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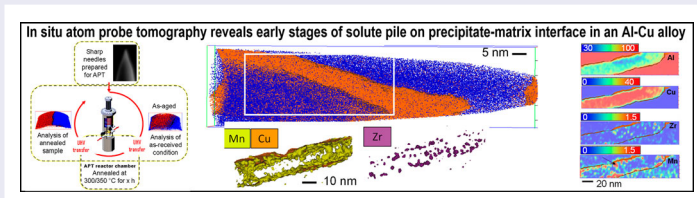
Rapid assessment of interfacial stabilization mechanisms of metastable precipitates to accelerate high-temperature Al-alloy development

Bharat Gwalani^a, Jia Liu^b, Sten Lambeets^a, Matthew Olszta^b, Jonathan Poplawsky^{b,c}, Amit Shyam^{b,d} and Arun Devaraj^a

^aPhysical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA, USA; ^bEnergy and Environmental Directorate, Pacific Northwest National Laboratory, Richland, WA, USA; ^cOak Ridge National Laboratory, Center for Nanophase Materials Sciences, Oak Ridge, TN, USA; ^dMaterials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

ABSTRACT

Precipitate strengthened high-temperature alloys are currently used in safety-critical applications. Understanding precipitate stability and solute segregation mechanisms at high temperatures is key to designing high-strength alloys. Rapid *in-situ* approaches, therefore, are pivotal in accelerating the alloy design process. Hereby using the test case of a promising high-temperature Al-Cu-Mn-Zr alloy, we demonstrate the value of *in-situ* atom probe tomography coupled with *in-situ* transmission electron microscopy to reveal atomic-scale mechanisms that lead to the emergence of non-equilibrium solute segregation. Mn and Zr segregation at strengthening precipitate(θ')-matrix interface increases the kinetic barrier for phase transformation thus retaining high-temperature strength.



IMPACT STATEMENT

Our rapid approach can essentially eliminate lengthy heat treatments, metallographic preparations, and ex-situ characterization steps and thus help accelerate the process of high-temperature alloy design.

ARTICLE HISTORY

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KEYWORDS

Solute-segregation; structural materials; phase transformation; *in-situ* characterization; atom probe tomography

Many safety-critical, high-strength applications rely on heat-treatable alloys that can be strengthened by formation of precipitates [1,2]. However, the high-temperature application of precipitation-strengthened alloys depends on the nucleation, growth, coarsening, and thermal stability of precipitates. As the precipitates increase in size, they become ineffective in moderating the dislocation activity by either Friedel or Orowan mechanisms [3,4], and thus, the material gradually loses its strength. Developing high-temperature alloys for such applications is a lengthy process, necessitating many iterations of alloy design, heat treatments, and ex-situ microstructural characterization to assess precipitate stability [5]. Hence, high throughput experimental approaches that can accelerate this process can have a broad impact across

many sectors [6]. In this work, using an example of a newly developed high-temperature Al-Cu-Mn-Zr alloy, we demonstrate the value of a high-throughput *in-situ* atom probe tomography (APT) approach in revealing the critical interfacial solute segregation mechanisms.

Alloys with multiple alloying elements possessing disparate diffusivities can stabilize precipitate-matrix interfaces through interfacial solute segregation, thereby extending the properties of the material to extreme environments. Interfacial segregation has been used for engineering multiple Al-based high-temperature alloys with enhanced mechanical properties [7–9]. One such class of non-rare earth-containing alloys is Al-Cu-Mn-Zr (ACMZ) which exhibits plate-shaped, metastable θ' precipitates (based on body-centered tetragonal Al_2Cu ,

CONTACT Bharat Gwalani bharat.gwalani@pnnl.gov Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA; Arun Devaraj arun.devaraj@pnnl.gov

