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ORIGINAL REPORT



Origin of high strength in the CoCrFeNiPd high-entropy alloy

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ABSTRACT

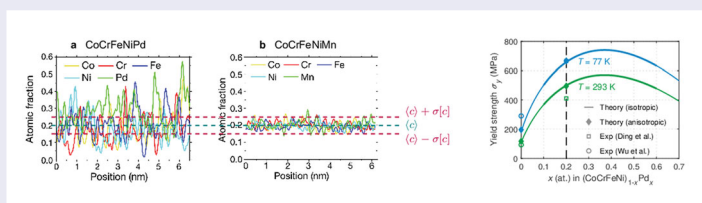
Recent experiments show that the CoCrFeNiPd high-entropy alloy (HEA) is significantly stronger than CoCrFeNi and with nanoscale composition fluctuations beyond those expected for random alloys. These fluctuations were suggested to be responsible for strengthening. Here, a recent parameter-free theory for initial yield strength in fcc random alloys is shown to predict the strength of CoCrFeNiPd in good agreement with experiments. The strengthening is due mainly to the large misfit volume of Pd in CoCrFeNi, indicating that effects of the non-random composition fluctuations are secondary. Analyses of strength variations and strengthening-associated length scales helps rationalize why dislocation motion is insensitive to such fluctuations. These findings point to the value of theory for understanding mechanical behavior of HEAs.

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KEYWORDS

High-entropy alloys; palladium; solute strengthening theory; yield strength



IMPACT STATEMENT

Experiments and theory are highlighting chemical ordering in high-entropy alloys (HEAs) as important for mechanical properties but the high strength in CoCrFeNiPd is predicted here to be achievable in the random alloy due to the large misfit volume of Pd, in spite of observed ordering. Ordering is thus not essential for attaining high-strength HEAs.

Introduction

High-entropy alloys (HEAs) are multicomponent alloys typically having near-equal concentrations of the constituent alloying elements. A number of new HEAs exhibit impressive mechanical properties such as high yield strength, high ultimate strength, high ductility, and/or high fracture toughness [1–4]. These results are driving investigation of a wide range of new alloys, including ‘doping’ with low concentrations of additional elements and non-dilute additions to widen alloy families. For instance, the Co–Cr–Fe–Mn–Ni family of fcc Cantor alloys has been studied over wider ranges of compositions [5] and extended with the addition of dilute Al [6–8], non-dilute V [9,10], and replacement of Mn with Pd to create CoCrFeNiPd [11–14].

The yield strength of CoCrFeNiPd at $T = 293\text{ K}$ and strain rate 10^{-3} s^{-1} was recently reported to be 410 MPa

at grain size $135\text{ }\mu\text{m}$ [14], which is much larger than the strength of CoCrFeNi (166 MPa at similar grain size) [15]. Similar to literature studies of Ni_3Pd [16], nanoscale compositional analysis showed that the atomic distribution of elements in the CoCrFeNiPd alloy is non-random (see Figure 1) over length scales of 1 nm [14]. It was thus asserted that the $2.5\times$ increase in strength of CoCrFeNiPd above CoCrFeNiMn (strength close to that of CoCrFeNi) is due to the non-random concentration variations (SRO), which were not observed in lower-strength CoCrFeNiMn (see Figure 1) or in CoCrNi.

Here we show that the measured strength in CoCrFeNiPd is well-predicted using the recent solute strengthening theory for random alloys. This parameter-free predictive theory for yield strength is within the framework of random alloys (without SRO), and has been successfully applied to a range of fcc HEAs [17–22].

