Achieving strong and stable nanocrystalline Al alloys through compositional design

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Al alloys often suffer from low mechanical strength and lack high-temperature microstructural and mechanical robustness. A series of binary and ternary nanocrystalline (NC) Al transition metal alloys with supersaturated solid solution and columnar nanograins have been recently developed by using magnetron sputtering, manifesting a new realm of mechanical properties and thermal stability. Distinct solutes cause evident differences in the phase transformations and efficiencies for grain refinement and crystalline-to-amorphous transition. Certain sputtered Al-TM alloys have shown room-temperature mechanical strengths greater than 2 GPa and outstanding thermal stability up to 400 °C. In addition, the NC Al alloys show mechanical anisotropy and tension–compression asymmetry, revealed by micromechanical tests. Through the process encapsulating various compositionally distinct systems, we attempt to illuminate the solute effects on grain refinement and properties and more importantly, tentatively unravel the design criteria for high-strength and yet thermally stable NC Al alloys.

Qiang Li earned his Ph.D. in Materials Engineering from Purdue University in 2019 and subsequently joined the Division of Materials Science and Engineering at Ames Laboratory of U.S. Department of Energy as a postdoc fellow devising new-generation high-temperature Al alloys. At Purdue University, his research focused on developing nanocrystalline and nanotwinned metals and alloys with mechanical, thermodynamic and corrosion-resistant merits as well as studying their deformation at nano/micro/meso scales. He was selected to receive the College of Engineering Outstanding Research Award. Li received his B.S. from Nanjing Tech University and his master's degree in Mechanical Engineering from the University of Texas - Pan American where he applied electrochemistry and high throughput technology to produce carbon- and oxide-based nanomaterials for energy applications, and received the Dr Hashim S. Mahdi Award in 2014. Dr. Li's research interest is to devise highly durable, damage-resistant nanostructured alloys and unveil the underlying principles behind their plasticity and thermodynamic properties via in/ex-situ multiscale techniques and advanced microscopy, with an emphasis on solving energy problems through materials solutions and multidisciplinary approaches.

Introduction

Mechanical and thermodynamic properties of a metallic material exceedingly depend on constituent selections as well as processing/treatment strategies. Lightweight Al alloys are indispensable in various energy sectors, but have been subjected to unsatisfactory strength for applications. In century-long quest

for high-strength Al alloys, mechanical strength could maximally reach 700 MPa by nanoprecipitation strengthening via aging treatment, e.g., T6 process, but often came at the cost of high-temperature performance due to microstructural instability at elevated temperatures below 200 °C [1, 2]. Grain refinement is effective in boosting mechanical strengths of metallic materials

and Hall–Petch relation becomes renowned for predicting the magnitude of strength increment as grain size reduces, in spite of its negligence of grain boundary (GB) chemistry, crystallographic, and defect features [3–5]. As a result, massive practices, such as adopting powder metallurgy, severe plastic deformation etc., have been executed to produce ultra-fine grained (UFG; grain size within 100 nm–1 μ m) and nanocrystalline (NC; grain size lower than 100 nm) metals and alloys to gain strength. In the meantime, it is considerably evident in various empirical and theoretical studies that a Hall–Petch breakdown could occur at a threshold grain size, causing softening. Under unceasing debate, it might nonetheless be reflective of a crossover from dislocation-mediated plasticity to GB-dominated deformation, such as GB sliding and grain rotation, or due to rapid grain growth under stress at low homologous temperatures or processing artifacts [6–9]. Moreover, GBs aspire to migration due to the excess free energy stored at intercrystalline regions, making the design of strong and yet thermally stable NC materials a major challenge [10–13].

Microstructural instability stimulates extensive research endeavors of studying the constituent and alloying effects to preserve nanograins at elevated temperatures. Thermodynamic and kinetic strategies have been devised to mitigate GB migration and grain coarsening [14]. Specifically, thermodynamic approach exerts GB energy relaxation by decorating GBs with selective solute atoms and the GB segregation-induced thermal stability has been realized in NC Al–Pb [15], Co–P [16], Cu–Ta [17], Fe–Zr [18], Ni–P [19], Ni–W [20], Ni–Mo [21], and W–Ti [22] alloys. On the contrary, the kinetic approach used particulate nanoprecipitates or atom clusters to hinder the GB migration. For instance, Al_3Sc and Al_3Zr nanoprecipitates were found effective in kinetically pinning GBs of UFG and NC Al alloys [23–25]. Especially, a stability criterion, supported by empirical evidences and simulations, has been developed to screen out thermally stable binary NC systems with GB segregation, wherein the enthalpy of GB segregated state should be large enough to overcome the sum of the GB energetic penalty and the enthalpy deficit from the formation of intermetallic compound [26–28].

In spite of those progresses, a majority of binary NC alloys exhibited microstructural and mechanical stabilities at temperatures below 50% of the melting points (T_m) of their matrix metals [21, 22, 29–31], except some exceptional successes [18, 32]. The binary NC systems are confronted with a lack of concurrent and customized properties. One limitation is the difficulty to reconcile high strength and thermal stability in binary NC alloys, because the elements effective for grain refinement do not necessarily render superb thermal stability and vice versa. For instance, Ni–Mn electrodeposits led to comparable or coarser grains sizes in comparison to that of the monolithic Ni electrodeposits, but could retain stability of nanograins at 500 °C via GB segregation [33]. In contrast, electrodeposited Ni–W achieved 5–7 nm

grain size, but was classified as a metastable/unstable NC system [26]. In the course of our recent developments of various binary NC Al alloys with supersaturated solid solution using sputtering technique, moderate addition of Co, Ni, or Fe has manifested exceedingly high effectiveness in shrinking the grain size of Al down to a few dozens of or a few nanometers, in striking contrast to Ag, Cr, Mg, Mo, Ti, W, and Zr [34–40]. Notwithstanding these NC Al–TM alloys endowed with strengths greater than 1.5 GPa, first principles calculations in combination with the NC stability criterion suggest that those Al–TM systems are subjected to very large weighted fraction of unstable segregated GBs, reflective of low propensity for good thermal stability [41]. Indeed, it was found that those NC Al–TM alloys were largely plagued by precipitous softening at low or moderate homologous temperatures upon the intermetallic formations [29, 42].

In this article, we collect and analyze various binary NC Al alloys with supersaturated solid solution, prepared by magnetron sputtering. We put our emphasis on two motives: First, we evaluate the changes in microstructural features and the resultant mechanical properties of different alloy systems in search of general tendencies and exceptions. While reflecting their property merits in comparison with conventional alloys, we attempt to perceive their underlying principles. Second, the aggregated collection of works permits us to illustrate the design criteria for high-strength and yet thermally stable NC alloys, which is expected to be in general helpful to instruct the following experimental and simulation efforts. In the meantime, the article covers anisotropy and tension–compression asymmetry of the NC Al alloys with GB directionality, revealed by systematic *in situ* micromechanical tension and compression investigation.

High-strength binary NC Al alloys

Fabrication

In search of the general trend through studies on different alloy compositions, magnetron sputtering had been chosen to fabricate these binary and ternary Al alloys, a majority of which are Al–TM systems. Electrodeposition is another non-equilibrium deposition technique and extensively used to prepared nanotwinned (NT) Cu [43–46], NC Ni [21, 47], Mo [48], Co [49] metals and their alloys. Electrodeposition in water-based solution is constrained to elements whose electrode potentials are greater than or close to the standard hydrogen electrode potential, howbeit more scalable and economic. First, it gives a limited selection of elements. Second, as to our objectives, a negative reduction potential of Al^{3+} of –1.68 V solely permits the electrodepositions using ionic liquids [50, 51]. Mechanical alloying has lower constraint in terms of element selection, but it has the risk of contamination

and the final grain size of NC alloys are largely affected by milling conditions and duration [32, 52].

Magnetron sputtering has been adopted to examine the effectiveness of different solutes in grain refinement, mechanical strengthening and enhancement of thermal stability in NC Al alloys. Sputtering is useful to rapidly and reliably prepare compositionally distinct alloys, followed by structural characterizations and mechanical analyses. It should be noted that sputtering parameters greatly affect the film quality and purity. A low base pressure, high deposition rate and pre-sputtering process are desired to minimize the potential reaction between residual gas molecules and metal atoms. Furthermore, the technique renders unique grain growth kinetics controlled by the surface diffusion of both matrix and solute atoms. The diffusion kinetics and the high quenching rate ($\sim 10^6$ to 10^{10} K/s) make alloys and the spatial dispersion of solute atoms stay at a far-from-equilibrium state [53, 54]. These solute atoms and/or their clusters are expected to affect the diffusivity of adatoms differently, thereby resulting in different effectiveness in grain refinement. Furthermore, the selection of solutes determines the decomposition temperature of solid solution,

the formation temperature of intermetallic compound and recrystallization temperature. Their occupancy at GBs and within grain interiors would also modify the GB migration and grain growth kinetics. These will be progressively revealed and elucidated in the following sections.

