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A hybrid aluminium alloy and its zoo of interacting nano-precipitates

Sigurd Wenner [a,*], Calin Daniel Marioara [b], Sigmund Jarle Andersen [b], Martin Ervik [a], Randi Holmestad [a]

[a] Department of Physics, NTNU, Høgskoleringen 5, NO-7491 Trondheim, Norway
[b] Materials and Chemistry, SINTEF, Høgskoleringen 5, NO-7491 Trondheim, Norway

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ABSTRACT

An alloy with aluminium as its base element is heat treated to form a multitude of precipitate phases known from different classes of industrial alloys: Al–Cu(–Mg), Al–Mg–Si–Cu, and Al–Zn–Mg. Nanometer-sized needle-shaped particles define the starting point of the phase nucleation, after which there is a split in the precipitation sequence into six phases of highly diverse compositions and morphologies. There are several unique effects of phases from different alloy systems being present in the same host lattice, of which we concentrate on two: the replacement of Ag by Zn on the Ω interface and the formation of combined plates of the θ′ and C phases. Using atomically resolved scanning transmission electron microscopy and energy-dispersive X-ray spectroscopy, we investigate the formation mechanisms, crystal structures and compositions of the precipitates.

1. Introduction

Optimizing the properties of metallic alloys requires control over crystalline phases: their volume fraction in the material, their extent and shape, and the structure and strain around phase boundaries. A classic and very important example of phase transformation is diffusion-controlled nucleation and growth from a solid solution in a host lattice. A phase nucleates when a sufficient amount of solute elements has converged on a location, after which it grows into its most energetically favorable shape. In addition to age hardenable Al alloys, examples of alloy systems exhibiting this mechanism are various Fe alloys [1,2], Cu–Co [3], Cu–Ni–Si [4], Mg–Y/Gd [5,6], and even doped non-metallic compounds such as the ferroelectric $BiFeO_3$–Nd–Ti [7]. There typically exists a precipitation sequence, where a phase with a lower bulk enthalpy nucleates in connection to another precipitate in the host lattice. In many cases, the sequence is branched, so that several different phases can precipitate at a given time in the microstructural evolution.

Focusing on alloys with fcc-Al as their host, the three main classes of wrought heat-treatable alloys are, in their most basic forms, Al–Cu (2*xxx*), Al–Mg–Si (6*xxx*), and Al–Zn–Mg (7*xxx*). For the improvement of mechanical strength, they all rely on nanometer-sized precipitate phases, which are partially coherent with the host lattice. The Al–Cu system is the oldest, predating the discovery that nanoprecipitates are responsible for strengthening during heat treatment [8,9]. Cu is often supplemented by Mg, Ag, and/or Li to improve properties, resulting in precipitate phases of diverse geometries and orientations [10,11]. The Al–Mg–Si system has the densest precipitation of the three classes, despite being relatively low-solute. This is mainly attributed to Si, which has a low solubility in Al and provides a driving force for homogeneous nucleation [12,13], that is why it is often added to all types of Al alloys in small amounts. In Al–Mg–Si–Cu, the most important strengthening phases are β″ needles [14], Q′ needles [15,16] and C plates [17]. The Al–Zn–Mg system is hardened by precipitation of the precursors to the equilibrium η-Zn_2Mg phase. These early phases come in several variants, some of which lack a repeated unit cell [18–20].

