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# *In situ* structural characterization of ageing kinetics in aluminum alloy 2024 across angstrom-to-micrometer length scales

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ABSTRACT

The precipitate structure and precipitation kinetics in an Al–Cu–Mg alloy (AA2024) aged at 190 °C, 208 °C, and 226 °C have been studied using *ex situ* Transmission Electron Microscopy (TEM) and *in situ* synchrotron-based, combined ultra-small angle X-ray scattering, small angle X-ray scattering (SAXS), and wide angle X-ray scattering (WAXS) across a length scale from sub-Angstrom to several micrometers. TEM brings information concerning the nature, morphology, and size of the precipitates while SAXS and WAXS provide qualitative and quantitative information concerning the time-dependent size and volume fraction evolution of the precipitates at different stages of the precipitation sequence. Within the experimental time resolution, precipitation at these ageing temperatures involves dissolution of nanometer-sized small clusters and formation of the planar S phase precipitates. Using a three-parameter scattering model constructed on the basis of TEM results, we established the temperature-dependent kinetics for the cluster-dissolution and S-phase formation processes *simultaneously*. These two processes are shown to have different kinetic rates, with the cluster-dissolution rate approximately double the S-phase formation rate. We identified a dissolution activation energy at (149.5 ± 14.6) kJ $mol^{-1}$, which translates to (1.55 ± 0.15) eV/atom, as well as an activation energy for the formation of S precipitates at (129.2 ± 5.4) kJ $mol^{-1}$, i.e. (1.33 ± 0.06) eV/atom. Importantly, the SAXS/WAXS results show the absence of an intermediate Guinier-Preston Bagaryatsky 2 (GPB2)/S″ phase in the samples under the experimental ageing conditions. These results are further validated by precipitation simulations that are based on Langer-Schwartz theory and a Kampmann-Wagner numerical method.


## 1. Introduction

The 2000 series aluminum alloys are important advanced functional materials due to their high yield strength, good fracture toughness and excellent fatigue properties [1]. The mechanism that accounts for these superior material characteristics is precipitation hardening, in which a heat treatment process produces fine precipitates due to changes in solid solute atom solubility in a supersaturated solid solution [2]. The presence of these fine precipitates, in turn, provides barriers to the motion of dislocations, thereby increasing the resistance of the alloy to plastic deformation.

Due to the extremely important role that the 2000 series aluminum alloys play in the aviation industry, much attention has been devoted to understanding their structures and properties [3–5]. Particularly, comprehensive investigations have been made to elucidate the morphological dependence of the precipitates on material composition [6], thermal treatment history [7], and impurity elements [8] to optimize the materials performance for designed applications. To achieve this, *ex situ* methods such as transmission electron microcopy (TEM) [4,9], three dimensional atom probe [10,11], and X-ray diffraction [12] have been used to examine the precipitate structure and morphology. Indirect methods such as hardness testing [13], specific resistivity [14], electrical conductivity [15], and differential scanning calorimetry [16] have also been used to provide information associated with the changes in the quantity of the precipitates. From a structure-characterization point of view, an *in situ* direct investigation of the entire precipitation process over all the relevant length scales,

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which acts to reveal the morphology and kinetic growth mode of the precipitation phases, remains elusive.

At the same time, despite the large amount of experimental, theoretical, and modeling effort which allows the precipitation processes to be understood on an atomic scale, the complete precipitation sequence in Al–Cu–Mg based aluminum alloys (AA20x4 series alloys) is still in debate [9,16–18]. For example, one of the possible precipitation sequences proceeds as follows: supersaturated solid solution → co-clusters/Guinier-Preston Bagaryatsky (GPB) zones → GPB2 zone/S″ → S' → S [2,19]. In this sequence, the co-clusters are predominantly a Cu–Mg binary phase and are transient [20]. The S phase, which is the thermal equilibrium phase, has an established crystal composition of $CuMgAl_2$ [20]. S′ has a crystal structure almost identical to that of the S phase, but is semi-coherent and slightly strained. Additionally, in Al–Cu–Mg alloys, the precipitation hardening is thought to be a two-stage process. In the first stage, the rapid formation of Cu–Mg co-clusters is responsible for the initial age hardening [21,22]. The second stage in the sequence accompanies the formation of the thermodynamic-equilibrium S phase, and does not finish until the transition towards S phase is complete [2]. It is also known that under identical physical and chemical conditions, the second stage requires a significantly longer time to complete. What is controversial is the presence of a transient, nonequilibrium phase of GPB2 zone/S″. To settle this debate, again, it calls for a direct and *in situ* probe that is capable of characterizing the entire precipitation process.

To meet these challenges, we sought to perform a systematic investigation of the formation kinetics and structure evolution of the precipitates in a commercial aluminum alloy 2024 (AA2024), mostly using synchrotron-based *in situ* small angle X-ray scattering (SAXS) and diffraction techniques. SAXS, as a scattering technique, examines the structural inhomogeneities within the materials under investigation. It is known to be highly sensitive to very small precipitates in alloys [23–26]. When combined with simultaneous *in situ* diffraction experiments, it offers an opportunity to unveil the structural transformations of the precipitates in AA2024.