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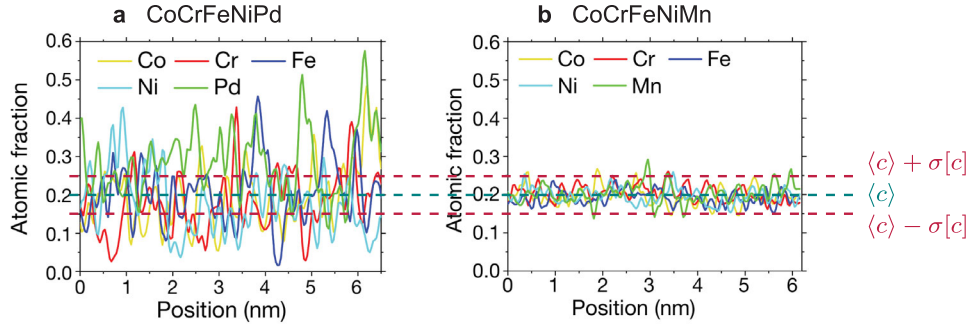


Figure 1. Solute concentrations versus position along $[\bar{1}12]$ in one $(\bar{1}\bar{1}1)$ atom plane, obtained from EDS line scans, in two HEAs (a) CoCrFeNiPd and (b) CoCrFeNiMn. The specimen thickness along $[110]$ is ~ 15 nm, leading to $N \approx 60$ atoms in each atom column. In a random alloy, the solute concentration in any finite domain of N atoms fluctuates around the mean value $\langle c \rangle = \bar{c}$ with a standard deviation $\sigma[c] = \sqrt{\bar{c}(1 - \bar{c})/N}$. For $\bar{c} = 0.2$ and $N = 60$, $\sigma[c] \approx 0.05$. The measured fluctuations in CoCrFeNiMn are consistent with the random alloy while those in CoCrFeNiPd show significantly larger fluctuations, typically two standard deviations (± 0.10) and larger, as indicated in the figure. Note that the average Pd concentration in this particular region of the CoCrFeNiPd alloy actually exceeds the nominal concentration $\bar{c} = 0.2$. Figure adapted from Ding et al. [14], reprinted by permission from Springer Nature.

The theory reveals the centrality of solute misfit volumes, over all other material properties, in strengthening. For instance, recent work [22] shows that the significant measured increases in strength due to V additions to various Co-Cr-Fe-Mn-Ni alloys can be attributed to the large atomic volume of V, leading to large misfit volumes and then high strengthening. Quantitatively, the theory predicts the strength of CoNiV in good agreement with experiment (399 MPa predicted; 383 MPa experiments), while the strength of CoCrNi is much lower (128–195 MPa predicted; 150–210 MPa experiments) and the strength of CoCrFeNi is even lower (107 MPa predicted; ~ 92 MPa experiments). Similarly, the origin of the high strength in CoCrFeNiPd here is due primarily to the large atomic/misfit volume of Pd in CoCrFeNi. The observed non-random concentration fluctuations are not necessary for strengthening. The reason that dislocations may be insensitive to such fluctuations is also discussed. We then conclude with a brief discussion of the value of theory for alloy design and discovery.

The justification for considering a random-alloy theory applied to a known non-random alloy follows from thinking about alloy processing routes. Starting from a solid-solution alloy in the random state at high temperature, quenching to low temperature would preserve the random order. The random alloy would then have some yield strength σ_y^{random} . Thermal aging, natural aging, or slow cooling, rather than quenching, could then induce various types or levels of chemical SRO that may or may not be detectable experimentally. With such SRO, the yield strength of the alloy would be σ_y^{SRO} . The difference between σ_y^{SRO} and σ_y^{random} would then reflect the net effects of SRO on strengthening. If $\sigma_y^{\text{SRO}} \approx \sigma_y^{\text{random}}$,

then the effects of SRO are either negligible or the SRO somehow significantly changes the microscopic strengthening mechanisms but not the macroscopic strength. In either case, there is no practical gain in strength due to the SRO. Thus, comparison of the predicted strength σ_y^{random} versus the measured strength provides a crucial insight into whether or not SRO is actually important for strength in an alloy. Here, we show indeed that $\sigma_y^{\text{SRO}} \approx \sigma_y^{\text{random}}$ for CoCrFeNiPd, and that the factor of $2.5\times$ increase in strength compared to random CoCrFeNi can be attributed to the effects of Pd as a large-misfit solute, independent of any non-random concentration fluctuations in the alloy.

