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Alloy Design Strategies and Future Trends in High-Entropy Alloys

JIEN-WEI YEH[1,2]

1.—Department of Materials Science and Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu 30013, Taiwan, ROC. 2.—e-mail: jwyeh@mx.nthu.edu.tw

High-entropy alloys (HEAs) are newly emerging advanced materials. In contrast to conventional alloys, HEAs contain multiple principal elements, often five or more in equimolar or near-equimolar ratios. The basic principle behind HEAs is that solid-solution phases are relatively stabilized by their significantly high entropy of mixing compared to intermetallic compounds, especially at high temperatures. This makes them feasibly synthesized, processed, analyzed, and manipulated, and as well provides many opportunities for us. There are huge numbers of possible compositions and combinations of properties in the HEA field. Wise alloy design strategies for suitable compositions and processes to fit the requirements for either academic studies or industrial applications thus become especially important. In this article, four core effects were emphasized, several misconceptions on HEAs were clarified, and several routes for future HEA research and development were suggested.

INTRODUCTION

Conventionally, the alloy design, alloy production, and alloy selection are almost confined by one-element or one-compound concept. This alloy concept obviously limits the degree of freedom in alloy's composition and thus limits the development of special microstructure and properties. It is safer to say that materials science and engineering of alloys are still not fully explored because those alloys outside this conventional scheme have not been included. In recognition of this tradition, a brand-new alloy concept of high-entropy alloys (HEAs) to break the confinement have been proposed and explored since 1995.[1–5] Up until now, it has been demonstrated that the explored alloys in this virgin field are feasible to be synthesized, processed, and analyzed contrary to the misconceptions based on traditional experiences. Moreover, there are many opportunities in this field for both academic studies and industrial applications.

As the combinations of composition and process for producing HEAs are numerous and each HEA has its own microstructure and properties to be identified and understood, the research work is truly limitless. Therefore, in this article, alloy design strategies and future trends for HEAs were focused on the technical and scientific viewpoints. But it is still very important to present basic concepts relating with HEAs in advance, including the origin of high entropy, definition, four core effects of HEAs, and misconceptions on HEAs, which are helpful in alloy design and research for HEAs.

DEFINITION AND THE REASON TO USE HIGH ENTROPY

The so-called HEAs contain multiple principal (or major) elements, often five or more in equimolar or near-equimolar ratios, and minor elements. The basic principle behind HEAs is that solid-solution phases are relatively stabilized by their significantly high entropy of mixing compared with intermetallic compounds, especially at high temperatures. This allows them to be feasibly synthesized, processed, analyzed, manipulated, and used by us. In a broad sense, HEAs are preferentially defined as those alloys containing at least five principal elements, each having the atomic percentage between 5% and 35%. The atomic percentage of each minor element, if any, is hence less than 5%.

Why are the new multicomponent alloys called HEAs? Let us consider an equimolar alloy at its liquid state or regular solid-solution state. Its configurational entropy per mole can be calculated by R

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$\ln(n)$ based on the well-known Boltzmann's hypothesis on the relationship between the entropy and the complexion of a system:

$$\Delta S_{\text{conf}} = -k \ln w = -R\left(\frac{1}{n}\ln\frac{1}{n} + \frac{1}{n}\ln\frac{1}{n} + \cdots + \frac{1}{n}\ln\frac{1}{n}\right) = -R\ln\frac{1}{n} = R\ln n$$

where R is gas constant, 8.314 J/K mol, and n is the number of elements.[4,5]

