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# Real-Time Atomic Scale Imaging of Nanostructural Evolution in Aluminum Alloys

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#### Supporting Information

**ABSTRACT:** We present a new approach to study the threedimensional compositional and structural evolution of metal alloys during heat treatments such as commonly used for improving overall material properties. It relies on in situ heating in a high-resolution scanning transmission electron microscope (STEM). The approach is demonstrated using a commercial Al alloy AA2024 at 100–240 °C, showing in unparalleled detail where and how precipitates nucleate, grow, or dissolve. The observed size evolution of individual precipitates enables a separation between nucleation and growth phenomena, necessary for the development of refined growth models. We conclude that the in situ heating STEM



approach opens a route to a much faster determination of the interplay between local compositions, heat treatments, microstructure, and mechanical properties of new alloys.

**KEYWORDS:** In situ (S)TEM, precipitation, aluminum alloys

Most commercial engineering alloys undergo heat treatments to change their intrinsic microstructural properties, such as elemental distribution and precipitate density, to enhance their extrinsic physical properties such as mechanical strength.<sup>1-3</sup> Despite the key importance of these treatments, studies of the compositional and structural evolution of alloys undergoing heat treatments are fragmented and timeconsuming as they have been carried out on a set of different samples taken at intermediate stages, which are in fact postmortem data that do not show the evolution of the same area.<sup>1-14</sup>

Here, we present a novel in situ method to investigate the (atomic) structural and compositional evolution of alloys with time and temperature. At the core of this method is a (scanning) transmission electron microscope ((S)TEM) fitted with a specimen holder that allows in situ heating at minimal specimen drift, three-dimensional precipitate structure retrieval

(tomography), and elemental mapping at the nanometer scale. We expect this in situ approach to become important for studying new compositions, such as those suggested by computational methods.

As proof-of-principle of our approach, we studied the wellknown commercial Al alloy AA2024. In short, from previous research it is established that subsequent heating stages induce the formation of precipitates inside the Al alloy, resulting in improved alloy strength through the well-known mechanism of "precipitation hardening".<sup>1–3</sup> Specifically, it is reported that during aging at 100–240 °C of a supersaturated solid solution obtained after quenching a heated Al alloy, clusters of 3–20 atoms are nucleated,<sup>9</sup> that either dissolve or grow into ~6-nmlong particles called Guinier–Preston–Bagaryatsky (GPB)

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**Figure 1.** (a) ADF-STEM image obtained on heating an AA2024 specimen at 250 °C for ~2 min, showing lath-like nanoprecipitates. From 91 such projections with tilt angles between  $-45^{\circ}$  to  $+45^{\circ}$ , the three-dimensional (3D) distribution of the lath-like precipitates has been extracted as shown in (b).

zones.<sup>3</sup> By a complex compositional and structural evolution at the atomic level,<sup>5–8</sup> these GPB zones grow into intermediate precipitates or GP-II zones with a thickness of 1–4 nm and a length of 10–100 nm.<sup>4,10</sup> Upon further aging, the precipitates grow into laths a few hundred nanometres long and up to 10 nm wide. The existing knowledge on the nanostructural hierarchy<sup>7</sup> of precipitates in aluminum alloys is from a combination of high-resolution microscopic techniques like atom probe tomography and high resolution (S)TEM on various specimens prepared from bulk samples that have undergone different heat treatments. However, information on all stages of the evolution of an individual precipitate is missing. Here, we show the evolution of precipitates in a TEM specimen through in situ heating.

Over the past 50 years, various in situ TEM studies have been performed on precipitation in Al alloys with limited success.<sup>15–19</sup> Factors that have prohibited successful in situ TEM studies are specimen drift, limitations with elemental analysis techniques, and electron beam damage. In recent years, new (e.g., MEMS-based) specimen holders<sup>20</sup> have succeeded in minimizing drift to 0.1 nm per 10–100 s,<sup>21</sup> whereas very fast Xray spectroscopy coupled with aberration-corrected (S)TEMs with a probe size of 0.1 nm using a low dwell time per pixel basically solves the latter two problems. TEM operation in scanning mode (STEM) has the advantage that it allows larger Al specimen thicknesses (150 nm) during high-resolution imaging in comparison to the TEM mode (50 nm). When combined, these instrumental innovations allow a powerful and fast approach to study the effects of heat treatment on alloys, of which we provide a first example.

