Materials Characterization 120 (2016) 30–37

Contents lists available at ScienceDirect

Materials Characterization

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

Continuous cooling precipitation diagram of aluminium alloy AA7150 based on a new fast scanning calorimetry and interrupted quenching method

Bin Yang [a,c,*], Benjamin Milkereit [a,b,c,**], Yong Zhang [d], Paul A. Rometsch [d], Olaf Kessler [b,c], Christoph Schick [a,c]

[a] *Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18051 Rostock, Germany*
[b] *Faculty of Mechanical Engineering and Marine Technology, University of Rostock, Albert-Einstein-Str. 2, 18051 Rostock, Germany*
[c] *Competence Centre CALOR, Faculty of Interdisciplinary Research, University of Rostock, Albert-Einstein-Str. 25, 18051 Rostock, Germany*
[d] *Department of Materials Science and Engineering, Monash University, Clayton, Melbourne, VIC 3800, Australia*

ARTICLE INFO

Article history:
Received 29 March 2016
Received in revised form 7 July 2016
Accepted 17 August 2016
Available online 19 August 2016

Keywords:
Aluminium alloys
Differential fast scanning calorimetry
Continuous cooling precipitation diagram
Critical cooling rate
Precipitation kinetics

ABSTRACT

Differential fast scanning calorimetry (DFSC) has been combined with a novel differential reheating method (DRM). Interrupted quenching at different temperatures followed by overcritical cooling enables both time- and temperature-dependent investigations of precipitation reactions in aluminium alloys during cooling from solution annealing at cooling rates between 1 K/s and 10^5 K/s. Together with conventional differential scanning calorimetry (DSC) results, for the very first time, a full continuous cooling precipitation (CCP) diagram for a highly concentrated wrought AlZnMgCu alloy has been developed. For alloy AA7150, three precipitation reactions with their respective start and end temperatures were observed by DFSC. The critical cooling rate for suppressing the high-temperature precipitation of *S*-Al_2CuMg was found to be ~10 K/s, whereas for the medium-temperature precipitation of η-Mg(Zn,Al,Cu)$_2$ it is ~100 K/s and for the low-temperature precipitation of *Y*-phase plates enriched in Zn and Cu it is ~300 K/s. The method can potentially be transferred to similar precipitate-forming metallic systems or related solid-state phase transformation systems also beyond the particular system analysed in the present study.

1. Introduction

The strength of precipitation hardening aluminium alloys is typically adjusted by means of a solid-state age hardening heat treatment procedure. The age hardening process contains three steps: solution annealing (in solid state), quenching and ageing. During the solution treatment all soluble phases should dissolve. During quenching, this solution should be retained and an unstable, supersaturated solid solution results. During ageing, nano-sized particles precipitate, which hinder dislocation movement by particle strengthening and thereby increase the strength of the alloy. The tendency to lose supersaturation of dissolved alloying elements during cooling from solution annealing is called quench sensitivity. The quench sensitivity or the precipitation behaviour of aluminium alloys during cooling from solution annealing is typically described in continuous cooling precipitation (CCP) diagrams. Such CCP diagrams need to cover a wide range of cooling rates from near-equilibrium slow cooling [1,2] up to beyond the upper critical cooling rate (CCR) [1,3,4]. The CCR is defined as the slowest cooling rate at which no precipitation occurs during cooling from solution annealing, which ensures maximum supersaturation after quenching and thereby maximum volume fractions of strengthening precipitates, and hence maximum strength, after subsequent artificial ageing.

During the last decade, measurement techniques to investigate the quench sensitivity of aluminium alloys were developed [1,3–10]. For example, one of the techniques combines microstructural analysis and mechanical testing with in-situ differential scanning calorimetry (DSC) [1,3,4]. DSC is able to detect the enthalpy changes caused by precipitation reactions, whereby the enthalpy change gives a direct link to the thermodynamics and volume fractions of the phases. The work [1,3,4], which combines microstructural analysis and mechanical testing with in-situ DSC, led to the first continuous cooling precipitation diagrams of low to medium alloyed AlMgSi (6000 series) and AlZnMg(Cu) (7000 series) wrought alloys.

