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Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys

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Phase stability is an important topic for high entropy alloys (HEAs), but the understanding to it is very limited. The capability to predict phase stability from fundamental properties of constituent elements would benefit the alloy design greatly. The relationship between phase stability and physicochemical/thermodynamic properties of alloying components in HEAs was studied systematically. The mixing enthalpy is found to be the key factor controlling the formation of solid solutions or compounds. The stability of fcc and bcc solid solutions is well delineated by the valence electron concentration (VEC). The revealing of the effect of the VEC on the phase stability is vitally important for alloy design and for controlling the mechanical behavior of HEAs. © 2011 American Institute of Physics. [doi:10.1063/1.3587228]

I. INTRODUCTION

High entropy alloys (HEAs) constitute a new type of metallic alloys for structural and particularly high-temperature applications, due to their high hardness, wear resistance, high-temperature softening resistance and oxidation resistance.^{1–3} HEAs are typically composed of more than five metallic elements in equal or near-equal atomic ratios, and interestingly they tend to form solid solution structure (mainly fcc and/or bcc) rather than multiple intermetallic compounds as expected from general physical metallurgy principles. They were termed as HEAs because the entropy of mixing is high when the alloying elements are in equiatomic ratio, and it was initially believed that the high entropy of mixing leads to the formation of the solid solution structure rather than intermetallic compounds.

The generally used alloying elements in HEAs are fcc-type Cu, Al, Ni, bcc-type Fe, Cr, Mo, V and hcp-type Ti, Co (crystal structure at ambient temperature). When these alloying elements are mixed with different combination, or with same combination but different amount of certain elements, fcc, bcc or mixed fcc and bcc structures may form. For example, cast CoCrCuFeNi (in atomic ratio, same afterwards) has the fcc structure while AlCoCrCuFeNi has the fcc+bcc structure;⁴ and the amount of Al in the Al_xCoCrCuFeNi system can tune the crystal structure from fcc to fcc+bcc and to fully bcc.⁴ The structure directly affects the mechanical properties, and to take again the Al_xCoCrCuFeNi system as an example: with increasing x , the structure changes from fcc to fcc+bcc and finally to bcc; the hardness and strength increase with the increasing amount of bcc phases but the alloys get brittle.^{4,5} Although the embrittlement mechanism by bcc phases still needs further exploration, it is certainly important to be able to control the formation of bcc phases. The target of this work is hence to

find out the physical parameters that control the stability for the fcc and bcc phases in HEAs.

II. ANALYSIS

Wang *et al.* briefly discussed the reason of addition of Al in the Al_xCoCrCu_{1-x}FeNiTi_{0.5} system causing the structural transition from fcc to bcc.⁶ They claimed that the alloying of larger Al atoms introduces the lattice distortion energy, and the formation of a lower atomic-packing-efficiency structure, such as bcc, can decrease this distortion energy. This does make sense but is far away from being satisfactory; besides, it can not quantitatively predict when the bcc structure will form as a function of Al additions. Ke *et al.* claimed that, in the Al_xCo_yCr₂Cu_{0.5}Fe_vNi_w system, Ni and Co are fcc stabilizers and Al and Cr are bcc stabilizers; 1.11 Co is equivalent to Ni as the fcc stabilizers and 2.23 Cr is equivalent to Al for the bcc stabilizers. Furthermore, if the equivalent Co % is greater than 45 at. %, the alloy has an fcc structure, and the alloy has a bcc structure if the equivalent Cr % is greater than 55 at. %.⁷ This empirical rule is useful but it has no scientific merits and is valid only for the specific alloy systems. The establishment of scientific principles to control the crystal structures in HEAs can also contribute to the alloy design of HEAs with desirable properties. For example, we can use less expensive Ni to partially or completely replace more expensive Co; or we can reduce the amount of Cu which is known to cause segregation issue because the mainly positive enthalpy of mixing between Cu and other alloying elements.⁴