On a ~150-nm-thick AA2024 specimen heated in situ to 250 °C for 2 min, annular dark-field STEM (ADF-STEM) imaging reveals the growth of lath-like nanoprecipitates (Figure 1a). We have performed six heat-treatment experiments on different specimens from room temperature to 500 °C, and a reproducible trend of elemental redistribution and precipitation is observed. From 180 °C upward, a change in the morphology of some grain-boundary precipitates is observed, whereas the formation of elongated nanoprecipitates is observed within the temperature range of 200–300 °C.

ADF-STEM also allows a full 3D tomography (Supplementary Movie S1) of the precipitates.<sup>22,23</sup> The reconstructed precipitate distribution (Figure 1b, Supplementary Movie S2) reveals the presence of three families of precipitates, oriented along the  $\langle 100 \rangle_{Al}$  directions. It is evident that one of the three  $(100)_{Al}$  families of the lath-like nanoprecipitates is present throughout the thickness of the specimen. Such precipitates are also reported for bulk precipitation.<sup>13</sup> Moreover, a precipitatefree zone at the grain boundary is observed (Figure 1a), which is noticed commonly in bulk specimens.<sup>24</sup> Analysis of two other STEM movies recorded at 250 °C show similar behavior. Although ~150 nm thick, the specimen clearly shows many features of relevance to bulk material. Surface effects are not fully absent, but their influence is suppressed due to the supersaturated condition of the Al alloy. The effective diffusion lengths of elements in the specimen are much shorter than suggested by diffusion coefficients from literature (see Supplementary Table S1), which are only valid for the very dilute limit. In our case, the distance to the nearest trapping site is much shorter than the distance to the surface, so that the surface effects are limited to a region very close to the surface.

Having witnessed the temperature range of precipitation (for more details on heat treatment, see Supporting Information), to follow growth kinetics at an optimum rate, heat treatment is carried out at 225 °C. The STEM movie (Supplementary Movie S3) recorded with an acquisition rate of one frame per 3 s shows the formation of individual precipitates after about 100 s. The snapshots (Figure 2a-c) from the movie show the intermediate stages. After 840 s, when no further changes are observed, the heating is stopped, and a tilt-series of ADF-STEM images is acquired for tomographic reconstruction. From the tilt-series (Supplementary Movie S4), it is observed that there are three families of precipitates, along the cube directions  $\langle 100 \rangle$  of the Al matrix. We have designated the precipitates oriented at 29° to the specimen surface (seen perpendicular to the specimen surface, Figure 2d) as [001] type, two of which are numbered 1 and 2, whereas the precipitates 3, 4 and 5, 6 are along the [100] and [010] directions, respectively. Precipitates 1 and 2 are connected to dislocation loops. The length evolution of these six individual precipitates (Figure 2e) is deduced from Supplementary Movie S3. The precipitates 1 and 2 nucleate earlier in time but show the same growth characteristics as precipitates that are formed in the matrix. Thus the average width and length of the precipitates is plotted as a function of  $t^{1/2}$  after synchronizing the nucleation moments to t = 0 (Figure 2f). The width remains nearly constant,

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**Figure 2.** (a-c) Snapshots from an in situ ADF-STEM movie showing the growth of lath-like precipitates in AA2024 specimen aged at 225 °C. (d) ADF-STEM image at 29° tilt showing that precipitates 1 and 2 are located on dislocation loops. (e) Plot of the length evolutions of the precipitates marked 1–6 with time. (f) Average length and average width of six precipitates monitored from the moment of nucleation, as a function of  $t^{1/2}$ . (g) Slice from a 3D reconstruction obtained from a tilt series of 91 ADF-STEM images. (h) Conceptual sketch illustrating the distribution of precipitates in this specimen across the thickness. The surface (position determined within an accuracy of 5 nm) is not exactly parallel to the viewing direction.

showing that growth in the lateral dimensions is interfacelimited. The average length increases approximately linearly



Figure 3. Snapshots from an HR-STEM movie obtained after heating an AA2024 specimen to 200  $^{\circ}$ C for (a) 10 min and (b) 48 min, showing Sphase type precipitates oriented parallel to the electron beam. The atomic clusters indicated by the arrows in (a) have disappeared in (b). At the same time, the precipitate close to the green arrow has become wider.



Figure 4. ADF-STEM image and corresponding EDX maps of Cu and Mg obtained at 250 °C showing the presence of lath-like hardening precipitates, identified as S-type. The vertical scales indicate atomic %.

with the square root of time, corresponding to classical volume diffusion controlled growth. The half-length is commonly expressed as: $^{25}$ 

$$1/2L(t) = 2(\beta D)^{1/2} t^{1/2}$$
<sup>(1)</sup>

where  $\beta$  is the dimensionless growth parameter, and *D* is the diffusivity of the slowest diffusing element in the precipitate (Cu,  $D_{Cu} = 4.0 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$  at 225 °C). The growth parameter is derived from the slope of the fitted linearity as  $\beta = 3.04$ .

