

Supplementary Materials

During TEM thin foil observation, the incident electron beam collides with atomic electrons of the particles, generating three effects: (1) radiolysis (ionization), (2) electron-beam heating (phonons), and (3) atomic displacement (knock-on damage), as addressed in the books [S1, S2] and in the paper [S3].

Regarding the radiolysis (ionization) effect [S1], owing to ion bonds and polar covalent bonds possessing low ability for neutralizing the attractive and repulsive electrostatic forces, lattice atoms are easily collapsed by accelerated electrons. On the other hand, metallic bonds, which are connected with the positive metallic ions and free electrons, can rapidly neutralize after the ionization induced by electron-particle interaction. Therefore, the effect of radiolysis on metals is negligible.

For the electron-beam heating (phonon) effect [S1-S3], after the sample absorbs the energy due to the electron-particle interaction, the vibration of atomic bonds generates phonons (i.e., the heating of the samples). If the mean free path of scattering is much smaller than the thickness of TEM samples, numerous phonons will be generated and the temperature of the sample will be elevated. However, metals usually possess a longer mean free path, resulting in a lower probability of scattering events. In addition, with good thermal conductivity, the rising temperature excited by phonons in metallic TEM samples is quickly dispatched, as reported in the two books [S1, S4] and in the two papers [S5, S6].

Three following examples [S4-S6] are illustrated for the issue of electron-beam heating in metals. In the work [S4], using a tungsten-filament 100 kV TEM, a Cr-metallic TEM thin foil (thermal conductivity of around 100 W/m K) was just slightly affected by electron beam heating with variable beam currents in the range of 0.1 to 1×10^4 nA. The elevated temperature was reported to be approximately smaller than 10 K. In the work [S5], under a typical tungsten-filament 100 kV TEM with 2×10^4 nA beam current, the elevated temperature of a Au-Ni thin foil (thermal conductivity of around 320 W/m K) was reported to be smaller than 8 K. Even for a beam current of 1×10^5 nA, the increment of temperature was only close to 15 K. In the work [S6], for a low-melting point metal Mg thin foil (thermal conductivity around 156 W/m K), under a LaB₆ 200 kV TEM with a 2.1 nA beam current, the resulting elevated temperature was reported to be smaller than 1 K. In summary, the effects of electron beam heating depend on the thermal conductivity of the material and the parameters of the accelerating voltage and the beam current.

In our work, we employed a Tecnai-F20 Schottky FEG 200 kV HRTEM having a range of beam currents (I_0), ($0.5 \text{ nA} < I_0 < 2.5 \text{ nA}$). The elevated temperature due to electron beam heating for Al thin foils can be estimated. It is presumed that the physical parameters of AA7050 aluminium alloy were similar to those of pure Al; i.e., thermal

conductivity of Al (~205 W/m K), and mean free path at 200 kV for Al (~164 nm) [S7], etc. We also assume that Al thin foils were covered with a thin-layer of Al₂O₃ aluminium oxides of around 5 to 35 nm (Al₂O₃: thermal conductivity of around 1 to 10 W/m K [S8]). Using Egerton's and Zheng's models [S3, S6], the elevated temperature for an Al thin foil is estimated to be a very small value (< 5 K) and can be considered negligible.

The primary damage to the metallic TEM thin foils is presumed to be caused by knock-on displacement (i.e., displacement damage) [S1-S3]. This process takes place due to the direct transfer of the beam energy to atoms in the samples, knocking out the atoms and creating vacancies and interstitials. Supposedly, it speeds up atom diffusion and promotes certain in-situ transformations. In the work [S6], under a LaB₆ 200 kV TEM with 2.1 nA beam current, the Mg thin foil was observed to be quickly drilled by the converged electron beam, thus forming some nano-pores. This phenomenon is associated with a cascade of atomic displacements, which occurs when the incident electron-beam energy (E) is higher than the threshold electron-beam energy (E₀) for atomic displacement. The determination of the threshold electron-beam energy (E₀) depends on the displacement energy of atoms (E_d) in the samples. Previous investigations have indicated that the displacement energy (E_d) has orientation dependence, such as Al_{<100>} ≈ 17 eV, Al_{<110>} ≈ 16 eV, and Al_{<111>} ≈ 14 eV [S9]; Cu_{<100>} ≈ 19 eV, Cu_{<110>} ≈ 23 eV, and Cu_{<111>} ≈ 76 eV [S10]; Mg_{<0001>} ≈ 14 eV, Mg_{<1010>} ≈ 11 eV, and Mg_{<1210>} ≈ 9 eV [S11]; and Zn_{<0001>} ≈ 11 eV, Zn_{<1010>} ≈ 9 eV, and E_{d<1210>} ≈ 7.6 eV [S12].

A formula [S3] for the displacement energy of atoms (E_d) of atomic weight (A) to determine the threshold electron-beam energy (E₀) is expressed as follows:

$$E_d = \frac{E_0 (1.02 + E_0 \times 10^{-6})}{465.7A} \text{ ----- (1).}$$

Equation (1) can be converted to be $E_0 = \frac{-1.02 + \sqrt{1.04 - (1.86 \times 10^{-3} \times A \times E_d)}}{2 \times 10^{-6}} \text{ ----- (2),}$ where E₀ is in eV, E_d is in eV, and A is in amu. The threshold energies (E₀) for different elements, such as Al, Cu, Mg, and Zn in Al alloys, have been estimated by using the above equation and are presented in Table R1.