For decades, precipitates in aluminium alloys have been studied extensively with transmission electron microscopy (TEM). A specimen used for TEM has a thickness of roughly 50 nm, which means that a nanometer-sized plate- or needle-shaped precipitate embedded in a host lattice can be imaged in cross-section (as a 2D projection) without any overlap with other phases in the viewing direction. High-angle annular dark-field scanning TEM (HAADF-STEM) has become a common technique for imaging nano-precipitates. This applies especially to cases where elements with a high difference in atomic number (e.g., Al and Cu) are present, as HAADF-STEM produces readily interpretable images with high atomic number-contrast [21]. Already in the 1970s, this technique was used to image single heavy atoms such as Au and Pt on carbon films [22,23]. The technique is at its most useful in an aberration-corrected microscope. Assuming the existence of high symmetry orientations having projected atom–atom distances longer than ~0.1 nm, every atomic column in a lattice may be imaged. Upon the combination with a spectroscopy technique such as electron energy loss spectroscopy (EELS) [24] or energy-dispersive X-ray spectroscopy (EDS) [25], compositional mapping with atomic resolution becomes feasible for a suitably thin and stable specimen.

The accumulated knowledge from both early X-ray diffraction and later TEM imaging/diffraction experiments should enable us to predict which precipitate phases are present in any industrial Al alloy with a specific heat treatment. In this paper, we transcend the boundaries

* Corresponding author.
E-mail address: sigurd.wenner@ntnu.no (S. Wenner).

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between the previously mentioned systems by investigating an alloy with a composition that accommodates the important strengthening phases in all three systems. The goal is to observe any interactions between the very different phases that may form, and to better understand how some phases heterogeneously nucleate on existing precipitates. Knowledge on precipitation in hybrid alloys has a great significance in industry as recycled material of varying composition constitutes a growing portion of all aluminium production. The main analytical tools are atomic-resolution HAADF-STEM imaging and simultaneous EDS acquisition with near-atomic resolution. In the Results and discussion section, we start by presenting all phases appearing during over-aging of the alloy. A discussion on nucleation follows, after which we focus on the two precipitate phases Ω and θ′, and how their interfaces with the host lattice are modified by introducing elements outside their "native" alloy systems into the material.

2. Experimental procedure

An alloy with the nominal composition Al–4.0% Zn–2.0% Cu–1.0% Mg–0.70% Si–0.55% Mn–0.20% Fe (by weight) was cast as a 4 kg billet. Mn and Fe were added to create Al(Mn,Fe)Si [26]/$Al_{20}Cu_2Mn_3$ [11,27] dispersoid phases which restrict grain growth, and are not present in any of the phases analyzed in the paper. The billet was homogenized at 480 °C for 3 h, which solutionizes all Zn, Cu and Mg. Some ≈20 μm large Si particles were left undissolved. The billet was extruded to a cylindrical profile with 20 mm cross-sectional diameter. Samples of the profile were kept for 1 h at 480 °C followed by water quenching and immediate immersion in an oil furnace at 150 °C for up to 32 days. The hardness values were measured with a Struers Duramin-A2500 using a 5 kgf. TEM specimens were prepared by mechanical polishing to 100 μm foils and subsequent electropolishing using a Struers TenuPol-5. The applied voltage was 20 V and the electrolyte was 1/3 nitric acid and 2/3 methanol kept at −25 °C.

HAADF-STEM was done primarily on a double Cs-corrected JEOL ARM-200F cold FEG microscope equipped with a JEOL Centurio EDS detector. A 200 kV, ≈21 pA electron beam with a convergence semi-angle of 27 mrad was used, and the collection semi-angle of the HAADF detector was 42–178 mrad. Some images are slightly distorted due to specimen drift during acquisition. No image processing was applied. For EDS mapping, a beam with ≈200 pA and convergence semi-angle

