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Quantitative measurement for the microstructural parameters of nano-precipitates in Al-Mg-Si-Cu alloys

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ABSTRACT

Size, number density and volume fraction of nano-precipitates are important microstructural parameters controlling the strengthening of materials. In this work a widely accessible, convenient, moderately time efficient method with acceptable accuracy and precision has been provided for measurement of volume fraction of nano-precipitates in crystalline materials. The method is based on the traditional but highly accurate technique of measuring foil thickness via convergent beam electron diffraction. A new equation is proposed and verified with the aid of 3-dimensional atom probe (3DAP) analysis, to compensate for the additional error resulted from the hardly distinguishable contrast of too short incomplete precipitates cut by the foil surface. The method can be performed on a regular foil specimen with a modern LaB_6 or field-emission-gun transmission electron microscope. Precisions around ±16% have been obtained for precipitate volume fractions of needle-like β″/C and Q precipitates in an aged Al-Mg-Si-Cu alloy. The measured number density is close to that directly obtained using 3DAP analysis by a misfit of 4.5%, and the estimated precision for number density measurement is about ±11%. The limitations of the method are also discussed.

1. Introduction

Quantification of typical microstructures plays an important role in deep understanding of phase transformations in materials and provides clues to the mechanisms controlling the materials' properties. Recent progress in quantitative simulations of the microstructures and mechanical properties based on methods such as CALculation of PHAse Diagrams (CALPHAD) [1,2], multi-phase field simulation [3,4] and yield strength modeling [5] further enhances this importance because all these methods need accurate experimental verifications concerning the microstructures. Among the many microstructural parameters, the combination of size and number density of particles drastically affects the hardness and strength of the materials. For example, an intra granular microstructure with fine needle-like nano-precipitates occurring in a high number density can double or triple the strength of Al-Mg-Si(-Cu) alloys [6,7].

Various methods have been established to quantify the many aspects of the microstructures such as texture, solute segregation, volume fraction (i.e. product of size and number density) of second phase particles, grain size and so on. For example, the recent progress in X-ray nano-tomography [8,9] and serial-sectioning using SEM/FIB (scanning electron microscopy with focused ion beam) [10,11] has made it possible to visualize different phases in 3D with varying sizes from several tens of microns down to several tens of nanometers. It is also possible to observe nano-objects (with at least one dimension below 10 nm) in 3D by quantitative electron tomography and thus to obtain their volume fraction [12–14]. However, a risk of beam damage exists due to the long exposure time (typically up to 46 min in total) required for the acquisition of serial images at a wide range of tilts. The risk and the sacrifice of time (including that of image interpretation) can be avoided if one is not interested in the very detailed shape of the particle/defect.

Generally, four methods have been applied to the measurement of size, number density and volume fraction of nano-precipitates in Al-Mg-Si(-Cu) alloys. By transmission electron microscopy (TEM), the number and size of

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nano-precipitates in a region can be measured from low-magnification bright field (BF) images and high-resolution TEM images. The volume of the observed region could be obtained by measuring the thickness of the region through electron energy-loss spectrometry (EELS) [15,16] (Method 1) and multiplying it with the area of the region. The thickness can also be estimated by counting the number of extinction fringes either at the edge of a wedge-shaped TEM foil (Method 2) or at an inclined grain boundary (Method 3) [17]. On the other hand, the precipitate size and relative volume fraction can be directly calculated from a small-angle X-ray scattering (SAXS) profile [18,19] (Method 4).

However, there are several issues with regard to precisions and limitations of these four methods. The uncertainty of Method 1 for measuring the foil thickness can be as large as ±20% [20]. Although in recent years due to the accurate measurement of mean free path this uncertainty can be reduced to ±8% (e.g., for Al [21]), the error brought about is still not negligible. Moreover, not every TEM instrument is equipped with an expensive EELS apparatus. Method 2 requires an ideal wedge-shaped foil with a starting thickness of 0–0.5 ξ_g (ξ_g is the extinction distance of the chosen reflection) at the edge of the hole (see Fig. 1a for an example). Moreover, it can give only a rough estimate of foil thickness (except at the fringes) when the wedge angle is not constant. Method 3 can only obtain the approximate thickness of a region near a grain boundary, as shown in Fig. 1b. The top and bottom ends of an inclined grain boundary in the foil are invisible, producing a large additional error. In Method 4, the relative volume fraction also has an uncertainty as large as ±15%. Additionally, different types of concurrent precipitates [19] may have similar contributions to a SAXS profile.

