Journal of Alloys and Compounds 579 (2013) 138–146

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Phase transformation and precipitation of an Al–Cu alloy during non-isothermal heating studied by in situ small-angle and wide-angle scattering

Cheng-Si Tsao [a,*], E-Wen Huang [b,*], Ming-Hsien Wen [b], Tsung-Yuan Kuo [c], Sheng-Long Jeng [a], U-Ser Jeng [d], Ya-Sen Sun [b]

[a] Institute of Nuclear Energy Research, Longtan, Taoyuan 32546, Taiwan
[b] Department of Chemical and Materials Engineering and Center for Neutron Beam Applications, National Central University, Taoyuan 32001, Taiwan
[c] Department of Mechanical Engineering, Southern Taiwan University of Science and Technology, Tainan 71005, Taiwan
[d] National Synchrotron Radiation Research Center, Hsinchu 30077, Taiwan

ARTICLE INFO

Article history:
Received 10 March 2013
Received in revised form 27 April 2013
Accepted 29 April 2013
Available online 16 May 2013

Keywords:
Al–Cu alloy
Precipitation
Phase transformation
Small-angle X-ray scattering
Wide-angle X-ray scattering

ABSTRACT

Understanding the classic precipitation sequence of Al–Cu alloys, solid solution → Guinier–Preston (GP) zones → θ″ → θ′ → stable θ, is of academic importance. In situ synchrotron small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) techniques were employed simultaneously to study the temperature-dependent behavior of various intermediate precipitation steps in the non-isothermal heating of Al–5.4 wt%Cu alloy. This study quantitatively demonstrates the concurrent evolution of the lattice structure, volume fraction (growth and dissolution) and structural growth in the thickness and length directions with temperature for various intermediate (metastable) precipitates for the first time. The detailed phase transformation mechanism and structural evolution in the precipitation sequence (for GP zones, θ″, θ′ and θ phases) can then be resolved. Our data analysis also considered the concurrent existence of multiple precipitates in the precipitation sequence. Moreover, the evolutional behavior of the orientation of precipitates in each precipitation step can be concurrently revealed. Different SAXS analysis models were proposed to successfully interpret the SAXS data. The new information presented by the SAXS/WAXS approach provides insight into the phase transformation mechanism of precipitation in Al–Cu alloys.

1. Introduction

Aluminum alloys have potential applications in various vehicles and portable devices due to their low weight and high strength. Precipitation hardening by heat treatment is critical in optimizing mechanical performance to achieve rational design. Al–Cu alloys, with metastable and spatially dispersed θ′ precipitates as the primary strengthening phase, have a long history and are of academic importance [1–9]. The θ′ phase of Al–Cu alloys has been a favorite model system for studying the theories or mechanisms of phase transformation in aluminum alloys [2]. The well-known classical precipitation sequence during heating, solid solution (SS) → Guinier–Preston (GP) zones (or GP I zones) → θ″ (or GP II zones) → θ′ → stable θ, is the textbook example of aging hardening [1–3]. The nucleation and growth of θ′ precipitates is arguably the model case for understanding the transition of intermediate (metastable) phases starting from the decomposition of a supersaturated solid solution. The formation and structure of metastable GP and θ″ (GP II) zones in the Al–Cu alloys has also attracted fundamental research interest [4,7,10–13].

Although extensive experimental studies have been conducted on the various precipitates in Al–Cu alloys, they focused on the lattice structures, interfacial characteristics and nanoscale morphology of precipitates using transmission electron microscopy (TEM) [2,4–7,13,14], atom-probe tomography [3] and X-ray diffraction, among other techniques. Several theoretical studies have also been conducted on the growth kinetics, morphology and strengthening mechanism of θ′ phase [1,8,9]. However, due to the lack of accurate information, such as the chemical free energies of metastable phases, lattice mismatch on the interface, interfacial energies and elastic strain, the development of model calculations has also focused on the θ′ phase under a certain set of simplified conditions [1,2]. On the other hand, microscopic observations have inherent drawbacks, such as limited sample preparation, local variation and counting statistics. Comprehensive quantitative or

* Corresponding authors. Tel.: +886 3 4711400x3420; fax: +886 3 4115851 (C.-S. Tsao), tel.: +886 3 4227151x34207 (E.-W. Huang).
E-mail addresses: cstsao@iner.gov.tw (C.-S. Tsao), ewhuang@ncu.edu.tw (E.-W. Huang).

