Applications of atomic-resolution HAADF-STEM and EDS-STEM characterization of light alloys

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Abstract. Precipitation-hardened aluminium and magnesium alloys often contain a uniform distribution of plate-shaped precipitates of intermediate or equilibrium phases that form on rational planes of the matrix phase. Micro-alloying additions can change the identity and/or distribution of these precipitate plates, but the precise roles of the micro-alloying elements in the formation of such precipitate plates are still a subject of debate. A key reason for this is the lack of direct experimental observation of the details of the distribution/segregation of these elements in and surrounding precipitates from conventional transmission electron microscopy. While the advent of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) provides much more information at the atomic-scale, there is still a need for performing atomic-resolution chemical mapping using advanced STEM techniques, such as energy-dispersive X-ray spectroscopy (EDS-STEM) and/or electron energy-loss spectroscopy (EELS-STEM), if the precise roles of the micro-alloying elements are to be revealed.

1. Introduction

Age hardening forms the backbone of light alloy development. The age hardening phenomenon in aluminium alloys was discovered in 1906. Since then, considerable progress has been made in the improvement of the age hardening response in aluminium alloys via the addition of micro-alloying elements. By the end of 1980s, the yield strength of precipitation-hardened aluminium alloys exceeded 700 MPa, already 2–3 times higher than obtained in 1906. For the development of age-hardenable magnesium alloys, remarkable progress was made between 2000 and 2015. In this period, the yield strength of magnesium casting alloys was raised from less than 200 MPa to over 300 MPa, and that of magnesium wrought alloys from typically 300 MPa to above 475 MPa. It is foreseeable that it will require a significantly shorter period, i.e. much less than 80 years, for magnesium alloys to reach the strength level currently enjoyed by ultrahigh strength aluminium alloys. One of the most important microstructural characterization facilities that have been used in the development of age hardenable light alloys is transmission electron microscopy (TEM). The imaging, diffraction and micro-analysis techniques of TEM have played a crucial role in revealing processing-microstructure-property relationships in these alloys. In conventional transmission electron microscopy, whilst information on the identity, spatial distribution and chemistry of precipitates could be readily obtained, it was difficult...
to reveal, at the atomic scale, the distribution of solute atoms or atoms of micro-alloying elements. It was for this reason that the roles of micro-alloying elements in precipitation of key strengthening intermetallic phases remained unresolved. Advances in scanning transmission electron microscopy (STEM) in the past 15 years, especially the aberration-corrected STEM techniques including high-angle annular dark-field (HAADF), energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS), provide opportunities for detecting segregated solute atoms at the atomic scale. The purpose of this article is to provide a review of the progress made in the understanding of precipitation and the role of micro-alloying elements in precipitation in selected aluminium and magnesium alloys, highlighting the importance of modern imaging and spectroscopy techniques of STEM in the characterization and development of these light alloys.