As a test to the equivalency of Ni and Co as fcc stabilizers, we prepared a series of Al_xCrCuFeNi₂ ($0.2 \leq x \leq 1.2$) alloys to study the effect of Al amount on the phase stability in this alloy system, in comparison to the well studied Al_xCoCrCuFeNi system. The alloys were prepared by arc-melting a mixture of the constituent elements with purity better than 99.9% in a Ti-gettered high-purity argon atmosphere. Repeated melting was carried out at least five times to

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improve the chemical homogeneity of the alloy. The molten alloy was drop-cast into a 10 mm diameter copper mold. The phase constitution of the alloy was examined by X-ray diffractometer using Co radiation (Bruker AXS D8 Discover). The X-ray diffraction patterns are shown in Fig. 1 where it is clear that at $x \leq 0.8$, the alloys have a single fcc structure and the bcc phase starts to appear at $x = 1.0$. In the $\text{Al}_x\text{CoCrCuFeNi}$ system, fully fcc structure is obtained at $x \leq 0.5$ and bcc phase starts to appear at $x > 0.8$.⁴ The experimental results indicate that Co is not necessarily required in obtaining the solid solution structure in HEAs, which is good for alloy design from economy concerns. This new alloy system also provides more data to study the phase stability in HEAs, ideally from the consideration of the fundamental properties of constituent alloying elements.

Zhang *et al.* studied the relationship between the phase stability and the atomic size difference, δ ($= 100 \sqrt{\sum_{i=1}^N c_i(1 - r_i/\bar{r})^2}$, $\bar{r} = \sum_{i=1}^N c_i r_i$, where c_i and r_i are atomic percentage and atomic radius of the i th component), and also the mixing enthalpy, ΔH_{mix} ($= \sum_{i=1}^n \sum_{j \neq i} \Omega_{ij} c_i c_j$, $\Omega_{ij} = 4\Delta_{\text{mix}}^{AB}$, where Δ_{mix}^{AB} is the mixing enthalpy of binary liquid AB alloys) for multi-component alloys.⁸ They found that the solid solution tends to form in the region delineated by $-15 \text{ KJ/mol} \leq \Delta H_{\text{mix}} \leq 5 \text{ KJ/mol}$ and $1 \leq \delta \leq 6$. The requirement of atomic size difference for formation of the solid solution structure is not surprising as basically it is in line with the well established Hume-Rothery rule.⁹ Other two requirements from the Hume-Rothery rule to form the solid solution are electronegativity and electron concentration. Fang *et al.* defined the electronegativity difference in a multi-component alloy system as $\Delta\chi (= \sqrt{\sum_{i=1}^n c_i(\chi_i - \bar{\chi})^2}$, $\bar{\chi} = \sum_{i=1}^n c_i \chi_i$, where χ_i is the Pauling electronegativity for the i th component).¹⁰ The effect of electron concentration is a little bit more complex. There are basically two definitions of the electron concentration: average number of itinerant electrons per atom, e/a , and the number of total electrons

including the d -electrons accommodated in the valence band, valence electron concentration or VEC.^{11,12} e/a or VEC for a multi-component alloy can be defined as the weighted average from e/a or VEC of the constituent components: $e/a = \sum_{i=1}^n c_i(e/a)_i$ or $\text{VEC} = \sum_{i=1}^n c_i(\text{VEC})_i$, where $(e/a)_i$ and $(\text{VEC})_i$ are the e/a and VEC for the individual element. Hume-Rothery rule works with the e/a definition and e/a has clear effect on the crystal structure for the so-called *electron compounds* or *Hume-Rothery compounds*.⁹ However, the HEAs comprise mainly transition metals (TMs) and e/a for TMs are very controversial.¹¹ Very recently, Mizutani reviewed the various definitions of e/a for TMs and concluded that e/a for TMs are small positive numbers.¹¹ Unfortunately, not all e/a for TMs have been determined and e/a for a TM element even varies in different environment. For convenience, VEC was used here to study the electron concentration effect on the phase stability in HEAs.