The 3D reconstruction of the precipitates (Supplementary Movie S5, Figure 2g) shows that the [001] type precipitates connected to dislocation loops are embedded within the specimen. The observation of precipitates nucleating at dislocations corresponds well with literature on bulk material.<sup>13,15</sup> The two precipitate families along [100] and [010] directions are predominantly present ~20-40 nm under the foil surface, as schematically summarized from the 3D analysis (Figure 2h). Possible explanations for this kind of a region include surface stresses due to lattice relaxations, thermal expansion differences between the alloy and a surface oxide

layer, specimen preparation effects, and a lower concentration of vacancies near the surface, leading to anisotropic vacancyassisted solute diffusion.

At a slightly lower heat treatment temperature (200 °C) to allow the recording of high-resolution (HR) STEM movie (Supplementary Movie S6), evolution of the precipitates at the atomic scale is observed. Two snapshots from the movie zoom in on the evolution of S-phase-type precipitates (Figure 3). Clusters of solute atoms are observed in the matrix (blue and red arrows) and near a precipitate (green arrow). Over time, the atom clusters marked by the red and blue arrows disappear and consequently must either dissolve into the matrix or diffuse elsewhere, whereas the atom cluster indicated by the green arrow contributes to the growth of the crystalline part of the precipitate (Figure 3b). The common characteristic of these precipitates are the rows of bright dots along the  $[210]_{Al}$ direction with a dot-dot distance of 4.5 Å, typical for the S phase (see for example<sup>4</sup>). The distance between these rows of dots is 6.3 Å, indicating a CuMgAl<sub>5</sub> composition (see Supplementary Text).

From the STEM movies (Figure 2 and Figure 3), timeresolved information is obtained from individual precipitates, which allows for separating nucleation and growth, in contrast to earlier TEM studies where average dimensions are considered of precipitates that nucleate at different moments in time. The detailed experimental information obtained using the current methodology will be required for developing and validating more advanced models, taking into account not only nucleation and growth of precipitates, but also the coalescence with precursor, GP zones.

As a final application of our in situ analysis approach, we combine STEM imaging with element-compositional analysis of the observed phase transformations through energy-dispersive X-ray spectroscopy (EDX) maps. STEM image and EDX maps of Cu and Mg taken at 250 °C of an area containing lath-like precipitates (Figure 4) show that all precipitates contain both Cu and Mg. The maps show that on average the precipitates have a Cu/Mg ratio of 0.9 ( $\pm$ 0.2), close to intermediate S-type precipitate compositions as reported in literature.<sup>4,12,13</sup> As the specimen is heated further to 300 °C, the lath-like precipitates start dissolving and are completely dissolved beyond 330 °C (see Supplementary Text).

Our experiments establish the analytical power of in situ heating combined with HR-STEM and compositional analysis. It succeeds in following the nanostructural hierarchy of nucleation and growth of precipitates in Al alloys: formation of clusters of solute atoms, nucleation of precipitates on dislocations, growth of lath-like intermediate precipitates, and the distribution of these precipitates in three dimensions and with nanoscale precision. The excellent correspondence of our in situ measurements on a submicrometer specimen with literature ex situ experiments on bulk highlights the validity of our approach for future studies of novel supersaturated composites. Even where the influence of the surfaces is felt (in a zone about 20–40 nm from both surfaces), the shape and evolution of the precipitates are nonetheless very similar to those in the bulk-like middle of the sample. In addition to the increased speed of the dynamic structural analysis, we introduce the possibility of in situ observation of the evolution of individual precipitates. The concept of nanostructural hierarchy of nucleation and growth of precipitates is not just limited to solid solutions like aluminum alloys but has also been observed during the nucleation and growth of calcium phosphate<sup>26,27</sup> and magnetite<sup>28</sup> from liquid solutions. We expect that by in situ TEM with liquid cells the evolution of a single particle in liquid solution can be followed, revealing much clearer the hierarchy. With the technology to achieve HR-STEM combined with in situ specimen heating and EDX now readily available, this analysis approach will accelerate and enrich the research on metallic alloys.

### ASSOCIATED CONTENT

#### **Supporting Information**

More details provided on heat treatment experiments, discrete tomography, analysis of growth kinetics, HR-STEM images, experimental limitations, and STEM movie analysis. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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