2. Aluminium alloys

2.1 Al–Cu–Sn alloys

In early 1950s, Hardy [1-2] discovered that additions of trace amounts (~0.1 at.%) of Sn to binary Al–Cu alloys could lead to a significantly enhanced age hardening response. The maximum hardness values achievable in the resultant Al–Cu–Sn alloy in the temperature range 100–200°C were substantially higher than those in the counterpart binary alloy, and this hardness increment is due to a refined distribution of $\theta'$ (Al2Cu) precipitates. At that time, X-ray diffraction was the technique used to collect indirect information that could be used to speculate on the role of Sn in enhancing the age hardening response. Based on the streaked diffraction maxima (so-called P diffraction spots) in the X-ray diffraction patterns obtained from samples in the early stages of ageing, Silcock [3] suggested that Sn atoms segregated to the $\theta'/\alpha$-Al interfaces, and that this segregation reduced the interfacial energy involved in $\theta'$ nucleation and thus increased the nucleation rate of $\theta'$ precipitates. Subsequent observations made by conventional electron microscopy in the 1970s led to different views. Sankaran and Laird [4] reported that their TEM observations supported the interpretation of Silcock, even though they did not provide any direct experimental evidence. On the other hand, based on observations made by TEM and energy-dispersive X-ray spectroscopy, Kamo and coworkers [5-7] reported the formation of a Sn-containing phase, which acts as heterogeneous nucleation sites for $\theta'$. It became possible in the 1990s to use combined techniques of imaging and microdiffraction of TEM, and one-dimensional atom probe, to examine the origin of enhanced nucleation of $\theta'$ in Al–Cu–Sn alloys. With the help of these techniques, Ringer and co-workers [8] showed the occurrence of clustering of Sn atoms in the very early stages of ageing and precipitation of incoherent particles of the equilibrium phase $\beta$-Sn at later stage of ageing. The $\theta'$ precipitates that form at the later stage of ageing were frequently found to be associated with $\beta$-Sn particles, with one $\beta$-Sn particle almost invariably located at one end facet of individual $\theta'$ plates. They further reported that Sn atoms did not segregate to the broad faces of the $\theta'$ plates. These observations have since then been widely used as direct experimental evidence for heterogeneous nucleation of $\theta'$ on $\beta$-Sn particles. Such interpretation is essentially based on the minimization of interfacial energy or volumetric misfit strain energy, and it supports the hypothesis made by Hardy [2] that Sn atoms precipitated first in the form of coherent Sn particles and subsequently act as heterogeneous nucleation sites for $\theta'$.

Based on observations made by high-resolution TEM and microdiffraction, Bourgeois and coworkers [9] reported that the $\beta$-Sn particles associated with $\theta'$ platelets, which formed at early stage of ageing, exhibited an orientation relationship that was distinctly different from those reported previously for the Al–Cu–Sn and Al–Sn alloys. This observation implies that, while tin may assist $\theta'$ nucleation, the formation of $\theta'$ also influences the crystallography of $\beta$-Sn that forms in association with $\theta'$. The continued ageing leads to coarsening of those $\beta$-Sn particles that are in contact with $\theta'$ plates, and eventual replacement of this orientation relationship by the one that is originally observed in the Al–Cu–Sn and Al–Sn alloys. More recent experimental observations using atomic-resolution Z-
contrast HAADF-STEM [10] revealed that Sn atoms segregate at the end facets of \(\theta'\) precipitate plates, as shown in figure 1. This observation indicates that the Sn particles formed in the early stages of ageing are not heterogeneous nucleation sites for \(\theta'\), and that the Sn particle that is in contact with a \(\theta'\) plate forms as the consequence of segregation of Sn atoms to the end facet of the \(\theta'\) nucleus. The solid solubility of Sn in the aluminium matrix is very low, and any excessive segregation of Sn atoms would lead to precipitation of \(\beta\)-Sn. The latest observation is consistent with the model that involves shear strain energy minimization [11-12]. The formation of \(\theta'\) precipitates generates a shear strain in the aluminium matrix phase. Since Sn has a large atomic size than Al, its segregation to the extension region of the matrix adjacent to the end facet of the \(\theta'\) nucleus allows a reduction in the shear strain energy in the region.

![Figure 1](image.png)

**Figure 1.** \(<011>\_a\) HAADF-STEM image showing Sn-rich columns (circled) attached to the end facet of \(\theta'\) plate in an Al–Cu–Sn alloy. The thickness of the \(\theta'\) plate is 2 nm [10].

### 2.2 Al–Cu–Mg–Ag alloys

Combined additions of small amounts of Ag and Mg, typically in the range 0.3–0.5 wt%, to Al–Cu alloys result in almost complete replacement of metastable \(\theta'\) phase by another metastable phase designated \(\Omega\) (Al\(_2\)Cu). The addition of Ag alone to binary Al–Cu alloys does not facilitate nucleation of \(\Omega\) precipitates. The uniform, dense and relatively thermally stable distribution of the \(\Omega\) precipitates enables the alloy to exhibit a tensile yield strength above 500 MPa at ambient temperatures and improved creep resistance at temperatures up to 180–200°C.