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$a = 4.04 \text{ \AA}$, and $c = 5.80 \text{ \AA}$) [10] that are responsible for the alloy's high strength [11,12]. Interfacial θ' Mn and Zr segregation in these face-centered cubic (FCC)-Al alloys has been shown to enhance the high-temperature stability of the strengthening θ' phase and retain high hardness extending to lengthy exposures to 350°C [13]. It was demonstrated using first-principle calculations that Mn and Zr diffusion towards the θ' interfaces is driven by a reduction in interfacial energy while the stabilization of θ' resulted from a combination of interfacial energy and solute drag effect of the solute elements [14–16]. Segregation assisted modification of phase transformations was used by Gao et al. taking advantage of Sc and Fe interface segregation in Al-Cu alloys [17–20]. Microalloying of Sc aided in grain refinement and coprecipitation $\text{Al}_2\text{Cu}-\text{Al}_3\text{Sc}$ is optimized by tuning Fe and Si in the alloy. A similar strategy of co-precipitation of $\gamma'-\gamma''$ improved creep properties and thermal stability in Ni-based superalloys [21–23]. However, the mechanism underpinning the tendency of solute segregation, and thereby extending the precipitate stability, is based on ex situ examinations after long-term exposure at elevated temperatures (hundreds and even thousands of hours) [15,24–26]. A direct assessment of microstructural changes, especially during the early annealing stages, is needed to ascertain the transformation pathway and guide computational models for future developments. Our work fills this knowledge gap by using a novel method of in-situ APT coupled with correlative scanning transmission electron microscopy (STEM). A reactor chamber attached to the APT vacuum chamber [27–29] allowed atomic-scale observations of the compositional changes on a well-characterized precipitate-matrix interface in the ACMZ alloy upon thermal exposure. We illustrated that the early-stage segregation of Mn on the prior-solute-free precipitate-matrix interface at 300°C and 350°C occurs within the first few hours of exposure, thus preventing the coarsening and transformation of metastable θ' to the stable θ phase. This initial segregation provides time for the formation of stable Zr rich pockets on coherent θ' -FCC interfaces leading to the stabilization of these interfaces for prolonged application at elevated temperatures. Previous work has shown that the non-equilibrium vacancy concentration rapidly annihilates in nano-sized samples and hence, phase transformations are predominantly governed by thermally induced diffusion in our approach [30,31]. However, an excess build-up of surface vacancies can be expected on the interfaces in nano-sized samples as explained by Bourgeois et al. [32] possibly modifying short-range diffusion and phase evolution. Our approach is a high-throughput technique that allows the study of phase transformations at an atomic scale. It can be widely applied for understanding pathways related

to precipitate nucleation, dissolution, initiation compositional fluctuations, and defect-solute interactions along with interfacial segregation.

The ACMZ alloy (6.40 at.% Cu, 0.20 at.% Mn, 0.15 at.% Zr, rest Al) considered in this study is strengthened via metastable θ' precipitates, which are known to be the strengthening phase in most Al-Cu and Al-Si-Cu alloys at temperatures extending to 200°C [11,16,25,33,34]. Prior work on ACMZ alloys has shown that the metastable intermetallic phase (Al_2Cu , θ') can be stabilized to much higher temperatures by microalloying with additions of Mn and Zr (while also maintaining low Fe and Si levels) resulting in substantial improvements in mechanical properties at elevated temperatures [14,16]. The initial microstructure of the as aged condition (aged at 240°C for 4.5 h) consisted of an FCC Al matrix with plate-like strengthening precipitates of Al_2Cu (θ') with a size aspect ratio of ~ 40 , mean interparticle spacing of $\sim 600 \text{ nm}$, and volume fraction of $\sim 2.5\%$ [13,24].

SEM images in Figure 1(a and low magnification inset) shows the aged alloy condition with the bright contrast intragranular θ' precipitates. The larger faceted precipitates are undesirable θ precipitates [14]. The phase fraction of θ precipitates is $< 0.05\%$ (calculated using image contrast thresholding by ImageJ software [35]) which does not change significantly in our experiments [14], hence, we will only focus on θ' precipitates for this study. The coherent faces of the precipitates are $[001] \theta' // [001]\text{Al}$ and semi-coherent faces are $[110] \theta' // [100]\text{Al}$ and as schematically displayed in Figure 1(b). There is an additional OR at the semi-coherent interface not shown here i.e. $[001]\theta' // [001]\text{Al}$ with a four-fold symmetry [24]. We chose precipitates aligned parallel to the evaporation direction (Z) in APT within a lift out made using a Xe ion-based plasma FIB (details given in the methods section) displayed in Figure 1(c). The APT reconstruction in Figure 1 (d-e) displays the top and side view of the needle with the Al-rich matrix region in blue and Cu rich, θ' precipitate in orange color. The crystallographically coherent interfaces of the precipitate are highlighted by white arrows in Figure 1 (d-e). We do not observe any trace Mn or Zr segregation in this condition (as aged) as depicted in Figure 1 (f-g) using both 2-D compositional maps (Figure 1(f)) and compositional profile across the interface (proximity histogram across 10 at.% Cu iso-concentration surface) in (Figure 1 (g)), which is consistent with the previous reports [16].