As a diffusion controlled process, precipitation during quenching depends on nucleation as well as on diffusion rate. Diffusion rate mainly

---

[*] Correspondence to: B. Yang, Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24, 18051 Rostock, Germany.

[**] Correspondence to: B. Milkereit, Faculty of Mechanical Engineering and Marine Technology, University of Rostock, Albert-Einstein-Str. 2, 18051 Rostock, Germany.

E-mail addresses: bin.yang@uni-rostock.de (B. Yang), benjamin.milkereit@uni-rostock.de (B. Milkereit).

http://dx.doi.org/10.1016/j.matchar.2016.08.016
1044-5803/

depends on the types of diffusing atoms and matrix (e.g. Zn in Al) and temperature. Nucleation mainly depends on supersaturation (homogeneous nucleation) and intrinsic nuclei (heterogeneous nucleation). Intrinsic nuclei may be grain boundaries, primary precipitates or dispersoids. Thus, the quench sensitivity of an aluminium alloy can be influenced by its chemical composition and solution annealing parameters (supersaturation) as well as by its microstructure (intrinsic nuclei). DSC always measures the enthalpy changes due to precipitation influenced by a superposition of all the above mentioned factors, i.e. diffusion rate, supersaturation and microstructure (intrinsic nuclei).

The precipitation process in AlZnMg(Cu) alloys is complex and may be divided into precipitation of different phases over different temperature and time ranges during different process steps [4,5,11,12]. More specifically, there are three different classes of precipitates. Firstly, relatively coarse primary precipitates tend to grow directly from the melt (e.g. via eutectic reactions) and reach dimensions of several μm. In this particular case, the Al_7Cu_2Fe intermetallic particles fall into this category. Such primary precipitates are assumed not to be influenced by the age hardening heat treatment. However, they may act as nucleation sites for coarse equilibrium phases that precipitate during slow cooling. Secondly, dispersoids occur. Dispersoids are based on minor alloying elements like Zr, Mn and Cr and form intermetallic particles of sizes typically in the range of 10–100 nm. Precipitation of dispersoids is a solid-state reaction that commonly occurs during homogenisation heat treatments. Dispersoids are also assumed not to be influenced by the age hardening heat treatment. However, they can strongly influence the quench sensitivity as dispersoids may act as nucleation sites for the quench-induced phases [12]. Thirdly, there are precipitates that form from the main alloying elements (here Zn, Mg, Cu and Al) and are greatly influenced by the age hardening procedure. In an ideal case, all these last-mentioned precipitates dissolve during solution annealing, and the quenching step should suppress any precipitation during cooling. During subsequent ageing, fine metastable nano-scale hardening precipitates are nucleated and evolve along a precipitation sequence with increasing ageing. As mentioned before, the aim of quenching from solution annealing is to retain the solid solution by avoiding any quench-induced precipitation that would lower the potential for subsequent hardening. Based on recent work from the present authors [4,12], the precipitation reactions during cooling of alloy AA7150 from solution annealing were divided into three main reactions: high-, medium- and low-temperature reactions (HTR, MTR and LTR, respectively). Nevertheless, the CCRs of MTR and LTR have so far only been inferred from ex-situ microstructure and property observations because conventional DSC is limited to cooling rates below ~10 K/s [13,14]. Furthermore, their precipitation temperature ranges at cooling rates above 3 K/s are unknown [4]. However, cooling rates between 1 and 10^3 K/s are highly relevant in technological processes, because such cooling rates are reached by water quenching (depending on the material thickness and water temperature) [15]. Besides, the more concentrated higher strength Al alloys have critical cooling rates in the range from ~10 to 10^3 K/s [3,4,16–19].

Recently it was shown that the chip-sensor based differential fast scanning calorimetry (DFSC), whose heating and cooling rates can reach up to some 10^6 K/s [20,21], could be utilised to follow precipitation reactions in Al alloy 7049A by the indirect differential reheating method (DRM) [22]. Based on this approach, the CCR of Al alloy 7049A was determined to be about 300 K/s. However, so far it was only shown that the DRM is able to detect the overall precipitation enthalpy at high cooling rates — unfortunately without any temperature-dependent information of individual precipitation reactions.