Solute strengthening theory

The theory for yield strength in a random alloy is based on the fundamental interaction energy between a dislocation and the atoms composing the alloy, all of which act as solutes in a hypothetical homogeneous version of the same alloy. The random arrangement of solutes gives rise to spatially-fluctuating concentrations at all length scales. A dislocation in the alloy minimizes its energy by becoming wavy, finding regions of random concentration fluctuations that lower the dislocation energy but at the expense of additional energy due to the increased dislocation line length. A characteristic wavelength $4\zeta_c$ and amplitude $w_c/2$ emerge naturally from the analysis [23]. Because the dislocation has lower energy in the regions over length ζ_c and faces barriers created by unfavorable regions at distance w_c along the glide direction, the dislocation motion is thermally activated. This leads to a temperature and strain-rate dependent yield stress with an activation volume that scales with $\zeta_c w_c b$ where b is the dislocation Burgers vector. The general theory for alloy

yield strength was reduced to an analytical model using the elastic approximation for the solute/dislocation interaction energy U^n of a type- n solute as $U^n = -p\Delta V_n$, where ΔV_n is the misfit volume of the type- n solute in the N -component alloy of composition $\{c_n\}$ and p is the (spatially varying) pressure field generated by the dislocation at the solute position. For fcc alloys, with dislocations dissociated into two partials separated by a stacking fault of width d , the theory predicts the zero-temperature shear yield stress τ_{y0} and the energy barrier ΔE_b (associated with dislocation segment of length ζ_c) given by

$$\begin{aligned}\tau_{y0} &= 0.01785 \left[\frac{\Gamma}{b^2} \right]^{-1/3} \left[\mu_{\text{alloy}} \frac{1 + \nu_{\text{alloy}}}{1 - \nu_{\text{alloy}}} \right]^{4/3} \\ &\quad \times \left[\frac{\sum_n c_n \Delta V_n^2}{b^6} \right]^{2/3}, \\ \Delta E_b &= 1.5618 \left[\frac{\Gamma}{b^2} \right]^{1/3} b^3 \left[\mu_{\text{alloy}} \frac{1 + \nu_{\text{alloy}}}{1 - \nu_{\text{alloy}}} \right]^{2/3} \\ &\quad \times \left[\frac{\sum_n c_n \Delta V_n^2}{b^6} \right]^{1/3},\end{aligned}\quad (1)$$

and a predicted tensile yield stress of

$$\sigma_y(T, \dot{\epsilon}) = 3.06\tau_{y0} \left[1 - \left(\frac{kT}{\Delta E_b} \ln \frac{\dot{\epsilon}_0}{\dot{\epsilon}} \right)^{2/3} \right]. \quad (2)$$

Here, $\dot{\epsilon}_0 = 10^4 \text{ s}^{-1}$ is a reference strain rate; 3.06 is the Taylor factor for untextured isotropic fcc polycrystals; μ_{alloy} and ν_{alloy} are the isotropic shear modulus and Poisson's ratio of the alloy; $\Gamma = \alpha\mu_{\text{alloy}}b^2$ is the edge dislocation line tension, with $\alpha = 0.125$ accurate for a number of fcc alloys. The above results are based on an edge dislocation and are independent of the stacking fault width for $d > 6b$. TEM results on 60° dislocations in CoCrFeNiPd show $d = 2.3\text{--}4.5 \text{ nm} \gg 6b = 1.56 \text{ nm}$ [14], making the above results valid for this alloy. The underlying length scales of the predicted wavy dislocation can be computed as

$$\begin{aligned}w_c &= [\pi/(2^{5/2} - 1)]^{1/3} [\Delta E_b^2/(\Gamma b\tau_{y0})]^{1/3}, \\ \zeta_c &= (\pi \Delta E_b)/(2w_c b\tau_{y0}).\end{aligned}\quad (3)$$

The application of the theory thus only requires the solute misfit volumes, the alloy elastic constants, and the alloy lattice constant. The details of the full and reduced theory can be found in Ref. [17,18,20].

