

Predicting the solid solubility limit in high-entropy alloys using the molecular orbital approach

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High-entropy alloys (HEAs) are currently at the research frontier of metallic materials. Understanding the solid solubility limit in HEAs, such a highly concentrated multicomponent alloy system, is scientifically intriguing. It is also technically important to achieve desirable mechanical properties by controlling the formation of topologically or geometrically closed packed phases. Previous approaches to describe the solid solubilities in HEAs could not accurately locate the solubility limit and have to utilize at least two parameters. Here, we propose to use a single parameter, the average energy of d-orbital levels, Md , to predict the solid solubility limit in HEAs. It is found that Md can satisfactorily describe the solid solubilities in fcc structured HEAs containing 3d transition metals, and also in bcc structured HEAs. This finding will greatly simplify the alloys design and lends more flexibility to control the mechanical properties of HEAs. When 4d transition metals are alloyed, Md alone cannot describe the solid solubility limit in fcc structured HEAs, due to the large increase of the bond strength that can be gauged by the bond order, Bo . The potential opportunities and challenges with applying the molecular orbital approach to HEAs are discussed. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935620>]

I. INTRODUCTION

High entropy alloys (HEAs), or multi-principal-element alloys, emerge in recent years as a new category of metallic materials.^{1–3} HEAs represent a ground breaking alloy design strategy in that there exist more than one or two principal elements in these alloys, fundamentally different to the situation in conventional alloys, where, for example, Fe dominates in steels, and Ti and Al are the two principal elements in TiAl-based intermetallics. The new alloy design concept intrigued great interest from researchers in the materials, metallurgy, and even condensed matter physics field, as it leads to an enormously unexplored compositional space, and potentially new materials with new structural and functional properties. During the last decade, the research towards HEAs has gradually become the frontier of advanced metallic materials, with more new alloy systems being developed, and more exciting mechanical and functional properties being discovered.^{4–9} Particularly, HEAs are widely regarded as very promising for becoming the new generation of high-temperature materials, mainly due to their compositional flexibility to improve the oxidation and corrosion resistance, and their excellent softening resistance and sluggish diffusion kinetics,^{6,7,10,11} at elevated temperatures. Having said that, however, HEAs are not yet to be able to replace current high-temperature materials, since in most of the HEA systems, the conflict between strength and ductility formulates the bottleneck for their engineering applications,^{12,13} and the high materials cost (high purity is normally required, and a large amount of basically all constituent elements) and high densities are also serious concerns.⁸ Essentially, the difficulties that are encountered by HEAs are

all related to the alloy design strategy in HEAs: know how to choose suitable constituent elements for desired phase constitution and the appropriate amount of them, and to replace expensive/heavier elements with cheaper/lighter elements if their effect can be comparable.

The phases formed in HEAs tend to be simple multi-component solid solutions, as the solid solutions are stabilized by the high entropy of mixing (this is how HEAs get their name) at high temperatures, and they can be easily frozen to the room temperature when prepared by solidification,^{1,11} the most commonly used method to prepare HEAs at the moment. In most cases, the formed solid solutions are of fcc and bcc structure, and a mixture of them,^{6,11} although in some cases other structured solid solutions also form.^{14–16} Fcc structured HEA solid solutions are known to be quite ductile, but their strength is low; bcc structured HEAs are much stronger, but quite often this high strength is accompanied by the brittleness, particularly under tension. This above mentioned conflict is still a big challenge to be tackled for the engineering application of HEAs. From the alloy design point of view, the formation of fcc or bcc solid solutions in HEAs can now be reasonably controlled by tuning the valence electron concentration (VEC),¹³ where adding elements of higher VEC can favor the fcc solid solutions, while adding element of lower VEC tends to favor the bcc solid solutions. However, the VEC rule is only valid when the alloying products are solid solutions: although the high mixing entropy is quite effective in stabilizing the formation of solid solutions, it cannot exclude the formation of intermetallic compounds, and in some conditions amorphous phases can also form.^{17–20} The current alloy design strategies to control the formation of solid solutions, intermetallics, and amorphous phases are essentially inherited from those used

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historically for binary solid solutions and metallic glasses, i.e., utilizing the atomic size mismatch, the mixing enthalpy, the electronegativity, variations or combinations of them, etc.²¹ Out of various parametric alloy design guidelines, a two-parameter δ - ΔH_{mix} approach is widely used in the HEA community,^{19,22} where δ describes the atomic size mismatch

$$(\delta = \sqrt{\sum_{i=1}^n c_i (1 - r_i / \sum_{j=1}^n c_j r_j)^2},$$

n is the number of alloying elements, c_i is the atomic percentage for the i th element, r_i or r_j is the atomic radius for the i th or j th element), and ΔH_{mix} is the averaged mixing enthalpy ($\Delta H_{mix} = \sum_{i=1, j>i}^n 4\Delta H_{AB}^{mix} c_i c_j$,