In this current work, we aim to close the former metrological gap by describing a method to obtain temperature-dependent enthalpy information of precipitation reactions in alloy AA7150 in the cooling rate range from a few up to several thousands of K/s. The DRM was developed further towards higher precision, larger cooling rate range of validity and particularly temperature dependency. Thereby, for the very first time, a full continuous cooling precipitation diagram covering all the technologically relevant cooling rates could be recorded for a highly concentrated AlZnMgCu wrought alloy (i.e. AA7150).

2. Materials and Methods

Bulk samples of alloy AA7150 (composition given in Table 1) were cut from the centre layer of a commercially produced 80 mm thick plate, supplied by the Aluminium Corporation of China Ltd. (Chalco). In order to obtain samples for DFSC measurements, a small piece of $5 \times 10 \times 20$ mm^3 was cut from the centre layer of the thick plate, as shown in Fig. 1(a). Then the material was heated up to 460 °C for 1 h followed by slowly heating up to 480 °C for another 1 h and finally quenched in cold water as a pre-solutionising treatment in a furnace [4]. This pre-treatment was done to reduce local chemical inhomogeneities in the thick industrially processed plate, thereby avoiding high local solute concentrations that could result in localised melting during the DSC and DFSC heating cycles. It therefore enabled the heating times in the calorimeter to be shortened significantly without any risk of incipient melting (which could occur if samples were heated rapidly directly to 480 °C without the prior removal of concentration gradients at a safe temperature of ~460 °C).

To obtain DFSC samples, a slice of about 300 μm thickness was cut parallel to the short transverse direction (STD)–long transverse direction (LTD) plane. Further, the slice was manually ground and polished to foils having a thickness of around 50 μm. As shown in Fig. 1(b), the foil thickness direction was aligned with rolling direction (RD) and was perpendicular to the sensor plane. The reason for this was to capture a more representative cross-section of the material, especially ensuring that sufficient grain boundaries were included in the thin foil. After that, the sample for DFSC measurements was cut into small rectangular pieces by a scalpel under an optical microscope and placed on the centre of the sensor by a thin copper wire, as shown in Fig. 1(c). In order to secure the small sample on the sensor, silicone oil was used, which would be evaporated during the first heating up to 480 °C.

DFSC is controlled by the power compensation method, which takes care of the heat losses on both sensors (loaded sample and empty reference) following the predefined temperature program very closely. Even at 10^4 K/s, the temperature difference between reference (T_R) and sample sensor (T_S) obeys the inequality, $T_R - T_S < 0.1$ K [21]. The nanocalorimeter sensor, XI-415 (Xensor Integrations, Netherlands), was used in this work. The sensor consists of an amorphous silicon-nitride membrane with a film-thermopile and a resistive film-heater placed at the centre of the membrane, as shown in Fig. 1(d). The sensor can effectively promote high heating and cooling rates up to 10^5 K/s through a preferable ratio between the added heat capacity of the sensor and sample heat capacity and applicable heating power. In a micron scale system, the most efficient cooling agents are gases because of their small heat capacity [23]. Considering these circumstances, we have chosen samples with a size of approximately 75 μm × 110 μm × 40 μm, as shown in Fig. 1(c). The DFSC temperature was calibrated by pure In, Sn, Pb, Zn and K_2SO_4 in an Ar7.5/H_2 (volume fraction in %) atmosphere at different heating and cooling rates up to 10^5 K/s. Further details about the temperature calibration method are given in Ref. [21].

In order to develop a complete CCP diagram, the CCR should be determined first. The CCR for alloy AA7150 is expected to be between 100 and 1000 K/s [24]. The low signal to noise ratio of the DFSC at these scanning rates, due to the very small thermal effects of

Table 1
Chemical composition of the investigated AA7150 alloy (in mass fraction).

Elements	Si	Fe	Cu	Mn	Mg	Zn	Zr	Al
Mass fraction (%)	0.02	0.05	2.04	0.04	2.15	6.33	0.12	Bal