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In situ small-angle scattering study of the precipitation kinetics in an Al–Zr–Sc alloy

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Abstract

A time-resolved small-angle X-ray scattering (SAXS) study was carried out to investigate the precipitation kinetics of L1$_2$ Al$_3$(Zr, Sc) precipitates in aluminium at temperatures ranging between 400 and 475 °C. It is shown that the chemical heterogeneity of the precipitates, which consist of a Sc-rich core and a Zr-rich shell, results in a characteristic SAXS signal, which can be fitted by a three-phase model to extract the chemical and morphological features of the precipitate size distribution. The experimental results show a strong effect of the heating rate on the precipitation kinetics, and a precipitate density strikingly constant with time in the investigated range. These results are discussed in view of the mechanisms proposed in the existing literature for the formation of the core–shell structure of these precipitates.

Keywords: Small angle X-ray scattering; Aluminium alloys; Al–Zr–Sc; Precipitation; Chemical heterogeneity

1. Introduction

Formation of Al$_3$Zr precipitates (called dispersoids) in aluminium alloys has been used for a long time, especially in alloys for aerospace applications (such as AA7000 series). This is due to their ability to pin grain and subgrain boundaries, leading to the desired very low recrystallized fractions; in addition, Al$_3$Zr dispersoids are less efficient sites for heterogeneous precipitation as compared with chromium-based dispersoids, for instance, leading to the development of less quench-sensitive alloys. The Al$_3$Zr precipitate's equilibrium crystal structure is DO$_{23}$; however, the metastable L1$_2$ form is always found in technologically relevant situations.

Since the mid-1980s, there has been a strong interest in the addition of scandium to zirconium as solutes in aluminium [1,2]. It was shown that such an addition resulted in a significant enhancement of the resistance to recrystallization, and consequently in better mechanical properties [3–10]. Scandium also forms L1$_2$ Al$_3$Sc precipitates with aluminium, which is in this case the stable phase [11–16]. When Sc and Zr are both present, Al$_3$(Zr,Sc) precipitates are formed, Sc and Zr having a complete miscibility [2,10,17]. Several studies have shown that these spherical precipitates have a distinct chemical heterogeneity [17–20]: the precipitate core is essentially scandium rich and the shell shows a higher zirconium concentration. This peculiar chemical structure was attributed to two complementary effects: the combination of the very different diffusion coefficients of the two species [21,22], associated with the fact that the energy for creating a vacancy in the L1$_2$ lattice is extremely high [20], which results in a conservation of the history of formation of the precipitate; and the decrease of interfacial energy by the presence at the sample surface of a high Zr concentration [4,17].

The aim of the present paper is to analyse in detail the precipitation kinetics in an Al–Zr–Sc alloy and, notably, to evaluate whether this particular chemical heterogeneity of the precipitate results in distinct kinetic features. For this purpose, small-angle X-ray scattering (SAXS), which provides a quantitative analysis of the precipitate size and

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volume fraction [23–25], will be used. It was shown recently in a former paper that SAXS is a quantitative tool which can provide measurements of several microstructural features in chemically heterogeneous precipitates. It will be shown how in situ measurements carried out with a synchrotron source can highlight the complex microstructural evolution in this system.

2. Experimental method

The alloy studied was provided by Alcan – Centre de Recherches de Voreppe. The composition is Al–0.16 wt.% Sc, 0.1 wt.% Zr (or 0.09 at.% Sc and 0.03 at.% Zr). Fe and Si contents are approximately 30 and 100 ppm, respectively. Ingots were cast at 695 °C, air cooled and subsequently homogenized at 630 °C for 360 h (to remove the micro-segregation of zirconium), followed by a 800 °C min^{-1} quench to room temperature. Subsequent heat treatments were carried out between 400 and 475 °C, with heating rates ranging between 5 and 430 °C min^{-1}.

All SAXS experiments have been carried out on the D2AM beamline (BM02-CRG) of the European Synchrotron Radiation Facility (ESRF). X-rays are generated by a bending magnet, are focused and monochromated to better than $\delta\lambda/\lambda = 2 \times 10^{-4}$ at a wavelength of 1.61 Å. Acquisition is carried out with a 2D-CCD camera. A sample-to-detector distance of 0.8 m was used, giving access to a range of scattering vectors [0.01, 0.2] Å^{-1}. CCD images are corrected for electronic noise, spatial distortion, pixel efficiency and background noise. A circular average is then performed for the calculation of the intensity scattered at a given angle. Intensity is converted in absolute units by measuring the sample transmission and by measuring reference samples, leading to an overall precision better than ±10%.

