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In situ heating TEM observations of evolving nanoscale Al–Mg–Si–Cu precipitates

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Summary
This research concerns the precipitation and subsequent dissolution of precipitate phases in an Al–0.86Mg–0.62Si–0.1Cu (at.%) alloy subjected to varying thermal exposure during an in situ heating transmission electron microscope (TEM) experiment. The distribution and crystal structure of precipitates were determined by a scanning diffraction approach at multiple stages, pinpointing the precipitates that underwent phase transformations during heating. Obtained results were compared with TEM studies of the material heated ex situ. This revealed differences in the transformation kinetics of precipitates in an electron transparent lamella (thickness \( \geq 90 \) nm) to that of macroscopic bulk specimens.

Introduction
Age-hardenable Al alloys are an important group of structural materials that are strengthened by nanosized, metastable precipitates formed during thermal ageing. The precipitates are conventionally studied using the TEM, with electron transparent specimens prepared from materials heat treated to different stages. Due to improvements in specimen preparation techniques and the advent of TEM heating holders with high mechanical and thermal stability, it has now become possible to study the evolution of precipitates in situ (Malladi et al., 2014; Liu et al., 2017; Park et al., 2019).

Al–Mg–Si(–Cu) alloys are important in automotive and construction applications, and form characteristic needle- or lath-shaped precipitates with long axes parallel to \( <100>_{\text{Al}} \) upon ageing (Edwards et al., 1998; Marioara et al., 2007). Previous in situ heating studies of precipitates in this alloy system have measured the overall changes to the distribution of precipitate parameters (lengths, densities, etc.) (Tsao et al., 2006; Chang et al., 2015; Flament et al., 2017). We have here conducted an in situ heating TEM study, using bright-field imaging and scanning precession electron diffraction (SPED) combined with data post-processing to study the distribution and identities of transforming precipitates. A single region of interest was systematically studied, enabling tracking of the evolution of individual precipitate phases. The results were compared to conventional TEM studies of the material heat treated ex situ (Sunde et al., 2019).

Material and methods
An extruded Al–0.86Mg–0.62Si–0.1Cu (at.%) alloy was subjected to solution heat treatment (SHT) at \( 540 \) °C for 12 min, and subsequently water-quenched to room temperature (RT). The specimens heat treated ex situ were kept 10 min at RT before artificial ageing at \( 180 \) °C. A peak-hardened material was obtained after approximately 3 h ageing. TEM specimens were made by standard electro-polishing using a Struers Tenupol-5 applying a 1:2 nitric acid:methanol mixture (\( T \approx -25 \) °C).

Electron backscatter diffraction was conducted in a Hitachi SU6600 FE scanning electron microscope (SEM) on an electropolished TEM specimen which enabled mapping and identification of grains close to \( (001)_{\text{Al}} \) orientation. The specimen had been heat treated 20 min at \( 180 \) °C ex situ to initiate the precipitation in bulk conditions. Subsequently, a focused ion beam (FIB) lamella of a \( (001)_{\text{Al}} \)-oriented grain was prepared and mounted on a DENSsolutions nanochip using a FEI Helios G4 FIB. The chip was placed in a DENSsolutions D6 wildfire TEM holder which kept the specimen at \( 180–240 \) °C in-between SPED scans. A JEOL 2100F microscope (200 kV) was used to run the in situ heating and SPED experiments. SPED was conducted using a NanoMEGAS ASTAR system. The nanobeam diffraction probe semi-convergence angle was 1.0 mrad and the precession angle employed was 1.0°. The scan step size was selected as 1.52 nm and pixel exposure time was 40 ms. SPED scans were recorded with the temperature held at RT (\( T = 23 \) °C) and typically comprised \( 400 \times 400 \) pixels, thus covering an area of \( \sim 600 \times 600 \) nm² and taking...
approximately 1.5 h to acquire. Specimen thickness was measured by electron energy loss spectroscopy. The obtained 4D SPED datasets, comprising a 2D PED pattern at each position of a 2D area scan, were analysed using the HyperSpy (de la Peña et al., 2019) Python library. The diffraction data were decomposed using an unsupervised machine learning algorithm based on non-negative matrix factorization, and subsequently matched with phases of the Al–Mg–Si–Cu system (Sunde et al., 2018).

Results and discussion

Figure 1 shows the evolution of the alloy microstructure after exposure to subsequent stages of heating. The time–temperature evolution is indicated in schematic B, showing the times $t_1$ at which bright-field images and SPED scans were obtained. In the initial stages ($t_1 - t_3$), the needle-shaped character of the majority of precipitates was hard to discern, and many likely existed as small atomic clusters or Guinier–Preston zones. Dislocations and surface impurities introduced by FIB (dark regions of Figs. 1C,D) gradually annealed out. At $t_4$ (image E), the needle morphology was clearly visible, and a high density of small precipitates had formed. The thermal exposure at this point corresponded with near peak hardness in isothermally heated bulk specimens. Figure 2 shows the phase mapping results obtained from SPED data. Figure 2(A) was constructed from SPED scan 1 acquired at $t_4$, and shows that the majority of precipitates in the region were $\beta''$. There was also a significant presence of $L$-phase and $\beta'/Q'$-phase precipitates.
After subsequent heating stages at $T > 180^\circ$C the precipitates coarsened and subsequently dissolved. The phase map in Figure 2(B) at $t_6$ shows a low presence of remaining $\beta''$ precipitates, and at time $t_7$ (Fig. 2C), there were none left. At this stage, there were only $L$-phase and $\beta'/Q'$-phase precipitates present. The six precipitates indicated by white and yellow arrows that existed throughout the full heating experiment support current hypotheses regarding the precipitation in this alloy system: The $L$-phase precipitates remained fixed as $L$ phases through the full experiment, and could be traced back to 1 h ageing (not shown). This observation indicates that this phase exhibits a separate evolution, likely tracing back to the clustering stage. No new $L$-phase precipitates were formed. The high thermal stability of this phase was also clearly demonstrated, as the majority of the $L$-phase precipitates at $t_4$ remained at $t_6$ and $t_7$ (Marioara et al., 2014). Two out of three yellow marked precipitates started out as $\beta''$ precipitates ($t_4$), but were at $t_6$ seen to have transformed to $\beta'$, in agreement with established knowledge about the precipitation in these alloys (Edwards et al., 1998; Marioara et al., 2007). The surrounding $\beta''$ precipitates at $t_4$ which were subsequently dissolved are thought to free solute to the matrix surrounding the evolving $\beta'$ precipitates.