Results

To obtain the misfit volumes of the elements, we follow the successful strategy of Ref. [17]. The apparent volumes $\{V_n\}$ of Co, Cr, Fe, and Pd in Ni are determined from

Table 1. Apparent volumes of each element in fcc HEAs, as deduced from room temperature experimental lattice constants of Ni-X alloys.

	fcc apparent volumes V_n ($\text{\AA}^3$)
Pd	15.3
Cr	12.27 ^a
Fe	12.09 ^a
Co	11.12 ^a
Ni	10.94 ^a

^aVarvenne et al. [17].

Vegard's law ($V_{\text{alloy}} = \sum_n c_n V_n$) and literature data on $\text{Ni}_{1-x}\text{X}_x$ binaries up to $x = 0.4$ [17,24], as summarized in Table 1. Application of Vegard's law and the volumes in Table 1 accurately captures the alloy atomic volumes for CoCrFeNiPd ($12.344 \text{ \AA}^3$ vs. $12.130\text{--}12.358 \text{ \AA}^3$ experiment [11,14]) and CoCrFeNiPd₂ ($12.837 \text{ \AA}^3$ vs. $12.733 \text{ \AA}^3$ experiment [11]). The solute misfit volumes ΔV_n are then computed as $\Delta V_n = V_n - V_{\text{alloy}}$. Table 1 shows that the apparent volume of Pd ($15.3 \text{ \AA}^3$) is much larger than those of all other alloying elements, immediately implying a large increase in yield strength upon Pd addition. The Pd apparent volume of $15.3 \text{ \AA}^3$ is larger than that in pure fcc Pd ($14.7 \text{ \AA}^3$ at room temperature [24]), a result supported by our DFT studies of Ni_2Pd (executed as in Ref. [21] using VASP-SQS [25,26] and EMTO-CPA [27]).

The elastic constants of CoCrFeNiPd must be determined. The single crystal and/or isotropic polycrystal elastic constants of fcc Ni, CoNi, CoCrNi, CoCrFeNi, and pure Pd are shown in Table 2. Ni, CoNi, CoCrNi, and CoCrFeNi are quite similar while Pd is significantly softer. The addition of Pd to CoCrFeNi should thus lead to softening. The polycrystalline shear modulus of CoCrFeNiPd μ^{poly} was only estimated as $\sim 89 \text{ GPa}$ [14], and so is uncertain. Thus, we have computed the anisotropic elastic constants C_{ij} of all the relevant alloys using DFT. Table 2 shows the results along with available experimental data. Based on C_{ij} , the Voigt-Reuss-Hill (VRH) shear modulus μ^H and Poisson's ratio ν^H are also computed (see Table 2). The DFT results are in broad agreement with experiments for all alloys. Most importantly, both CoCrFeNiPd and Ni_2Pd show significant softening relative to CoCrFeNi and Ni, respectively, as expected.

We now make strength predictions for random CoCrFeNiPd with no adjustable parameters. We compute the alloy lattice constant and misfit volumes based on Table 1 and use the DFT elastic constants C_{ij} for the alloy directly. As shown in Nag et al. [31], the strength of elastically anisotropic alloys is accurately predicted by using (i) the Voigt-averaged isotropic elastic constants, $\mu^V = (C_{11} - C_{12} + 3C_{44})/5$, $\nu^V = (C_{11} + 4C_{12} - 2C_{44})/(4C_{11} + 6C_{12} + 2C_{44})$, in Equation (1);

Table 2. Elastic constants of various fcc metals, as measured from room temperature and/or low-temperature experiments and computed from DFT (vasp-SQS). μ^H and ν^H are Voigt-Reuss-Hill average. μ^{poly} and ν^{poly} are polycrystal elastic moduli. C_{ij} and μ are in GPa.