Although total mixing entropy has four contributions such as configurational, vibrational, magnetic dipole, and electronic randomness, configurational entropy is dominant over other three excess contributions.[6,7] Among these three, the excess vibrational entropy at high temperatures could be calculated from Debye temperatures before and after mixing.[6] Negative contribution of excess vibrational entropy to overall mixing entropy might occur and could be enhanced by attractive interactions between unlike atomic pairs. Table I lists the configurational entropies of equimolar alloys in terms of the gas constant R. The entropy increases as the number of element increases. From Richards' rule, the entropy change per mole, ΔS_f, from solid to liquid during melting is about one gas constant R for metals. Moreover, the enthalpy change or latent heat per mole, ΔH_f, can be correlated with ΔS_f by the equation: $T_m \Delta S_f = \Delta H_f$. Because ΔH_f can be regarded as the energy required to destroy about one twelfth of all bonds in the solid, a mixing entropy of R per mole due to mixing in an alloy state would be quite large to decrease the mixing free energy by an amount of RT at high temperatures, e.g., RT = 8.314 kJ/mol at 1000 K, and to compete with the mixing enthalpy of intermetallic compounds arising from the interaction between unlike metallic atoms. That means the tendency to form the mixing state of constituent elements would be increased by increased mixing entropy. This tendency will be further discussed in the "High Entropy Effect" section.

It can be seen from Table I that configurational entropy of a three-element equimolar alloy is already slightly higher than $1R$ and that of a five-element alloy is higher than R by 61%. Thus, it is reasonable to think that $1.5R$ (even not include other three mixing entropy contributions mentioned above) is large enough to compete with mixing enthalpy, as well as to be used as a border line between HEAs and medium-entropy alloys. This could be understood from the fact that if the formation enthalpies of two typical strong intermetallic compounds such as NiAl and TiAl are divided by their respective melting points, then the resulting equivalent ΔS_{conf}, $1.38R$ and $2.06R$, are in the same range as the entropy changes of mixing in a system with more than five elements.[4] That means, $1.5R$ could be competitive with most strong bonding energies of unlike atomic pairs at high temperatures. In addition, $1R$ can be used as the border line for medium-entropy and low-entropy alloys because a mixing entropy smaller than $1R$ is expected to be much less competitive with those strong bonding energies. Table II gives the configurational entropies calculated for typical traditional alloys at their liquid state or random state. We can see from this table that most alloys have low entropy, whereas some concentrated alloys of Ni-base, Co-base superalloys, and bulk metallic glasses (BMGs) have medium entropy between 1 and $1.5R$. That means very few traditional alloys could have a high mixing entropy $>1.5R$. Based on this, the alloy world is schematically shown in Fig. 1. Previously, the border lines are set as $0.69R$ and $1.61R$, respectively, and thus, they have some difference from the current picture. This is simply because the previous ones are based on the number of principal elements, i.e., 2 and 5, respectively.[5,8]

Based on the defined border lines, the definition of HEAs in a broad sense can be also understood from configurational entropy calculation. From the configurational entropy equation, we can obtain that an element with a concentration of 5 at.% would contribute a mixing entropy of $0.05R\ln 0.05 = 0.15R$, which is just 10% of minimum requirement of $1.5R$ for HEAs. So, we could regard an element in an amount >5 at.% as a principal element. As for 4 at.%, 3 at%, 2 at.%, and 1 at.%, the contributions are $0.129R$, $0.105R$, $0.078R$, and $0.046R$, respectively, and thus their percentages based on $1.5R$ are 8.6%, 7%, 5.2%, and 3.1%, respectively. So, we regard an element in an amount <5 at.% as a minor element.

A question is raised from the HEAs definition: What is the upper bound of the number of metallic principal elements? For 5-element, 10-element, and 12-element alloys, as well as 13-element, 14-element, 15-element, 20-element, and 40-element equal-mole alloys, the total configurational entropies are $1.61R$, $2.3R$, $2.49R$, $2.57R$, $2.64R$, $2.71R$, $3.0R$, and $3.69R$, respectively. Because the increase in $0.07R$, from a 13- to a 14-element alloy is relatively small (0.07/2.57 = 2.7%), a practical number of principal element between 5 and 13 was suggested for HEAs.[5] That means more principal elements will not get a significant benefit from the

Table I. Configurational entropies of equimolar alloys with constituent elements up to 13

n	1	2	3	4	5	6	7	8	9	10	11	12	13
ΔS_{conf}	0	$0.69R$	$1.1R$	$1.39R$	$1.61R$	$1.79R$	$1.95R$	$2.08R$	$2.2R$	$2.3R$	$2.4R$	$2.49R$	$2.57R$