The \(\Omega\) precipitates form as thin plates on \(\{11\}_a\) planes. Although the number density and volume fraction of \(\Omega\) plates is similar to those of \(\theta'\) in Al–Cu binary alloys, the aspect ratio of \(\Omega\) plates is much larger than that of \(\theta'\). The formation of such \(\{11\}_a\) precipitate plates, and the increased aspect ratio of these plates, reduce the effective inter-particle spacing and thus increase the alloy tensile strength. The improved creep strength is attributable to the thermal stability of the \(\Omega\) phase, which is associated with a low interfacial energy between \(\Omega\) and matrix phases on the habit plane.

The precise roles of Ag and Mg in stimulating the nucleation and thermal stability of the \(\Omega\) phase have received considerable interest in the past, but are still not fully understood. Studies made in late 1980s and early 1990s using X-ray microanalysis [13] and one-dimensional atom probe [14] revealed the strong segregation of Ag and Mg to the broad \(\Omega/\alpha\)-Al interface and the absence of these two elements in the interior part of the \(\Omega\) phase. In the following years, the development of the three-dimensional atom probe technique allowed the detection of Ag–Mg co-clusters that form in the very early stages of decomposition of the Al–Cu–Mg–Ag alloys. The Ag–Mg clusters do not have any
well-defined shape at the start. During further ageing, these clusters absorb Cu atoms and gradually evolve into discs on \( \{111\} \alpha \) planes. Once \( \Omega \) nuclei have developed from these clusters, Ag and Mg atoms are rejected to the broad surfaces of the \( \Omega \) plates. There were controversial reports on the number of the Ag/Mg segregation layers. Early studies made by atom probe field ion microscopy claimed that Ag and Mg were segregated in a single atomic layer [15]. But subsequent work made in 2001 by atomic-resolution HAADF-STEM concluded that the Ag and Mg atoms form a double-layer in the broad surface of the \( \Omega \) plate [16]. Observations made in more recent years using HAADF-STEM with better spatial resolution confirmed the existence of the double layer in the \( \Omega \)/matrix interface [17]. However, in this double-layer, the Ag atoms are all distributed in a single layer adjacent to the aluminium matrix, and Cu atoms are in the next layer that is close to the precipitate, as shown in figure 2. The Ag atoms in the monolayer have a graphene-like hexagonal arrangement, with Mg atoms in the centre of individual hexagons. First-principles calculations based on these observations indicated that the Mg atoms in the layer stabilize the interfacial structure and consequently the thermal stability of the \( \Omega \) phase. The segregation of Ag–Mg atoms was observed at all thicknesses of the \( \Omega \) plates. It is the presence of the layer of the Ag and Mg atoms that facilitates the nucleation of \( \Omega \) precipitates by reducing the interfacial energy. The presence of this layer at the \( \Omega \) plate surfaces is also considered to restrict ledge formation, thereby minimizing thickening at temperatures up to 200 °C.

![Figure 2](image)

**Figure 2.** \(<112>\)\( _\alpha \) HAADF images showing Ag segregation at the \( \Omega \)/matrix interface in an Al–Cu–Mg–Ag alloy [17].

While the latest interpretation of the roles of Ag and Mg in \( \Omega \) precipitation seems to be rational, it is still based on incomplete STEM observations. Since the intensity in the HAADF-STEM image is approximately proportional to the square of atomic number, it is difficult to unambiguously distinguish Mg from Al, and Ag from Cu, in HAADF-STEM images. It is for this reason that the latest interpretation remains to be validated. To resolve such issues, it will be necessary to use EDS-STEM or EELS-STEM (EELS: electron energy loss spectroscopy) in the near future to perform atomic-scale...
chemical mapping of the Ω/matrix interface. The latest STEM instruments are equipped with
innovative technologies that significantly enhance X-ray signal collection. For example, the
ChemiSTEM technology of the FEI Titan G2 has four windowless silicon drift detectors arranged
symmetrically around the specimen and the objective lens pole pieces, figure 3, which greatly
facilitates the chemical mapping along some critical directions of the precipitate-matrix interface.
While it is relatively easy to obtain atomic-resolution chemical maps from ceramics and high-
temperature metallic materials, it is still a real challenge to obtain such maps from aluminium alloys
and magnesium alloys.