		C_{11}	C_{12}	C_{44}	Shear modulus		Poisson's ratio	
					μ^H	μ^{poly}	ν^H	ν^{poly}
Ni	Exp RT	251 ^a	150 ^a	124 ^a	86	76 ^e	0.297	0.31 ^e
	Exp OK	261 ^a	151 ^a	132 ^a	93		0.287	
	DFT	276	154	125	94		0.293	
CoNi	Exp RT	248 ^b	157 ^b	132 ^b	86	84 ^e	0.301	0.29 ^e
	Exp OK	269 ^c	161 ^c	141 ^c	96		0.290	
	DFT	278	162	144	100		0.286	
CoCrNi	Exp RT	249 ^d	156 ^d	142 ^d	91	87 ^e	0.291	0.30 ^e
	Exp OK	261 ^c	159 ^c	150 ^c	97		0.284	
	DFT	262	163	139	92		0.297	
CoCrFeNi	Exp RT	—	—	—	—	84 ^e	—	0.28 ^e
	DFT	219	126	130	86		0.268	
CoCrFeNiPd	DFT	208	125	107	73		0.293	
Ni ₂ Pd	DFT	236	151	95	69		0.330	
Pd	Exp RT	227 ^a	176 ^a	72 ^a	47	44 ^f	0.386	0.39 ^f
	Exp OK	234 ^a	176 ^a	71 ^a	50		0.383	
	DFT	199	148	72	48		0.369	

^aSimmons et al. [28].

^bLeamy et al. [29].

^cProf. K. Tanaka (Kobe University), personal communication, 2018.

^dJin et al. [30].

^eWu et al. [15].

^fVarvenne et al. [20].

(ii) the shear modulus for fcc slip $\mu_{110/111} = (C_{11} - C_{12} + C_{44})/3$ in the dislocation line tension Γ ; and (iii) a small anisotropy correction based on the Zener anisotropy $A = 2C_{44}/(C_{11} - C_{12})$. (See Ref. [32] for details.) From the DFT C_{ij} , we obtain $\mu^V = 80.8$ GPa, $\nu^V = 0.275$, $\mu_{110/111} = 63.3$ GPa, and $A = 2.6$ for CoCrFeNiPd. The predicted strength of CoCrFeNiPd at $T = 293$ K and experimental strain rate 10^{-3} s^{-1} is shown in Figure 2 along with the experimental value. The prediction of 495 MPa is in generally good agreement with the one experimental value 410 MPa, with no adjustable parameters. The theory is fully temperature and strain-rate dependent. With the same elastic constants, Figure 2 also shows the prediction of the strength at $T = 77$ K, and excellent agreement is obtained. In prior applications [17], the theory usually underestimates the strength at $T = 77$ K, as seen in Figure 2 for CoCrFeNi (at $x = 0$, predicted also with DFT C_{ij}), for reasons discussed in Ref. [17]. The good agreement at $T = 77$ K may thus be in part due to the overestimate of CoCrFeNiPd strength at $T = 293$ K.

From the above analysis, we can conclude that the non-random composition fluctuations observed in CoCrFeNiPd provide no significant strengthening relative to the random alloy. The large increase in strength relative to CoCrFeNi is simply a consequence of the large misfit volume of Pd in CoCrFeNi with only a small decrement due to the reduced alloy elastic moduli. The theory

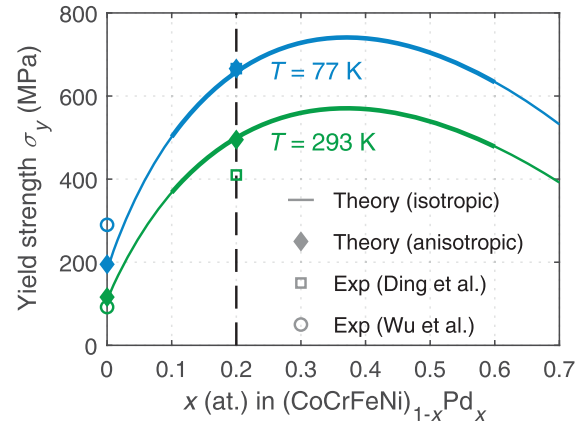


Figure 2. The prediction of initial yield strength of pseudo-binary alloy $(\text{CoCrFeNi})_{1-x}\text{Pd}_x$ as a function of x , at loading strain rate 10^{-3} s^{-1} and various temperatures. Here, isotropic theory uses the ROM polycrystal elastic moduli; the anisotropic theory predictions are based on DFT C_{ij} . The experimentally measured yield strengths [14,15] are also indicated. For CoCrFeNi, the strengths shown are from Hall-Petch extrapolation to infinite grain size; for CoCrFeNiPd, the strengths are from experiments at grain size of $135 \mu\text{m}$.

