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Transformations and structures in the Al–Zn–Mg alloy system: A diffraction study using synchrotron radiation and electron precession

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ABSTRACT

The structure of the hardening η'-phase precipitates in Al–Zn–Mg alloys has been investigated by using precession electron diffraction and X-ray synchrotron radiation diffraction. The latter was recorded as a three-dimensional, continuous intensity distribution from a single alloy grain, from which patterns of remarkable sharpness from the precipitate particles could be extracted. High resolution electron microscopy revealed extensive structural variations with prolific faults in the η' precipitates. The η'-structures are described in terms of two structure models based on two icosahedral elements that are inherent in the equilibrium η-$MgZn_2$ structure. The role of these icosahedra in the transformations of the alloy system is discussed.

1. Introduction

Age-hardening 7xxx alloys are based on precipitation in the Al–Zn–Mg system, in the composition range (wt.%) 3–7% zinc and 0.8–3% magnesium. Due to the high strength that is attained in the hardened state, the alloys are used in aerospace and automotive applications for highly stressed components, such as automobile bumpers. The chief hardening agent is the metastable, semicoherent precipitate phase η', which is a main theme of this article. The precipitation sequence is described as: supersaturated solution → GP-zones → η' → η'-$MgZn_2$. In industrial practice the aging treatment of the supersaturated solid solution is usually performed in two stages, after quench from the solution temperature. Two types of zones appear during the early stage [1]: the equiaxed GP(I)-zones are formed over a wide temperature range; diffraction patterns indicate local substitutional order of solute atoms [2]. Disc-shaped GP(II)-zones, one to two atom layers thick on $\{1\,1\,1\}_{Al}$ are formed by aging at temperatures above 75 °C, after quenching from temperatures above 450 °C [1,3]. The (pseudo)hexagonal η'-phase is formed during the second aging stage. Upon prolonged aging η' is transformed to the stable hexagonal Laves phase η-$MgZn_2$ (a = 0.5221 nm, c = 0.8567 nm) [4–6], as larger incoherent particles, in a set of well-defined orientation relationships to the Al-matrix [7,8].

The hardened state thus appears as a dispersion of η'-precipitates, at different stages throughout the transition from GP-zones to the stable η-phase. The hexagonal η' unit cell first proposed by Graf and Roy [9] is now generally recognized, with parameters a = 0.496 nm, c = 1.403 nm – and the hexagonal axis parallel with one $\langle 1\,1\,1\rangle_{Al}$. Several attempts to derive a structure model for the η'-phase have been made. Auld and Cousland [10] collected X-ray intensities from a single alloy grain by the Buerger precession technique. They proposed a structure model in the assumed space group $P\bar{6}m2$ (187) and composition $Mg_4Zn_{11}Al$. However, Li et al. [11] found that high-resolution electron microscopy (HRTEM) images of an η'-precipitate did not fit the Auld and Cousland structure, and suggested a different model in $P\bar{6}$ (174), with approximate composition $Mg_2Zn_{5-x}Al_{2+x}$. Atom probe (APFIM) studies [12–14] indicate considerable variations in the composition of the η'-precipitates, with a substantial aluminum content. High-resolution electron microscope images (HRTEM)

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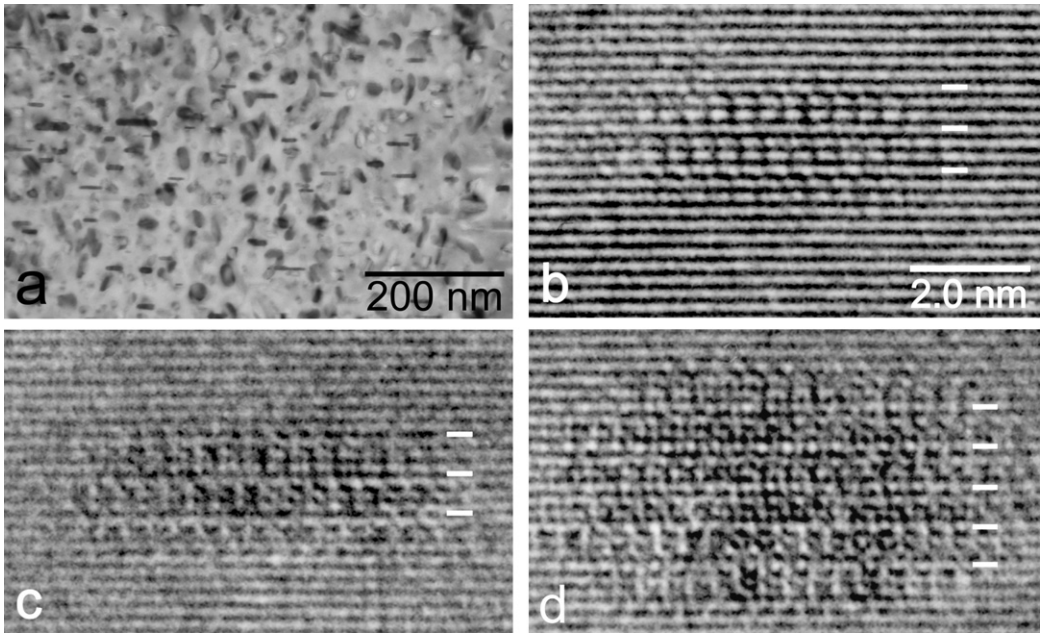

Fig. 1. Images of the age hardening state in $[1\,1\,2]_{Al}$. (a) Bright field image and (b)–(d) HRTEM images of the η'-phase, $[1\,0\,0]_{\eta}$.

reveal substantial variations in the internal structure of the precipitates.