Table II. Configurational entropies calculated for typical traditional alloys at their liquid state or random state

Systems	Alloys	ΔS_{conf} at liquid state
Low-alloy steel	4340	0.22*R* low
Stainless steel	304	0.96*R* low
	316	1.15*R* medium
High-speed steel	M2	0.73*R* low
Mg alloy	AZ91D	0.35*R* low
Al alloy	2024	0.29*R* low
	7075	0.43*R* low
Cu alloy	7-3 brass	0.61*R* low
Ni-base superalloy	Inconel 718	1.31*R* medium
	Hastelloy X	1.37*R* medium
Co-base superalloy	Stellite 6	1.13*R* medium
BMG	$Cu_{47}Zr_{11}Ti_{34}Ni_8$	1.17*R* medium
	$Zr_{53}Ti_5Cu_{16}Ni_{10}Al_{16}$	1.30*R* medium

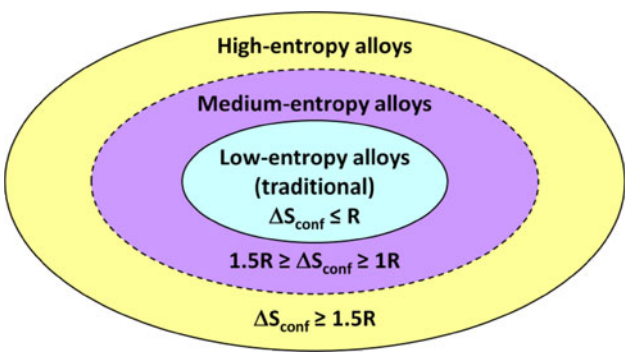

Fig. 1. Alloy world based on configurational entropy.

high-entropy effect but might increase the complexity in handling raw materials or recycling the alloys.

Indeed, it is not easy to give a clear-cut composition definition for HEAs. The composition definition is just a guideline. An alloy with some deviation from this composition definition might also be regarded as an HEA. For example, an alloy with 21-element equal-mole alloy is surely an HEA, even though each element has a concentration smaller than 5 at.%. In the common definition of low-alloy carbon steels, they can, from a technical standpoint, contain about 1 wt.% to 4 wt.% alloying elements.[9] If a higher amount is added, then it is considered as a different type of steels. Surely, the upper limit of 4 wt.% is also a guideline because 5 wt.% and 8 wt.% were ever proposed from different standing points.

Under the above definition and practical upper bound of 13 principal elements, at an arbitrary choice of a group of 13 metallic elements, we can obtain a total of 7099 possibilities for designing equal-mole HEAs systems from 5 to 13 elements[5]:

$$C_5^{13} + C_6^{13} + C_7^{13} + C_8^{13} + C_9^{13} + C_{10}^{13} + C_{11}^{13} + C_{12}^{13} + C_{13}^{13} = 7099 \quad (5)$$

We may design an equal-mole AlCoCrCuFeNi alloy. We may also design unequal-mole alloys with minor alloying elements like $AlCo_{0.5}CrCu\ Fe_{1.5}\ Ni_{1.2}B_{0.1}C_{0.15}$ for further modification of microstructure and properties. As a result, HEAs are countless in number.

FOUR CORE EFFECTS OF HEAs

Many factors affect the microstructure and properties of HEAs. Among these, four core effects are more basic.[5] For thermodynamics, a high entropy effect could interfere with complex phase formation. For kinetics, a sluggish diffusion effect could slow down phase transformation. For structure, severe lattice distortion effect could alter properties to an extent. For properties, the cocktail effect brings excess quantities to the quantities predicted by the mixture rule due to mutual interactions of unlike atoms and severe lattice distortion. The next section further explains these four effects.