The metastable θ' precipitates have been shown to coarsen and transform into the thermodynamically stable incoherent θ phase following elevated temperature exposure [34]. To further understand the destabilization mechanism of the θ' precipitates in this alloy, we first conducted *in-situ* hot-stage TEM experiments at 300°C ,

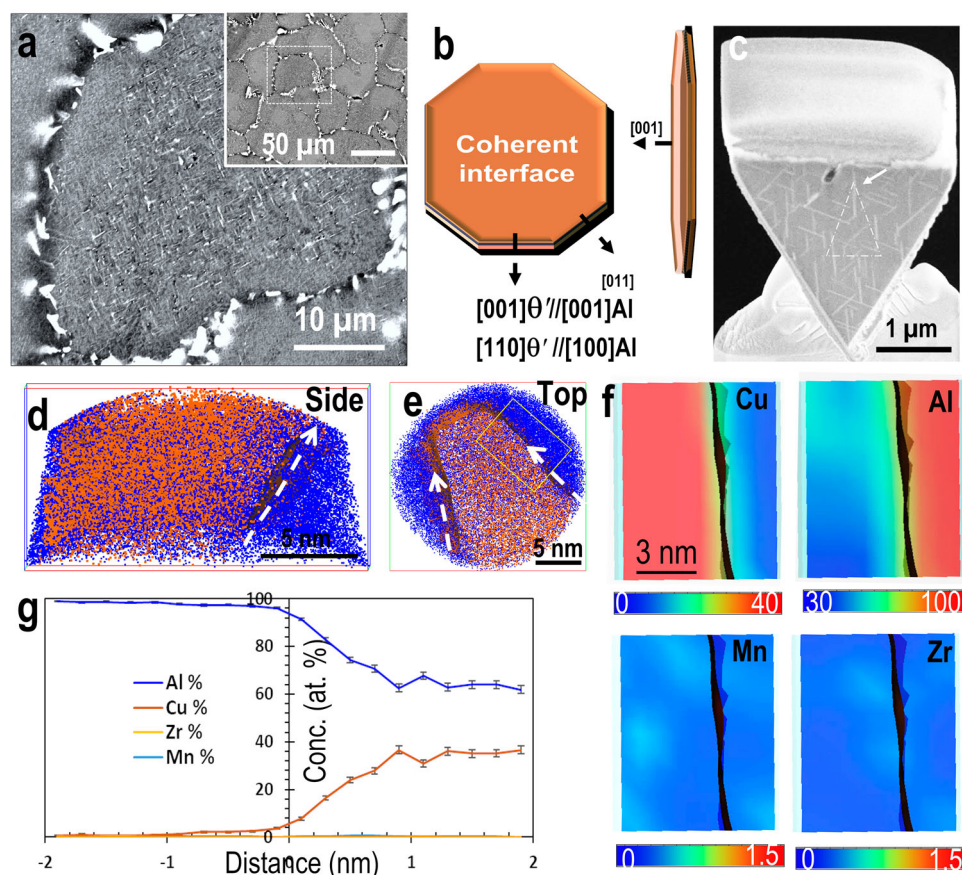


Figure 1. ACMZ alloy in as-aged condition: (a) SEM images (b) schematic showing the alignment of θ' with Al matrix. (c) SEM image of the wedge-shaped liftout. (d-e) APT reconstructions showing the top and side views. (f) 5 nm slice from the APT reconstruction shows the 2-D compositional maps. (g) proximity histogram across the interface.

350°C, and 400°C for 30 mins each. We did not observe a significant change in the phase fraction of θ' precipitates at 300°C and 350°C while a rapid phase transformation occurs at 400°C. A high rate of transformation at 400°C in thin TEM foils was probably achieved due to the excess surface vacancies [32]. The observations at lower temperatures are consistent with the earlier ex situ examinations where θ' precipitates were found to be stable for up to at least 5000 h [14,16] at 300°C and 2000h at 350°C in the current alloy. The in-situ observation of θ' precipitate dissolution at 400°C is displayed in Figure 2. The plate-shaped θ' precipitates, appearing as needles on projecting in the 2-D TEM image in Figure 2(a) (white arrows) similar to Figure 1a, were noted during in-situ annealing. Figures 2 (a-d) show the sequence of disappearing θ' precipitates transforming to the stable θ phase (red arrows). The EDS maps from the boxed region in Figure 2(e) confirm that the θ' is replaced with the blocky θ phase (tetragonal space group ($a = b = 6.067$ Å and $c = 4.877$ Å, I4/mcm)) [36]. The HAADF STEM BF images in Figure 2 (e-f) further confirm the crystal structure and crystallographic orientation of the two precipitates and the matrix. The video graphic file provided

as the supplementary information (Movies S1-3) shows the precipitation sequence and the spatial orientation of the θ phase to the θ' phase and the matrix.

These *in-situ* TEM results demonstrated that the θ' phase rapidly transforms upon thermal activation forming more stable θ phase at 400°C. To understand atomic-scale mechanisms underpinning the stabilization of this metastable phase below 400°C, *in-situ* APT was utilized. The atomic-scale changes at the interface of the θ' -matrix at 300°C and 350°C are rather sluggish and are difficult to capture within a reasonable experimental timeframe using 3-D resolution in TEM. For this, the needles from the as aged condition were exposed to an annealing treatment for 1 h in the APT reactor chamber as described in the methods section. Upon annealing, APT data is collected and this process is repeated multiple times. Our approach for doing *in-situ* APT experiments is presented in Supplementary Figure S4 and described in the methods section.