Microstructural and crystallographic features

Magnetron sputtering was used to prepare compositionally distinct Al alloys on Si (111) substrates and a few exceptions, including Al–Mg, Al–Zr and Al–Ti systems, were grown onto Ag (111) template on Si (111). In contrast to NC systems with exquiaxed nanograins, sputtered monolithic Al, Al–Mg and Al–Fe alloys have columnar grain morphology and GBs with a clear directionality, typical of metallic materials produced by the sputtering technique, supported by the representative plan-view TEM (PVTEM) and cross-section TEM (XTEM) micrographs in Fig. 1. Fe appears more effective in refining grain structure of Al than Mg. Specifically, in reference to 450 nm grain size of the Al (Fig. 1a and 1b), 2.5 at% Fe in $\text{Al}_{97.5}\text{Fe}_{2.5}$ is able to reduce the grain size to 40 nm (Fig. 1d and

Figure 1: Plan-view, cross-section transmission electron microscope (TEM) micrographs, and x-ray diffraction pole figures of (a-c) pure Al, (d-f) $\text{Al}_{95}\text{Mg}_5$, and (g-i) $\text{Al}_{97.5}\text{Fe}_{2.5}$ alloys. Plan-view TEM imaging and pole figure measurements were taken along $\langle 111 \rangle$ zone and cross-section TEM imaging along $\langle 110 \rangle$ zone. Figures are adapted with permission from Ref. [35, 38].

1e), in contrast to 82 nm in $\text{Al}_{95}\text{Mg}_5$ (Fig. 1g and 1h). Al-Fe alloys have a homogeneous dispersion of Fe solutes in Al [29, 35], whereas a heterogeneous Mg distribution was witnessed in the sputtered Al-Mg alloys [38]. Pun et al. observed that Mg segregated to GBs in mechanically alloyed NC Al-Mg [55]. Impurity solubility at equilibrium in Al is very limited at room temperature, but these NC Al alloys could uphold solute supersaturation in Al lattice. Unlike equiaxed NC materials, Al and Al alloys possess a strong out-of-plane (111) texture, evidenced by the selected-area electron diffraction (SAED) patterns and x-ray diffraction (XRD) pole figures. While monolithic Al shows a three-fold symmetric pole figure in Fig. 1c, both $\text{Al}_{95}\text{Mg}_5$ and $\text{Al}_{97.5}\text{Fe}_{2.5}$ instead manifest a six-fold symmetry with nearly equally bright diffraction spots in Fig. 1f, i, implying that the neighboring columnar nanograins in these alloyed films have a twin relation. Differing from the face-centered cubic (FCC) metals and alloys with low or low-to-intermediate stacking fault energies (SFE), such as Ag, Cu and stainless steels comprised of $\Sigma 3[110](111)$ coherent twin boundaries (CTBs) [44, 56–58], a majority of the twin boundaries (TBs) in these Al alloys are $\Sigma 3[110](112)$ incoherent TBs (ITBs) mostly vertically aligned [35, 38], which is attributed to the high SFEs of Al and its alloys ($\gamma_{\text{Al}} = 120\text{--}144 \text{ mJ/m}^2$) [59]. Therefore, these NC Al alloys have been often referred to as NT Al alloys.

The growth direction of ITBs is largely orientation-dependent as ITBs without kinks are perpendicular to {111} planes [60]. Ideally, in (111) texture, the nuclei made of the adatoms either have identical orientation or have a relative 60° in-plane rotation along the [111] film growth direction, giving rise to a twin relation between two nuclei. Then, the process of free surface annihilation leads to vertical ITBs. It was found that pure Al could be grown epitaxially on different Si substrates, i.e., Si (111), (110) and (112), and the texture and the TB networks changed in concert with the change of Si substrates [61]. However, the sputtered NC Al-Fe alloys could preferentially grow (111) texture even on amorphous SiO_2 substrates as Fe content exceeds a threshold value, suggesting that the (111) texture of Al-Fe alloys may be more energetically determined rather than epitaxial growth determined. In addition, a lattice expansion in reference to the lattice parameter of pure Al was witnessed in Al-Fe alloys, notwithstanding that Fe possesses a smaller atomic radius ($r_{\text{Fe}} = 0.124 \text{ nm}$ vs. $r_{\text{Al}} = 0.143 \text{ nm}$) [29]. Abundant low angle GBs (LAGBs) formed as Fe content is greater than 2.5 at%. All these signs signify excess strain energy stored in these NC Al alloys at non-equilibrium, and the formation of (111) texture that renders the lowest surface energy in FCC structure may alleviate the excess system energy [62].

Solute effect on grain refinement and phase transformation

Most of the compositionally distinct Al alloys formed supersaturated solid solution in a single FCC phase prior to phase transformation. Figure 2a reflects how the increase in Fe concentration drastically decreases the average grain size of NC Al-Fe alloys. It should be noted that within relatively dilute Al-Fe alloys, the average ITB spacing can be equated with the grain size; as Fe content is greater than $\sim 2.5\%$, the grain size is smaller than the ITB spacing due to the presence of abundant LAGBs. LAGBs formed in multiple studied Al-TM systems [35, 37, 40]. LAGBs would ultimately determine grain size and the neglect of LAGBs could cause an overestimation of the GB barrier strength. LAGBs have been proven to be the major obstacles to dislocation transmission in various experimental and discrete dislocation dynamics simulation studies [63, 64]. Figure 2d exhibits different solute effects on grain refinement and in general, a higher solute concentration generates a smaller grain size. Co, Ni and Fe show strikingly higher effectiveness in grain refinement compared to Ti, Zr and Mg [35–38, 40]. 5–6 at% addition of Ni, Co and Fe managed to bring the grain size down to about 14, 5 and 5 nm, respectively.

Most of our studied binary Al-rich systems experienced a two-stage phase transformation, i.e., FCC-to-amorphous transition, as solute concentration increased, on condition that matrix element is predominant. In one exceptional system, Al-Cr exhibits a multistage transformation from FCC to intermetallic Al_7Cr to amorphous phase [34]. For liquid-quenched amorphous alloys, larger T_g/T_m (T_g is glass transition temperature), difference in atomic radius and mixing enthalpy in general lead to a higher glass-forming ability [65], and this suggests that the amorphization is highly composition- and rate dependent [66, 67]. An amorphous phase started to form as Fe content (C_{Fe}) reached $\sim 8\%$ in Al-Fe, $C_{\text{Cr}} \sim 13\%$ in Al-Cr and $C_{\text{Zr}} \sim 15\%$ in Al-Zr system [29, 34, 36]. Ophus et al. revealed that 12% Mo was the onset of composition for the amorphous formation [68]. If we crudely consider the amorphous state as the ultimate form of NC structure with exceedingly high fraction of GBs, solutes with high effectiveness in grain refinement may have relative ease in the glass forming in these sputtered binary Al alloys and atomic size misfit plays critical roles in the amorphization process. The determination of specific compositional range for amorphization is affected by the local solute segregation, the formation of intermetallic compound, energetics and other potential factors. We mostly investigated Al-rich compositions and thus lack data for fully amorphous alloys. Masui et al. found the compositional ranges for the formation of a glassy phase were roughly within 10–25% in RF-sputtered Al-TM (TM = Co, Ni or Fe) alloys [69].

Figure 2: (a) Hardness and grain size of Al–Fe alloys as a function of Fe concentration. (b) Ashby map highlighting the high specific strengths and specific moduli of the sputtered NC Al–Fe alloys. (c) Hardness versus solute concentration of a variety of binary Al alloy systems. (d) Average grain size of different binary Al alloy systems versus solute concentration. a and b are reprinted with permission from Ref. [35]. Data for (c), (d) were collected from Refs. [34–40].

Solute effect on mechanical properties

Figure 2a presents the hardness evolution of NC Al–Fe alloys as Fe concentration increases. The peak hardness of ~ 5.5 GPa is reached at 5–6 at% Fe and the translated flow stress approximates to 2 GPa, according to the Tabor relation of $H = 2.7 \sigma$ (the proportionality constant of 2.7 was chosen for high-strength materials with a deformation mode of elastic–plastic transition) [70]. Figure 2b shows that both specific strength and specific elastic moduli, normalized by density, of NC Al–Fe alloys are higher than those of conventional alloys. Figure 2c shows the composition effects on hardness of various binary NC Al alloys and it clearly suggests that Co [37], Ni [40] and Fe [35] are more effective in strengthening Al than other solutes. With 5–6 at% solutes, Al–Co, Al–Ni and Al–Fe produce hardnesses as high as 5.5–6 GPa, whereas the hardnesses of Al–X ($X = \text{Ag}$ [35], Cr [34], Mg [38], Mo [35, 71], Ti [39], Zr [36] or W [35]) alloys could hardly exceed 3 GPa.

Composition-dependent microstructural refinement primarily contributes to the high strengths of these NC Al alloys in comparison to single-phase solid solution Al alloys [72]. Solute-associated effects on strengthening, plasticity and

thermodynamic properties will be discussed subsequently. This intrinsic size effect can be depicted by the Hall–Petch relation linking the mechanical strength to the reciprocal square root of the grain size [4, 5]:

$$\sigma = \sigma_0 + \frac{K}{\sqrt{d}} \quad (1)$$

where σ_0 and K are lattice friction stress and the Hall–Petch slope, respectively, and d denotes the grain size. Figure 2c and d imply that the composition-dependent evolution of grain size considerably affects the hardness and strength. In general, a smaller grain size, decided by the solute type and concentration, leads to a higher hardness. In the Al–Fe system, a softening is captured as Fe content increases to 8–10% and mechanical behaviors deviate from the Hall–Petch linearity as the grain size approaches or falls below ~ 5 nm. Due to the columnar grain morphology, it is possible that the softening mechanism differs from the GB sliding and rotation responsible for the Hall–Petch breakdown in conventional equiaxed NC metals and alloys [3, 48]. We attribute the softening to the trace formation of glassy phase that causes structural heterogeneity and thus the easier

nucleation of dislocations [29, 35]. It requires dedicated endeavors to comprehend the softening in metallic materials with columnar nanograins.

