Available online at www.sciencedirect.com

SciVerse ScienceDirect

Acta Materialia 60 (2012) 633–644

Acta MATERIALIA

www.elsevier.com/locate/actamat

The magic thicknesses of θ′ precipitates in Sn-microalloyed Al–Cu

Laure Bourgeois [a,b,c,*], Christian Dwyer [a,b,c], Matthew Weyland [a,c], Jian-Feng Nie [b,c], Barrington C. Muddle [b,c]

[a] Monash Centre for Electron Microscopy, Monash University, Victoria 3800, Australia
[b] ARC Centre of Excellence for Design in Light Metals, Monash University, Victoria 3800, Australia
[c] Department of Materials Engineering, Monash University, Victoria 3800, Australia

Received 13 August 2011; received in revised form 7 October 2011; accepted 9 October 2011
Available online 22 November 2011

Abstract

θ′ is an effective strengthening precipitate phase in high-strength Al alloys; unfortunately its nucleation is difficult and usually requires assistance, such as that provided by Sn in Sn-microalloyed Al–Cu. In order to clarify the mechanisms by which Sn promotes the nucleation of θ′, we investigated the structure and thickness of θ′ precipitates in a Al–1.7 at.% Cu alloy with trace additions of Sn (0.01 at.%). Scanning transmission electron microscopy imaging reveals that θ′ platelets recently nucleated at 160 and 200 °C exhibit a discrete distribution of specific, or "magic", thicknesses, corresponding to minima in the residual volumetric and shape misfit strain. This observation is unique to the Sn-assisted nucleation of θ′: θ′ platelets that undergo growth or form in the Sn-free alloy do not display this discrete distribution, although preference for the magic thicknesses persists. Direct evidence is presented that Sn does not accommodate volumetric misfit strain. Instead, it is shown that Sn in its solute form reduces either the interfacial energy of θ′ and/or the transformation shape strain associated with thicknesses intermediate to the magic thicknesses.

Keywords: Aluminium alloys; Precipitation; Heterogeneous nucleation; High-angle annular dark field (HAADF)

1. Introduction

The effect of Sn on the precipitation behaviour of an Al–1.7Cu alloy (all alloy compositions will hereafter be given in at.%) is a classic example of how specific trace alloying additions can significantly improve the precipitation-hardening response of an alloy. In this case the introduction of a mere 0.01 at.% Sn results in a 100% increase in peak hardness and a dramatic acceleration in the hardening response (e.g. 1 h instead of 24 h to reach peak hardness at 200 °C) [1,2]. Other microalloying additions such as Cd, In and Ag have been observed to have similarly beneficial effects on the mechanical properties of Al alloys [2–3], thus making this phenomenon one of great practical importance. In fact, microalloying additions are commonly used ingredients in the development of high-strength Al alloys [4,5].

Although the advantageous role of microalloying additions in strengthening Al alloys has been known empirically for many decades [2,3], the mechanisms at play remain poorly understood. The case of Sn-microalloyed Al–1.7Cu studied here is no exception, despite the fact that Al–Cu is one of the most-studied and characterized precipitation-hardened Al alloy systems [3,5,6].

It has long been established that precipitation hardening of Al–1.7Cu takes place via the decomposition of a Cu solid solution in the α-Al matrix phase into a series of metastable Cu-rich solid-state precipitate phases: GP(I) (Guinier–Preston) zones, the intermediate precipitate phases θ″ and θ′ (of nominal stoichiometries Al_3Cu and Al_2Cu, respectively), and the equilibrium phase θ (Al_2Cu). At moderate ageing temperatures (below about 160 °C),

* Corresponding author at: Monash Centre for Electron Microscopy, Monash University, Victoria 3800, Australia. Tel.: +61 3 99055368; fax: +61 3 99053600.
E-mail address: laure.bourgeois@monash.edu (L. Bourgeois).

1359-6454/$36.00 © 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2011.10.015

Table 1
Crystallographic data for the three crystal phases encountered in the present study. The data for α-Al and β-Sn are given for their bulk form at 25 °C.

Phase	Space group	Lattice parameters (Å)	Atomic positions in asymmetric unit cell	Ref.
α-Al	$Fm\bar{3}m$	$a_\alpha = 4.05$	Al at (0,0,0)	
θ′	$I4/m$	$a_{\theta'} = 4.04$; $c_{\theta'} = 5.8$	Cu at (0,0,0) Al at (0,0.5,0.25)	[8]
β-Sn	$I4_1/amd$	$a_\beta = 5.83$; $c_\beta = 3.18$	Sn at (0,0,0)	[11]

the full precipitation sequence of GP(I) → θ″ → θ′ → θ can be observed [7]. The θ′ phase, and to a lesser extent the θ″ phase, are the main strengthening constituents of the precipitation-hardened Al–1.7Cu alloy [8]. GP(I) zones, θ″ and θ′ precipitates all contain Cu atomic planes coherent with the {1 0 0} atomic planes of the α-Al matrix. The θ′ phase, in particular, precipitates from the solid solution in the form of thin platelets of high aspect ratio (~40 at peak hardness) with their broad face parallel to $\{100\}_\alpha$ [9,10]. The crystal structure of θ′ is distinct from α-Al, with an orientation relationship ($(001)_{\theta'}//(001)_\alpha$, $[100]_{\theta'}//[100]_\alpha$) [8] that allows near full coherence along the $\langle 100\rangle_{\theta'}$ directions. The crystallographic data for the α-Al and θ′ phases is provided in Table 1.