ΔH_{AB}^{mix} is the enthalpy of mixing for the binary equiatomic AB alloys). The δ - ΔH_{mix} approach (and also some other parametric approaches) can quite reasonably delineate the formation of solid solutions, intermetallic compounds, and amorphous phases in HEAs merely from given alloy compositions:^{19,21} solid solutions form when δ is small and ΔH_{mix} is not significantly negative, and almost on the opposite amorphous phases form at large δ and quite negative ΔH_{mix} , although the formation of amorphous phases is also known to depend on the kinetic factors. Intermetallic compounds form in the intermediate conditions in terms of δ and ΔH_{mix} , or in other words, there exists an overlapping region in the two-dimensional δ - ΔH_{mix} map where both solid solutions and intermetallics can form, and both intermetallics and amorphous phases can form.¹⁹ There is certainly a need to avoid such an overlapping between solid solutions and intermetallics from the alloy design point view. On the one hand, it relates to the more strict definition of what HEAs are,²³ and on the other hand, from at least the mechanical properties perspective, it is desirable to be able to control the formation of intermetallic compounds, particularly topologically closed-pack (TCP) phases and geometrically closed-pack (GCP) phases, since these TCP and GCP phases have been known to play a critical role in strengthening or embrittling conventional alloys.²⁴

The search for new guidelines to distinguish the formation of solid solutions and intermetallic compounds, and more specifically, the TCP and GCP phases, constitutes the motivation and target of this work. Alternatively, it can be said that we aim to locate the solid solubility limit in HEAs. We intend to explore the possibility of using the parameter Md , the average energy level of the d orbitals of the alloying transition metals,^{25,26} an effective parameter to predict the phase boundary between solid solutions and TCP/GCP phases in transition-metal-based alloys such as Ni-based, Co-based, and Fe-based alloys, to delineate the solid solubility in HEAs. An obvious reason for trying this parameter is because HEAs normally comprise mainly transition metals. In Secs. II–V, we will first give a brief introduction to the Md method and its success in non-HEAs, and then apply this parameter to test its usefulness for the prediction of solid solubility in fcc and bcc structured HEAs, before some discussions and the final conclusion are made.

II. THE Md METHOD

The parameter Md and its application to the estimation of solid solubility are clearly introduced in a seminal paper

by Morinaga *et al.*²⁵ There were several motivations behind this relatively new parameter at the time when it was proposed: using the electronegativity and atomic size mismatch (by Hume-Rothery *et al.*²⁷ and Darken and Gurry²⁸) and the electron vacancy numbers of the d bands (the so-called PHACOMP method by Decker²⁹) encountered many problems when addressing to alloy systems containing transition metals; the electronegativity and the atomic size parameters are not independent of each other; the electron vacancy number does not include a reflection of the atomic size factor; and also very importantly, the use of only one parameter, instead of more parameters, is quite appealing. Morinaga *et al.* also critically pointed out that in previous methods to estimate the solid solubilities, the alloying effect and the nature of the second-phase precipitates were not considered, and features associated with the transition metals should be taken into consideration when designing new parameters. The parameter Md , a d-electron parameter, was then proposed to estimate the solubility limit of terminal solid solutions in transition-metal-based alloys (the new PHACOMP method³⁰), on the basis of discrete-variational DV-X α molecular orbital method for calculations of the electronic structure and properties of molecules.²⁶ The d-orbital energy level of an alloying transition metal, M, in a base metal, X, can be obtained from the cluster calculation. For example, in the case of a pure Fe cluster, the levels of $8e_g$ to $16t_{2g}$ originate mainly from the Fe 3d orbitals and form the Fe 3d band where the Fermi energy level lies.²⁶ In the case of an alloyed Fe cluster, new energy levels mainly due to the d-orbitals of the alloying transition metal appear above the Fermi energy level. These levels are called Md levels, and their energy height changes systematically with the order of elements in the periodic table. The Md levels correlate with the electronegativity and the atomic radius of elements in that the Md levels increase as the electronegativity of the alloying element decreases, and increase with increasing atomic radius of the element. The average energy of these two d-orbital levels, e_g and t_{2g} , is referred to as Md . The Md values are listed in Table I, for various commonly used transition metals (M) in fcc Ni, bcc Fe, and bcc Cr (X).^{26,31} It is noted that in Table I, Al and Si are non-transition metals, and their Md values are determined from the interpolation of the curve of Md versus the metallic radius, and therefore, they are only empirical values. The average value of Md for alloys is defined by taking the compositional average, $Md = \sum_{i=1}^n c_i (Md)_i$. When

Md increases beyond a critical value, the Md method assumes that the phase instability will occur and that a secondary phase will appear in a terminal solid solution. In other words, a single parameter, the critical Md value determines the solubility limit of the terminal solid solution and also depends on the type of the secondary phase. Also, as the solid solubility changes with the temperature, the critical Md value also depends on the temperature, but the dependence is normally weak. The Md method has been proven quite useful in predicting the phase boundaries of terminal solid solutions in fcc structured Ni-based alloys, Co-based alloys, and Fe-based alloys.²⁵ The situation becomes more complicated for bcc