Figure 3. Schematic diagram of the ChemiSTEM™ design, showing 4 silicon drift detectors that are
arranged symmetrically around the sample and the objective lens pole pieces [Brochure of FEI Titan™
G2 with ChemiSTEM™ Technology].

2.3 Al–Cu–Li–Mg–Ag alloys
The key strengthening precipitate phase in Al–Cu–Li alloys is the T1 phase (Al6(CuLi)). The T1
precipitates form as plates on {111}α planes, with an aspect ratio typically larger than 50:1. Although
the T1 phase is almost fully coherent with the aluminium matrix phase within its habit plane, it is
difficult to nucleate during conventional isothermal ageing treatments. Consequently, it is common
practice to cold deform the aluminium matrix phase prior to ageing, or to add micro-alloying additions
of Ag and Mg to such alloys, to facilitate nucleation of the T1 phase. The dislocations introduced by
the cold-work act as heterogeneous nucleation sites for the T1 phase and hence result in an increased
number density of T1 precipitates. The combined additions of trace amounts of Ag and Mg (typically
0.3–0.5 wt%) to Al–Cu–Li alloys remarkably enhance the nucleation and formation of T1 phase [18].
The resultant Al–Cu–Li–Mg–Ag alloys, such as the Weldalite 049™ series of ultra-high strength
aluminium alloys, can exhibit a tensile yield strength exceeding 700MPa. While the number density
and volume fraction of T1 plates are both comparable to those of Ω in Li-free Al–Cu–Mg–Ag alloys,
the T1 plates are much thinner (typically less than 2 nm), and their aspect ratio is significantly larger
than that of Ω. The ultra-high strength achieved in the Al–Cu–Li–Mg–Ag alloys is attributable to the
uniform distribution and an almost continuous network of T1 plates. The Al–Cu–Li–Mg–Ag alloys
also have an increased creep strength. The improved creep resistance is attributable to higher thermal
stability of the T1 phase.

Similar to the case of Al–Cu–Mg–Ag alloys, the precise roles of Ag and Mg in the precipitation of
the T1 phase have received considerable interest in the past, but are still far from being well
understood. While the roles of Ag and Mg are considered to be similar to those in the precipitation of
Ω phase, there have been conflicting reports on whether Ag and Mg segregate into the T1 precipitate
or just to the T1/matrix interface. The presence of Li in the T1 precipitate as well as its thinness make
it extraordinarily difficult to accurately detect the distribution of Ag and Mg atoms within the region containing the \(T_1\) precipitate, when conventional TEM is used alone. Even studies made by atom probe tomography gave controversial reports. Murayama and Hono [19] and Araullo-Peters and co-workers [20] reported that both Ag and Mg segregate into the \(T_1/\)matrix interface, whereas Gault et al. [21] reported that Ag and Mg segregate to the internal part of the \(T_1\) precipitate rather than the \(T_1/\)matrix interface. It is unclear whether such controversial reports are due to the variation of the spatial resolution of the atom probes used. However, recent studies made by atomic-resolution HAADF-STEM [22-23] suggest that Ag atoms segregate into the \(T_1/\)matrix interface, certainly at the later stage of \(T_1\) growth but probably also at the nucleation stage of the \(T_1\) precipitate. The segregated Ag atoms are distributed in a single atomic layer that is adjacent to the aluminium matrix phase, similar to that observed in the \(\Omega/\)matrix interface. Again, due to the limitations of the imaging technique, it is still difficult to accurately detect the distribution of Mg atoms in the \(T_1/\)matrix interface. Therefore, the precise roles of Ag and Mg in stimulating the nucleation and thermal stability of \(T_1\) precipitate remain vague. It again seems necessary to employ atomic-resolution EDS-STEM or EELS-STEM in the following years to determine the distribution of Ag and Mg atoms in the \(T_1/\)matrix interface.