From a technique point of view, it has been over 60 years since Guinier's pioneering studies of precipitates in alloys using SAXS [27,28]. Nevertheless, it is important to recognize that the low X-ray flux from lab-based X-ray sources makes *in situ* and *in operando* characterization of precipitate formation processes challenging, if not completely impossible, and a fixed X-ray energy may present problems with X-ray fluorescence that is usually difficult to mitigate. Synchrotron sources, with their energy tunability and high X-ray flux, overcome these restrictions and greatly expand the applicability of SAXS in probing the static morphology and kinetics of precipitates in alloys. Despite this, other hurdles still exist. For example, precipitates in alloys often have multiple length scales, complex shapes, and high volume concentrations. Elucidating these parameters *in situ* often involves a scattering-vector magnitude, $q$, range (where $q = (4\pi/\lambda) \times \sin(\theta)$, with $2\theta$ being the scattering angle and $\lambda$ being the X-ray wavelength) that is not commonly accessible using a pinhole SAXS camera setup alone, and the determination of scattering background, necessary for characterization of small precipitates such as Guinier-Preston zones or cluster defects, often requires the scattering intensity to be extended to higher $q$ regimes to determine the level of thermal fluctuations and instrumental background scattering [29]. These requirements demand new measurement capabilities.

To address these needs, we have recently developed an *in situ*, synchrotron-based measurement technique that is capable of rapidly quantifying atomic structures and microstructures over a size range from less than 0.5 Å up to ≈30 μm. Employing this technique, in conjunction with TEM and thermodynamic modeling, we have investigated the precipitate growth and dissolution kinetics in solution-annealed AA2024 under different artificial ageing conditions. With the unprecedented scale range that this technique covers, we were able to follow, for the first time, the *in situ*, *simultaneous* growth of the S precipitates and dissolution of GPB zones/small clusters in AA2024 alloys under different isothermal ageing conditions and resolve the evolution of the precipitates both in atomic structure and in microstructure. It is worth noting that many critical aspects of the performance of AA2024 alloys, such as mechanical behavior [30,31], resistance to corrosion [32], *etc*. are closely related to the microstructures that emerge at different processing states. Therefore, it is vital to understand the microstructures across all relevant length scales for the ultimate goal of comprehensive material design and optimization.

In the next section, we will briefly introduce the details of the materials, the characterization techniques, experimental procedures, and computational methods. We will then discuss the data reduction and analysis procedure, followed by a presentation of our detailed experimental results and finally offer some concluding remarks.

## 2. Materials and Methods

### 2.1. Materials

Commercially available bare T3-temper aluminum alloy 2024 (AA2024) sheets were acquired and used for the experiments discussed in this paper. The AA2024 sheets were manufactured by AMAG rolling[1] and meet the standard specification of ASTM B209 [33]. The nominal thickness of the sheet was 0.508 mm (0.020 inch). The as-received alloy was cut into pieces of ≈5 mm × 5 mm.

### 2.2. In situ USAXS/SAXS/WAXS experiments

This technique is based on the ultra-small angle X-ray scattering (USAXS) instrument at the Advanced Photon Source (APS), Argonne National Laboratory and combines USAXS with pinhole-camera-based small-angle X-ray scattering and wide-angle X-ray scattering (WAXS).

We conducted our measurements at the USAXS beamline 15-ID at the APS [34]. This instrument makes use of Bonse-Hart type double-crystal optics and extends the scattering vector range of small-angle X-ray scattering (SAXS) down to $10^{-4}$ Å$^{-1}$($2 \times 10^{-5}$ Å$^{-1}$ when using higher energy X-rays [35]), which is normally inaccessible to pinhole SAXS cameras. Additionally, the scattering intensity from a Bonse-Hart instrument is absolute calibrated, i.e., we measure the quantitative differential scattering cross section, a characteristic property of the sample material, without the need for a separate scattering intensity standard. We used collimated, monochromatic X-rays in the standard 1-D collimated transmission geometry to measure the scattering intensity as a function of $q$. In our experiments, the X-ray wavelength was 0.738 Å, which corresponds to an X-ray energy of 16.80 keV. The beam size was 0.8 mm × 0.8 mm, and the X-ray flux was ≈$10^{13}$ photon/s. The measured USAXS $q$ range was from $1 \times 10^{-4}$ Å$^{-1}$ to 0.2 Å$^{-1}$.

To provide better statistics and a lower scattering background at high $q$, we used a PILATUS 100 K detector (Model: 100 K-S, Dectris, Baden, Switzerland) [36] in a conventional pinhole small-angle

[1] Certain commercial equipment, instruments, software or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the Department of Commerce or the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.