequent lowering of the nucleation barrier.

2. Experimental procedures

2.1. Alloy preparation

Al-1.7Cu and Al-1.7Cu-0.02Au alloy (in at. %) were prepared using high purity Al (5N8, 99.9998), Cu (5N8, 99.9998) and high purity Au (5N, 99.999). The amount of Au 0.02 at.% in this alloy, is lower than the maximum solid solubility of Au achievable in Al—Au binary alloy (~0.055 at.%) at 540 °C [17,18]. As experimentally verified, there are no distinct Au-rich particles at the grain boundaries, suggesting all Au atoms were solid solutioned into this alloy. Trace Fe and Si which are believed to originate from the high purity Al (even with a high purity of 5N8), were also detected by inductively coupled plasma optical emission spectrometry (ICP-OES) but were found to have no significant effect on the precipitation of θ′ as they were concentrated along grain boundaries. The alloy was arc-melted under high vacuum (10^{-6} mbar) to ensure homogenisation. The as-cast buttons were subsequently cold-rolled at room temperature into plates 0.5 mm thick and 20 mm wide.

2.2. Heat treatments and TEM sample preparation

These as-cast materials were cut into discs 3 mm in diameter and 0.5 mm in thickness to ensure a spatially even thermal history within the whole materials for comparison. These samples were subjected to a solution treatment in a nitrate salt bath for 30 min at 540 °C, followed by a water quench to room temperature. Isothermal ageing was applied in an oil bath for different times at 200 °C and 160 °C in order to study the ageing response, and the aged samples were water quenched to room temperature. The heat-treated disks were ground to a thickness of 0.15 mm and twin-jet electropolished in a solution of 33% nitric acid and 67% methanol at −25 °C using a voltage of 12.7 V. Vickers' microhardness was measured using a Shimazu MVK-E hardness tester using a load of 50 g.

2.3. Scanning transmission electron microscopy

Preliminary microstructural imaging of PSDs was performed on a JEOL JEM 2100F operated at 200 kV. For ADF imaging, a 10 mrad convergence semi-angle was used, with an inner collection semi-angle of 65 mrad and an outer collection angle of about 200 mrad. The specimen thickness was determined by comparing on-zone ⟨100⟩ convergent beam electron diffraction (CBED) patterns with the simulated pattern using JEMS software [22]. The precipitate number density was then calculated by combining the number of precipitates counted from ADF imaging and the measured thickness. Automatic image thresholding within the ImageJ software did not allow precipitates to be characterised due to the noise in the ADF images. To characterise the precipitate length distributions, we have used a manual size analysis method to outline precipitates for lower magnification imaging and subsequently applied the thresholding approach within ImageJ.

Quantitative ADF imaging was performed on an FEI Titan^3 electron microscope with double aberration correctors (CCOR, CEOS GmbH) operating at 300 kV. A 15 mrad probe-forming aperture was used, corresponding to ~1.1 Å resolution, and an inner collection semi-angle of 43.5 mrad and an outer collection semi-angle of 200 mrad. To quantify the Au concentration of each atomic column in the θ′ (Al_2Cu) precipitates, the experimental image was firstly normalized by the incident beam intensity to the fractional intensity of the probe following the method in Ref. [23]. ADF image simulations were carried out for a series of $Al_2Cu_{1-x}Au_x$ compositions ($0 \leq x \leq 0.5$) via the quantum excitation of phonons model [24] in the μSTEM code [25], where the two-dimensional response function of the ADF detector was included. Twenty phonon passes were used to obtain adequate convergence over a wide range of thickness. The Voronoi cell intensity around the Cu/Au column was calculated and a similar parameterization method to that in Ref. [26] was used to evaluate Au concentrations. The image intensity from the pure Al_2Cu precipitate region was used to fit the thickness. Subsequently, extrapolation using a two dimensional first order polynomial function for the regions containing Au atoms gave an averaged thickness of 295 Å. This was in close agreement with an independent thickness determination via position averaged convergent beam electron diffraction (PACBED) [27], further supporting the validation of this quantification method. By comparing the experimental intensity for each atomic column with the simulated concentration-thickness matrix, the Au concentration for each atomic column was obtained.