Available online at www.sciencedirect.com

ScienceDirect

Scripta Materialia 74 (2014) 92–95

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

Atomic-resolution electron energy loss studies of precipitates in an Al–Mg–Si–Cu–Ag alloy

Sigurd Wenner,[a,*] Calin D. Marioara,[b] Quentin M. Ramasse,[c] Despoina-Maria Kepaptsoglou,[c] Fredrik S. Hage[c] and Randi Holmestad[a]

[a]*Department of Physics, NTNU, Høgskoleringen 5, Trondheim NO-7491, Norway*
[b]*Materials and Chemistry, SINTEF, Høgskoleringen 5, Trondheim NO-7491, Norway*
[c]*SuperSTEM Laboratory, STFC Daresbury Campus, Keckwick Lane, Daresbury WA4 4AD, UK*

Received 13 September 2013; accepted 6 November 2013
Available online 11 November 2013

Aberration-corrected scanning transmission electron microscopy combined with electron energy loss spectroscopy has been used to determine the distribution of Cu and Ag atomic columns of precipitates in an Al–Mg–Si–Cu–Ag alloy. Cu columns were commonly part of C and Q′ phases, with the atomic columns having large projected separations. Columns containing Ag were more tightly spaced, in areas lacking repeating unit cells and at incoherent precipitate–host lattice interfaces. Cu-rich and Ag-rich areas were not found to intermix.

Keywords: Aluminum alloys; Precipitation; Scanning transmission electron microscopy; Electron energy loss spectroscopy

Al–Mg–Si alloys are heat-treatable and exhibit a significant increase in strength upon nucleation and growth of hardening nanosized metastable phases. Detailed investigations of the precipitation sequence have been performed over the years, and the crystal structures of most metastable phases have been solved by means of quantitative transmission electron microscopy (TEM) combined with first-principles calculations [1,2]. When Cu is added to the alloys, the precipitate phases of the Al–Mg–Si system are suppressed [3], and new, Cu-containing phases such as C [4] and Q′ [5–7] form. Additionally, areas with no repeating unit cell become more common in the structure of the precipitates. One characteristic of all metastable precipitates in the Al–Mg–Si(–Cu) system is that they have one main coherency (and growth) direction, along $\langle 0\,0\,1\rangle_{Al}$. Consequently, they all are needle-, lath- or plate-shaped. Moreover, they contain a common network of Si columns along their main growth direction, with a projected near-hexagonal structure [8]. Atomic columns of Mg, Al and Cu occupy positions between these Si columns, all three having different preferred local atomic configurations and site symmetries. Small additions of Cu to Al–Mg–Si alloys have been found to increase the mechanical strength [3], and additions of Ag have a similar effect [9]. The reason for this is that Cu and Ag promote precipitate nucleation, and create a microstructure of smaller precipitates with higher number density. Recent work has shown that Ag enters the (Cu-free) β' precipitate and replaces 1/3 of its Si atomic columns, creating its own local symmetries [10]. In this paper we reveal the different roles played by Cu and Ag atoms in metastable precipitates in Al–Mg–Si–Cu–Ag alloys.

High-angle annular dark-field scanning TEM (HAADF–STEM) has proven to be a very useful technique for investigating the structure of precipitates in Al alloys. This is due to the properties of high-angle scattered electrons: they are incoherent and form an easily interpretable image, as the contrast is generally unaffected by small changes in objective lens defocus and specimen thickness [11–13]. In addition, the scattered intensity (Rutherford and thermal diffuse scattering) from an atomic column increases with its atomic number Z. The development of C_s aberration correctors [14,15] has improved the technique by achieving spatial resolutions below 0.1 nm. These attributes make the identification of pure Cu ($Z = 29$) and Ag ($Z = 47$) atomic columns straightforward, and even enable the

* Corresponding author. Tel.: +47 93820647; fax: +47 73597710; e-mail: sigurd.wenner@ntnu.no

1359-6462/$ - see front matter © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.scriptamat.2013.11.007

Table 1. Nominal composition of the studied alloy (at.%).

Mg	Si	Mn	Fe	Cu	Ag	Al
1.00	0.62	0.27	0.10	0.14	0.03	Balance

Si ($Z = 14$) columns to be distinguished from Al ($Z = 13$) and Mg ($Z = 12$) columns [10]. However, the technique has certain limitations: elements close in Z (such as Al and Mg), mixed atomic columns and columns with partial occupancies make it difficult to form atomic models of entire precipitates. On the other hand, electron energy loss spectroscopy (EELS) does not suffer from these limitations. This TEM technique is commonly used to extract compositional information and properties of the electronic structure from nanosized regions in materials. The combination of EELS and aberration-corrected STEM has been successfully used for atomic-resolution elemental mapping and electronic fine structure studies in, for example, metal oxides [16,17]. There have been few attempts to copy this success for the case of Al alloys. Al and its neighbours in the periodic table are not particularly suitable for EELS analysis because their L-edges overlap with the Al plasmon peaks, and their K-edges are of high energy and will thus give poor statistics. However, recent advances such as dual energy range EELS [18] make the Al–K, Mg–K and Si–K edges more available for analysis.