III. RESULTS

Following Zhang *et al.*'s method,⁸ the atomic size difference, δ , and the mixing enthalpy, ΔH_{mix} for the $\text{Al}_x\text{CoCrCuFeNi}$ ⁴ and $\text{Al}_x\text{CrCuFeNi}_2$ systems are plotted in Fig. 2. The electronegativity difference, $\Delta\chi$, and VEC are also plotted to show how these factors referred in the Hume-Rothery rule affect the solid solution formation. ΔH_{mix} , $\Delta\chi$ and VEC are all plotted as a function of δ in Fig. 2 for convenience, and this does not indicate these parameters are mutually dependent. For comparison, δ , ΔH_{mix} , $\Delta\chi$ and VEC for three additional systems of HEAs [CoCrCuFeNiTi_x (see Ref. 13), $\text{Al}_{0.5}\text{CoCrCuFeNiTi}_x$ (see Ref. 14), $\text{Al}_{0.5}\text{CoCrCuFeNiV}_x$ (see Ref. 15)], where compounds will form in the originally fcc-typed alloy by increasingly doping the amount of one alloying element (Ti or V), are also plotted in Fig. 2. The calculation required physicochemical and thermodynamic

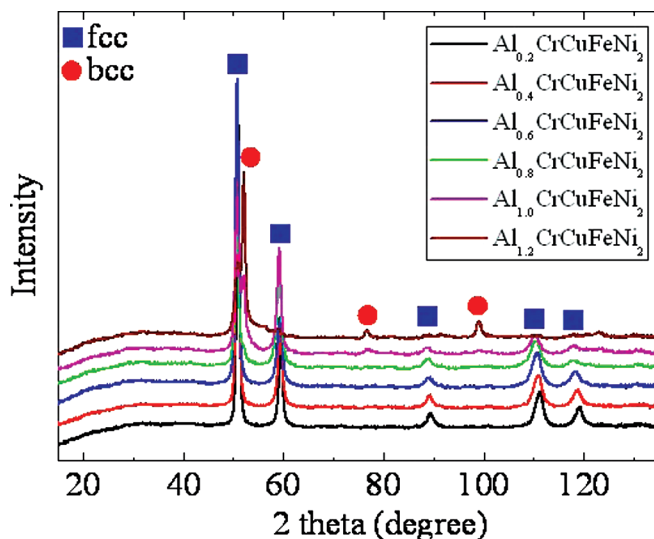


FIG. 1. (Color online) X-ray diffraction patterns for $\text{Al}_x\text{CrCuFeNi}_2$ alloys ($x = 0.2 \sim 1.2$).

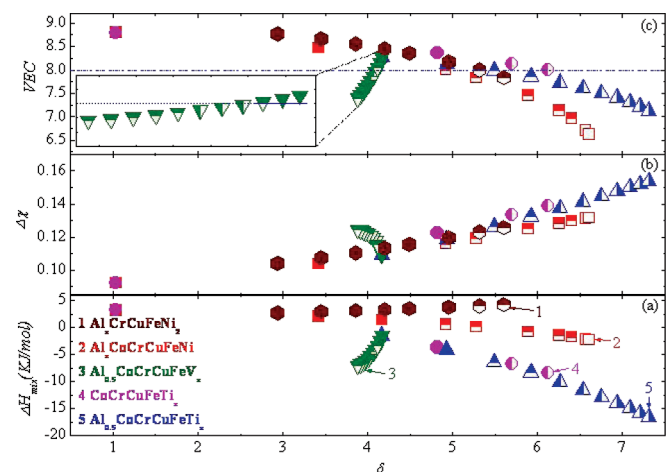


FIG. 2. (Color online) Relationship between the mixing enthalpy, ΔH_{mix} (a), the Electronegativity, $\Delta\chi$ (b) and the valence electron concentration, VEC, (c), and the atomic size difference, δ , for five HEA systems: $\text{Al}_x\text{CoCrCuFeNi}$, CoCrCuFeNiTi_x , $\text{Al}_{0.5}\text{CoCrCuFeNiTi}_x$, $\text{Al}_{0.5}\text{CoCrCuFeNiV}_x$, and $\text{Al}_x\text{CrCuFeNi}_2$. Note on the legend: fully closed symbols for sole fcc phases; fully open symbols for sole bcc phase; top-half closed symbols for mixtures fcc and bcc phases; left or right-half closed symbols for phases containing at least one compound phase (left or right half simply indicates different types of compounds).