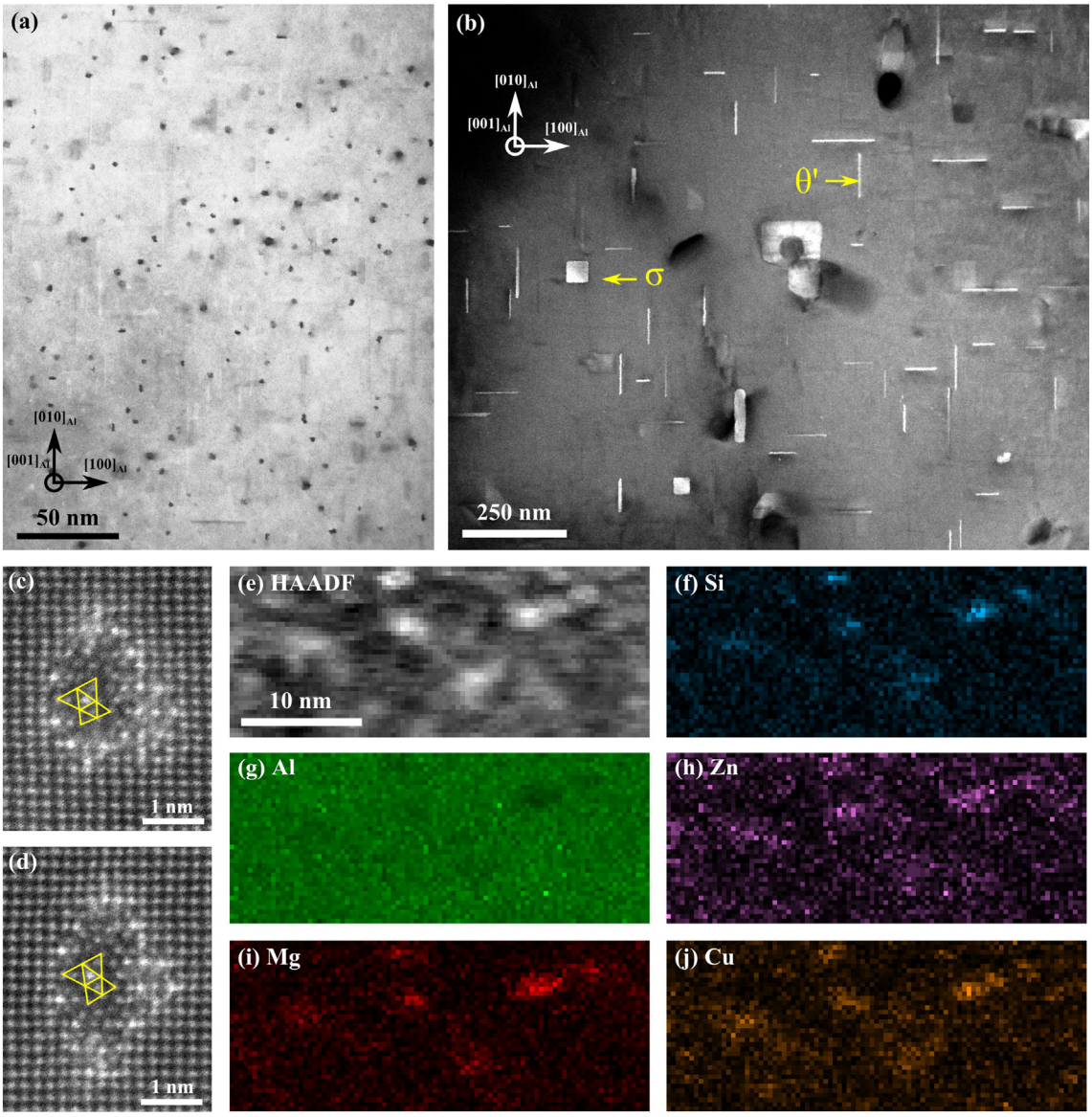

Fig. 1. Precipitate microstructure. (a) Overview bright-field TEM image of the peak-aged condition, 150 °C for 17 h. (b) HAADF-STEM image of the precipitate microstructure in a very over-aged condition, 150 °C for 32 days. (c–d) HAADF-STEM images of the peak-aged condition, showing example cross-sections of needle-shaped particles. Somewhat distorted Si networks are marked with yellow lines. (e–j) STEM-EDS map of a group of precipitates in the peak-aged condition, showing the presence of Mg, Si, Zn and Cu.