is not perfect (typical deviations in other applications being $\pm 15\%$) and the experiments of CoCrFeNiPd are on polycrystals with grain size $\sim 135 \mu\text{m}$ while the theory is for infinite grain size. Nonetheless, these differences are minor compared to the fact that 20 at.% addition of Pd to CoCrFeNi leads to a significant $\sim 2.5\times$ increase in

the yield stress at room temperature according to both experiments and theory.

We now examine why the alloy may be insensitive to such fluctuations. The experimental alloy shows concentration fluctuations, predominantly for Pd. We use the theory further to show that the expected variations in strength across a range of pseudo-binary (CoCrFeNi)_{1-x}Pd_x alloys is relative small. The theory is applied using the misfit volumes as before (from Table 1) and the simple rule-of-mixtures (ROM) approximation for the alloy elastic moduli,

$$\begin{aligned}\mu_{\text{alloy}} &= (1-x)\mu_{\text{CoCrFeNi}} + x\mu_{\text{Pd}}, \\ B_{\text{alloy}} &= (1-x)B_{\text{CoCrFeNi}} + xB_{\text{Pd}}, \\ \nu_{\text{alloy}} &= \frac{3B_{\text{alloy}} - 2\mu_{\text{alloy}}}{2(3B_{\text{alloy}} + \mu_{\text{alloy}})}.\end{aligned}\quad (4)$$

Using the DFT-based μ^H and ν^H , the ROM elastic moduli for CoCrFeNiPd are computed as $\mu_{\text{ROM}}^H = 78$ GPa and $\nu_{\text{ROM}}^H = 0.288$. The DFT ROM shear modulus μ_{ROM}^H agrees fairly well with the full DFT result μ^H (78 GPa vs. 73 GPa), typically within $\sim 15\%$ higher as found in previous studies [21]. The ROM applied to Ni₂Pd gives similar conclusions. This indicates the reliability of using the ROM to estimate the elastic constants of (CoCrFeNi)_{1-x}Pd_x alloys. In the predictions below, the elastic constants are calculated from ROM (Equation (4)) and the room temperature polycrystal moduli of CoCrFeNi and Pd.

The predicted strength vs. Pd composition x using the isotropic theory (Equation (1)) is shown in Figure 2. At $x = 0$ and $x = 0.2$, the isotropic results are very close to the anisotropic predictions of CoCrFeNi and CoCrFeNiPd as discussed above. The strengthening associated with Pd concentrations in excess of $x = 0.2$ is not significantly greater than that at $x = 0.2$. The maximum predicted strengthening is at $x = 0.35$ and exceeds that at $x = 0.2$ by only 70 MPa. The theory predicts that this alloy system is relatively insensitive to concentration variations of Pd in the range $x = 0.1$ – 0.6 . Similar conclusions are found at $T = 77$ K.

Moving beyond the pseudo-binary, thermodynamic studies [33] showed that interactions between Pd and both Ni and Co are repulsive, and these have the largest volume differences. Conversely, Pd forms intermetallic phases with both Fe and Cr, and these have the smallest volume differences. Therefore, concentration variations that are deficient/enhanced in Ni and Co and enhanced/deficient in Pd, Fe, and Cr could be expected to arise. However, for example, the predicted strength for Co_{0.1}Cr_{0.2}Fe_{0.2}Ni_{0.1}Pd_{0.4} is only 57 MPa higher, and that of Co_{0.29}Cr_{0.14}Fe_{0.14}Ni_{0.29}Pd_{0.14} is only 43 MPa lower,

than the equi-composition alloy (assuming the same elastic moduli). Thus, an alloy that has non-random concentration fluctuations with Ni/Co enhanced and deficient regions would have a strength comparable ($\pm 10\%$) to the random equi-composition alloy.