Table R1. The threshold electron-beam energies (E₀) for atomic displacement.

Element	Atomic mass (A) (amu)	Displacement energy* (E _d) (eV)	Threshold energy (E ₀) (keV)	Reference
Al	26.98	14.0 - 25.0	150 - 263	[S3, S4, S9]
Cu	63.55	19.0 - 79.0	396 - 1101	[S10]
Mg	24.31	9.0 - 23.2	91 - 211	[S11, S12]
Zn	65.38	7.6 - 11.0	191 - 261	[S12]

*The range of the displacement energy is caused by the crystal directions such as <100>, <110>, and <111> directions, etc.

For nominal compositions of η'-Mg₂Zn_{5-x}Al_{2+x} (x = 2 to 4) and η-MgZn₂

precipitates, both Mg and Zn atoms might dominate the corresponding threshold energies (E_0). Moreover, detailed information about the respective directional displacement energies (E_d) of Mg and Zn atoms were reported in previous investigations [S11, S12]; i.e., $E_{d\langle 1\bar{2}10 \rangle} \approx 7.6$ eV for Zn, and $E_{d\langle 1\bar{2}10 \rangle} \approx 9.0$ eV for Mg. As shown in Table R1, the corresponding threshold energies (E_0) (i.e., 191 keV for Zn and 91 keV for Mg) were estimated to be lower than the electron voltage generated in a 200 kV microscope. It is presumed that Mg atoms are easily susceptible to the accelerating voltage of 200 kV and thus dramatically diffuse out along the $\langle 11\bar{2}0 \rangle$ direction, causing the transformation from relative Mg-rich η' phase to Mg-depleted η phase (i.e., Zn-rich η phase). It is appropriate to conclude that the atomic displacement caused by the electron beam might have a strong impact on speeding up in-situ nucleation $\eta' \rightarrow \eta$.

Three references illustrating the transformation behaviors with the electron beam between the snapshots of in-situ TEM.

In two previous works [S13, S14] for Al-Cu alloys and the other work [S15] for a Fe-Cu alloy, in-situ TEM has been conducted for the investigations of the precipitate transformation with the electron beam between the snapshots.

Wenner et al.'s work for an Al-Cu alloy [S13] indicated an example of transformation of Al_2Cu phase (θ') in the Al-Cu alloy. Under Cold FEG 80 kV observation, a new structure Al_5Cu_3 was generated within the original Al_2Cu precipitate. From their first principle calculation, the calculated energies required to initiate atomic diffusion in $\text{Al}_2\text{Cu}/\text{Al}_5\text{Cu}_3$ in the Al-Cu alloy are determined to be in the range of 1.74 to 2.34 eV, which is far lower than the atomic displacement energy of Al atoms (14 eV) in the Al matrix. Therefore, even under the exposure of the Cold FEG 80kV TEM electron-beam, the structural modification of the Al_2Cu precipitate still occurred. On the other hand, under Cold FEG 200kV TEM observation after a short duration of 15 s, the internal structure of Al_2Cu precipitates was found to be dramatically damaged.

Lu et al.'s work [S14] investigated the GPII zone in an Al-Cu alloy under LaB₆ 300 kV TEM observation for three different duration times (0 s, 240 s and 420 s). The TEM snapshots indicated that with 240 s of holding, the Cu-rich layer of GPII zones slightly dissolved; with 420 s, they completely dissolved. The minimum threshold energy (E_0) of Cu atoms is 396 keV; that of Al, 150 keV. It is clear that under the exposure of the 300 keV electron-beam, the atomic displacement of Al atoms promptly occurred, inducing the diffusion of Al atoms adjacent to the interface of the GPII/Al matrix. The in-situ TEM snapshots displayed the course of dissolution of the GPII zone.

In Nicol et al.'s investigation of a Fe-Cu alloy [S15], they found that Cu precipitates possessed variable structural transformations; i.e., BCC $\rightarrow$ 9R (twinned

structure) $\rightarrow$ 3R (un-twinned structure) $\rightarrow$ FCC. Under LaB₆ 400 kV TEM observation for a duration of 600 s, two respective HRTEM micrographs showed that a twinned 9R structure apparently developed into an un-twinned 3R structure. It is noted that the threshold energies (E_0) of Fe [S16] and Cu atoms, around 373 and 396 keV, respectively, are lower than an incident electron beam (E) of 400 keV. Hence, the HRTEM images of snapshots provide strong evidence that the atomic displacements of Fe and Cu atoms were triggered by the higher energy electron beam.

In the present work, after the Zn-rich GPII zone dissolved, the formation of η' was observed with serial in-situ frames of HRTEM micrographs. It is appropriate to conclude that the atomic displacements of Mg, Al and Zn atoms in the GPII zone were enhanced by the 200 keV electron beam, leading to the dissolution of the GPII zone and hence providing adequate Zn atoms to nucleate an η' phase. On the other hand, the electron beam heating of the aluminium alloy sample has been estimated by theoretical calculations, and the elevation in temperature is extremely small. Therefore, the separated nucleation of GPII zone $\rightarrow$ η' precipitates, which was associated with diffusion, was presumed to be mainly speeded up by the atomic displacement effect.

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