Figure 3 (a) highlights the reconstruction of a needle specimen with a θ' -matrix interface after *in-situ* annealing at 300°C for 1 h. A 15 nm x 10 nm x 5 nm region is selected containing the interface in the center (Figure

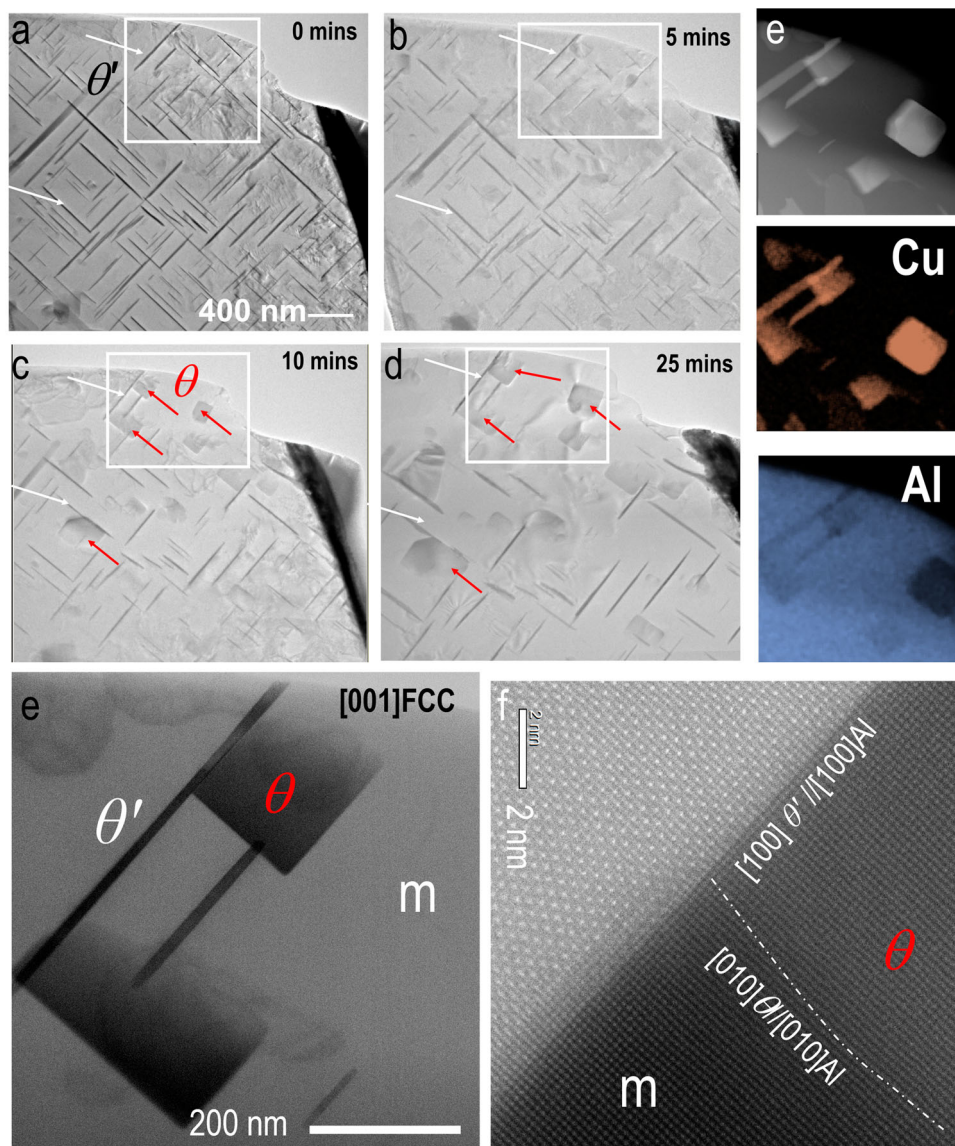


Figure 2. *In-situ* hot stage TEM results. (a-d) The θ' in the matrix is highlighted by white arrows disappear as a function of time forming θ (cyan arrows). (e) HAADF-STEM image of the region boxed in (d) and the corresponding EDS maps. (e-f) HAADF-STEM images showing the interface of transforming θ' , precipitating θ phase, and Al matrix.

