



## Regular Article

Stabilization of nanocrystalline alloys at high temperatures *via* utilizing high-entropy grain boundary complexionsNaixie Zhou<sup>1</sup>, Tao Hu<sup>1</sup>, Jiajia Huang, Jian Luo<sup>\*</sup>

Department of NanoEngineering; Program of Mater. Sci. Eng., University of California, San Diego, La Jolla, CA 92093, USA

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## ABSTRACT

Multicomponent alloying can be utilized to enhance the thermal stability of nanocrystalline alloys. The grain boundary energy can be reduced significantly *via* both bulk and grain-boundary high-entropy effects with increasing temperature at/within the solid solubility limit, thereby reducing the thermodynamic driving force for grain growth. Moreover, grain boundary migration can be hindered by sluggish kinetics. To test these new theories, numerical experiments were conducted; subsequently, several nanoalloys, including a Ni-based alloy ( $\text{Ni}_{80}\text{Mo}_{6.6}\text{Ti}_6\text{Nb}_6\text{Ta}_{1.4}$ ) and Ni-containing high-entropy alloys ( $\text{Ni}_{29}\text{Fe}_{23}\text{Co}_{23}\text{Cr}_{23}\text{Zr}_2$  and  $\text{Ni}_{25}\text{Fe}_{23}\text{Co}_{23}\text{Cr}_{23}\text{Mo}_2\text{Nb}_2\text{Zr}_2$ ), were designed and fabricated to demonstrate outstanding thermal stabilities that outperform the Ni-based binary nanocrystalline alloys.

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Although nanocrystalline metals can exhibit superior properties such as high strength and hardness [1–4], their applications are often hindered by the extreme susceptibility to grain growth. For example, nanocrystalline Al, Sn, Pb, and Mg are subjected to grain growth even at room temperature [5–7]. There are two general approaches to stabilize nanocrystalline materials against grain growth [8–11]. First, kinetic stabilization by the solute-drag effects and/or Zener (particle) pinning can slow down grain boundary (GB) migration [12–14], which become less effective at high temperatures. Second, thermodynamic stabilization can be achieved by reducing the GB energy ( $\gamma_{\text{GB}}$ ) *via* solute segregation (*a.k.a.* GB adsorption) to reduce the thermodynamic driving force for grain growth. Specifically, Weismuller originally proposed that an “equilibrium” grain size can be reached when the effective  $\gamma_{\text{GB}}$  vanishes [15,16]. Yet, Kirchheim [17] showed that the equilibrium-grain-size binary nanocrystalline alloys generally represent metastable states in supersaturated regions if (and only if) the precipitation is hindered kinetically. In such cases, the kinetic inhibition of the precipitation also becomes more difficult with increasing temperature, triggering abrupt grain growth. These challenges motivate the present study to develop and test new theories and strategies to enhance the thermal stability of nanocrystalline alloys at high temperatures *via* utilizing high-entropy GB complexions (where the term “complexion” refers to an interfacial “phase” that is thermodynamically two-dimensional [18]).

Experimentally, stabilization of nanocrystalline alloys (nanoalloys) have been achieved in several binary systems, including Pd–Zr [19],

W–Ti [20], Fe–Zr [21,22], and Cu–Zr [23] (where the primary phases are underlined). Li et al. also showed that addition of 1–4 at.% Hf could further enhance the thermal stability of the binary Fe–Zr alloys [24]. Specifically, an electrodeposited  $\text{Ni}_{79}\text{W}_{21}$  nanoalloy was found to be stable up to 600–700 °C [25], which represents the best reported result for Ni-based nanoalloys. To test the proposed new strategies, this study demonstrated the stabilities of a Ni-based alloy ( $\text{Ni}_{80}\text{Mo}_{6.6}\text{Ti}_6\text{Nb}_6\text{Ta}_{1.4}$ ) and two Ni-containing high-entropy alloys ( $\text{Ni}_{29}\text{Fe}_{23}\text{Co}_{23}\text{Cr}_{23}\text{Zr}_2$  and  $\text{Ni}_{25}\text{Fe}_{23}\text{Co}_{23}\text{Cr}_{23}\text{Mo}_2\text{Nb}_2\text{Zr}_2$ ) up to ~1000 °C, representing a noteworthy improvement from the binary Ni-based nanoalloys reported previously.