TABLE I. List of Md and Bo for commonly used transition metals in HEAs.^{26,31,32}

Element	M in fcc Ni		M in bcc Fe		M in bcc Cr		
	Md (eV)	Bo	Md (eV)	Bo	Md (eV)	Bo	
3 d	Ti	2.271	1.098	2.497	2.325	2.87	5.109
	V	1.543	1.141	1.61	2.268	1.998	5.041
	Cr	1.142	1.278	1.059	2.231	1.301	4.938
	Mn	0.957	1.001	0.854	1.902	0.752	4.801
	Fe	0.858	0.857	0.825	1.761	0.694	4.548
	Co	0.777	0.697	0.755	1.668	0.658	4.496
	Ni	0.717	0.514	0.661	1.551	0.213	4.276
	Cu	0.615	0.272	0.637	1.361	-0.346	4.123
4 d	Zr	2.944	1.479	3.074	2.551	3.359	5.475
	Nb	2.117	1.594	2.335	2.523	2.662	5.403
	Mo	1.55	1.611	1.663	2.451	1.968	5.286
5 d	Hf	3.02	1.518	3.159	2.577	4.518	5.517
	Ta	2.224	1.67	2.486	2.57	3.605	5.471
	W	1.655	1.73	1.836	2.512	2.768	5.368
others	Re	1.267	1.692	1.294	2.094	2.037	5.221
	Al	1.9	0.533	1.034 ^a	...	1.034 ^b	...
	Si	1.9	0.589	1.034	0	1.034 ^b	...

^a Md for Al in bcc Fe cannot be found. The same Md value of 1.034 for Si was assumed for Al, as Md for Al and Si in fcc Ni are determined from interpolation of the curve of Md vs. metallic radius, and they are of the same value.

^bNo values of Md for Al and Si in bcc Cr can be found. The same Md values for Al and Si in bcc Fe were then assumed for them in bcc Cr.

structured alloys though, where another alloying parameter, bond order, Bo ,²⁶ which can also be obtained from the cluster calculation, has to be also considered. Bo is a measure of the strength of the covalent bond between M and X atoms, and Bo also changes according to the position of elements in the periodic table (a list of Bo for various elements in fcc Ni, bcc Fe, and bcc Cr is given in Table I). The main reason for the complication in bcc alloys is due to the more significant second-nearest-neighbor interaction, and shorter second-nearest-neighbor interatomic distance that is only 15% larger than the first-nearest-neighbor distance, while in fcc alloys this distance is 41% larger and hence the second-nearest-neighbor interactions are much less significant. The description of solid solubilities in bcc structured Fe and Cr alloys using Md and Bo were discussed in Refs. 31 and 32. In all previous efforts to correlate Md (and Bo) with the solid solubilities, the context was set to terminal solid solutions. Can the Md method be extended to highly concentrated alloys, such as HEAs? And more importantly and more interestingly, can it solve the inadequate capabilities of current alloy design approaches, such as the two-parameter $\delta - \Delta H_{mix}$ plot, to accurately delineate the solid solubilities, or the phase boundaries between solid solutions and intermetallic compounds, in HEAs? Below we will apply the Md method to fcc and bcc structured HEAs, and test how it works in these concentrated alloy systems. Bo is not the focus of this work, and we only mention Bo when it is helpful for the discussion.

III. Md AND SOLID SOLUBILITIES IN HEAs

To test the effect of the parameter Md on predicting the phase boundaries between solid solutions and TCP/GCP

TABLE II. Phase constitutions in fcc structured HEAs containing 3 d transition metals only, together with their mixing enthalpy, ΔH_{mix} , atomic size mismatch, δ , and d-orbital energy level, Md .