TABLE I. Physiochemical properties for commonly used elements in HEAs.

Element	Atom radius (Å)	Pauling electronegativity	VEC
Al	1.432	1.61	3
B	0.820	2.04	3
C	0.773	2.55	4
Co	1.251	1.88	9
Cr	1.249	1.66	6
Fe	1.241	1.83	8
Mn	1.350	1.55	7
Mo	1.363	2.16	6
Nb	1.429	1.6	5
Ni	1.246	1.91	10
Ta	1.430	1.50	5
Ti	1.462	1.54	4
V	1.316	1.63	5
W	1.367	2.36	6

parameters for the constituent alloying elements are from Refs. 16–19 and some of them are listed in Table I.

As seen from Fig. 2, using the definitions of atomic size difference, mixing enthalpy, valence electron concentration and electronegativity defined here, ΔH_{mix} is the only effective parameter that can predict the formation of sole solid solutions (hence no formation of compounds) in HEAs. Solid solution form when $-5 \text{ KJ/mol} \leq \Delta H_{\text{mix}} \leq 5 \text{ KJ/mol}$, and compounds would form once ΔH_{mix} is more negative. On the other hand, δ , $\Delta\chi$ and VEC all fail to effectively predict the formation of solid solution phases or compounds. Figure 2 provides some clues to obtain the solely solid solution structure in HEAs based simply on the fundamental properties of constituent elements. This is certainly useful but from Fig. 2 it is still unclear when the bcc phase will form and what is the determining factor controlling the bcc phase formation.

A careful examination of Fig. 2, however, suggests that bcc phases start to form when VEC reaches ~ 8.0 [Fig. 2(c)]. The other three parameters, ΔH_{mix} , δ , and $\Delta\chi$ do not behave such a clear indicator function. To make the point clearer, VEC for three HEA systems, $\text{Al}_x\text{CoCrCuFeNi}$ (see Ref. 4), $\text{Al}_x\text{CoCrCu}_{0.5}\text{FeNi}$ (see Ref. 7), and $\text{Al}_x\text{CoCrCuFeNi}_2$ (this work) in which increasingly doping of the same element Al would cause phase constitution from sole fcc to mixed fcc

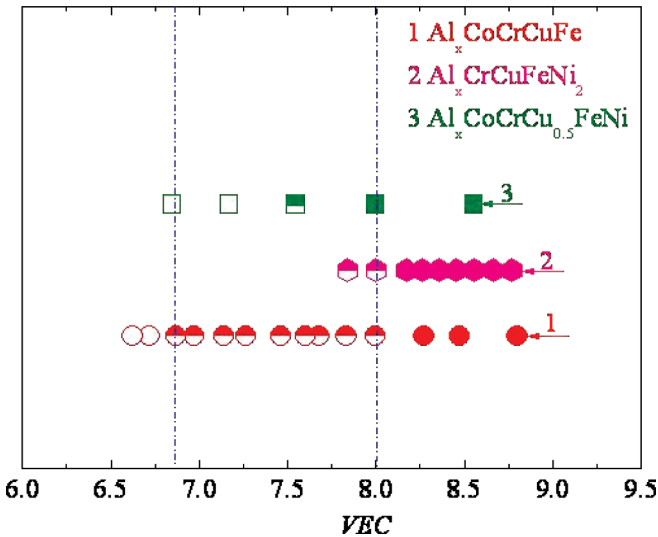


FIG. 3. (Color online) Relationship between VEC and the fcc, bcc phase stability for three HEA systems: $\text{Al}_x\text{CoCrCuFeNi}$, $\text{Al}_x\text{CrCuFeNi}_2$ and $\text{Al}_x\text{CoCrCu}_{0.5}\text{FeNi}$. Note on the legend: fully closed symbols for sole fcc phases; fully open symbols for sole bcc phase; top-half closed symbols for mixes fcc and bcc phases.