Table 1 shows a comparison of measured precipitate statistics at time $t_4$ to that of $ex$ $situ$ heated specimens studied after 3 and 24 h isothermal ageing at $180^\circ$C, corresponding with a peak-hardened and a slightly overaged condition, respectively. Bright-field images of the material microstructures for the conditions listed in Table 1 are shown in Figure 3. It is observed that the precipitate statistics in the studied region of the $in$ $situ$ heated lamella (thickness ~ 90 nm) showed a more refined microstructure of smaller precipitates relative to the isothermally heated bulk specimens. This indicated that the material was still in an underaged state. This is thought to have occurred primarily due to a lack of solutes which instead have diffused towards the top and bottom surfaces of the TEM lamella. It has previously been shown that there was a significant migration of Si and Mg to the surface of an Al–Mg–Si–Li alloy at 200$^\circ$C, with concentrations exceeding 10 at.% for both atomic species in the top nanometre of the specimen (Cooil et al., 2016). Mg was shown to migrate towards grain boundaries (GBs), whereas Si was ubiquitous. It is important to note that the surface oxide was removed by Ar$^+$ bombardment in the cited study. The specimen in the present study was exposed to air before insertion into the TEM, and therefore formed several nanometre thick surface oxide layers. Due to the similarities in element additions and temperature, surface segregation of solutes is also thought to have occurred for the alloy studied in this work. Decreased levels of precipitate forming elements, most notably Si, are thought to be the main reason for the observed reduction in precipitate growth as compared to specimens prepared.
from bulk conditions. In addition, because the TEM lamella is free to bend and expand in one dimension, different from a bulk material, strain relaxation could also have contributed to reduced precipitate growth. Heterogeneous nucleation of precipitates in cold worked materials is known to accelerate precipitation significantly, with dislocations acting as high-diffusion pathways. However, as the bulk material was not subjected to any cold deformation and the resulting division of precipitate types formed was similar, the effect is thought to be less important than surface segregation of solutes.

The precipitates in the studied region did not grow larger than 30 nm in length (see Fig. 1H). In a thicker region of the specimen (Fig. 1J, ~130 nm thickness), some precipitates grew to reach above 100 nm in length, similar to significantly overaged conditions in the isothermally aged bulk material (Sunde et al., 2019). There is a striking difference between the scarcely populated region of Figure 1(I) to that of Figure 1(J), both acquired at the same condition. The dissolution of precipitate phases in a thin region of the lamella further indicated that the concentration of solutes (and potentially vacancies) in the specimen had developed in a significantly different manner than for the bulk material.

As the material was pre-aged before FIB specimen preparation, the vacancy concentration was likely near equilibrium concentration initially. Before in situ ageing, below the surface oxide layers, the top and bottom surfaces of the material were rich in dislocations and Ga$^{+}$ ions from the FIB. Metal/amorphous interfaces serve as dislocation sinks (Legros et al., 2009; De Knoop & Legros, 2014), and the initial bright-field imaging observations showed that the dislocations and surface impurities were annealed out after a relatively short time. It is not known whether the metal/oxide interfaces act as net sources or sinks of vacancies. In situ observations of precipitate-free zones (PFZs) surrounding dispersoids near the studied region showed that the PFZs grew at similar rates as for PFZs surrounding dispersoids and GBs in the bulk material. The comparable growth rates are taken as a qualitative indication that the concentration of vacancies in the lamella was comparable to that of the bulk material.

Our hypothesis regarding precipitate dissolution is that with a driving force causing solutes to segregate to the specimen surfaces with ageing, the precipitates that were positioned near or grew to reach in proximity of the surfaces dissolved, thus initiating the formation of PFZs. Subsequently, the continued segregation of solutes to the surfaces lead to further growth of the PFZ regions, and the growing PFZs reached precipitate phases buried progressively deeper in the lamella thickness, causing further dissolution. In addition, the lack of solutes through the lamella thickness might eventually have caused dissolution of the remainder precipitate phases. High-resolution high-angle annular dark-field scanning TEM imaging was attempted at $t_{5}$, but the precipitates were buried too deep in the material to be imaged, which supports the PFZ hypothesis. Future experiments will attempt SHT and re-ageing in situ to see whether the experiment can be repeated on the same lamella. Thickness effects will also be studied more carefully to assess the transferability of the results to bulk precipitation behaviour.

Conclusions

The high thermal resistance of the $L$ phase was demonstrated, being one of the main phases remaining after multiple stages of high thermal exposure ($180$–$240^\circ$ C). $\beta''$ was the main precipitate phase near peak-hardened conditions, and formed a high number density of precipitates. A few percentage of the $\beta''$ precipitates subsequently transformed to $\beta'/Q'$ phases, whereas the rest dissolved. Specimen thickness had a pronounced effect on the ageing kinetics, and additional experiments comparing in situ and ex situ heating TEM results are necessary to investigate this aspect further.
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Conflict of interest
The authors declare no conflict of interest.

References