Besides strengthening, although not put emphasis on, solutes also result in different GB stability. In the processes of thermally and mechanically driven GB migration and grain growth, alloying is an effective tactic to impeding GB movement through the Zener drag and/or Zener pinning [23–25]. The decoration of distinct solutes at GBs modifies the detwinning process in these sputtered Al alloys comprised of ITBs. ITBs are made of two mixed Shockley partials with the Burgers vectors $1/6[\bar{2}11]$ and $1/6[1\bar{2}1]$ and a Shockley partial edge dislocation with the Burgers vector $1/6[11\bar{2}]$, and would migrate under stress through collective glides of partials [73–75]. Indeed, the sputtered Al–Fe and Al–Ni alloys with ITBs exhibited different deformation behaviors under uniaxial compression, in spite of comparable effectiveness of Fe and Ni in grain refinement and strengthening [29, 40, 76]. During plastic straining, Al–Ni micropillars underwent severe dilation at the pillar heads, reflective of highly localized deformation [40], whereas Al–Fe showed more homogeneous deformation [29, 35, 76]. Micropillars of NC Al–Fe–Ti alloys with an approximately identical grain size were deformed via the formation of shear bands rather than the ITB migration-driven grain coarsening in multiple binary NC Al alloys [77]. These deformation behaviors imply that solutes residing at ITBs or GBs have different solute-drag effects on ITB movement and appreciably modify the boundary energy landscape and influence the plastic deformation [78].

Strengthening mechanisms

Grain boundary strengthening

In the prior section, we declared that Hall–Petch strengthening greatly contributes to the hardening of NC Al alloys. Hall–Petch relation relies on the dislocation pile-up against GBs. The composition-dependent grain size limits the pile-up length and therefore affects the strength of NC Al alloys. However, GB strengthening in these NC Al alloys is more intricate by virtue of the nanoscale grain size as well as the change in GB characters due to the solute and GB types. The Hall–Petch relation faces various constraints upon some practical applications. First, it has different mathematic formulas in different material systems [79]; for example, Cordero et al. plotted available data into the Hall–Petch equation and found the grain size exponent spanning from -0.03 for Hf to -0.95 for W [3]. Second, it neglects certain effects from the metallurgical processing, GB chemistry, texture and defects [3, 80]. In addition, when its application is extended to nanoscale length, a softening has been witnessed in both metals and alloys,

referred to as the inverse Hall–Petch relation [9, 81]. Given that the processing artifacts and grain growth under stress do not come into play, the breakdown of Hall–Petch relation is mostly attributed to a transformation of deformation mechanism from dislocation-dominated activities to GB-mediated ones, such as GB sliding, grain rotation and diffusional creep, as the grain size falls below a critical value for a given metal [6–9, 82–85]. Mohamed used the model of dislocation-accommodated boundary sliding and associated the critical size to the sliding rate, the activation energy and volume and decided the critical grain size for Al to be ~ 110 nm [86]. Empirical evidences reflected a critical size of ~ 40 nm at the crossover of deformation mechanism transition for Al [87].

In the sputtered NC Al alloys, the grain size mostly ranges from 120 to 5 nm (Fig. 2d). When grain size is large enough (approximately $d > 20$ nm) to abide by the linearity of the Hall–Petch relation [35, 36], the full dislocation-dominated mechanism is presumably operative in these Al alloys. It is noteworthy that different GB types lead to different barrier strengths and Hall–Petch slope, K . We fitted the available data pertaining to CG, UFG, and NC Al and estimated K to be $4.7 \pm 0.2 \text{ GPa}\cdot\sqrt{\text{nm}}$, eligible for the conventional high angle GBs. However, the studied NC Al alloys are mainly comprised of ITBs and LAGBs. The solute concentration affects both GB and solid solution strengthening. To reasonably estimate the K value, we subtracted the solute-associated strengthening from the measured flow stresses of NC Al–Fe alloys and as a result, the K was calculated at $\sim 6 \text{ GPa}\cdot\sqrt{\text{nm}}$ [29, 35].

As grain size further decreases, the mechanical behaviors of NC Al alloys deviate from the linearity of the Hall–Petch relation and a stress plateau and even a drop in stress emerge [35]. Within this grain size region, GBs more engage in the deformation. Though Al prefers deforming through full dislocation activities [6–8], owing to the high SFE of Al, stacking faults might transect the entire nanograins and in the other scenario, GBs could emit partial dislocations and the emitted trailing partials need to travel a splitting distance to react with the emitted leading partials when the grain size is nanoscale. In deformed $\text{Al}_{94.5}\text{Fe}_{5.5}$ with a 5 nm grain size, the formations of 60° dislocations and Shockley partials were witnessed [76]. In order to predict the GB strengthening for NC Al alloys with nanoscale grain size, the maximum barrier strength for a single dislocation transmission, τ^* , across a vertical GB has been estimated. Misra et al. derived the following equation based on classic dislocation mechanics [88]:

$$\sigma = m \left(\tau_0 + \sqrt{\frac{\tau^* \mu b}{\pi(1-\nu)L}} \right) \quad (2)$$

where m and L stand for the Taylor factor and mean distance between a dislocation source to an obstacle, respectively, and ν ,

μ , and b are the Poisson's ratio, the shear modulus for Al alloy and the magnitude of Burgers vector. The shear moduli of these Al alloys were modified using $\mu = \frac{E}{2(1+\nu)}$ (Elastic modulus, E , was obtained from nanoindentation experiments). Then, τ^* can be obtained:

$$\tau^* = \left(\frac{K^2 \pi (1 - \nu)}{\mu b} \right) \quad (3)$$

Therefore, the maximum GB strengthening in NC Al alloys with very fine nanograins can approximate to 2.2 GPa after a Tylor factor is applied. This approach sets forth the predicted maximum strength upon an inoperative Hall–Petch relation, but it does not take into account further grain size variation and possible GB-mediated activities.

Solid solution strengthening

Solid solution strengthening also significantly contributes to the strength of these NC Al alloys, considering the solute supersaturation benefitting from the far-from-equilibrium process. Upon the occupancy of solute atoms at the substitutional/interstitial sites, extra strengthening originates from the dislocation-obstacle interactions [89–92]. Macroscopically, the applied shear stress needs to overcome a critical stress for a continuous deformation. Locally, the solutes closest to the dislocation cores make larger strengthening contribution. Most of quantitative models and calculations have been focused on the dilute alloy systems [91]. Fleischer model alleged that the critical shear stress in solid solution alloys is affected by the solute-induced variations in the lattice parameter and the shear modulus. The solid solution strengthening based on Fleischer model can be expressed as [89]:

$$\sigma_{SS} = m \cdot \alpha \cdot \mu_{Al} \cdot \varepsilon_s^{3/2} \cdot c^{1/2} \quad (4)$$

where α is material-sensitive constant depending on the specific alloy system, e.g., α taken as 1/700 for FCC Cu, 1/240 for $Al_{50}Co_{50}$, 1/120 for Al–Mo [29, 47, 71, 93], c is the solute concentration and ε_s is the interaction factor reflective of the solute effects on lattice parameter, a , and shear modulus:

$$\varepsilon_s = \left| \frac{\frac{1}{\mu_{Al}} \cdot \frac{\partial \mu}{\partial c}}{1 + 1/2 \left| \frac{1}{\mu_{Al}} \cdot \frac{\partial \mu}{\partial c} \right|} - 3 \cdot \frac{1}{a_{Al}} \cdot \frac{\partial a}{\partial c} \right| \quad (5)$$

In these sputtered Al alloys, the solute concentration must far exceed the solubility at equilibrium in Al matrix. In the Al–Fe system, a lattice expansion took place while Fe content surpassed 2.5 at%, indicative of the formation of Fe–Fe clusters and/or occupancy of Fe atoms at interstitial sites. The Fleischer model assumed uniformly dispersed solutes in rather dilute solution

and might not be ideally applicable to these Al alloys, thereby requiring modification. On the contrary, the Labusch model takes into account the distribution of dislocation-obstacle interaction force and the distance between neighboring obstacles [90]. In supersaturated solid solution alloys, two models tend to manifest large difference [91, 92]. The Labusch model is expressed as:

$$\sigma_{SSS} = M \cdot \varphi \cdot \mu_{Al} \cdot \varepsilon_L^{2/3} \cdot c^{2/3} \quad (6)$$

where φ is 1/550 for FCC alloys. The interaction factor, ε_L , is expressed as:

$$\varepsilon_L = \left| \left(\frac{\frac{1}{\mu_{Al}} \cdot \frac{\partial \mu}{\partial c}}{1 + 1/2 \left| \frac{1}{\mu_{Al}} \cdot \frac{\partial \mu}{\partial c} \right|} \right)^2 + \left(16 \cdot \frac{1}{a_{Al}} \cdot \frac{\partial a}{\partial c} \right)^2 \right| \quad (7)$$

Please note that Labusch model suggests that the solid solution strengthening in FCC alloys is more governed by edge dislocation-obstacle interactions [90, 94]. Some efforts have been spent adjusting these models to distinguish the substitutional and interstitial solid solution strengthening [95].