In this work metastable precipitates formed in an Al–Mg–Si–Cu–Ag alloy have been imaged by probe C_s-corrected HAADF–STEM and the distribution of Ag and Cu atomic columns has been analyzed by atomic-resolution EELS elemental mapping. These two elements were chosen since their edges Ag–$M_{4,5}$ at 367 eV and Cu–$L_{2,3}$ at 931 eV, combined with their high HAADF–STEM Z contrast, make them suitable for detailed analysis. This model system is thus used to emphasize the advantages of atomic-resolution EELS for precipitate structure determination.

The composition of the extruded profiles used in the study is given in Table 1. The elements Mn and Fe were added to form dispersoid particles that reduce the grain size of the material, and do not participate in precipitation of hardening phases. To achieve an over-aged microstructure composed of finely dispersed Cu-containing precipitates, the following heat treatment was applied: 30 min of solution heat treatment at 530 °C, quenching in water and storage for 4 h at room temperature, aging to peak hardness with 12 h of annealing at 155 °C and lastly over-aging for 21 days at 200 °C. The TEM specimen was prepared by mechanical polishing, dimpling and ion milling with energies from 4.0 keV down to 1.5 keV. To prevent carbon contamination, the specimen was baked in vacuum at approx. 135 °C for 6 h before loading in the microscope, and was given regular electron beam showers during microscopy. Tests were performed to ensure that the baking procedure does not alter the microstructure significantly.

HAADF–STEM and EELS spectrum imaging were performed using an aberration-corrected Nion UltraSTEM™ 100 at the SuperSTEM facility at Daresbury, UK. Its cold field emission gun electron source gives a native energy resolution of 0.35 eV, and the minimum expected probe size is 0.08 nm. A voltage of 100 kV was applied. The beam convergence angle was 30 mrad, the HAADF–STEM detector angles were 74–185 mrad

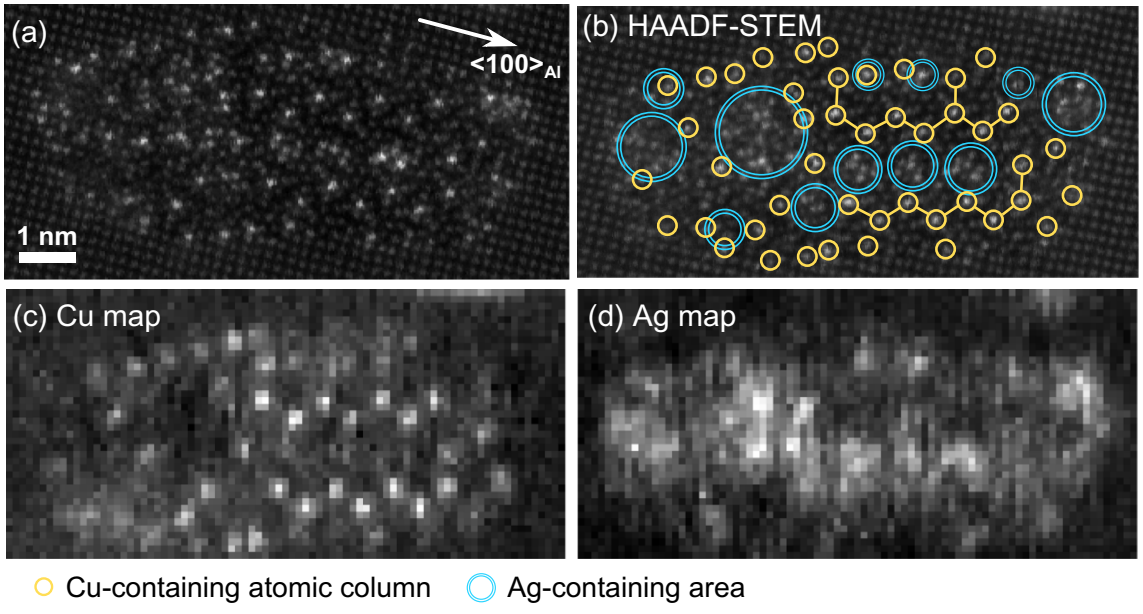

Figure 1. (a and b) Raw HAADF–STEM images of a precipitate cross-section, taken respectively before and during the STEM–EELS acquisition. (c and d) EELS elemental maps of Cu and Ag. The location of Cu atomic columns and areas rich in Ag are marked in (b). Cu columns in a Q′ configuration are connected by lines.