Alloy system	Phase	$\Delta H_{mix}/$ (kJ·mol ⁻¹) δ * 100				Reference
		ΔH_{mix}	δ	Md		
CoCrCuFeNi	fcc	3.20	1.03	0.822	34	
CoCrCu _{0.5} FeNi	fcc	0.49	0.83	0.845	37	
CoCrFeMnNi	fcc	-4.16	3.27	0.89	2	
CoCrFeNi	fcc	-3.75	0.30	0.874	38	
CoCrCuFeNiTi _{0.5}	fcc	-3.70	4.81	0.954	39	
Al _{0.3} CoCrCuFeNi	fcc	0.16	3.42	0.883	34	
Al _{0.5} CoCrCuFeNi	fcc	-1.52	4.16	0.92	34	
CoCrCuFeMnNi	fcc	1.44	2.99	0.844	2	
CoCuFeNiV	fcc	-2.24	2.20	0.902	22	
Al _{0.25} CoCrCu _{0.75} FeNi	fcc	-0.71	3.24	0.886	40	
Al _{0.5} CoCrCu _{0.5} FeNi	fcc	-4.60	4.36	0.95	40	
Al _{0.25} CoCrFeNi	fcc	-6.75	3.47	0.934	41	
Al _{0.375} CoCrFeNi	fcc	-7.99	4.11	0.961	41	
Al _{0.5} CoCrCuFeNiV _{0.2}	fcc	-2.50	4.14	0.942	42	
CoCrFeNiTi _{0.3}	fcc	-8.89	4.34	0.971	43	
CoCrFeNiSi _{0.05}	fcc	-5.49	0.88	0.886	44	
CoCrFeNiSi _{0.1}	fcc	-7.14	1.20	0.899	44	
CoCrFeNiSi _{0.15}	fcc	-8.70	1.44	0.911	44	
CoCrFeNiSi _{0.25}	fcc	-11.62	1.80	0.934	44	
CoCrFeNiTi _{0.5}	fcc+ σ +Laves+R	-11.56	5.32	1.029	43	
CoCrCuFeNiTi _{0.8}	fcc+Laves	-6.75	5.69	1.022	39	
CoCrCuFeNiTi	fcc+Laves	-8.44	6.10	1.063	39	
Co _{1.5} CrFeNi _{1.5} Ti _{0.5}	fcc+ η	-10.74	4.87	0.978	45	
Al _{0.3} CoCrFeNiTi _{0.1}	fcc+ η	-8.93	4.39	0.975	46	

phases in HEAs, we scrutinized a decent number of HEA systems where fcc solid solutions and fcc solid solutions plus TCP/GCP phases (σ phase, R phase, μ phase, and Laves phase/ η phase), and also bcc solid solutions and bcc solid solutions plus TCP phases (σ phase and Laves phase) are formed. All chosen alloys are prepared by the casting route, the most commonly used materials preparation method, to simplify the data interpretation by avoiding the interruption from the material preparation aspect. The chosen alloy systems are listed in Tables II–IV, in the sequence of fcc structured HEAs containing 3 d elements only (for transition metals), fcc structured HEAs containing also 4 d elements,

TABLE III. Phase constitutions and d-orbital energy level, Md , in fcc structured HEAs containing 4 d transition metals.

Alloy system	Phase	Md	Reference
CoCrFeMo _{0.3} Ni	fcc	0.921	47
Al _{0.3} CoCrFeMo _{0.1} Ni	fcc	0.959	46
CoCrFeMo _{0.5} Ni	fcc + σ	0.949	47
Co _{1.5} CrFeMo _{0.5} Ni _{1.5} Ti _{0.5}	fcc + σ	1.025	48
Co _{1.5} CrFeMo _{0.8} Ni _{1.5} Ti _{0.5}	fcc + σ	1.05	48
CoCrFeMo _{0.85} Ni	fcc + σ + μ	0.992	47
CoCrFeNb _{0.103} Ni	fcc + Laves	0.905	49
CoCrFeNb _{0.155} Ni	fcc + Laves	0.92	49
CoCrFeNb _{0.206} Ni	fcc + Laves	0.934	49
CoCrFeNb _{0.309} Ni	fcc + Laves	0.963	49
CoCrFeNb _{0.412} Ni	fcc + Laves	0.99	49
Co _{1.5} CrFeMo _{0.1} Ni _{1.5} Ti _{0.5}	fcc + η	0.988	45 and 48

TABLE IV. Phase constitutions and d-orbital energy level, Md , in bcc structured HEAs. Md for elements (M) in both fcc Fe and bcc Cr (X) are adopted for the calculation.

Alloy system	Phase	Md (in bcc Fe)	Md (in bcc Cr)	Reference
Al ₃ CoCrCuFeNi	bcc	0.88	0.703	34
AlCoCrCu _{0.25} FeNi	bcc	0.856	0.726	22
Al _{1.25} CoCrFeNi	bcc	0.875	0.792	50
Al _{1.5} CoCrFeNi	bcc	0.882	0.803	50
Al ₂ CoCrFeNi	bcc	0.895	0.822	50
Al _{2.5} CoCrFeNi	bcc	0.905	0.839	50
Al ₃ CoCrFeNi	bcc	0.915	0.853	50
Al _{0.5} CrFe _{1.5} MnNi _{0.5}	bcc	0.888	0.826	51
CoCrCuFeMnNiSi _{0.2}	bcc	0.806	0.561	52
AlCoCrFeMo _{0.1} Ni	bcc	0.882	0.803	53
AlCoCrFeNb _{0.1} Ni	bcc	0.896	0.817	54
AlCoCrFe _{0.6} Mo _{0.5} Ni	bcc + σ	0.948	0.903	55
AlCoCrFeMo _{0.5} Ni	bcc + σ	0.939	0.888	55
AlCoCrFe _{1.5} Mo _{0.5} Ni	bcc + σ	0.93	0.872	55
AlCoCrFe ₂ Mo _{0.5} Ni	bcc + σ	0.922	0.858	55
AlCo _{0.5} CrFeMo _{0.5} Ni	bcc + σ	0.958	0.911	56
AlCoCrFeMo _{0.5} Ni	bcc + σ	0.939	0.888	56
AlCo _{1.5} CrFeMo _{0.5} Ni	bcc + σ	0.924	0.869	56
AlCoCrFeNb _{0.25} Ni	bcc + Laves	0.937	0.87	54
AlCoCrFeNb _{0.5} Ni	bcc + Laves	1	0.951	54
AlCoCrFeNb _{0.75} Ni	bcc + Laves	1.058	1.025	54