NC solute pinning strengthening

As to nanograins, dislocations get emitted from GBs and traverse a nanograin. Therefore, the solute atoms dispersed in the lattice would no longer be the only obstacles interacting with dislocations and the dislocation-obstacle spacing is equivalent to the grain size. These NC Al alloys possess nanograins and GBs could dictate the pinning sites for dislocation movement, besides the dispersed solutes. Rupert et al. [47] developed a model to explain extra solid solution strengthening from the NC solute pinning effect:

$$\Delta \sigma_{NC,SS} = \frac{\mu_{Al} \cdot b}{d} \cdot \left| \frac{1}{\mu_{Al}} \cdot \frac{\partial \mu}{\partial c} + \frac{1}{a_{Al}} \cdot \frac{\partial a}{\partial c} \right| \cdot c. \quad (8)$$

The model bears a resemblance to the Fleischer equation. The later describes the effect of individual solute atom on the local lattice properties, i.e., lattice parameter and shear modulus; the former provides one more strength-controlling mechanism by considering the change of elastic properties at GBs that spatially limit the dislocation bowing.

Design of high-strength binary NC Al alloys

Various compositionally distinct Al alloys are gathered in search of a general tendency for the solute effect on grain refinement and strengthening. During the nucleation and growth processes of these NC Al alloys with ITBs, adatoms diffuse and are being built upon {111} free surface. Well-dispersed solute atoms sets kinetic barriers for the diffusion process, thereby affecting the

Figure 3: Hardness of a variety of binary Al alloy systems with 5–6 at% additions of solutes, exhibiting distinct effectiveness in strengthening. Data were collected from Refs. [34–40].

grain size. The nanoindentation hardnesses of these studied binary NC Al-TM (TM = Ag, Cr, Co, Fe, Mg, Mo, Ni, Ti, W or Zr) alloys with 5–6 at% additions of solutes are plotted against the discrepancy in atomic radius, i.e., $r_{Al} - r_{Solute}$ in Fig. 3. It manifests that the hardness increment may be closely related to the difference in the matrix-solute atomic radius and a general tendency emerges especially for Al-TM systems with smaller solutes, except an outlier, i.e., Al–Cr system. The hardness and mechanical strength change jointly with the solute-controlled grain refinement (Fig. 2c, d). Effective grain refiners, such as Co, Fe and Ni, with comparably large atomic size mismatch with Al, gave rise to more effective strengthening than others did. From the perspective of system energy, the solute supersaturation and the larger matrix-solute atomic size mismatch result in the substantially excess elastic strain energy and the generation of high-density ITBs and LAGBs is to in part alleviate it. Studies alleged that a larger GB area is necessitated in response to the solute saturation [22, 96]. From the kinetic point of view, distinct solutes alter the diffusivity of Al differently. Fallis et al. showed that a substitutional defect could trap the diffusing adatoms [97]. A separate investigation is being dedicated to comprehend the discrepancies in diffusion activation energy and extra binding energy in these compositionally distinct Al alloys, which will help reveal the kinetic effect each solute represents on the diffusivity [98]. In UFG and NC single-phase alloys prepared by severe plastic deformation (SPD), impurity solutes exert the solid solution strengthening by modifying elastic properties to interact with dislocations and in the meantime, they were found able to contribute extra grain refinement. Edalati et al. gathered

available data and found that the steady-state grain sizes of SPD UFG and NC alloys are approximately linearly proportional to the $\mu \varepsilon_L^{2/3} c^{2/3}$ (see the discussion of solid solution strengthening) [94]. A steady state of grain size is achievable only if a balance is reached between the mechanically refined grain structure and the dynamic softening processes related to dislocation recovery, recrystallization and GB migration [99]. The sluggish GB movement in the presence of solutes tailoring the local stress is in concert with the hindered grain coarsening processes. The matrix-solute atomic size mismatch accounts for the extra grain refinement in these SPD UFG and NC Al-, Cu- or Ni-based alloys [94]. In these NC Al alloys, the GB stability ought to be discussed because the boundary migration could counteract the grain refinement effect. ITBs could potentially migrate through collective glides of partials [73–75]. The corresponding detwinning process largely relies on the ratio of unstable SFE over stable SFE, $\gamma_{USFE}/\gamma_{SFE}$. In the Al–Fe system, density-functional theory (DFT) calculations showed that Fe increases both the absolute SFE and $\gamma_{USFE}/\gamma_{SFE}$, suggesting that the ITB migration in Al–Fe system requires a higher energy penalty [35].

An outlier from the general tendency is seen, i.e., Al–Cr system (Fig. 3). In contrast to other present Al–TM alloys with mostly homogeneous solute distribution in Al, Al–Cr alloys encountered a severe Cr segregation, which weakens the solute effect on grain refinement [34]. In the binary Al systems with bigger solutes relative to Al, i.e., Al–Mg, Al–Zr and Al–Ti alloys, no general trend has developed by far. In NC Al–Mg alloys, an Mg segregation was also witnessed, presumably responsible for the underperforming refinement and strengthening effects [38, 55].

Exception: Al–Cr system

Cr segregation

We now turn our attention to one exceptional system, i.e., Al–Cr alloys. Particular efforts were spent inspecting this binary system because Cr shares many similarities with other TM elements in terms of crystallographic parameters and heat of mixing with Al but behaves strikingly differently as to the effectiveness in grain refinement and strengthening. Prepared using identical conditions, the Al–Cr alloys remain a polycrystalline form, disagreeing with other Al–TM systems with a strong (111) texture. Within the compositional range $< \sim 10$ at%, Al–Cr alloys remain fully crystalline prior

to the emergence of amorphous phase (Fig. 4a and b). Cr is less effective in grain refinement than Co, Ni and Fe. Specifically, 5% Cr gave rise to a grain size of 95 nm but similar amount of Fe of ~ 5 nm. PV-STEM images in Fig. 4c, f exhibit obvious Cr segregations in $\text{Al}_{93}\text{Cr}_7$ and $\text{Al}_{87}\text{Cr}_{13}$. The increment in Cr content made the Cr-segregated areas thicken progressively and eventually become prevalent (Fig. 4a). The segregation-induced deprivation of the solute atoms from the FCC lattice appreciably weakens the effect of grain refinement. However, the segregation results in a multistage phase transformation and grant us opportunity to build up different single- and dual-phase structures for mechanical investigations.

Figure 4: (a) The average grain size of binary Al–Cr alloys, the thickness and volume fraction of Cr-segregated phases as a function of Cr composition. (b) Hardness of Al–Cr alloys versus Cr composition. The phase transformations occur along with the increasing Cr. (c) PV-STEM and (d, e) PVTEM micrographs showing that $\text{Al}_{93}\text{Cr}_7$ alloy has Cr segregation at GBs, forming intermetallic Al_7Cr . (f) PV-STEM and (g, h) PVTEM micrographs of $\text{Al}_{87}\text{Cr}_{13}$ showing nanocomposite structure consisting of FCC and amorphous phases. Figure 4a and b are reprinted with permission from Ref. [34]. Figure 4c–4 h were adapted with permission from Ref. [34].

Multistage phase transformation

Differing from other sputtered Al-TM systems [35, 37, 40, 71, 76], Al-Cr experiences a FCC-monoclinic-amorphous phase transformation. Specially, Al-Cr has a single FCC phase despite some noticeable Cr segregation at GBs as $C_{Cr} < 3\%$; then, it transfers to a FCC/monoclinic nanocomposite as $3 < C_{Cr} < 10\%$ and to a FCC/amorphous composite structure as $10 < C_{Cr} < 21\%$; eventually, Al-Cr forms fully amorphous structure before Cr dominates (Fig. 4a, b). Figure 4d and e show that $Al_{93}Cr_7$ are made of FCC nanograins surrounded by a 5–8 nm thick Al_7Cr with a monoclinic structure. In contrast, $Al_{87}Cr_{13}$ has FCC nanograins dispersed amid the amorphous phase (Fig. 4g, h). The amorphization process is highly composition dependent [66, 67]. The Cr segregation led to Cr-rich and Cr-lean regions, which locally accelerated the formation of glassy phase at the Cr-segregated regions. Amorphous binary Al alloys could hardly form through liquid quenching [65]. The rapid quenching rate in the sputtering process, solute saturation and the $\sim 13\%$ mismatch strain between Al and Cr ($\gamma_{Al} = 1.432 \text{ \AA}$; $\gamma_{Cr} = 1.249 \text{ \AA}$) facilitated the transformation processes [66, 100, 101]. The intermediate Al_7Cr phase with low-symmetry monoclinic structure might serve as the precursor for the formation of amorphous phase,

which might help to reduce the system energy within a specific compositional range.

Merits of building nanocomposites

By forming the amorphous phase, $Al_{79}Cr_{21}$ has reached a peak hardness of 6.1 GPa (Fig. 4b). Micro-compression experiments were conducted to compare the deformation behaviors among these single-phase and dual-phase structures. $Al_{97}Cr_3$, $Al_{93}Cr_7$, $Al_{87}Cr_{13}$ and $Al_{79}Cr_{21}$ were chosen as the embodiment of each region, namely FCC, FCC/monoclinic, FCC/amorphous and full amorphous regions. Figure 5a shows the engineering stress–strain curves of pure Al and four selected Al-Cr alloys. By analyzing the relations between the flow stress and the elastic modulus (Fig. 5b), it is clearly evident that the Al-Cr alloys with amorphous phase delivered higher flow stresses than their full crystalline counterparts. $Al_{79}Cr_{21}$ produced a strength as high as 2.4 GPa, outperforming a majority of Al alloys.