3 (b)) for examining the local composition fluctuations after annealing. The 2-D compositional maps showing the enrichment of Cu (0-40 at.%), Mn(0-1.5 at.%), and Zr(0-1.5 at.%) in this selected window are given in Figure 3(b) in this order. Both Mn and Zr show pockets of local enrichment near the interface. A range of 0-1.5 at.% in the 2-D maps for Mn and Zr is kept constant throughout the analysis to compare the color maps in different annealing conditions. The brighter spots in the maps here show a composition near ~ 1.0 at.% for both Mn and Zr. When compared to the as-aged condition (Figure 1 (f)) the diffusion of Mn and Zr to the coherent interface is evident. Note that the piling-up of Mn is more obvious after 1 h annealing at 300°C compared to Zr, which is in the form of nanoclusters instead of continuous segregation. In a

proximity histogram (3-D averaged composition profile), the interface captures the change in the elemental distribution from the matrix to θ' (shown in Figure 3 (c)). The θ' composition is consistently recorded at ~ 35 -36 Cu at.% (remainder Al). Considering the distribution of minor elements (Figure 3 (d)), we note a substantial enrichment of Mn (~ 1.08 at.%). Even though the average increase in Zr composition on the interface (close to 0.25 at.%) is not as profound as Mn, it is indicative of higher Zr than either side of the interface.

Subsequent annealing treatment for additional 3 h at 300°C was performed on the same batch of the APT needle. Before APT re-analysis the needles were transferred to the TEM to observe the crystal structure at the precipitate-matrix interface (Figure 4 (a)). A

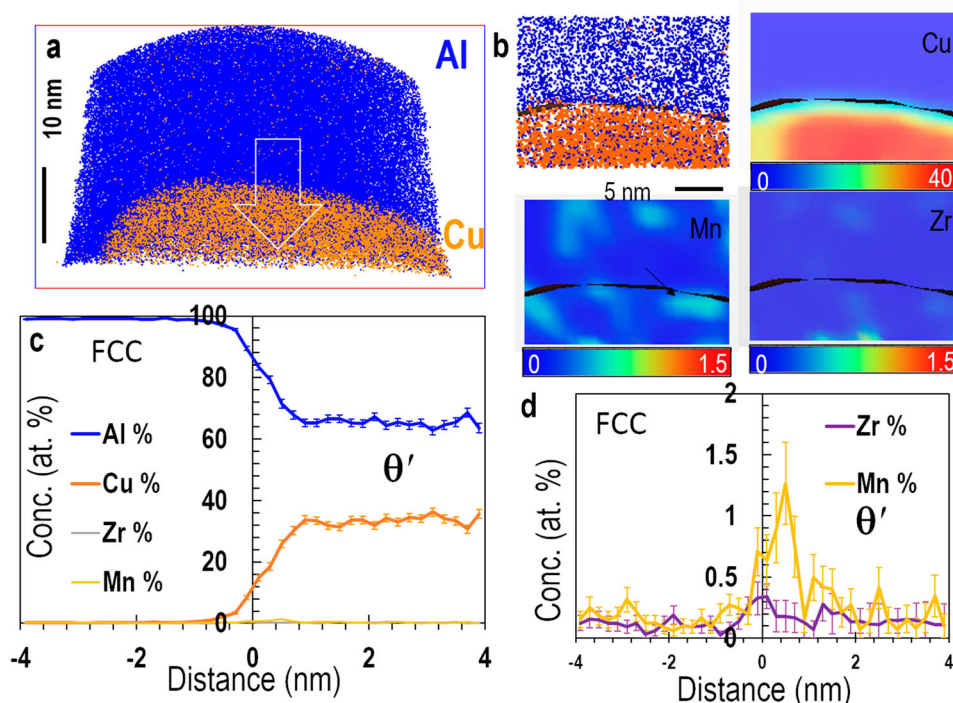


Figure 3. APT results after 300°C/1h: (a) Overall reconstruction. (b) A 20nm x 15nm x 5 nm across the interface (c-d) proximity histogram across the FCC- θ' interface.

STEM-HAADF image illustrates the precipitate (bright-contrast-side) and the matrix (dark-contrast-side) (Figure 4(b-c)). We also note a layer of bright atoms on the Al-matrix side suggesting a solute pile-up of a heavy element. In order to minimize surface contamination in TEM, the sample was imaged quickly, and EDS analysis was avoided. The composition across this interface was analyzed by APT (Figure 4 (d)). The compositional change is shown using 1-D composition across the cylindrical region marked by white arrow. Figure 4 (e) shows the profile of Cu and Al while Figure 4 (f) shows Zr and Mn along the same cylindrical region. The vertical black dotted lines in Figure 4 (e-f) indicate the precipitate/matrix interface and the red dotted lines indicate the extent of the interfacial region. In addition to 1-D composition profile, the proximity histogram across the precipitate-matrix interface is shown in Figure 4 (g-h). The Mn enrichment increased from 1.08 at.% at 300 °C/1 h to 1.25 at. % at 300°C/4 h while the Zr increased from 0.25 at.% to 0.45 at.% for these sample conditions. While the compositional analysis so far was done across the θ' -matrix interface using Cu iso-concentration surface, the local Mn and Zr rich pockets at the interface are examined by making iso-concentration-surfaces using Mn and Zr and 2-D composition maps (Figure 5).