and bcc structured HEAs. The listed phase constitutions are mainly determined by the X-ray diffraction method. For the calculation of Md values in Tables II and III, Md values for various alloying elements (M) in fcc Ni (X)^{25,26} are used and all chosen alloy systems contain Ni. This can be understood that we treat the solid solubilities in Ni-M pseudo binary systems, where M here are alloy components other than Ni. According to Morinaga *et al.*, these Md values are less sensitive to the choice of the base element (X) in transition metal based fcc structured alloys, i.e., being they Ni, Co, or Fe.²⁵ All chosen fcc structured alloy compositions that are listed in Tables II and III contain Ni, as otherwise the assumption of Ni-M pseudo binary systems is invalid. However, for bcc structured alloys, Md values are sensitive to the choice of the base element (see Table I). As an example, here we choose two base elements, Fe and Cr (X), and the Md values for various elements (M) in both bcc Fe and bcc Cr (X) from Table I are used for the calculation in Table IV, and of course all chosen alloys contain both Fe and Cr.^{26,31,32} We will show later that the choice of base element does not affect the existence of threshold Md values separating the solid solution and TCP phases, and it is simply a matter of shifting the threshold Md values when choosing different base elements, Fe or Cr in this case.

To compare with the two-parameter $\delta - \Delta H_{mix}$ approach, δ and ΔH_{mix} for fcc structured HEAs containing 3 d elements only are also listed in Table II. Figure 1 shows the two-dimensional $\delta - \Delta H_{mix}$ plot delineating the phase formation in fcc structured HEAs containing 3d elements only. All fcc solid solutions form in the shaded region ($\delta \leq 0.066$, $\sim -11.6 < \Delta H_{mix} < 3.2$ kJ/mol), where it has been shown previously within which solid solution phases can form.¹⁹ However, TCP and GCP phases can also form in this region,

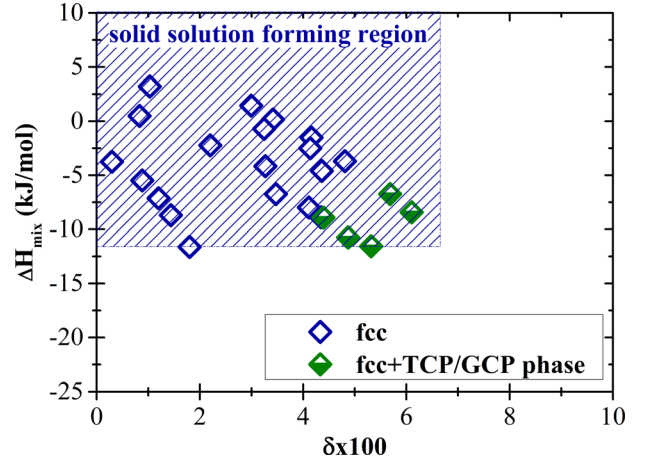


FIG. 1. $\delta - \Delta H_{mix}$ plot delineating the phase formation in fcc structured HEAs containing 3 d elements only.

indicating the requirements on δ and ΔH_{mix} are necessary conditions, but not sufficient conditions to form solid solutions in HEAs. This is exactly the motivation for us to search for new parameters to replace the $\delta - \Delta H_{mix}$ approach, to robustly determine the solid solubility limits in HEAs.

Figure 2 shows the application of the parameter Md to fcc structured HEAs containing 3 d transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) only. Interestingly, there exists a clearly defined critical Md value, ~ 0.97 , below which only fcc solid solutions form, and beyond which TCP/GCP phases such as the σ phase, Laves phase, R phase and η phase will form. This result is certainly exciting, as it shows the possibility of using a simple and single parameter to predict the solid solubility limit in fcc structured HEAs, the most studied HEA systems. The convergence of critical Md values between fcc solid solutions and different TCP/GCP phases is also surprising, as, for example, in terminal solid solutions, the critical Md values vary in different alloy systems. The critical Md for the γ/σ phase boundaries in Ni-based superalloys is 0.915, and it is 0.90 in γ/μ phase boundaries in Co-based alloys and in γ/σ phase boundaries in Fe-based alloys.²⁵ The lack of well-defined solvent and solutes, and