Then, a question arises as to whether there exists differences in plastic deformation in these Al-Cr alloys that were differently microstructurally constructed? It was noteworthy

Figure 5: (a) Representative engineering stress–strain curves, collected from *In situ* micro-compression experiments, of pure Al, $Al_{97}Cr_3$, $Al_{93}Cr_7$, $Al_{87}Cr_{13}$, and $Al_{79}Cr_{21}$. (b) The flow stresses, converted from hardness measurements and collected from compression tests, of various Al-Cr alloys as a function of elastic modulus. The reference lines for E/85, E/50, and E/70 are marked. After taking into account the straining-induced geometric evolutions of different Al-Cr alloys, the spontaneous true stress–strain relations were obtained for (c) $Al_{97}Cr_3$, (d) $Al_{93}Cr_7$, (e) $Al_{87}Cr_{13}$, and (f) $Al_{79}Cr_{21}$ with their corresponding SEM images of micropillars before and after deformation. Figures 5a and 5b are reprinted with permission from Ref. [34]. Figure 5c–5f were adapted with permission from Ref. [34].

that the Al-Cr alloys with different microstructure and phases respond differently to the deformation, evidenced by the different geometric evolutions during the straining (Fig. 5c–f). This causes challenges interpreting the inherent hardening and softening. Thus, a procedure taking into account the spontaneous geometric change of the deforming micropillars was developed. $\text{Al}_{97}\text{Cr}_3$ and $\text{Al}_{93}\text{Cr}_7$ have comparable grain sizes but the former underwent a strain softening and the latter a strain hardening (Fig. 5c, d). Post-mortem analyses discovered that single-phase $\text{Al}_{97}\text{Cr}_3$ was subjected to localized grain coarsening underneath the pillar-indenter contact, whereas FCC/monoclinic $\text{Al}_{93}\text{Cr}_7$ instead had a more homogeneous deformation, for which the constraint effect from the intermetallic boundaries on the deformation of FCC phase was responsible. Moreover, $\text{Al}_{87}\text{Cr}_{13}$ and $\text{Al}_{79}\text{Cr}_{21}$ exhibited different serrated flows on the stress–strain curves in Fig. 5e, f. Sun et al. described a method to determine the amplitude and frequency of these stress drops [102]. $\text{Al}_{87}\text{Cr}_{13}$ with the FCC/amorphous composite structure displayed a lower amplitude but a higher frequency of stress drops compared to the amorphous $\text{Al}_{79}\text{Cr}_{21}$, suggestive of improved plasticity in metallic glasses (MGs) [103–106]. MGs have often suffered from catastrophic failure due to the formation of major shear bands [107]. Wu et al. showed that a Mg-based MG with embedded nanocrystals rendered a strength as high as 3 GPa but underwent instant fracture after yielding under compression [108]. Various factors can influence the deformation of MGs. Spaepen used free volume concept to interpret the strain rate dependence of homogeneous and inhomogeneous flow of MGs [109]. Maaß et al. showed that the shear band arrest is related to the glass transition temperature [110]. Ke et al. showed the sample size and base element could affect the serrated flow [111]. Sun et al. showed that the serrated plastic flow arises from the intrinsic instability of the sliding of shear bands, which is affected the elastic properties [112]. Compared to $\text{Al}_{79}\text{Cr}_{21}$, the improved plasticity in $\text{Al}_{87}\text{Cr}_{13}$ benefits from the interactions between shear bands and FCC nanocrystals. The initiated shear bands in the amorphous phase are arrested by the nanocrystallites, promoting the nucleation and propagation of new shear bands, and this interaction brings about the delocalized shear deformation in the FCC/amorphous composite structure [34]. In addition, except the major strengthening mechanisms, nanovoids were identified at GBs in Al-Cr, which might influence the mechanical properties of Al-Cr alloys. Thermal behaviors of those nanocomposites are unknown. Age-hardened Al alloys with nanoprecipitation often suffer from microstructural instability at temperatures below 200 °C [1, 2], but a composition modification strategy may be promising to inhibit the nanoprecipitation coarsening [113].

Orientation-dependent mechanical properties

Various strengthening mechanisms responsible for the extremely high strengths of these NC Al alloys have been discussed. As we have noticed, these Al alloys mainly consist of ITBs and LAGBs with a clear directionality. Meanwhile, some other NC alloys with columnar nanograins also manifested superb mechanical properties [114, 115]. However, the orientation-dependent mechanical properties of metals and alloys with columnar structure or non-equiaxed grains were less understood. The anisotropy of single-crystal metals relies on the activation of different slip systems, verified by many experimental and theoretical inspections [116–118]. You et al. exhibited anisotropic plastic behaviors of NT Cu with lateral CTBs, rationalized by the different orientation-dependent dislocation-CTB interactions [45, 119]. In some nanocolumnar metals and alloys, the tensile results were inconsistent with the hardness results and the proportionality constant in Tabor equation, i.e., $H = C\sigma$, is noticeably off. This phenomenon has been mostly ascribed to the voids residing at GBs owing to the sluggish kinetics of adatoms as well as the shadowing effect from the surface roughness in coarse columnar structures. However, the void formation in thin films is considerably dependent on the columnar grain size and surface roughness [120]. A dedicated study is required to investigate the anisotropy and tension–compression asymmetry of the nanocolumnar structure and the orientation-dependent deformation mechanisms. An attempt to explicate these behaviors is bound to run into peculiar difficulties when it comes to the limited thickness of thin films and coating materials. A rigorous *in situ* micromechanical tension and compression study is present.

In situ micromechanical tension and compression

NC $\text{Al}_{94.5}\text{Fe}_{5.5}$ was chosen to investigate the orientation-dependent properties. Few voids at GBs were identified in $\text{Al}_{94.5}\text{Fe}_{5.5}$ in the underfocus TEM imaging condition (Note that voids were readily identified in texture-less Al-TM alloys with coarse columnar structure) and the elemental selection is relatively exempted from the GB embrittlement according to Gibson and Schuh model [121, 122]. Figure 6a shows that $\text{Al}_{94.5}\text{Fe}_{5.5}$ has an ITB spacing of 22 nm and a grain size of 5 nm. With the aid of a commercially available flat punch indenter and a self-built tensile grip fabricated out of a boron-doped diamond blank tip, four types of *in situ* tests were devised, that is, out-of-plane compression (OPC), in-plane compression (IPC), out-of-plane tension (OPT), and in-plane tension (IPT). They can be also named based on the force loading direction with respect to the GB direction, namely OPC ($\sigma_C \parallel \text{GB}$), IPC ($\sigma_C \perp \text{GB}$), OPT ($\sigma_T \parallel \text{GB}$) and IPT ($\sigma_T \perp \text{GB}$) (Fig. 6b–f).

Figure 6: (a) Dark field XTEM micrograph, taken along $[\bar{1}11]_g$ vector, and HRTEM micrograph showing the columnar nanograins and vertical GBs in $Al_{94.5}Fe_{5.5}$. The GB statistic shows that the respective average ITB spacing and columnar grain size are ~ 22 and ~ 5 nm. (b) Schematics of the NC Al-Fe with vertical GBs and the tensile and compressive loading directions relative to GB direction. Low- and high-magnification SEM micrographs showing micropillars or micro-coupons prepared for (c) in-plane compression, IPC ($\sigma_c \perp GB$), (d) out-of-plane compression OPC ($\sigma_c \parallel GB$), (e) in-plane tension, IPT ($\sigma_T \perp GB$), and (f) out-of-plane tension experiments, OPT ($\sigma_T \parallel GB$). Figures 6a and 6b were adapted with permission from Ref. [76]. Figure 6c-6f are reprinted with permission from Ref [76].

Anisotropy

The IPC ($\sigma_c \perp GB$) tests led to an average strength of 1.6 GPa and the formation of a shear offset at a 45° inclination angle, whereas the OPC ($\sigma_c \parallel GB$) resulted in a higher strength of 2 GPa and a deformation accommodated by the dilation of the upper pillar sector (Fig. 7a, b). A strength ratio of ~ 1.25 between OPC and IPC was obtained. It is noteworthy that the collected mechanical contributions from the aforementioned GB strengthening, solid solution strengthening and NC solute pinning strengthening are incapable of accounting for anisotropic behaviors under the compression mode. According to Eq. 2, i.e., $\sigma = m(\tau_0 + \sqrt{\frac{\tau^* \mu b}{\pi(1-\nu)L}})$ that takes into account the texture effect, two variables are operative to affect strength, which are microstructural feature length, L , and the Taylor factor, m . Due to the nanocolumnar structure, the length for dislocation movement is $d/\cos 70.53^\circ$, where d is average columnar grain size, for both IPC and OPC experiments. Taylor factor is intimately associated with the SFE as well as the ratio, ξ , of critical resolved shear stresses for twinning and slips for FCC metals. Taylor factors were estimated using criterion of maximum work principle

of Bishop-Hill [123, 124] and were well depicted by Chen et al. [125] For Al and its alloys with ultrahigh SFE, ξ is greater than $2/\sqrt{3}$ and the Taylor factor for $[111]$ direction is ~ 3.67 . The Al-Fe alloy has a strong out-of-plane (111) texture and the nanograins experienced in-plane rotation; hence, the texture along $Si[2\bar{1}1]$, the in-plane test direction, is either polycrystalline or approximates to $\langle 112 \rangle$. In either case, the Taylor factor along the in-plane direction is proximately equal to 3.06 [125, 126]. The ratio of two Taylor factors is 1.2, in accordance with the experimentally measured 1.25, suggestive of a texture-determined anisotropy under the compression mode.