Kverneland et al. [15] collected electron diffraction data by the Vincent–Midgley precession technique [16]. Double scattering via matrix reflections was suppressed at the expense of a high background, which is due mainly to inelastic scattering from the matrix. This limited severely the number of reflections that could be measured with any precision. Systematic absences were observed, and two basic models, I and II, within space group $P6_3/mmc$ were proposed.

In the present work the electron diffraction study has been augmented by X-ray diffraction from a synchrotron source. A three-dimensional continuous intensity distribution was collected from a single matrix grain exsolved from the alloy. A three-dimensional set of 84 unique precipitate reflections, referred to the either of the Laue classes $6mmm$ or $\bar{3}1m$, was extracted. It appears that such application of synchrotron radiation to embedded, coherent particles had previously not been reported.

Standard crystallographic techniques failed to produce a unique average structure model representing the whole range of η' precipitates. The reason is seen in the wide structural variations that are revealed by HRTEM as a range of disordered transitional structures. The limitations in the data due to overlap between reflections and uncertainties as to composition are seen as less important. Distorted icosahedra are main structural elements in either of the models I and II – as indeed in the equilibrium phase η-$MgZn_2$. Mechanisms for the transition from cubooctrahedron to icosahedra are discussed.

2. Experimental

An alloy of nominal composition (wt.%) 88.12% Al, 10.2% Zn, 1.68% Mg was cast to yield fairly large matrix grains, of size 100 μm. A distribution of disk-shaped η'-precipitates with thicknesses 2–4 nm, and widths up to 10 nm, was obtained by a standard heat treatment procedure: 20 min at 500 °C + 20 h at 20 °C + 5 h at 100 °C + 15 h at 140 °C. Electron microscope specimens were prepared by conventional twin-jet polishing (Tenupol 3) and examined in a Jeol EM 200CX and a Jeol EM 4000EX microscope. The original Vincent–Midgley precession system [16] mounted on a Philips EM 400 was used to collect electron diffraction data from selected projections. Intensities were recorded on Fuji image plates, which were read using the Fuji FDL 5000 equipment. The intensities were measured using the software Fujifilm Multigauge V2.1.

Single crystal grains for synchrotron radiation were exsolved from the matrix using liquid gallium and subsequently cleaned by "Kellers etch" (water, 2.5% nitric acid, 1.5% hydrochloric acid and 1.0% hydrofluoric acid). The grains were mounted in a standard way on the tip of a glass thin rod. Two full data sets with resolution 0.1 nm were measured on two different samples at room temperature, at the Swiss–Norwegian Beam Line (SNBL) at ESRF, Grenoble, France. Monochromatic X-rays, $\lambda = 0.08$ nm, were obtained by a $Si_{(1\,1\,1)}$ double crystal monochromator. Focusing was obtained with the second, sagitally bent crystal. The resulting beam cross-section was 0.6 mm × 0.6 mm at the sample. A three-dimensional continuous distribution of intensities was collected, on a MAR 345 image plate detector, by performing a φ-rotation of the crystal in steps of 0.5°. Actual camera length was set to 155 mm. Image reconstructions were extracted from the raw data, using the software CrysAlis RED V1.171.24 beta [17] and intensities were recorded manually by Fujifilm Multigauge V 2.1.

Patterson maps were calculated using an algorithm developed in the Pascal programming language (Turbo Pascal 7). Geometrical simulations of the diffraction patterns were carried out in Mathematica V 5.0 [18].

3. Electron diffraction and microscopy

Electron microscopy images of the age hardening state taken in $[1\,1\,2]_{Al}$-projection (Fig. 1) revealed mostly η'-particles. The bright field image (a), shows high density of nanometer sized precipitates. The precipitate particles in the HRTEM images, (b), (c) and (d), could be identified as the $[1\,0\,0]_{\eta'}$-projection by the 1.4 nm repetition distance along $c_{\eta'}$ as well as by Fourier transforms of the images. The images, taken with defocus values slightly lower than the Scherzer defocus ($\Delta f = -47.5$ nm), reveal extensive variations in the internal structure of the η'-precipitates. Note that the reproduced images were obtained from the same illuminated area, and hence with identical imaging conditions. The apparent variation in stacking order in the precipitates, from scant inter-