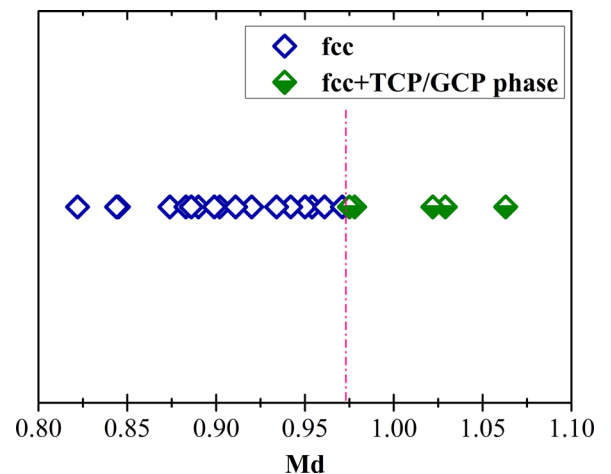


FIG. 2. The parameter Md and the phase formation in fcc structured HEAs containing 3 d transition metals only.

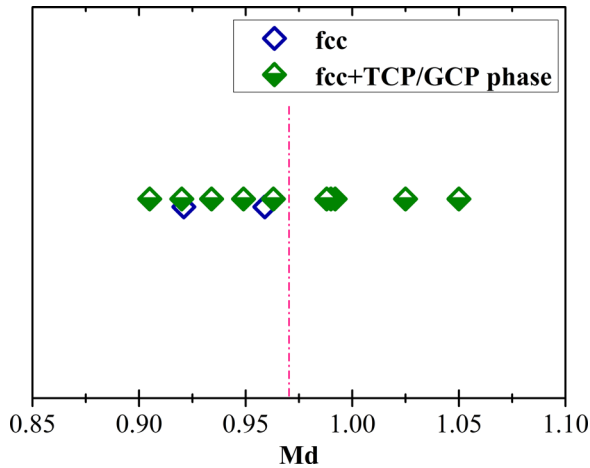


FIG. 3. The parameter Md and the phase formation in fcc structured HEAs containing 4 d transition metals.

the multi-principal-element nature of solid solutions in HEAs probably render the critical Md in different alloy systems converge to the similar value. The higher critical Md value (0.97) in HEAs, compared to those in conventional alloys, can be understood by the enhanced solid solubility in HEAs and hence the increased compositional average. The situation, however, becomes more complicated when 4 d transition metals (Nb and Mo) are alloyed. As seen in Fig. 3, although TCP/GCP phases (σ phase, Laves phase, and μ phase/ η phase) are almost the same as those in the alloys containing 3 d elements only, a clearly defined phase boundary in terms of Md is not existing. The fcc solid solution seems to still form below the critical Md of 0.97 (the robustness of this argument needs more data to support though), but TCP/GCP phases can form in a wide range of Md values, down to much lower Md than 0.97. This abnormality can be very possibly connected to the larger bond strength, or Bo of 4 d elements Nb and Mo (in fcc Ni, Table I), similar to the situation occurring to bcc alloys. For example, Morinaga *et al.* showed that the solid solubility in bcc Fe cannot be described by Md only, and Bo has to be taken into consideration.³² They also pointed out that a large increase of Bo by alloying can lead to the occurrence of more closely packed phases such as the Laves phase, hence restricting the solid solubility.³² This scenario is also observed in the fcc structured HEAs containing 4 d elements, as in almost all those alloys with low solid solubilities (forming TCP phases at low Md), the Laves phase formed. It can be envisaged that when 5 d elements, Hf, Ta, and W, are alloyed into fcc structured HEAs, the chances are that the solid solubility in these 5 d elements containing alloy systems would be low as well, since Hf, Ta, and W also have large Bo .

Naturally, it would be expected that the parameter Md alone cannot describe the solid solubilities in bcc structured HEAs.³² However, very surprisingly, Fig. 4 shows that Md alone can indeed work quite effectively, in both bcc Fe and bcc Cr (assumed X), with different critical Md values of ~ 0.92 and ~ 0.86 , respectively, even when 4 d elements Nb and Mo are present. The phase boundaries are between bcc solid solutions and TCP phases, the σ phase and the Laves

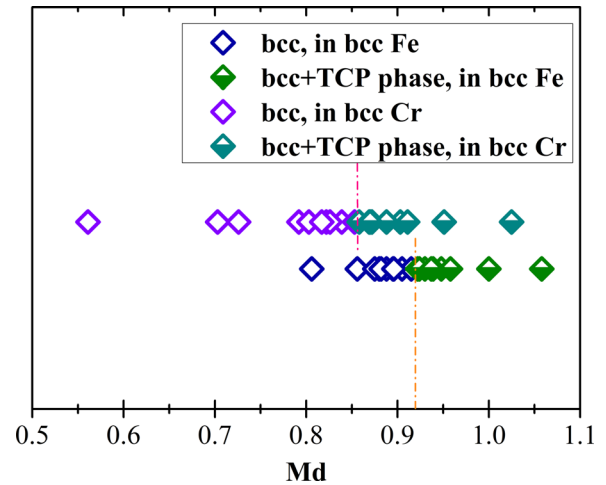


FIG. 4. The parameter Md and the phase formation in bcc structured HEAs. Md for elements (M) in both fcc Fe and bcc Cr (X) are adopted.