High Entropy Effect

As the name implied, high entropy is the unique and most important of HEAs because its effect could enhance the formation of solution phases and makes the microstructure much simpler than previously expected. Why? It is well known that there are three possible categories of competing states in the solid state of an alloy, that is, elemental phases, intermetallic compounds, and solid-solution phases. The competition involving liquid phase during solidification is not considered. Elemental phase means the terminal solid solution based on one metal element. Intermetallic compound means stoichiometric compounds having specific superlattices, such as NiAl having B2 structure and Ni_3Ti having $D0_{24}$ structure. Solid solution means the phase with the complete mixing of all elements or with a significant mixing of constituent elements in the structure of body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close packed (hcp). Intermetallic phases or intermediate phases are also included because they are solid solutions based on intermetallic compounds.[10,11] In such phases, different constituent elements tend to occupy different sets of lattice sites. According to the Thermodynamic Second Law, the state having the lowest mixing free energy ΔG_{mix} among all possible states would be the equilibrium state. To elucidate a high entropy effect in enhancing the formation of solid-solution phases and inhibiting the formation of intermetallic compounds, HEAs composed of constituent elements with stronger bonding energies between each other are considered. By the comparison in Table III, which does not consider strain energy con-

tribution (due to atomic size difference) to mixing enthalpy for simplicity, elemental phases based on one major element have small ΔH_{mix} and ΔS_{mix}, and compound phases have large ΔH_{mix} but small ΔS_{mix}; on the other hand, solid-solution phases containing multiple elements have medium ΔH_{mix} and high ΔS_{mix}. As a result, solid-solution phases become highly competitive for equilibrium state and more stable especially at high temperatures. It should be explained why multielement solid solutions have medium ΔH_{mix}. This is because a proportion of unlike atomic pairs exists in solution phases. For example, a mole of atoms, N_0, of NiAl intermetallic compound (B2) in complete ordering has $(1/2) \times 8N_0$ Ni-Al bonds, whereas a mole of NiAl random solid solution would have $(1/2) \times (1/2) \times 8N_0$ Ni-Al bonds. That means the mixing enthalpy in the random state is half that of the completely ordered state. Similarly, for a five-element equimolar alloy, the ratio is 4/5 and for an eight-element equimolar alloy, the ratio is 7/8 assuming that all heats of mixing for unlike atom pairs are the same. In brief, a higher number of elements would allow the random state to have the mixing enthalpy closer to that of the completely ordered state and to become even more competitive with the ordered state under the aid of its high mixing entropy.

In general, if the heats of mixing for unlike atomic pairs do not have large difference, simple solid solution phase would be dominant in the equilibrium state. For example, the FeCoCrMnNi alloy can form a simple fcc solution even full-annealed at all temperatures.[12,13] The ductile refractory HfNbTaTiZr alloy having the melting point around 2250°C as predicted by the rule of mixture has a simple bcc phase in the as-cast state.[14] Conversely, a large difference might generate more than two phases. For example, Al has stronger bonding with transition metals, but Cu has no attractive bond with most transition metals. As a result, AlFeCoCrCuNi alloy forms Cu-rich fcc + multi-element fcc + multi-element bcc (A2) at high temperatures above 600°C, and has B2 precipitates in the Cu-rich fcc and spinodally decomposed structure of A2 + B2 phases from A2 phase during cooling. The B2 solid solution containing multielements is in fact derived from the NiAl-type compound.[15] Even larger difference as found in the alloys containing O, C, B, or N would generate oxides, carbides, borides or nitrides in the microstructure.

To include the effect of atomic size difference, Zhang et al.[16] first proposed the forming trend of disordered solid solutions, ordered solid solution, intermediate phases, and BMG by comparing ΔS_{mix}, ΔH_{mix}, and atomic size difference (δ). Guo and Liu[17] also used these factors to lay out the phase selection rule for such kinds of phase. Moreover, Yeh,[18] Chen and Yeh,[19] and Yang and Zhang[20] used δ and the ratio of $T\Delta S_{mix}$ to ΔH_{mix} to describe the order–disorder competition in HEAs and the existing range of intermetallics and BMG. All these studies pointed out that solution-type phases including disordered and intermediate phases tend to form in highly alloyed multicomponent alloys. Disordered solutions preferentially form under smaller δ, smaller ΔH_{mix}, but higher ΔS_{mix}, i.e., a higher ratio of $T\Delta S_{mix}$ to ΔH_{mix}.