Under tension, the engineering stress-strain responses of $Al_{94.5}Fe_{5.5}$ under IPT ($\sigma_T \perp GB$) exhibited a typical brittle fracture and a fracture stress of 1.1 GPa (Fig. 7c). The fracture surface was made of a horizontal regime and an inclined shear lip. In the other hand, OPT ($\sigma_T \parallel GB$) produced an average tensile strength of 1.8 GPa and a progressive shear propagation during the deformation (Fig. 7d). No apparent elongation was seen due to the spatial limitation for dislocation accumulation, but the apparent engineering strain and the slow

Figure 7: Engineering stress–strain curves and the corresponding SEM micrographs before and after deformation for (a) in-plane compression, IPC ($\sigma_c \perp GB$), (b) out-of-plane compression OPC ($\sigma_c \parallel GB$), (c) in-plane tension, IPT ($\sigma_T \perp GB$), and (d) out-of-plane tension experiments, OPT ($\sigma_T \parallel GB$). The fracture surface morphologies after IPT and OPT tests are also present. It should be noted that the global plastic strain cannot be equated with a true strain for elongation for bulk tensile tests. Figures were adapted with permission from Ref [76].

propagation of the shear at $\sim 45^\circ$ are distinguished from the catastrophic fracture under IPT mode. A stress ratio between OPT and IPT modes is ~ 1.64 , much higher than ~ 1.25 under compression. In the meantime, post-mortem analyses identified few dislocation events in IPT deformed specimens. All signify a premature fraction taking place under the IPT ($\sigma_T \perp GB$) mode. The collected stresses from different modes were plotted against the extrinsic sample dimension in Fig. 8a. An extrinsic size effect often emerges in single-crystal and CG metals and the dislocation starvation or truncation in the spatial constraint demands higher critical stress to nucleate dislocations [127]. No apparent extrinsic size effect was captured for the NC Al–Fe, at least under OPC mode, which also differs from the NC metals with equiaxed nanograins [128, 129]. The reduced extrinsic dimensions magnify the free surface effect, thereby facilitating the GB sliding and the softening of equiaxed NC metals.

Tension–compression asymmetry

Compression-tension asymmetry, σ_y^C/σ_y^T , in UFG and CG metals and alloys is not significant. For example, Yu et al. showed that Al produced by equal channel angular extrusion had σ_y^C/σ_y^T values of 1.1–1.2 [130]. Kabirian et al. showed that AA5182 alloys delivered comparable compressive and tensile strengths at different strain rates [131]. Within the grain size range where dislocation-mediated activities prevail, Cheng, Spencer and Milligan developed a model explaining that σ_y^C/σ_y^T arises from the pressure dependence of the self-energy of bow-out dislocation [132]. Jiang and Weng developed a micromechanics-based composite model treating

GBs as a pressure-dependent phase and estimated the yield stress of metals with grain sizes of a dozen or a few dozens of nanometers under both tension and compression [133]. Lund and Schuh adopted molecular simulations to predict the σ_y^C/σ_y^T as the deformation shifts from shear transformation zone-mediated to dislocation-mediated plasticity and they further analyzed prior models to cover the strength asymmetry across all grain sizes [134].

Figure 8b shows that σ_y^C/σ_y^T of FCC metals with equiaxed grain structure increases monotonically from ~ 1 when grain size is a few hundred nanometers to ~ 1.6 when grain size decreases to 10–20 nm. Such a phenomenon is speculated as a consequence of transitions from dislocation-mediated to GB-mediated plasticity (including GB sliding and grain rotation), and from shear-stress dependent to hydrostatic pressure-dependent deformation. For UFG metals with low σ_y^C/σ_y^T values, a better ductility is anticipated due to the ability for dislocation multiplication, whereas for the NC metals with σ_y^C/σ_y^T approaching 1.6, the GB-mediated deformation often results in limited plasticity and tensile strength due to the GB susceptibility to fracture [132, 134]. For the NC Al–Fe with columnar nanograins and a grain size of ~ 5 nm, the in-plane measurements showed that σ_y^C/σ_y^T is ~ 1.5 , in agreement with the general trend in Fig. 8b, but intriguingly, the out-of-plane measurements showed that σ_y^C/σ_y^T is ~ 1.1 , close to that of the CG and UFG metals and alloys. This indicates that NC Al alloys could carry better plasticity as tested along the out-of-plane direction and the out-of-plane direction of the NC Al alloys is subjected to alleviated susceptibility of GB fracture. In addition, unlike the equiaxed NC metals and alloys, the strength asymmetry does not monotonically depend on the grain size in these nanocolumnar structures.

Figure 8: (a) Strengths of $\text{Al}_{94.5}\text{Fe}_{5.5}$, collected from each mode are plotted in the relation between yield strength and extrinsic sample dimension. (b) Compression-tension asymmetry (σ_c/σ_t) of FCC metals is plotted against grain size. Schematics illustrate primary deformation/fracture mechanisms for (c) IPC ($\sigma_c \perp \text{GB}$), (d) OPC ($\sigma_c \parallel \text{GB}$), (e) IPT ($\sigma_t \perp \text{GB}$), and (f) OPT ($\sigma_t \parallel \text{GB}$). Figures are reprinted with permission from Ref [76].

Deformation and fracture mechanisms

NC Al-Fe was subjected to an intergranular shear propagation along GBs under IPC mode (Fig. 8c). Aitken et al. found a shear stress-driven GB sliding along the inclined GB in bi-crystal Al pillars [135]. The extensive deformability under OPC tests were accommodated by the partial migration-induced grain coarsening (Fig. 8d). Moreover, a premature fracture along GBs, dominated by nominal stress, occurred in NC Al-Fe under IPT mode (Fig. 8c). You et al. found that the columnar GBs in NT Cu were subjected to larger plastic strain as well as inhomogeneous deformation [46]. Conversely, OPT experiments underwent an intragranular shear propagation deflected by the vertical GBs (Fig. 8d).

Thermally stability and high-temperature properties of NC Al alloys

Thermal properties of binary NC Al alloys

The excess energy stored at GBs drives the grain growth. It remains a challenge to equip the NC materials with both high strength and thermal stability. Multiple tactics that aimed to enhance the thermal stability of NC alloys were referred to in the introduction section. A question naturally arises as to what the thermal stability and high-temperature behaviors of these high-strength NC Al alloys would be? Fig. 9 shows PV-STEM micrographs of NC $\text{Al}_{94.5}\text{Fe}_{5.5}$ annealed at temperatures from 200 to 400 °C. In comparison to the microstructural stability at

200 °C (Fig. 9a), Fe segregation occurred first at the free surface and caused the faceted cellular contours of Fe segregation at 280 °C (Fig. 9b). Fe evidently congregated at 330 °C, signifying the recrystallization process and the decomposition of solid solution into FCC/intermetallic composite structure (Fig. 9c, d). According to the hardness variations in response to the annealing temperature, the softening temperatures for high-strength $\text{Al}_{95.5}\text{Ni}_{4.5}$, $\text{Al}_{94.2}\text{Co}_{5.8}$ and $\text{Al}_{94.5}\text{Fe}_{5.5}$ are ~120, ~200 and ~280 °C, respectively [29, 42]. Masui et al. found the recrystallization temperatures for RF-sputtered amorphous Al-Ni, Al-Co and Al-Fe are 220, 260 and 360 °C [69], in line with our observations. The softening at low or moderate temperatures for these binary systems can be assigned to the facile decomposition of solid solution and the severe formations of the relevant intermetallic phases, which deprived the lattice and GB sites of the solute atoms operative to stabilize nanograins.

Limitations of binary systems

One effective method to suppress the microstructural instability is to decorate the GBs with impurity atoms in order to create an energetically favorable GB state against the grain growth. Kalidindi et al. developed a stability criterion to handpick binary NC alloys able to achieve thermal stability via solute segregation at GBs. These stable systems should have the enthalpy of GB segregated state, ΔH_{seg} , greater than the sum of the excess energy of GBs, $k\gamma$, and the enthalpy deficit from the

Figure 9: STEM micrographs and corresponding EDS compositional mapping for Al and Fe of binary $\text{Al}_{94.5}\text{Fe}_{5.5}$ annealed at (a1-a3) 200, (b1-b3) 280, (c1-c3) 330, and (d1-d3) 400 °C. Figures are reprinted with permission from Ref. [29].

intermetallic compound formation, i.e., $\Delta H_{\text{mix}} - \frac{1}{x_S^C} \Delta H_{\text{form}}$, where ΔH_{mix} and ΔH_{form} are the enthalpy of mixing and the formation enthalpy of the compound, respectively, and x_S^C is the stoichiometry of the formed compound [26–28]. The stability criterion is expressed as.

$$\Delta H_{\text{seg}} > \Delta H_{\text{mix}} - \frac{1}{x_S^C} \Delta H_{\text{form}} + k\gamma \quad (9)$$

This criterion was improved by considering the compound formation-induced solute deficiency at GBs when compared to the criterion based on the Gibbs adsorption isotherm, proposed by Weissmüller [27].