phase. For comparison, the critical Md value to form the Laves phase in Cr-Mo ferritic alloys ($X = \text{Fe}$) is ~ 0.85 ,³³ lower than 0.92 in HEAs. We currently do not have a definite answer to why adding 4 d elements does not cause any issue, as in the case of fcc structured HEAs containing 4 d elements. Certainly, this unexpected result will be subject to further inspections when more data are available. However, one note can already be added here. In bcc structured HEAs, the ordering of the bcc phase almost accompanies its formation and quite often, NiAl-like B2 phase (β) forms as the result of such ordering.³⁴ Morinaga *et al.* once noted that the Md method cannot only be applied to GCP phase such as γ' and η , but also to β -NiAl ($\gamma/(\gamma + \beta)$ phase boundary).²⁵ If one considers the formation of β -NiAl phase as the secondary phase in bcc alloys, then the phase boundaries between bcc solid solutions and intermetallic compounds will definitely be blurred. However, it is practically difficult to tell critically whether β -NiAl phase forms or not in bcc structured HEAs, from quick structural identification methods like the X-ray diffraction, due to their normally weak superlattice diffraction intensities in HEAs.³⁴ Therefore, we made it clear in Fig. 4 that the critical Md values are between bcc solid solutions and TCP phases, and we did not consider the complication by the β phase in this case.

IV. DISCUSSION

A. How about Bo is used together with Md ?

Previously, it was claimed that the parameter Md needs to be combined with Bo , to describe the solid solubilities in bcc alloys. Here, in fcc structured HEAs, we also argued that Md alone cannot explain the low solid solubilities in 4 d elements containing alloy systems, and we ascribed that to the large Bo of 4 d elements. However, this explanation is qualitative in nature and does not offer much quantitative information to account for the solid solubility limit in 4 d and even 5 d elements containing HEAs. Will Md together with Bo lead to a better prediction? Using again the 4 d elements containing fcc structured HEAs as an example (Table III), Fig. 5 shows the $Md - Bo$ plot for the phase formation in

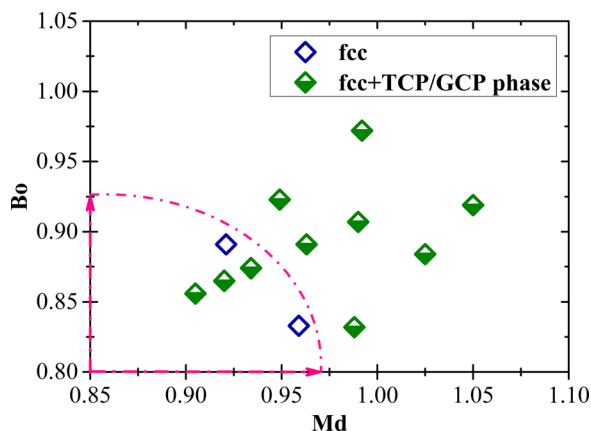


FIG. 5. The $Md - Bo$ plot and the phase formation in fcc structured HEAs containing 4d transition metals.

these systems. The dashed-dotted line defined region ($Md < 0.97$, $Bo < 0.93$) therefore can be assumed to delineate the solid solubility limit. Comparing Fig. 5 with Fig. 3, the $Md - Bo$ plot does improve the solubility limit prediction by using the parameter Md alone, however, the Laves phase is still seen to form in this region, indicating that the problem is not solved. There remains a challenge on how the molecular orbital approach can be further improved, to account for the difficulty in predicting the solid solubility limit when alloying of 4d and 5d elements in fcc structured HEAs, and possibly also in bcc structured HEAs, causes the large increase of Bo .

B. The potential of applying the molecular orbital approach to HEAs

The molecular orbital approach can be of significant importance beyond predicting the solid solubility limit. It can also be used to design alloys with desirable mechanical properties. For example, in commercial cast Ni alloys, the 0.2% yield strength shows a maximum at Md : ~ 0.98 and Bo : ~ 0.67 , the creep strength also shows a maximum around this position, and all of the single crystal superalloys are located near the position.²⁶ Every alloy around such a position contains a large volume fraction (about 60%) of the γ' phase, without any TCP phase precipitating in it, resulting in the high strength of the alloy.²⁶ TUT92 and other second-generation single-crystal superalloys, such as PWA 1484 and CMSX-4, are located in a very limited region around Md : 0.985 and Bo : 0.665.²⁶ Similarly, the alloy design in HEAs can be correlated with the molecular orbital approach, like the use of $Md - Bo$ plot for cast Ni alloys. Such a correlation remains to be established and verified for HEAs. The molecular orbital approach can also be used to guide the modification of alloy compositions in HEAs, by utilizing the equivalence of elements in terms of Md and Bo . This was exemplified in the modification from PWA 1480, the first-generation superalloy, to PWA 1484, the second-generation superalloy.²⁶ The Cr content of PWA 1484 decreases by 6 mol. %, whereas the Re content increases by 1 mol. % compared to the respective values of PWA 1480. Further decrease of the Cr content and corresponding increase of the

Re content lead to René N6, the third-generation superalloy. The molecular orbital approach is thus expected to greatly advance the alloy design in HEAs.