A magnified view of the θ' precipitate highlighted by the box in the reconstruction uses iso-concentration surfaces (10 at.% Cu, 1 at.% Mn, and 1 at.% Zr) to delineate

the Cu, Mn and Zr enriched regions (Figure 5(a)). The 2-D maps from the boxed region in Figure 4 (d) are given in Figure 5(b) show a more continuous Mn pileup on the interfaces (compared to 300°C/1 h), together with localized segregation of Zr on the interface. On observing just the color maps generated from the thin 5 nm slices in Figure 5, it can appear that one interface has high segregation of solutes than the other. However, it is most likely due to the heterogeneity of the segregation at that scale. At a lower magnification in Figure 4 (f) the average composition of Mn spikes near both interfaces, as well in supplementary Figure 5 (at 350°C) the compositional segregation occurs on both coherent sides. So, based on our current assessment we do not believe that there is any special tendency of solute to pile up on one vs another coherent side of the precipitate. The local composition of Mn and Zr rich pockets is measured using the proximity histogram analysis of the Mn and Zr rich nano-regions respectively and is shown in Figure 5 (c-d). The proximity histograms (Figure 5 (c)) from Mn-rich nano-regions depict ~ 6 at.% Mn in these pockets ($\sim 67\text{Al}_{27}\text{Cu}_6\text{Mn}$) and that of Zr-rich region has a ~ 20 at.% Zr ($\sim 64\text{Al}_{16}\text{Cu}_{20}\text{Zr}$) (Figure 5 (d)). Hence, the results imply that the local Mn enrichment saturates at ~ 6 at.% while that of Zr reaches ~ 20 at.%. Volumetrically more Mn-rich regions are observed along with the interface whereas Zr-rich regions are more dispersed and sparsely located. The localization of Mn on the interface