and bcc, are plotted in Fig. 3. Figure 3 clearly shows that VEC can be used to quantitatively predict the phase stability for fcc and bcc phases in HEAs: at $VEC \geq 8.0$, sole fcc phase exists; at $6.87 \leq VEC < 8.0$, mixed fcc and bcc phases will co-exist and sole bcc phase exists at $VEC < 6.87$. Note that at the boundary $VEC = 8.0$, sometimes bcc phases also form but they are minor phases (see Fig. 1 and Ref. 4). Although there is one exception for the $\text{Al}_x\text{CoCrCu}_{0.5}\text{FeNi}$ alloy where $6.87 \leq VEC < 8.0$ but the stable phase is sole bcc (not fcc+bcc), we suspect this VEC -defined phase stability shall work effectively for most cases. To prove this, VEC for more HEA systems with fcc, fcc+bcc, or bcc structure containing other alloying elements like Ti, V, Mn, Nb, Mo, Ta, W even metalloid B and C, are plotted in Fig. 4 (data are from literatures in Ref. 7 and 20–24). Although there are still some exceptions, the fcc/bcc phase boundary can clearly be delineated by VEC . With a note to those exceptions, the VEC -defined fcc/bcc phase boundary seems to work unsatisfactorily for Mn-containing HEA systems.

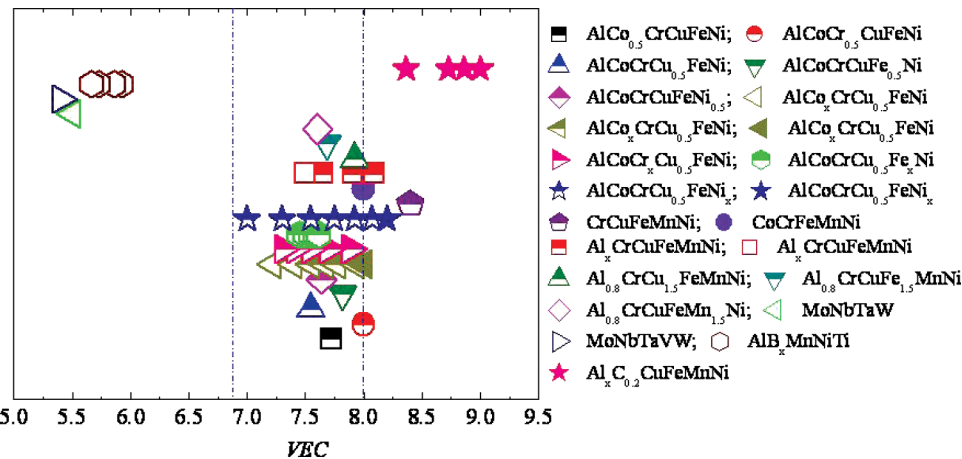


FIG. 4. (Color online) Relationship between VEC and the fcc, bcc phase stability for more HEA systems further to Fig. 3. Note on the legend: fully closed symbols for sole fcc phases; fully open symbols for sole bcc phase; top-half closed symbols for mixes fcc and bcc phases.