In summary, a high entropy effect is important for HEAs to avoid the formation of many different kinds of stoichiometric compounds, which are very brittle and complex to analyze and understand. Conversely, it enhances the formation of solution-type phases and thus reduces the number of phases as predicted by Gibbs phase rule which permits the number of phases in equilibrium to increase with the number of components.

Sluggish Diffusion Effect

We know that the formation of new phases requires cooperative diffusion of many different kinds of atoms to accomplish the partitioning of composition in HEAs. However, the vacancy concentration for substitutional diffusion is still limited in HEAs as found in traditional alloys because each vacancy in crystalline HEAs is also associated with a positive enthalpy of formation and an excess mixing entropy, which render a minimum free energy of mixing at a certain equilibrium concentration for a given temperature.[21] A vacancy in the whole-solute matrix is in fact surrounded and competed by different-element atoms during diffusion. It has been proposed that slower diffusion and higher activation energy would occur in HEAs due to larger fluctuation of lattice potential energy (LPE) between lattice sites.[13] The abundant low-LPE sites can serve as traps and hinder atomic diffusion, leading to the sluggish diffusion effect.

To verify this effect, a near-ideal solution system of Co-Cr-Fe-Mn-Ni with stable single fcc solid solution was selected by Tsai et al.[13] to make diffusion couples and analyze the diffusion data of each element in the matrix. Four quasi-binary diffusion

Table III. Comparisons of ΔH_{mix}, ΔS_{mix}, and ΔG_{mix} between elemental phases, compounds, and solid solutions

Possible states	Elemental phases	Compounds	Solid solutions
ΔH_{mix}	~0	Large negative	Medium negative
$-T\Delta S_{mix}$	~0	~0	$-RT\ln(n)$
ΔG_{mix}	~0	Large negative	Large negative

Strain energy from atomic size difference is not included in ΔH_{mix}.

couples were made as listed in Table IV. In the two end members of each couple, only two elements differed in concentration. The diffusion couple was tightly fixed in a molybdenum tube, which was further sealed in a vacuum quartz tube. From the concentration profiles obtained after diffusion at different elevated temperatures, 1173 K, 1223 K, 1273 K, and 1323 K, diffusion coefficients and activation energy were obtained. The results showed that the sequence in the order of decreasing diffusion rate was Mn, Cr, Fe, Co, and Ni. It was also found that diffusion coefficients of each elements at T/T_m in the Co-Cr-Fe-Mn-Ni alloy system were the smallest in similar fcc matrices including Fe-Cr-Ni (-Si) alloys and pure Fe, Co, and Ni metal. In addition, the melting point normalized activation energies, Q/T_m, in the HEA were the largest as shown in Fig. 2. These figures show direct evidence for the sluggish diffusion effect in HEAs. It was also noted that for the same element, the degree of sluggish diffusion is related to the number of elements in that matrix. For example, the Q/T_m values in the present HEAs are the highest, those in Fe-Cr-Ni (-Si) alloys are the second, and those in pure metals are the lowest.

It is expected that sluggish diffusion effect might provide several important advantages as found in many related publications[15,22–29]: easy to get supersaturated state and fine precipitates, increased recrystallization temperature, slower grain growth, reduced particle coarsening rate, and increased creep resistance. These advantages might benefit microstructure and property control for better performance. For example, Liu et al.[28] studied the grain growth of cold-rolled and annealed sheet of CoCrFeMnNi HEA and found that the activation energy is much higher than AISI 304LN stainless steels, which is consistent with the sluggish diffusion effect.