The insensitivity of strength to concentration variations on the scale of 1 nm can further be rationalized by considering the length scales ζ_c and w_c that control strength in the random alloy. The predicted ζ_c is the scale over which the dislocation can respond to, and take advantage of, concentration fluctuations in the random alloy. The inability of the dislocation to have a shorter wavelength is due to the additional line tension cost of such configurations. In CoCrFeNiPd, we predict $\zeta_c \approx 6$ nm for the edge dislocation, which is much longer than the length scales of the concentration fluctuations (1 nm). While a dislocation in the non-random alloy can attempt to become wavier in response to smaller-scale non-random concentrations fluctuations, there is an energetic (line tension) cost that inhibits such behavior.

Discussion and conclusions

The observation of non-random composition fluctuations in the CoCrFeNiPd HEA is interesting. However, we show that the high strengthening in this alloy can be understood qualitatively and quantitatively by considering the random alloy, which represents the strength of the alloy before any processing-induced ordering effects have occur. We further show that the predicted strength is relatively insensitive to composition variations while the predicted length scale ζ_c relevant for strengthening in the random alloy suggest that dislocation motion may be insensitive to concentration fluctuations on much smaller scales. It remains possible that the strength in the non-random CoCrFeNiPd alloy is controlled by the non-random solute distributions via some mechanism(s) not yet established. However, this could only be verified by quantitative parameter-free predictions of the strength based on that mechanism, which would nonetheless have essentially the same strength as an initial quenched random alloy.

Inhomogeneous (non-random) concentration variations may be important for other mechanical phenomena. However, this remains to be demonstrated explicitly. For instance, the work in Ref. [13,14] on CoCrFeNiPd and CoCrNi reported significant cross-slip observed in TEM in both alloys but only CoCrFeNiPd has non-random concentration fluctuations. Recent theoretical work [34] suggests that the barriers for cross-slip can be much lower in HEAs as compared to elemental metals with the same average stacking fault energy due to

the energy fluctuations associated with random concentration fluctuations. Thus, enhanced cross-slip does not appear to be significantly altered by concentration fluctuations.

Finally, we put our findings here in a broader context of general importance to researchers working in complex alloys. First, predicting alloy strength using the random alloy model provides an *a priori* assessment of the possible strength in any HEA of interest; this is useful for alloy design and ideation. For instance, Varvenne et al. considered pseudo-ternaries alloys (e.g. (RhIr)-(NiCu)-(AgAu)) in the Rh-Ir-Pd-Pt-Ni-Cu-Ag-Au family. They used the simple Vegard's law and fcc elemental atomic volumes and isotropic elasticity, and then identified compositions in the region around (RhIr)_{0.38}(NiCu)_{0.38}(AgAu)_{0.24} with predicted strengths of ~ 1 GPa due to the large size differences between (NiCu) and (AgAu) and the added benefit of the stiffness of (RhIr) [20]. Closer to the present alloys, a AuNi₃ alloy is estimated to have a strength of 918 MPa due to the large size difference between Au and Ni. While not addressing phase stability, the theory quickly provides promising domains for examination. Second, the experimental verification of any chemical ordering is extremely difficult. Researchers should understand that, as shown here, the presence of chemical order may be of limited importance (unlike in precipitation alloys that achieve long-range order) and so not worth the cost of investigation. Third, if experiments do show notable deviations from the predictions of the random alloy, then it becomes important and useful to probe the origins for such differences. For instance, new work shows that the AuNiPdPt alloy has an exceptional strength of ~ 1300 MPa as compared to a predicted strength, using estimates based on fcc atomic volumes, of 513 MPa [35]. In-depth study of any such alloys may then uncover new mechanisms of strengthening and thus open entirely new avenues for discovery of complex non-random alloys with promising properties. These points highlight the multifaceted power of theory: it can be used to predict performance *a priori* within a set of broadly applicable assumptions but, if it fails for any given system, it can point toward directions for new mechanisms beyond those embedded in the theory.

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

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