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http://dx.doi.org/10.1016/j.jallcom.2013.04.201

qualitative understanding of the phase transformation between the intermediate phases and complex structural evolution in this precipitation sequence is still lacking. So far, no experimental work has simultaneously measured both the phase (lattice structure) transformation and the morphological evolution (including the growth and dissolution of the volume fraction) of various intermediate phases in the precipitation sequence for Al–Cu alloys. Differential scanning calorimetry (DSC) can be used to effectively investigate the precipitation kinetics (relative volume fraction) or qualitative temporal behavior of the precipitation sequence [15–19]. This method is based on simplified assumptions and previously known information. The non-isothermal theoretical model was developed simply based on the response of a metastable phase into stable phase without considering the transformations of a series of intermediate phases and multiple phases.

Small-angle X-ray scattering (SAXS) is a powerful tool for non-destructively investigating the shape and size distribution of a large number of particles in the bulk sample [20–25]. The combination of SAXS and wide-angle X-ray scattering (WAXS; i.e., X-ray diffraction) was used to study the phase separation of amorphous alloys [26–28]. In this study, we employed simultaneous synchrotron SAXS and WAXS [29,30] to measure the temperature-dependent behavior and various corresponding precipitation steps in Al–5.4 wt%Cu alloy subjected to non-isothermal heating. The concurrent evolutions of lattice structure, volume fraction (growth and dissolution) and structural growths in the thickness and length directions with temperature for various plate-like intermediate precipitates were determined by in situ WAXS and SAXS measurements for the first time. The detailed phase transformation mechanism and structural evolution in the precipitation sequence (comprised of the GP zones and θ″, θ′ and θ phases) can be thus resolved, unlike in previous experimental studies. Our data analysis also considered the concurrent existence and transformation of θ′ and θ phases (i.e., multiple precipitates) in the precipitation step. Moreover, the evolutional behaviors of the orientation and spatial distribution of precipitates relative to the lattice planes of the Al matrix during each precipitation step are concurrently determined from our in situ two-dimensional (2D) SAXS patterns. Due to the distinctive SAXS profiles contributed by the GP zones (spatially ordered), θ″ and θ′ phases, different SAXS analysis models were proposed herein to successfully interpret the SAXS data.

The in situ SAXS and WAXS measurements characterizing the concurrent evolutions of lattice phase, morphology and spatial orientation can determine whether the new phase is nucleated from another site or is formed by the transformation of the precursor into a nucleation site. In the present study, the new information provides insight into the phase transformation mechanism of non-isothermal precipitation for the aluminum alloys. The phase transformations and morphological behavior of a series of metastable intermediate precipitates are correlated with a simple non-isothermal precipitation kinetics theory herein. The results advance the current fundamental understanding of this process. These data can serve as the basis for modifying or improving future theoretical studies. Finally, this study is relevant to industrial applications because several important processes and treatments are non-isothermal, such as welding.