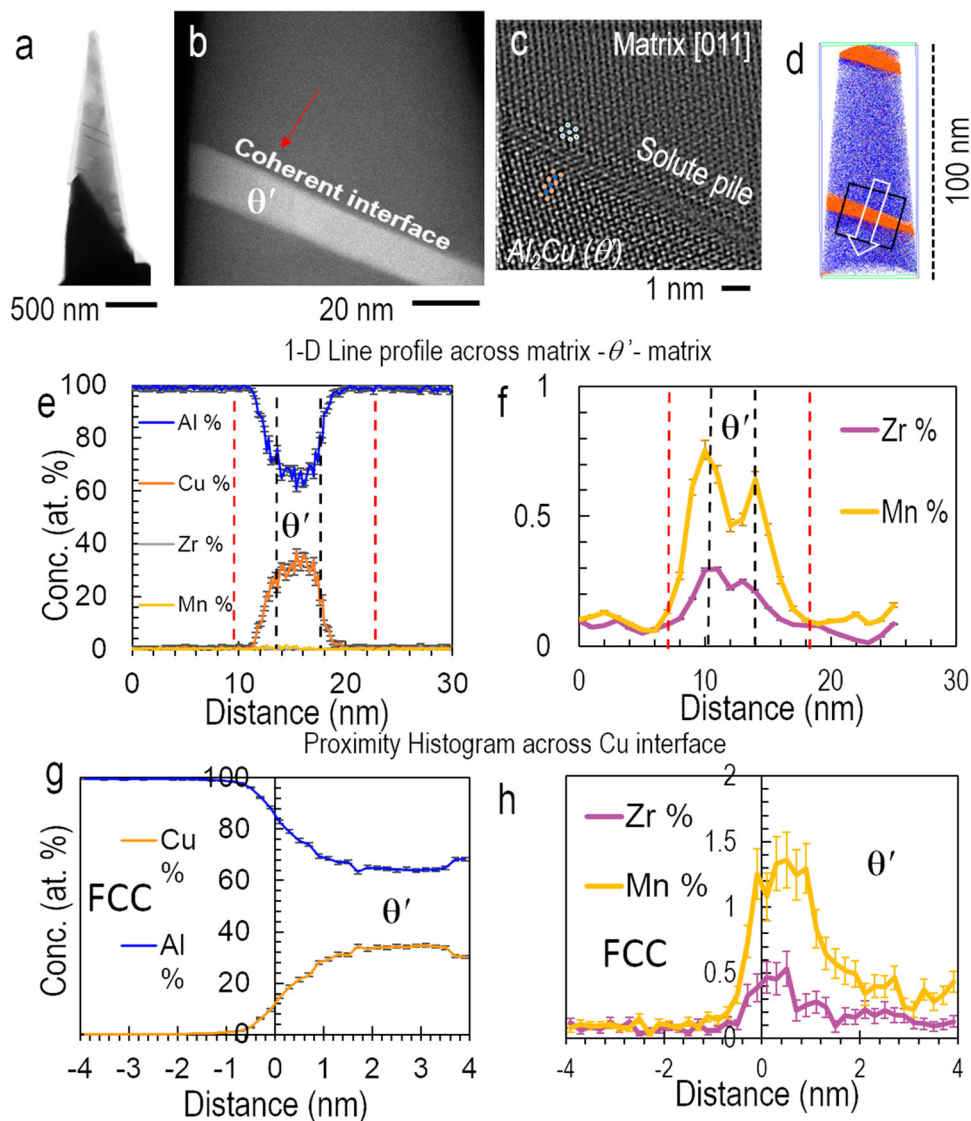


Figure 4. Solute segregation on a coherent θ' -matrix interface after a 300°C/4h: (a-c) STEM results from the interface after annealing (d) APT reconstruction (e-f) 1-D compositional profile across the θ' -matrix interfaces.

can have a strong stabilization effect on this interface at 300°C, thus slowing down the coarsening kinetics of the θ' phase and its subsequent transformation into the equilibrium θ phase. Figure S5 has the APT results from 350°C for 4 h condition. The Mn-enriched regions are seen to be highly continuous compared to the 300°C/4 h condition, while the Zr-rich regions are globular and still discontinuous similar to the 300°C/4 h condition given in Figure 5.

The early-stage solute segregation after annealing at 300/350°C plays a key role in increasing the $\text{Al}_2\text{Cu}-\theta'$ precipitate stability. The interfacial energy of coherent θ' -matrix interface is $\sim 170\text{--}250 \text{ mJ/m}^2$ [25]. Based on density functional theory (DFT) calculations there is a 10% reduction in the energy by Zr segregation [26]. The ordering of Zr and Al further results in the release of

energy, lowering the driving force for coarsening of θ' -precipitates. Shyam et al. showed that both Mn and Zr on the 2nd nearest neighbor can result in lowering the interfacial energy [13]. Our current observations (for 300/350°C) suggest saturation of Mn pileup at 6 at.%, though the volume fraction increases as the continuity of the Mn-rich network increases with time and temperature. The accumulation of Mn is followed by Zr segregation to the interface. The sparse and small Zr-rich regions rapidly reach a local composition of ~ 20 at.% Zr indicates an early stage pre-ordered composition with Al_3Zr structure. Hence, the extension of stability of the coherent interface, accomplished by early-stage Mn segregation, slows the precipitate coarsening kinetics and transformation at 300 and 350°C. This scenario then provides enough time for the slower diffusing Zr