There are a few notes relevant to applying the $Md (Bo)$ parameter to HEAs that we want to further clarify here. First, on the choice of base elements and the criterion of Md values, as said in Section III, the choice of base elements has a small effect on the Md values in fcc structured HEAs, and using Ni as the base element can be a good option, if the target alloy systems contain Ni. In bcc structured HEAs, the choice of different base elements does have a noticeable effect on the Md values, but it does not change the existence of the threshold Md value; it simply shifts the threshold Md value. For example, in Fe-containing bcc structured HEAs, a threshold Md value of 0.92 using Fe as the base element exists, so when one designs solid solution forming Fe-containing HEAs, one simply designs the Md to be less than 0.92. Similarly, for solid solution forming Cr-containing HEAs, one designs the Md (using Cr as the base element) to be less than 0.86. As long as one is aware of the choice of the base element (Fe or Cr in this case), and what is the threshold Md value (0.92 or 0.86) according to the choice of the particular base element, using the Md method to design HEAs is straightforward, and the different threshold Md values are not a concern. Second, for cases beyond what we exemplify here, essentially, our work is providing a methodology, and not giving all solutions, as giving all solutions in one work is almost unlikely. We show examples on how the Md method can be used to design solid solution forming HEAs without the formation of TCP/GCP phases. More specifically, for the fcc structured HEAs case, we use Ni as the base element and for the bcc case, we use both Fe and Cr as base elements. In cases one needs to use the Md method to design new bcc structured HEAs without Fe and Cr, one cannot use the threshold values of 0.92 or 0.86 anymore, as these two threshold values only work if Fe or Cr is present and the assumption of Fe-M or Cr-M pseudo-binary alloys is therefore valid. Assuming these new bcc structured HEAs contain Ti, such as derivatives of the refractory TaNbHfZrTi alloy,³⁵ what one needs to do, when designing bcc solid solution forming refractory alloys, is firstly to find out the threshold Md value from a sizeable database of Ti-containing bcc-structured HEAs, using bcc-Ti as the base element,³⁶ then to design the Md to be smaller than this identified threshold Md value. This process is exactly what we exemplify here, and also applies to other HEA systems. We do not use these refractory HEAs to exemplify the application of the Md method to bcc structured HEAs due to two considerations: (1) this work aims to find the phase boundary between the bcc solid solution and TCP phases. There currently lack sufficient data for refractory HEAs (containing the same element that can be assumed as the base element, e.g., Ti) for this purpose, as most reported refractory HEAs are in the bcc solid solution side and not so much in the bcc solid solution plus TCP phase side. Statistically, more data points are required to generate a convincing conclusion; and (2) although Md and Bo have been used for the alloy design in Ti-based alloys (not HEAs), the phase boundary is rather between, like bcc-Ti (β -Ti) and hcp-Ti (α -Ti), than between

the solid solution and TCP phases. To avoid the unnecessary confusion, we choose to use bcc-Fe and bcc-Cr, rather than bcc-Ti, as the base element for the exemplification purpose. However, how much the Md method can help the alloy design of refractory HEAs is an interesting topic, and we are now working on that direction.

V. CONCLUSIONS

Understanding solid solubility limits is critical for the alloy design in HEAs, considering the need to achieve the single-phase solid solution and to control the formation of TCP/GCP phases. In this work, the molecular orbital approach previously applied to describe the solid solubilities in transition-metal-based terminal solutions is first applied to HEAs. It was found that the single parameter Md , the d-orbital energy level, can well describe the solubility limit in fcc structured HEAs containing 3d transition metals only. The critical Md value of 0.97 is higher than that in terminal solid solutions, due to the enhanced solid solubility in HEAs. Md alone, however, cannot describe the solid solubilities in fcc structured HEAs containing 4d elements, as alloying of these 4d elements will cause a large increase of bond order, Bo , measuring the strength of covalent bonds. The use of two parameter $Md - Bo$ plot can improve the prediction of solid solubility limit when 4d elements are alloyed, but the problem remains and needs further work. Surprisingly, Md alone can describe the solid solubilities in bcc structured HEAs, even when 4d elements are present. This statement, however, also needs more data to support, and the complication by the formation of β -NiAl phase requires further clarification. Overall, the molecular orbital approach offers new opportunities to advance the alloy design in HEAs, although the approach itself needs also to be advanced.

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