Severe Lattice Distortion Effect

Because the multielement matrix of each solid-solution phase in HEAs is a whole-solute matrix,[15] every atom is surrounded by different kinds of atoms and thus suffers lattice strain and stress mainly due to atomic size difference as shown in Fig. 3. Besides the atomic size difference, both different bonding energy and crystal structure tendency among constituent elements are also believed to cause even higher lattice distortion because non-symmetrical bindings and electronic structure exist between an atom and its first neighbors and moreover, this non-symmetry varies from site to site in the lattice.[13,32] As a result, the distortion severity of lattice is much larger than that in conventional alloys that are based on a major element. In conventional alloys, most matrix atoms (or solvent atoms) have the same kind of atoms as their neighbors.

Lattice distortion not only affects properties but also reduces the thermal effect on properties. Hardness and strength effectively increase because of large solution hardening in the heavily distorted lattice. For example, hardness values of refractory bcc HEAs: four equimolar alloy NbMoTaW and five equimolar alloy VNbMoTaW are Hv 4,455 MPa and 5,250 MPa, respectively. These values are three times that obtained by the mixture rule.[30] In addition, electrical and thermal conductivity significantly decrease due to electron and phonon scattering.[31] X-ray diffraction peak intensity decreases due to x-ray diffuse scattering in the distorted atomic planes.[32] All these properties in HEAs become quite insensitive to temperature. This is explainable because the lattice distortion caused by thermal vibration of atoms is relatively small compared with the severe lattice distortion.[32] For

Table IV. The concentrations of end members of three diffusion couples[13]

Couple	Alloy	Composition (at.%)				
		Co	Cr	Fe	Mn	Ni
Cr-Mn	1	22	29	22	5	22
	2	22	17	22	17	22
Fe-Co	3	33	23	11	11	22
	4	11	23	33	11	22
Fe-Ni	5	23	24	30	11	12
	6	23	24	12	11	30

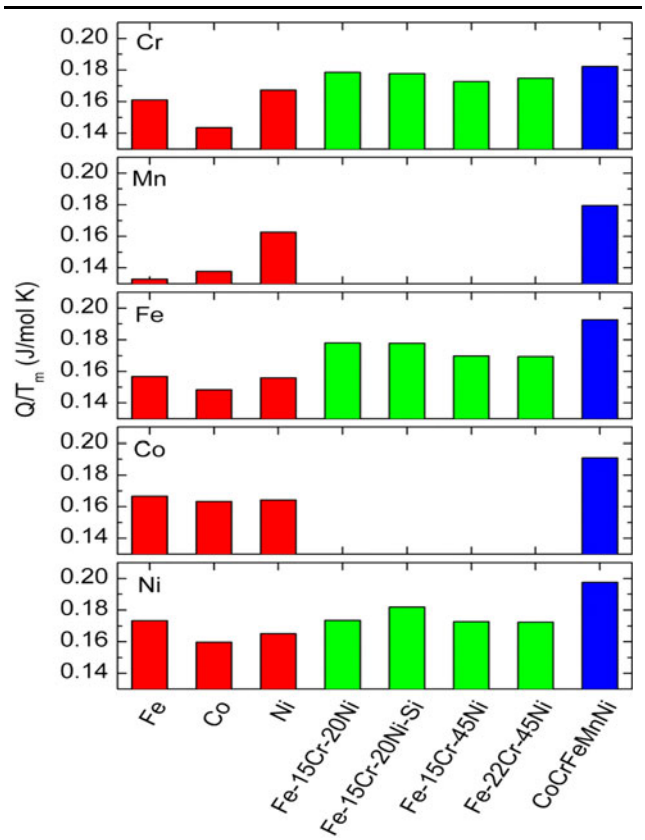

Fig. 2. Melting-point normalized activation energy of diffusion for Cr, Mn, Fe, Co, and Ni in different matrices.[13]

example, Lu et al.[33] studied the thermal diffusivity as a function of temperature for four HEAs and pure Al as shown in Fig. 4. It was found that the thermal diffusivities of HEAs are positively small and insensitive to temperature, whereas that of conventional metal is positively large and sensitive to temperature.[33]