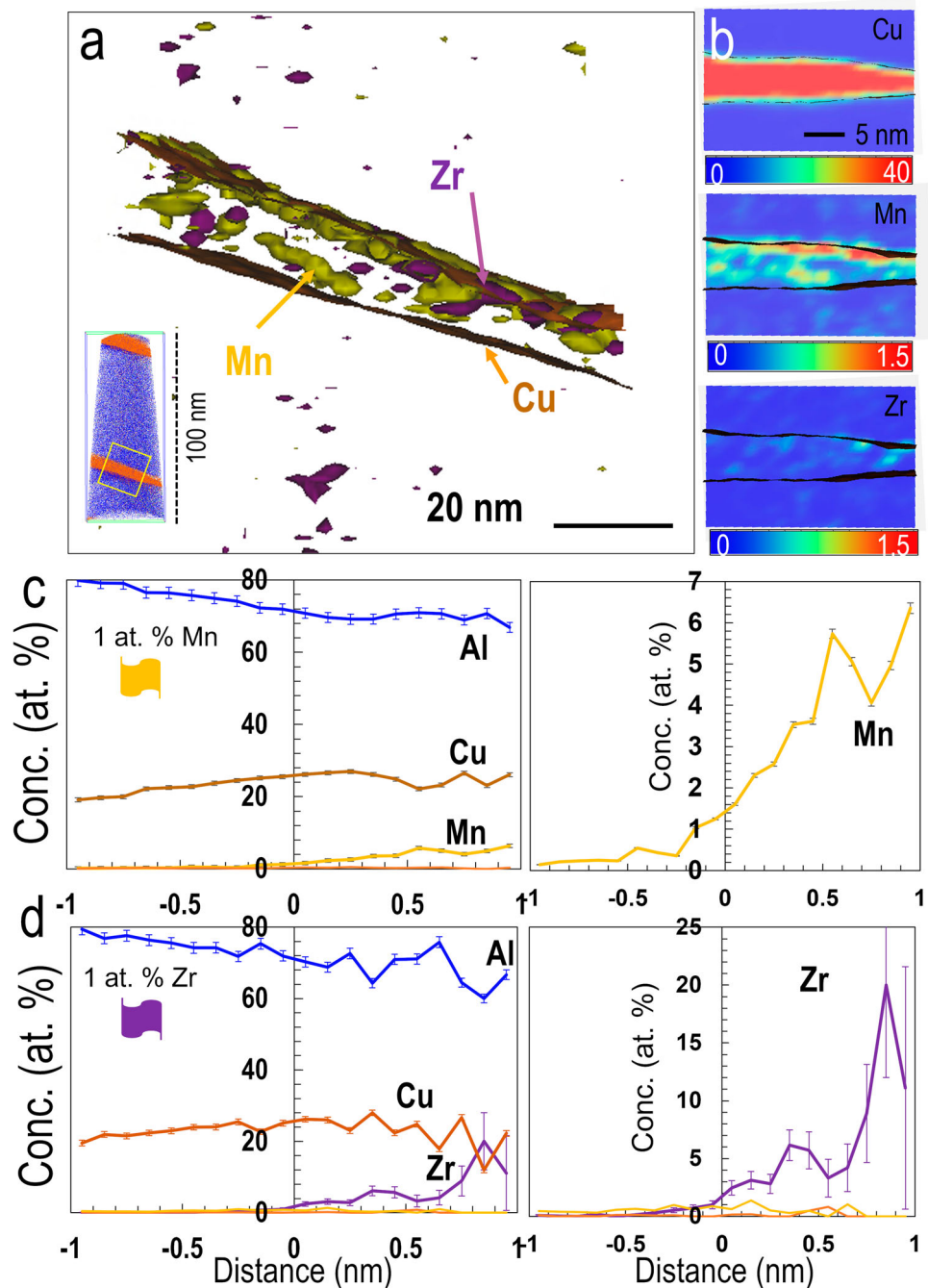


Figure 5. Composition of solute clusters on the θ' -matrix interface after a 300°C/4h: (a) 10 at. % Cu, 1 at. % Mn, and 1 at. % Zr iso-concentration surfaces. (b) 2-D maps (c-d) proximity histogram analysis of Mn-rich and Zr-rich clusters, respectively.

atoms to segregate at the coherent interfaces and form an $L1_2/\theta'$ co-precipitate structure that has a near-zero interfacial energy [26]. The very stable Al_3Zr structure pins the θ' coherent interfaces preventing the nucleation of ledges that can coarsen the precipitate (ledge poisoning). The reduced interfacial energy and ledge poisoning effect from the $L1_2/\theta'$ co-precipitate structure prevents θ' from coarsening.

The thermodynamically stable θ phase in Al-Cu alloys is undesirable as it is ineffective in providing precipitation

strengthening to the alloy at elevated temperatures. However, the transformation of θ' to the θ phase requires overcoming a thermodynamic nucleation energy barrier posed by the increased interfacial energy of the θ phase [37,38]. The diffusion of Mn and Zr to the coherent interfaces further increases this barrier thus stabilizing the θ' phase to 350°C. However, at 400°C the interfacial energy stabilization is insufficient to prevent the transformation that is driven by much lower Gibbs free energy of the θ phase compared to θ' . Additionally, the θ' formation

energy increases rapidly above 350°C further reducing the stabilization effect [38].

The interplay between Mn/Zr diffusion rates and modification of the barrier for θ - θ' phase transformation assisted in enhancing the relative stability of the strengthening phase.

In conclusion, we demonstrated the atomic-scale mechanisms that lead to the emergence of this non-equilibrium solute segregation during the early stages of annealing. The atomic-scale observation that leads to the emergence of this non-equilibrium solute segregation, especially during the early stages of annealing, provides direct evidence for the stabilization of metastable θ' precipitates resulting in the observed high-temperature strength of this alloy.

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Author contributions

Conceptualization: BG, AD
 Methodology: BG, JL, SL
 Investigation: BG, JL, SL, MO
 Visualization: BG, MO, JP
 Funding acquisition: AD, AS
 Project administration: AD
 Supervision: AD, AS
 Writing – original draft: BG
 Writing – review & editing: All Authors

Data and materials availability

All data are available in the main text or supplementary materials.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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ORCID

Jonathan Poplawsky  <http://orcid.org/0000-0002-4272-7043>

Amit Shyam  <http://orcid.org/0000-0002-6722-4709>

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