2. Experimental

The 2-mm-thick Al–5.4 wt%Cu alloy sheets were fabricated by ALCAN International. The composition of impurity of the alloy is listed in Supplementary data. The alloy sheets were heat-solution treated at 542 °C and then drop-quenched in water at room temperature (RT). Before the SAXS/WAXS experiment, one alloy sample was aged at RT for one month (i.e., naturally aged) and another was aged at 200 °C for 1 h, respectively. These samples are denoted as NA and A1h, respectively, for simplification. The simultaneous SAXS/WAXS experiment was performed at the National Synchrotron Radiation Research Center, Taiwan. The experimental procedure and scattering instrument configuration (see Fig. 1) were described elsewhere [29]. The optimum thickness for the Al–Cu samples is ~200 μm. The grain size in the alloy samples observed by the optical microscope is averagely 120 μm. The beam size (~1 mm^2) allows us to probe the precipitates lying on several oriented grains (like powder-like sample). The sample being studied was placed in a program-controlled heating container. In situ SAXS/WAXS measurements were conducted to study the precipitation behavior during heating from RT to 500 °C for the NA and A1h samples. The heating rate for both samples was 20 °C/min. The 2D SAXS and WAXS patterns collected were reduced into 1D SAXS and WAXS profiles as a function of the scattering vector, Q (=$4\pi/\lambda \sin(\theta/2)$; θ is the SAXS scattering angle, λ is the incident radiation wavelength), respectively, using standard data reduction procedures (e.g., background subtraction, angular averaging). Because the SAXS and WAXS data collection times per frame differed, the measured temperatures were slightly shifted between the SAXS and WAXS data.

3. Results

The temperature-dependent 1D WAXS patterns of the samples after natural aging (NA) or artificial aging (A1h) pretreatment during non-isothermal heating are shown in Fig. 2. The theoretical X-ray diffraction (XRD) patterns of the θ″, θ′, θ and α matrix phases in the Al–Cu alloy were calculated using Powder Cell software (see Supplementary data). The peak positions and relative intensities of the experimental WAXS patterns corresponding to the θ″, θ′, θ and α matrix phases (Fig. 2) are consistent with the theoretical XRD patterns. The temperature dependence of the peak positions in the WAXS patterns during heating signifies the phase (lattice structure) transformation between the intermediate phases of each step in the precipitation sequence. For the NA sample (Fig. 2a), the precipitation sequence identified by WAXS is as follows: GP (RT ~ 210 °C) → θ′ (210–390 °C) → θ′ + θ (390–450 °C) → θ (450–510 °C). For the A1h sample (Fig. 2b), the corresponding precipitation sequence is as follows: θ″ (RT ~ 270 °C) → θ′ (270–350 °C) → θ′ + θ (350–410 °C) → θ (410–510 °C). The temperatures and WAXS peak positions of the various phases are listed in Tables S1 and S2 of the Supplementary data. Moreover, the temperature evolution of the relative peak intensities in the WAXS patterns qualitatively indicates the dissolution or growth of the precipitate phase in each step. According to the WAXS result, we can describe the precipitation sequence more definitely and generally than previous reports: (1) dissolution of the θ″ (GP II zones) or GP zones (formed in the pretreatment) → (2) formation and growth of the θ′ phase → (3) dissolution of θ′ concurrently with the formation of the θ phase → (4) growth of only the θ phase (also see Table S1). This information is reported for the first time based on direct evidence from in situ structural characterization. The 2D WAXS patterns corresponding to (1) the initial GP zones, (2) the initial θ″ phase, (3) the intermediate θ′ phase, (4) the concurrent existence of the θ′ and θ phases and (5) the final stable θ phase are demonstrated in Fig. 3.

Simultaneous SAXS measurements were conducted to correlate the phase transformation to the concurrent morphological

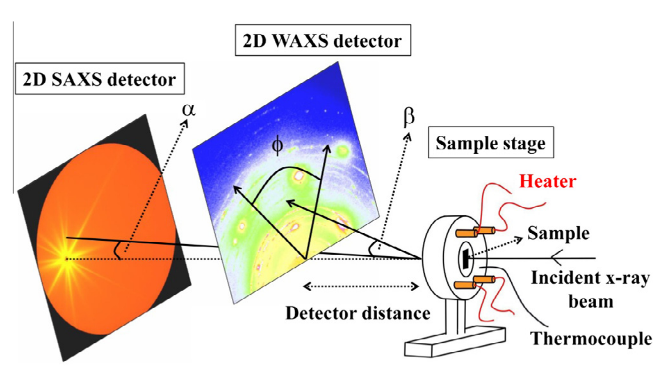

Fig. 1. Instrumental configuration of simultaneous SAXS/WAXS measurement.