However, these binary NC alloys have difficulties to reconcile high strength and thermal stability. In binary NC alloys, the solute that acts as the effective grain refiner might be incapable of rendering the thermal stability of its own accord. On the other hand, the solute that is a superb stabilizer might be ineffective to refine the grain size for significant gain in strength. For instance, Talin et al. showed that Mn did not effectively refine the electrodeposited Ni–Mn but it was able to preserve the nanostructure up to 500 °C through the GB segregation [33]. Schuh et al. showed that W reduced the grain size of Ni down to

5–7 nm but Ni–W alloys are thermally metastable/unstable [26, 136]. An et al. showed that Al could effectively refine the grain size of Cu, but the microstructure of Cu–Al alloys coarsened at low homologous temperatures [137, 138]. In sputtered Al alloys, Co, Ni and Fe demonstrated astounding ability to refine grain sizes of Al down to less than 10 nm, but Al–Ni, Al–Co and Al–Fe manifested unsatisfactory thermal stabilities [29, 35, 37, 40, 42]. Mohjoub et al. used first principles calculations to predict general tendency for solute segregation at GBs in Al and found that Sr, Mg, Si and Ca were expected to achieve stable segregated GB state and on the contrary, Ni, Co and Fe are bound to lead to metastable or unstable segregated state due to the formation of stable intermetallic compounds [41]. To integrate the thermal stability into the high-strength NC Al alloys, binary systems encounter certain inherent weakness.

Thermal properties of ternary NC Al alloys

In the following, we demonstrate that coupling binary alloys with a second wisely selected solute could substantially enhance the resistance to microstructural coarsening up to 400 °C while retaining ultrahigh strength. $\text{Al}_{94.5}\text{Fe}_{5.5}$ underwent the recrystallization process and the mechanical softening as temperature

exceeded $\sim 280^\circ\text{C}$ (Fig. 10a, b). In contrast, no apparent changes of microstructure and chemical distribution were noticed in $\text{Al}_{89.8}\text{Fe}_{5.5}\text{Ti}_{4.7}$ alloys at 350°C (Fig. 10c). Fe segregation at ITBs was witnessed at 400°C (Fig. 10d), while Ti remained homogeneously distributed and the columnar nanograins were preserved. Then, as temperature continued to rise, both Fe and Ti started to precipitate out as orthorhombic cmcm Al_6Fe and L1_2 , $\text{D0}_{22}\text{Al}_3\text{Ti}$ phases and the columnar nanograins transferred to the equiaxed nanograins (Fig. 10e, f).

The microstructural and mechanical stabilities of ternary Al–Fe–Ti alloys in reference to those of binary Al–Fe are substantially enhanced, evidenced by the hardness and grain size evolutions in response to temperatures. Figure 11a exhibits that the onset of softening of ternary NC $\text{Al}_{89.8}\text{Fe}_{5.5}\text{Ti}_{4.7}$ is 400°C (maintaining hardness of 5.8–6.6 GPa), equivalent to $0.72T_m$ of Al, a drastic improvement from the 250 to 280°C of binary Al–Fe alloys. According to a series of HRTEM statistical analyses, columnar nanograins in NC $\text{Al}_{89.8}\text{Fe}_{5.5}\text{Ti}_{4.7}$ were well preserved at temperatures lower than or equal to 400°C (Fig. 11b). Notably, the microstructural and mechanical stabilities of ternary NC Al–Fe–Ti alloys outperform most of CG, UFG and NC Al and Al alloys. It is imperative to maintain the microstructural and mechanical stabilities of NC alloys at high service temperature. *In situ* compression experiments at elevated temperatures revealed that a precipitous softening occurred at 300°C for NC $\text{Al}_{94.5}\text{Fe}_{5.5}$ [29], whereas NC $\text{Al}_{89.8}\text{Fe}_{5.5}\text{Ti}_{4.7}$ was able to produce ~ 1.7 GPa flow stress at a testing temperature of 300°C and the softening to 360 MPa took place as testing temperature reached 400°C (Fig. 11c). The superb preservation of flow stress

and the low rate of strength reduction at high temperatures for NC $\text{Al}_{89.8}\text{Fe}_{5.5}\text{Ti}_{4.7}$ suggest that the constituent elements profoundly change the elemental interactions and the solute–solute, solvent–solute bonding (Fig. 11d, e).

Discussion on high-strength and thermally stable ternary NC Al alloys

Ti in binary Al–Ti was insufficient to refine grain size [39]. In the ternary system, Fe acts as the grain refiner and Ti as a stabilizer. Ti solutes are positioned at substitutional sites adjacent to Fe solutes, forming a more energetically favored Fe–Ti pairs in Al matrix (Fig. 12a). This suggests that it is bound to take a higher energy to expel Fe solutes from the solid solution. Various studies found that the formation temperature for Al_3Ti is higher than that of Al_6Fe , suggesting a higher decomposition temperature of Ti solid solution in Al. Ti could remain in the lattice, exerting solute drag to inhibit the Fe diffusion and agglomeration prior to the formation of Al_6Fe . In addition, a Fe segregation at ITBs was identified and a GB segregated state causes an energy minimal state at 400°C before the precipitations (Fig. 10d). DFT calculations were carried out to estimate the energies of solute pairs in vicinity of ITBs (Fig. 12b, c). The lowest and 2nd lowest energy configurations both have Fe atoms residing at ITBs and Ti atoms being adjacent to Fe, in accordance with the experimental observations. Compared to the binary Al–Fe system wherein the decomposition of solid solution and the accompanying Al_6Fe precipitation determine the stability (Fig. 12d), Al_6Fe and Al_3Ti formed upon temperatures greater than 400°C

Figure 10: XTEM micrographs and the corresponding EDS elemental mapping with line profiles of (a, b) binary NC $\text{Al}_{94.5}\text{Fe}_{5.5}$ and (c-f) ternary NC $\text{Al}_{89.8}\text{Fe}_{5.5}\text{Ti}_{4.7}$ at various annealing temperature. Figures are reprinted with permission from Ref. [77].

Figure 11: (a) Hardnesses of $Al_{97}Fe_3$, $Al_{94.5}Fe_{5.5}$, $Al_{95.3}Fe_{2.8}Ti_{1.9}$, and $Al_{89.8}Fe_{5.5}Ti_{4.7}$ as a function of annealing temperature. (b) Grain size evolution of UFG Al, $Al_{94.5}Fe_{5.5}$, and $Al_{89.8}Fe_{5.5}Ti_{4.7}$ in response to annealing temperatures. (c) Representative engineering stress–strain curves of compressions at elevated temperatures of $Al_{89.8}Fe_{5.5}Ti_{4.7}$ and $Al_{94.5}Fe_{5.5}$, and the corresponding SEM images of the deformed micropillars of $Al_{89.8}Fe_{5.5}Ti_{4.7}$. (d) The Flow stress and (e) the normalized flow stress reduction of NC $Al_{94.5}Fe_{5.5}$, $Al_{89.8}Fe_{5.5}Ti_{4.7}$ and various UFG, NC, and NT Al alloys as a function of testing temperature. Figures were adapted with permission from Ref. [77].

Figure 12: Density functional theory (DFT) calculations compute the formation energies of substitutional solute pairs in Al solvent and (a) Formation energies of Fe-Ti, Fe-Fe, and Ti-Ti solute pairs at different substitutional sites in Al. (b) The comparable energies of Fe-Ti pairs in vicinity of ITBs. 25 configurations were calculated. (c) Optimal atomic configurations with the lowest and 2nd lowest energy states. Schematics illustrating the microstructural and chemical evolutions in (d) binary Al-Fe alloys and (e) ternary Al-Fe-Ti alloys in response to temperatures. Figures were adapted with permission from Ref. [77].

TABLE 1: Thermal stability and mechanical properties of NC Al alloys.