In this work, efforts have been devoted to the establishment of a facile method for determination of size, number density and finally volume fraction of nano-precipitates with acceptable accuracy and precision. Such a method can be implemented on a modern TEM instrument with a LaB_6 filament or field emission gun (FEG) accessible to most microscopists (i.e., with no special additional apparatus equipped). Two techniques are used to establish such a method. The conventional technique of convergent beam electron diffraction (CBED) was reported to have a small uncertainty of ±3% [22] in determining TEM foil thickness. Moreover, its output does not contain the influence from the amorphous layer on the foil surface as is the case for EELS [20]. It is the most precise method for crystals that are thicker than ξ_g [23], and is thus used for measuring the volume fractions of the needle-like nano-precipitates in Al-Mg-Si(-Cu) alloys in this work. On the other hand, in recent years 3-dimensional atom probe (3DAP) can be applied for determining the number densities of nano-sized objects, such as atomic clusters, G.P.-zones and β″ precipitates [24], although acquiring the average sizes of such objects is believed to be less reliable due to the errors produced when selecting precipitates [25]. Therefore, in the present work the measurement of size, number density and volume fraction of nano-precipitates based on CBED has been performed first, followed by verification using 3DAP. Limitations of the systematically established method are also discussed.

2. Materials and methods

The Al-Mg-Si-Cu alloy studied in this work has a nominal composition of Al-1.0 wt.% Mg-1.1 wt.% Si-0.65 wt.% Cu. The alloy was cast, solutionized at 550 °C for 4 h and quenched, and then immediately aged at 175 °C for different times. Details about casting, solution and ageing (at 175 °C) heat treatments of the alloy as well as preparation of TEM foils have been described elsewhere [26,27]. TEM observations were performed on a FEI G2 F20 microscope operated at 200 kV. The tip specimen for 3DAP analysis was prepared from a thin bar of $0.5 \times 0.5 \times 15$ mm^3 cut from the alloy aged for 8 h, via the standard two-step electro-polishing procedures [28]. The tip was then examined in a LEAP 3000 SI instrument under a high vacuum of 10^{-12} Torr, at a specimen temperature of 20 K, a pulse repetition rate of 200 kHz and a pulse voltage fraction of 20%. The parameters used for analyzing the 3DAP results are separation distance (d) of 0.6 nm, surround distance of $L = 0.5$ nm for including solvent atoms and minimum cluster size (N_{min}) of 10 solutes. For identification of the boundary between the matrix and an elongated precipitate like β″, an isosurface at 5 at.% Mg [24,29] has been defined, which reproduces a similar precipitate size to that measured by TEM. Similar methods for defining nano-precipitate surfaces have also been applied in other 3DAP investigations of Al alloys to obtain precipitate number densities [24,25,30,31].

3. Results and discussion

The precipitation sequence of the alloy at 175 °C has been identified as follows: super-saturated solid solution (SSSS) → G.P.-zones → β″ + C (for 8 h) → Q + Si (for 30 d), according to our previous studies [26,27]. Two typical intragrannular microstructures, i.e. the peak-aged (2#, for 8 h) and over-aged (1#, for 30 d), are selected for this work since they typically contain short and long needle-like nano-precipitates growing along $\langle 001 \rangle_{Al}$ directions in high and low densities, respectively. According to high-resolution TEM (HRTEM) and high-resolution scanning transmission electron microscopy (HRSTEM) observations, the peak-aged microstructure is comprised of β″ (~83%, identified in a previous work [26]) and C (~17%, identified as shown in Fig. S1 in the Supplement [32]) needle-like precipitates, while the over-aged microstructure contains coarser needle-like Q precipitates and micro-sized plate-like Si precipitates (identified in a previous work [27]). The microstructural parameters of Si precipitates are not measured in this work.

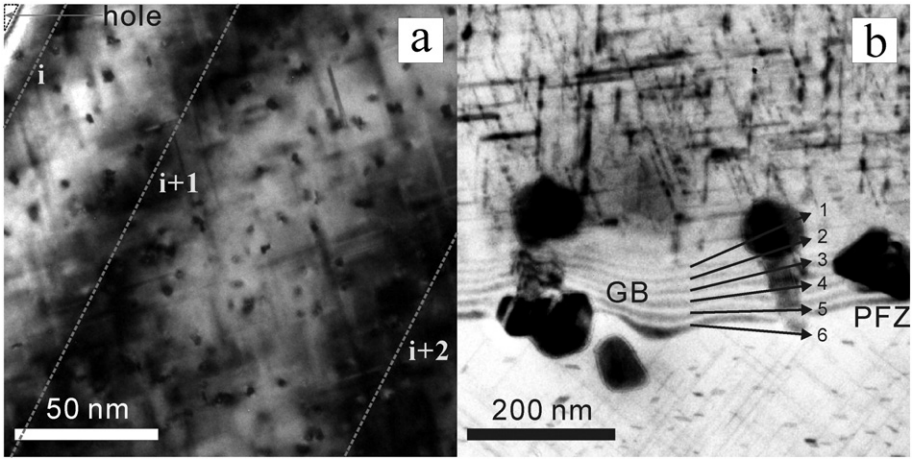

Fig. 1. Two examples are shown of measuring the thickness by counting the extinction fringes in TEM images. The images were taken from: (a) the edge of a hole and (b) an inclined grain boundary (GB) in an aged Al-Mg-Si-Cu sample containing nano-precipitates. The orders of the fringes are indexed in the images, among which the value of *i* is not known. The zone axis of (a) and the lower grain in (b) is $[001]_{Al}$.