The Gibbs adsorption theory states:

$$d\gamma_{\text{GB}} = S^{\text{XS}}dT - \sum_i \Gamma_i d\mu_i \quad (1)$$

where  $S^{\text{XS}}$  (entropy) and  $\Gamma_i$  (adsorption) are the GB excess quantities,  $T$  is temperature, and  $\mu_i$  is the chemical potential of the  $i$ -th element. Eq. (1) implies that the GB energy ( $\gamma_{\text{GB}}$ ) can be reduced by segregation at a constant  $T$  and this effect can be enhanced for multicomponent (high-entropy) GBs under certain conditions. We should note that generally  $(\partial\gamma_{\text{GB}}/\partial T)_{P, X_i} > 0$  for a specimen of a constant bulk composition ( $X_{\text{bulk}}^i$ ) due to thermally-induced desorption. In a recent article [26], we proposed that a high-entropy GB effect can be achieved for a saturated specimen (in equilibrium with precipitates), when the bulk composition moves long the solvus line, where the solutes' bulk chemical potentials are pinned by the precipitates so that  $(\partial\gamma_{\text{GB}}/\partial T)_{P, X_{\text{bulk}}^i}$  on solvus  $\approx (\partial\gamma_{\text{GB}}/\partial T)_{P, \mu_i} = -S^{\text{XS}}$ ; thus,  $\gamma_{\text{GB}}$  can be reduced with increasing temperature for a high-entropy GB with positive and

<sup>\*</sup> Corresponding author.

E-mail address: [jluo@alum.mit.edu](mailto:jluo@alum.mit.edu) (J. Luo).

<sup>1</sup> Contributed equally to this work.

large  $S^{XS}$  [26]. This high-entropy GB effect has been verified by modeling [26]; however, realization of this strategy for a Ni-based alloy with common segregating elements like Zr, Nb, Ta, Mo, and W would require adding a substantial amount of total non-FCC alloying elements that often leads to a large amount of precipitates and/or formation of ordered phases, which complicates the explanation. Thus, we propose two new strategies *via* using a bulk high-entropy effect (that can occur in conjunction with the GB high-entropy effect) and sluggish kinetics in this study.

As one new strategy to stabilize nanoalloys at high temperatures, we propose that the coupling between bulk high-entropy effects (e.g., high-entropy matrix NiFeCoCr) and the effect of including one (or more) strong GB segregating element(s) (e.g., Zr) can effectively reduce  $\gamma_{GB}$  as the driving force for grain growth, and this effect can occur concurrently with the high-entropy GB effect proposed in Ref. [26] (e.g., introducing additional GB segregating elements like Nb and Mo) to enhance one another. This bulk high-entropy effect is consequence of a competition between GB segregation and bulk precipitation. Specifically, precipitation limits GB segregation. The mixing entropy can effectively lower the free energy of the bulk high-entropy phase with respect to precipitates, thereby increasing the solid solubility of individual segregating elements to allow more reduction in  $\gamma_{GB}$  within the solubility limit.

To examine the above hypotheses, we conducted numerical experiments using a statistical thermodynamic model for multicomponent GB adsorption [26] that is a generalization of the binary Wynblatt-Chatain model [27]; this multicomponent model, as well as a few simplifications adopted, was derived and discussed in the Supplementary Material and it was briefly described (in a more general form) in Ref. [26]. Assuming ideal mixing (as a simplification, which is discussed in the Supplementary Material), the equilibrium GB composition of an  $N$ -component alloy can be obtained *via* a McLean-Langmuir type adsorption equation:

$$\frac{X_{GB}^i}{X_{GB}^1} = \frac{X_{Bulk}^i}{X_{Bulk}^1} \exp\left(-\frac{\Delta h_{ads.(i-1),0}}{kT}\right) \quad (2)$$

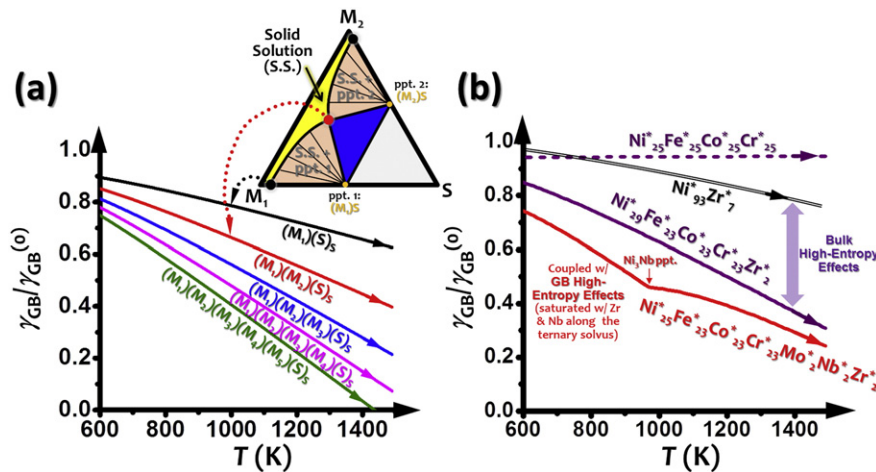
where  $X_{GB}^i$  and  $X_{Bulk}^i$  are the GB and bulk compositions (atomic fractions), respectively, of the  $i$ -th element/component ( $i = 1, 2, \dots, N$ ),  $\Delta h_{ads.(i-1),0}$  is the GB adsorption (segregation) enthalpy (i.e., the enthalpic change of swapping one atom of the  $i$ -th element inside the bulk material with one atom of the first element at the GB, where the “0” in the subscript denotes ideal mixing, which is a simplification adopted here to focus our numerical experiments on the bulk and GB