Composition (at%)	Synthesis	Phase	Microstructure	RT strength (GPa)	HT strength (GPa)	Softening/coarsening temperature	Ref.
Al _{93.5} Mn _{6.5}	ED	FCC	Equiaxed nanograins with Mn segregated GBs; $d = 66$ nm	–	–	~300 °C	[140]
Al ₉₅ Fe ₅	MA + SPS	FCC + Al ₆ Fe	Equiaxed nanograins; $d = 25$ –50 nm	$\sigma_C = 1$ –1.1	$\sigma_C = 0.5$ –0.6 at 250 °C; $\sigma_C = 0.35$ –0.5 at 350 °C	≤350 °C	[52]
Al _{99.3} Fe _{0.5} Zr _{0.2}	MA + SPS	FCC + Al ₆ Fe + Al ₃ Zr	Equiaxed nanograins; $d = 65$ nm	$\sigma_C = 0.85$	$\sigma_C = 0.46$ at 250 °C; $\sigma_C = \sim 0.2$ at 350 °C	~250 °C	[141]
Al _{95.3} Zr _{4.0} Fe _{0.7}	EBE	FCC + Al ₃ Zr	Equiaxed nanograins; $d = 70$ –260 nm	$H = 2.5$ $\sigma_T = 0.82$	$\sigma_T = 0.54$ at 150 °C; $\sigma_T = 0.43$ at 200 °C	~200 °C	[142]
Al _{93.1} Ti ₆ Cu _{0.9}	MA + extrusion	FCC + Al ₃ Ti + Al ₂ O ₃ + Al ₄ C ₃	Equiaxed nanograins; $d = 30$ –70 nm	$\sigma_T = 0.56$	$\sigma_T = 0.27$ at 200 °C; $\sigma_T = 0.14$ at 375 °C	–	[143]
Al ₉₃ Fe ₃ Cr ₂ Ti ₂	MA + extrusion	FCC + Al ₁₃ Fe ₄ + Al ₃ Ti	Equiaxed nanograins; $d = 80$ nm	$\sigma_C = 0.56$	$\sigma_C = 0.4$ at 200 °C; $\sigma_C = 0.17$ at 400 °C	–	[144]
Al ₉₇ Fe ₃	DC-MS	FCC	Columnar nanograins; ITBs + LAGBs	$H = 4.7$	–	250 °C	[29, 77]
Al _{94.5} Fe _{5.5}			$d = 48$ nm $d = 5$ nm	$H = 5.6$; $\sigma_C = 1.73$ ($\epsilon = 5\%$)	$\sigma_C = 1.3$ at 200 °C; $\sigma_C = 0.1$ –0.15 at 300 °C; ($\epsilon = 5\%$)	280 °C	
Al _{95.3} Fe _{2.8} Ti _{1.9}	DC-MS	FCC	Columnar nanograins; ITBs + LAGBs	$H = 5$	–	330 °C	[77]
Al _{89.8} Fe _{5.5} Ti _{4.7}			$d = 5$ nm	$H = 6.6$; $\sigma_C = 2.2$ –2.3 ($\epsilon = 7\%$)	$\sigma_C = 1.7$ at 300 °C; $\sigma_C = 0.36$ at 400 °C; ($\epsilon = 7\%$)	400 °C	
Al _{95.5} Ni _{4.5}	DC-MS	FCC	Columnar nanograins; ITBs + LAGBs; $d = 39$ nm	$H = 5.4$; $\sigma_C = 1$ ($\epsilon = 10\%$)	–	100 °C	[42]
Al _{92.5} Ni _{4.5} Ti ₃	DC-MS	FCC	Columnar nanograins; ITBs + LAGBs; $d = 30$ nm	$H = 6.3$; $\sigma_C = 1.8$ ($\epsilon = 10\%$)	–	250 °C	[42]
Al ₈₇ Ni ₇ Ce ₆	DC-MS	FCC + amorphous	Nanograins; Amorphous Ce, Ni co-segregated GBs; $d = 10$ nm	$H = 5.16$; $\sigma_T = 1.65$	$\sigma_T = 1.35$ at 250 °C; $\sigma_T = 0.23$ at 325 °C;	325 °C	[145]

ED, DC-MS, MA, SPS, and EBE denote electrodeposition, direct current-magnetron sputtering, mechanical alloying, spark plasma sintering, and electron-beam evaporation, respectively. RT and HT stand for room temperature and high temperature. H , σ_C , σ_T , and σ_I are hardness, compressive strength or flow stress at certain strain, tensile strength, and flow stress translated from indentation measurements, respectively.

in ternary NC Al–Fe–Ti (Fig. 12e). The presence of Ti delays the Fe agglomeration and the formation of intermetallic Al_6Fe . The thermal stability and high-temperature mechanical behaviors of various NC Al alloys selected from the literature are summarized in Table 1. Some NC Al systems fabricated by mechanical alloying are selected and there are more NC Al systems prepared using this route. The determination of coarsening and softening temperatures for those compositionally distinct alloys may be ambiguous owing to the excess mechanical energy stored at GBs, contamination and the intermetallic formation amid the milling process. Using mechanical alloying technique, Mula et al. studied the thermal stabilities of NC Al–Zr alloys with different Zr contents as well as the influences of Nb, Y and Zr on the thermal stability of NC Al–Cu alloys [25, 139]. In contrast to sputtered and electrodeposited NC Al alloys with stable nanograins prior to coarsening temperature, the nanograins and mechanical properties of mechanically alloyed NC Al alloys are sensitive to low and moderate temperatures.

NC Al–Fe–Ti underwent recrystallization and mechanical softening as temperature exceeded 400 °C, whereas Al–Ni–Ti coarsened and softened at ~250 °C [42]. This strongly suggests that the solute as the grain refiner considerably influences the thermal stability of the NC ternary Al alloys as well. Kube et al. stated that in a situation wherein a stabilizing solute induces a co-segregation of the other desegregating solute at GBs, thermodynamic stability of the ternary NC system could be deteriorated once the desegregating solute governs the precipitation process [96]. Sputtered NC Al–Ni was subjected to severe precipitation at ~120 °C, in comparison to the ~280 °C of Al–Fe alloys. The comparably facile formation of the intermetallic Al_3Ni in Al–Ni to a large extent affects the thermal stability of its ternary NC system. The established stability criterion could reasonably predict the segregation tendency in binary NC systems to improve the thermal stability of NC alloys, but estimating the stability of a ternary system becomes much more intricate [26]. Saber et al. constructed a model predicting the stability of ternary NC alloys, taking into account the effects of elastic enthalpy and the interaction energy parameter associated to the mixing enthalpy [146]. Considering the atomic size mismatch between Ti and Al, adding Ti into Al–Fe is expected to cause insignificant change in elastic enthalpy. Moreover, a calculation of interaction energy parameter, based on the heat of mixing, –17 kJ/mol for Ti–Fe and –11 kJ/mol for Al–Fe, may infer that adding Ti to Al–Fe might not increase the effectiveness of thermodynamic stability through GB segregation [147]. This suggests that the Ti-driven Fe segregation at ITBs took place within a narrow temperature window around ~400 °C, and the improved microstructural stability up to 400 °C might be more kinetically determined because of the delayed precipitation of intermetallic Al_6Fe in the presence of Ti. A classic relation between solubility of various TM solutes in solid Al and temperature is reconstructed [148].

The relation was initially adopted to deduce the heat of mixing and the stability and metastable phases in commercial Al alloys with limited impurity solubility. Its applicability and validity might be better held to explain the decomposition tendency of supersaturated solid solution in these far-from-equilibrium NC Al alloys with solute supersaturation. The reduction of solubility in systems, such as Al–Ni and Al–Fe, is highly sensitive to the decreasing temperature, suggestive of a facile decomposition of solid solution, whereas the solubility in systems, such as Al–Ti and Al–Zr, is relatively insensitive to the temperature. In the ternary Al–Fe–Ti system, Fe manifests high effectiveness in the grain refinement but encounters comparably facile precipitation; nevertheless Ti solutes are ineffective in grain refinement but manage to remain a solid solution at higher temperatures, suppressing the diffusion of Fe and the formation of intermetallic Al_6Fe , so that the precipitation-induced deprivation of solute atoms from GBs was significantly delayed and GBs could be sufficiently stabilized by the solutes against the grain coarsening. The application of this kinetic approach in a different ternary system might require extra considerations pertaining to the solute–solute interactions and the facile formation of certain stable intermetallic phases. More empirical and theoretical studies need to be dedicated to robustly predict the thermodynamically stable ternary NC systems. In this coupled-solute-effect approach, the high strength and thermal stability can be well reconciled in the ternary Al–Fe–Ti system.

Conclusion

In summary, in light of the aggregated collection of recent works on non-equilibrium NC Al alloys prepared by sputtering, we analyzed the discrepancies as to their microstructural characteristics and property in an effort to understand the solute effects on grain refinement and mechanical and thermodynamic properties. Comprehension toward characters of each constituent helps direct a design of high-strength and yet thermally stable NC alloys. This literature also presents the anisotropic behaviors and compression-tension asymmetry of NC Al alloys with clear boundary directionality. Based on these studies, the findings and alloy design principles discovered from the sputtered Al alloys can be, to certain extent, transferred to other non-equilibrium processes, such as mechanical alloying, after taking into account factors including boundary type and energy state, elemental solubility, and phase formation at different synthetic conditions, etc. More dedicated studies are necessary to identify design principles for achieving thermally stable NC alloys with compositional complexity. Despite new findings on mechanical behavior of different NC Al alloys, a major obstacle for the application of these NC alloys is their limited tensile ductility. Scaling up the fabrication of these high-strength Al alloys remains a technical challenge.

The major findings from the literature review are summarized below:

- (1) In sputtered binary NC Al alloys, Fe, Co, and Ni appear most effective in strengthening Al alloys, as evidenced by high hardnesses greater than 5 GPa and high flow stresses approaching 2 GPa.
- (2) The solute-induced microstructural refinement and strengthening exhibit a relationship with the atomic size mismatch for Al solid solution alloys, with a few exceptions.
- (3) In Al-Cr alloys, the Cr segregation promotes a multistage phase transformation, forming FCC/intermetallic and FCC/amorphous nanocomposites that display improved plasticity compared to single-phase counterparts.
- (4) A thorough *in situ* micromechanical investigation reveals that certain NC Al alloys with columnar nanograins have mechanical anisotropy and compression-tension asymmetry. Out-of-plane direction gives rise to better plasticity and alleviated susceptibility to GB fracture, whereas in-plane tension is prone to premature fracture.
- (5) Solutes effective in the grain refinement generally render limited thermal stability in the binary NC Al alloys owing to the facile precipitation of intermetallic phase. Coupled solute effects have been observed, that is, a solute serves as the effective grain refiner and selective second solute serves as the stabilizer to appreciably improve the microstructural and mechanical stabilities as well as high-temperature mechanical behaviors through GB segregation and the suppression of intermetallic formation. NC Al-Fe-Ti system as a case study produces a strength greater than 2 GPa, a high-temperature strength of ~1.7 GPa at 300 °C, and microstructural stability up to 400 °C.

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Declarations

Conflict of interest The authors have no financial or personal relationship with a third party whose interests could be positively or negatively influenced by the article's content.

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