For in situ experiments, the 70-μm-thick samples are placed in a resistance furnace in vacuum which enables a maximum heating rate of 10 K s^{-1}.

3. Evidence of the core–shell structure of the precipitates

As detailed above, it is now widely recognized that the $Al_3(Zr,Sc)$ precipitates are not chemically homogeneous. The precipitates have been shown to consist of a Sc-rich core, surrounded by a shell rich in Zr, this chemical heterogeneity evolving with time. Since Zr and Sc atoms have very different atomic numbers, it can be expected that such a chemical inhomogeneity results in a specific SAXS signal, such as been observed in the Al–Ag system [26]. In a previously published paper [20], it was shown that the chemical heterogeneity results in oscillations of the SAXS signal, which can be used for quantification of the microstructural features. Moreover, the outcome of this quantification was demonstrated to be consistent with that of two other experimental techniques, namely tomographic atom probe and high angle annular dark field (HAADF) transmission electron microscopy (TEM).

Fig. 1 shows an example of an experimental scattering curve, represented both in a log(I) vs q plot, and in an Iq^4 vs q plot. The latter plot converges in a classical two-phase system with sharp interfaces to a horizontal curve reflecting the asymptotic $1/q^4$ behaviour (called Porod approximation). In the present case, both curves show strong oscillations, which are highly unusual in metallic systems.

It is possible to predict the scattering curve of a size distribution of spheres, and compare it with the experimental spectrum. It was shown in former studies of binary systems such as the Fe–Cu system, to enable a very good descrip-

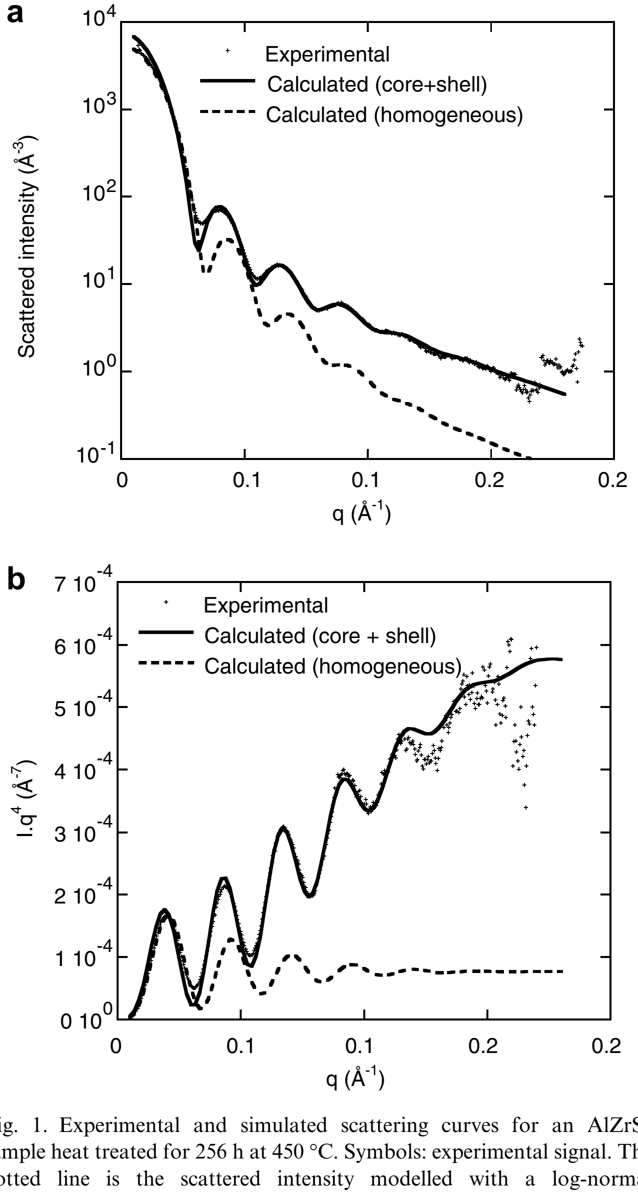

Fig. 1. Experimental and simulated scattering curves for an AlZrSc sample heat treated for 256 h at 450 °C. Symbols: experimental signal. The dotted line is the scattered intensity modelled with a log-normal distribution of spheres of homogeneous composition, and the solid line is the intensity modelled with a log normal distribution of spheres with a core–shell chemical structure; parameters of the simulation: log normal distribution ($s = 0.08$, $R = 13$ nm), shell 13% of the precipitate size, composition in solute atoms of the shell 55% Zr. (a) ln(I) vs q plot; (b) Iq^4 vs q plot.