3. Magnesium alloys

3.1 Mg–RE–Ag and Mg–RE–Zn alloys

Binary Mg–Gd and Mg–Y alloys with Gd or Y less than 6 wt% are not age hardenable. Ternary additions of 2 wt% or more Ag to these alloys can generate a remarkable age hardening response in the temperature range 200–250 °C [24-25]. Ternary additions of 1–2 wt% Zn to Mg–6wt%Gd alloys can also induce a remarkable age hardening response, which leads to a significant improvement in tensile and creep properties [26]. This enhancement in mechanical properties is associated with a uniform and dense distribution of basal precipitate plates that do not form in binary Mg–Gd or Mg–Y alloys. These basal plates look remarkably similar in the Mg–Gd–Ag, Mg–Y–Ag, Mg–Gd–Zn and Mg–Y–Ag–Zn alloys. These precipitate plates are very thin and their characterization and analysis using conventional TEM is difficult. However, it is now possible to obtain atomic-resolution images of these precipitates using HAADF-STEM, as shown in in figure 4, although it remains difficult to distinguish columns rich in RE atoms from columns rich in Zn or Ag in these images. Therefore, it is again necessary to use atomic-resolution EDS-STEM or EELS-STEM in order to identify the factors that are critical in controlling the thickness of the plates.

**Figure 4.** \(\langle 1\bar{2}10\rangle_{\alpha}\) HAADF image showing a basal precipitate plate comprising Mg, Gd and Zn in a Mg–Gd–Zn alloy [27].
3.2 Mg–Sn–Zn alloys

Ternary additions of 1wt% Zn to binary Mg–Sn alloys remarkably enhance the age hardening response. Microstructural observations made by conventional TEM [28-29] indicated that the enhanced age hardening response was due to a finer distribution of β precipitates (Mg2Sn). These observations suggested that the Zn addition stimulate the nucleation of the β precipitate, but the precise role of Zn in the precipitation process was unclear. A key reason was that it was difficult to establish the distribution of Zn element in the Mg–Sn–Zn alloys from conventional TEM images. Given that both Sn and Zn have much higher atomic numbers than Mg, it is also difficult to distinguish Zn from Sn in HAADF-STEM images. A recent study made by EDS-STEM mapping [30] indicated unambiguously that Zn segregates strongly to the β/matrix interface, for a variety of boundaries associated with different orientation relationships of the β phase. One such example is shown in figure 5. These segregation layers are quite thin, and it has proven difficult to accurately establish their thickness and structure. For this reason, it was difficult to assess why Zn atoms prefer to segregate to the β/matrix interface and whether this segregation reduces the interfacial energy to such a level that ultimately leads to a significantly enhanced nucleation rate of the β phase. Again, the use of atomic-resolution EDS-STEM may provide vital clues to the accurate thickness and structure of the segregated Zn atoms in the β/matrix interface.

Figure 5. (a) HAADF-STEM image, and (b) EDS-STEM showing Zn segregation at the β-Mg2Sn/matrix in a Mg–Sn–Zn alloy [30].

4. Summary

The advent of aberration-corrected STEM techniques has greatly facilitated the atomic-scale characterization of precipitates in a group of scientifically and commercially important aluminium and magnesium alloys, and has advanced our understanding of the roles of micro-alloying elements in the precipitation process. However, it is still necessary to combine the HAADF-STEM imaging technique with spectroscopy techniques such as EDS-STEM or EELS-STEM in order to reveal the mechanism via which the segregation of solutes or micro-alloying elements stimulates the nucleation and formation of the key strengthening precipitate phases in these alloys.
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