entropic effects instead of the non-ideal interactions), and  $k$  is the Boltzmann constant. The GB energy can be expressed as:

$$\gamma_{GB} = \gamma_{GB}^{(0)} - 2n + 2n \cdot \sum_{i \neq 1} X_{GB}^i \Delta h_{ads.(i-1),0} \sum_i kTX_{GB}^i \ln\left(\frac{X_{GB}^i}{X_{Bulk}^i}\right) \quad (3)$$

where  $\gamma_{GB}^{(0)}$  is the “clean” GB energy of the first component (without GB adsorption) and  $n$  is the number of atoms per unit area in the atomic plane parallel to the GB. This model has been used to numerically illustrate the high-entropy GB effect [26], where the GB energy can be reduced with increasing temperature when the bulk composition moves along the multicomponent solvus line (for a specimen saturated with many different segregating elements), as shown in Fig. 6 in Ref. [26].

To further illustrate the bulk high-entropy effect (that is distinct from the GB high entropy effect shown in Fig. 6 in Ref. [26]), we first conducted numerical experiments using a hypothetical, symmetrical, ideal, high-entropy solution of  $N$  matrix elements ( $M_i$ ;  $i = 1, 2, \dots, N$ ) and one segregating element ( $S$ ), where stoichiometric line compounds ( $M_i$ ) $S$  can form to limit the solubilities (solvus curve). More details of the model and parameters used are described in the Supplementary Materials and the computed results are shown in Fig. 1(a). The inset of Fig. 1(a) shows that the solid solubility can be increased in the ternary system  $M_1$ - $M_2$ - $S$ , as compared with two binary subsystems,  $M_1$ - $S$  and  $M_2$ - $S$ . Subsequently, Fig. 1(a) shows that increasing  $N$  (the number of matrix elements  $M_i$ ) results in more reduction in  $\gamma_{GB}$  and makes  $d\gamma_{GB}/dT$  more negative to reduce the thermodynamic driving forces for grain growth at high temperatures. Furthermore, Fig. 1(b) shows the computed  $\gamma_{GB}$  vs. temperature curves for several cases, where the bonding and segregation energies were selected to represent the real Ni based alloys (see the Supplementary Material). Fig. 1(b) suggests that a  $Ni_{29}Fe_{23}Co_{23}Cr_{23}Zr_2$  alloy will have substantially lower  $\gamma_{GB}$ , as compared with both a binary counterpart ( $Ni_{93}Zr_7$ ) and the conventional high-entropy counterpart ( $Ni_{25}Fe_{25}Co_{25}Cr_{25}$ ); here, only Zr is a strong segregating element (Supplementary Table S-1). Fig. 1(b) further suggests that adding two additional segregating elements, Nb and Mo, can further reduce  $\gamma_{GB}$  for a  $Ni_{25}Fe_{23}Co_{23}Cr_{23}Mo_2Nb_2Zr_2$  alloy *via* a GB high-entropy effect, in addition to the bulk high-entropy effect to reduce  $\gamma_{GB}$ ; this GB high-entropy effect is evident by the kink in the  $\gamma_{GB}$  vs. temperature curve in Fig. 1(b), below which more reduction in  $\gamma_{GB}$  and more negative  $d\gamma_{GB}/dT$  are a result that both Zr and Nb are saturated so that the bulk composition moves along a ternary solvus line to



**Fig. 1.** (a) The computed  $\gamma_{GB}/\gamma_{GB}^{(0)}$  vs. temperature curves along the bulk solvus curves for symmetrical ideal solutions of 1–5 matrix elements ( $M_i$ ) and one segregating element ( $S$ ). The subscript “s” denotes that all specimens are saturated with element  $S$  at all temperatures (in equilibrium with  $S$ -enriched precipitates). The inset is an isothermal section of a ternary phase diagram, where the binary and ternary compositions on the solvus (labeled by the black and red dots) correspond to the specimen compositions for calculating the first two (black and red) curves. (b) The computed  $\gamma_{GB}/\gamma_{GB}^{(0)}$  vs. temperature curves for several “Ni-like” alloys. Here, the superscripts “\*s” are used acknowledge that the calculations were conducted by using a lattice model with segregation enthalpies and bonding energies to represent real alloys, but with simplifications, to capture the most important trends. The model and parameters are described in the Supplementary Materials. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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