IV. DISCUSSION

The effect of the *VEC* on the phase stability has been studied before by the current authors for the intermetallic compounds only. One example is on the (Fe, Co, Ni)₃V intermetallic alloys with long-range-ordered (LRO) structures.²⁵ We found that these LRO alloys are characterized by specific sequences of stacked close-packed ordered layers and the stacking character can be altered systematically by controlling the *VEC* of these alloys. With the decreasing *VEC* by partial substitution of Co and Ni by Fe, the LRO changes from purely hexagonal, to L1₂-type cubic ordered structure, through different ordered mixtures of hexagonal and cubic layers. As the hexagonal structure exhibits brittle fracture while the cubic ordered structures are ductile, the control of *VEC* can hence be used to tune the mechanical properties of LRO alloys. We also investigated the role of *VEC* in the phase stability of NbCr₂-based transition-metal Laves phase alloys.²⁶ It was found that when the atomic size ratios were kept nearly identical, the *VEC* is the dominant factor in controlling the phase stability (C14, hexagonal or C15, cubic) in this type of high-temperature structural alloys. Our results in the present work prove that *VEC* also plays a decisive role in the stability of fcc and bcc solid solution phases in the multi-component HEAs. Mizutani has shown that *VEC* is crucial in determining the Fermi level when first-principles band calculations are carried out to study the band structure.¹¹ In the first-principles band calculations, the integration of the density of states (DOS) actually results in *VEC*, which includes not only *s*- and *p*-electrons but also *d*-electrons forming the valence band.¹¹ Mizutani emphasized that the parameter *VEC*, instead of *e/a*, should be used in realistic electronic structure calculations to take into account the *d*-electron contribution.¹¹ More theoretical work needs to be carried out to understand the physical basis for the mechanism behind the *VEC* rule on the phase stability, for example from the *VEC*-electronic structure-band structure energy perspective.²⁷

Two issues need to be emphasized here for the discussion of the *VEC* rule on the phase stability. First, the *VEC* ranges for different phases to be stable might overlap and these ranges also vary depending on the specific alloy systems. A very close example is in some ternary Mg alloys that possess typical Laves structures.⁹ It was found that the electron concentration (*e/a* though) ranges for MgCu₂-type (cubic, with packing *ABCABCABC*), MgNi₂-type (hexagonal, with packing *ABACABAC*) and MgZn₂-type (hexagonal, with packing *ABABAB*) structures differ in various alloy systems, and the *e/a* ranges for MgNi₂-type structure and MgZn₂-type structure overlap for the Mg-Cu-Al system. This can probably explain the exceptions that appear in Figs. 3 and 4. Second, the phases referred in this work are all identified in the as-cast state and they are hence very possibly in the metastable state. However, evidences have shown that these *metastable* phases have quite good thermal stability^{28–31} and can hence be regarded as very close to the stable phases. This gives confidence to the general applicability of the *VEC* rule, considering it works so well for such an extended series of various alloy systems. More work is certainly needed to further verify this. Admitting these two issues mentioned above, one solid

result out of our study is that, in HEAs the bcc phase is stable at lower *VEC* while the fcc phase is stable at higher *VEC*. This trend already sheds some light on the alloy design, and the fact that most HEA alloy systems satisfying the *VEC* (<6.87, bcc; ≥8, fcc) rule even simplifies the process. As the *VEC* rule on the phase stability between the fcc and bcc phases is tested only for the HEAs in this work, its applicability to other alloy systems other than the nearly equiatomic HEAs (i.e., in the traditional alloys where only one or two primary elements dominate), awaits further analysis. In addition, it would be interesting to know whether this *VEC* rule can be used to predict the phase stability for other structured phases, like the hcp-typed phases. More work along these directions is under way.

V. CONCLUSIONS

In summary, the phase stability in HEAs and its relationship to the physicochemical and thermodynamic properties of constituent alloying elements are systematically studied. The mixing enthalpy determines whether the solid solution phases or compounds form in the nearly equiatomic multi-component alloy systems. Most importantly the *VEC* is found to be the physical parameter to control the phase stability for fcc or bcc solid solutions. Fcc phases are found to be stable at higher *VEC* (≥8) and instead bcc phases are stable at lower *VEC* (<6.87). This work provides valuable input for understanding of the phase stability and to design ductile crystal structures in HEAs.

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