Unaided, the θ′ phase nucleates with great difficulty in Al–Cu alloys, in which case it forms a coarse and inhomogeneous distribution that is ineffective in impeding stress-generated dislocations and consequently at strengthening the alloy. It was recognized more than 50 years ago [12,13] that the substantial improvement in the hardening response of Al–Cu alloys microalloyed with Sn [2] is the consequence of a large increase in the nucleation rate of θ′ at the expense of the θ″ phase and GP(I) zones. Subsequent works [6,14–16] revealed the presence of Sn nanoparticles, presumably of β-Sn phase (see Table 1 for the β-Sn crystal structure) adjacent to the majority of θ′ platelets, strongly suggestive of Sn playing a direct role in the precipitation of θ′. However, to date there exists no satisfactory description of the specific mechanisms by which Sn promotes the nucleation of θ′ precipitates. Indeed, studies on the subject have yielded widely varying answers to the question as to which contributions to the nucleation rate of θ′ are enhanced by microalloying additions X (where X = Sn, Cd, In) [1,2,12,14–26]. Kinetics [2,12,19,21,23], volumetric misfit strain [14], shear strain [16,18] and interfacial energy [12,15,17,22–24] have all been invoked as factors in the role of X. There is also disagreement on the active form taken by Sn in promoting the nucleation of θ′: solute atoms [2,12,21,25,26] and/or β-Sn precipitates [12,14,15,22,23]. One reason for the persisting confusion is that despite much research on microalloyed Al–1.7Cu systems, there has been surprisingly little detailed structural examination of θ′ precipitates since Silcock's pioneering X-ray experiments. In addition, although high-resolution transmission electron microscopy (TEM) imaging has been used successfully to determine the crystallography of β-Sn precipitates [25,26], this technique fails to provide accurate information about particle morphology, size and interfacial structure for nanoscale precipitates embedded in a matrix.

The present work aims to address these deficiencies through a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) study of the θ′ phase in Al–1.7Cu–0.01Sn. This imaging technique has already proven to be extremely valuable for atomic-scale structural studies of other Al alloys [27–28]. The large relative difference in atomic number (Z) of the three elements contained in the alloy (Al ($Z = 13$), Cu ($Z = 29$) and Sn ($Z = 50$)) makes HAADF-STEM particularly suited to this system. We demonstrate that Sn favours the nucleation of θ′ with special precipitate thickness values, and that the nucleation mechanism involves solute Sn rather than pre-existing particles of β-Sn phase.

2. Experimental and computational procedures

2.1. Alloy fabrication

Two alloys of nominal compositions Al–1.7Cu and Al–1.7Cu–0.01Sn were investigated. They will be referred to hereafter as AC and ACS, respectively. They were prepared from high-purity elements (Al: 99.92%, Cu: 99.8%, Sn: 99.9%). The cast ingots were homogenized for 48 h at 520 °C and hot extruded at 450 °C into plates 14 mm thick and 60 mm wide. The extrusion ratio was 16:1. The actual compositions of the alloys were determined spectroscopically to be Al–1.67Cu–0.009Sn (0.03Si, 0.01Fe) and Al–1.63Cu (0.03Si, 0.01Fe) at.%, where Si and Fe are impurity elements. TEM showed these impurities to be concentrated at grain boundaries.

2.2. Heat treatments and TEM sample preparation

The ingots were cut into disks 3 mm in diameter and 0.5 mm in thickness. These were then heat treated according to a conventional age-hardening regime: solution treatment in a nitrate salt bath for 30 min at 525 °C, followed by a cold water quench, then isothermal ageing in an oil bath for times ranging from 2 min to 24 h at 200 or 160 °C, and a final cold water quench. The heat-treated disks were ground to a thickness of 0.2 mm and twin-jet electropolished in a solution of 33% nitric acid and 67% methanol at –20 °C using a voltage of 13 V.

2.3. Scanning transmission electron microscopy (STEM)

All images shown in this work were taken in HAADF-STEM mode. A JEOL JEM 2100F field-emission gun scanning transmission electron microscope operated at 200 kV was used to obtain most of the results. The instrument has a point resolution of 2.3 Å and a STEM resolution of 1.9 Å. Except where otherwise, specified HAADF-STEM