Cocktail Effect

The term "multimetallic cocktails" was first proposed by Ranganathan[34] to emphasize alloy pleasures in alloy design and development. To treat AIDS, cocktail treatment was invented by David Ho using the concept of three-drug therapy in 1996, which shows an impressive benefit with a 60–80% decline in rates of AIDS, death, and hospitalization. In HEAs, the cocktail effect is also emphasized majorly because at least five major elements are used to enhance the properties of the materials. As stated above, HEAs might have a simple phase, two phases, three phases, or more depending on the composition and processing. As a result, the whole properties are from the overall contribution of the constituent phases by the effect of phase shape, phase distribution, phase boundaries, and properties of each phase. However, each phase is a multielement solid solution and can be regarded as atomic-scale composites. Its composite properties come from not only the basic properties of elements by the mixture rule but also the mutual interactions among all the elements and from the severe lattice distortion. Interaction and lattice distortion would bring excess quantities to the quantities predicted by the mixture rule. As a whole, the "cocktail effect" ranges from an atomic-scale, multielement composite effect to a microscale, multiphase composite effect. Therefore, it is important for an alloy designer to understand the related factors involved before selecting suitable composition and processes. For example, refractory HEAs developed by Air Force Research Laboratory have melting points very much higher than that of Ni-base and Co-base superalloys.[24,30] This is simply because refractory elements were selected as constituent elements. By the mixture rule, four-equimolar-alloy NbMoTaW and five-equimolar-alloy VNbMoTaW have melting points above 2600°C. As a result, both alloys display much higher softening resistance than superalloys and have yield strengths above 400 MPa at 1600°C as shown in Fig. 5.[24] Such refractory HEAs are thus also expected to have potential applications at very high temperatures. In another example, Zhang et al.[35] studied $FeCoNi(AlSi)_{0-0.8}$ alloys for finding the composition with the optimum combination of magnetic, electrical, and mechanical properties. The best was achieved in alloy $FeCoNi(AlSi)_{0.2}$ with saturation magnetization (1.15 T), coercivity (1,400 A/m), electrical resistivity (69.5 $\mu\Omega$ cm), yield strength (342 MPa), and strain without fracture (50%), which lets the alloy be an excellent, soft magnetic material for many potential applications. Obviously, this alloy design relied on the selection of equimolar ferromagnetic elements (Fe, Co, and Ni) for forming ductile fcc phase with higher atomic packing density than bcc, and suitable addition of nonmagnetic elements (Al and Si having slightly anti-parallel magnetic coupling with Fe, Co, and Ni) to increase lattice distortion. It led to a positive cocktail effect in achieving high magnetization, low coercivity, good plasticity, high strength, and high electrical resistance.

Finally, it should be mentioned that the four core effects are much more pronounced in HEAs and

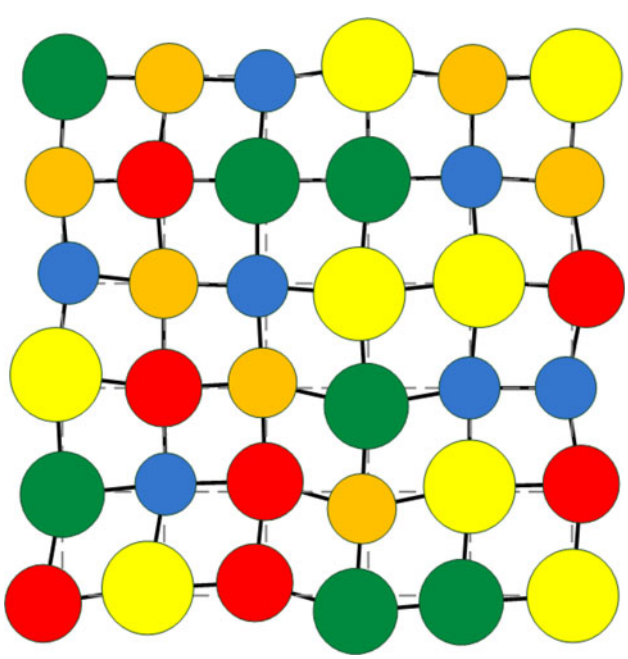

Fig. 3. Severely distorted lattice in a multielement crystal structure.

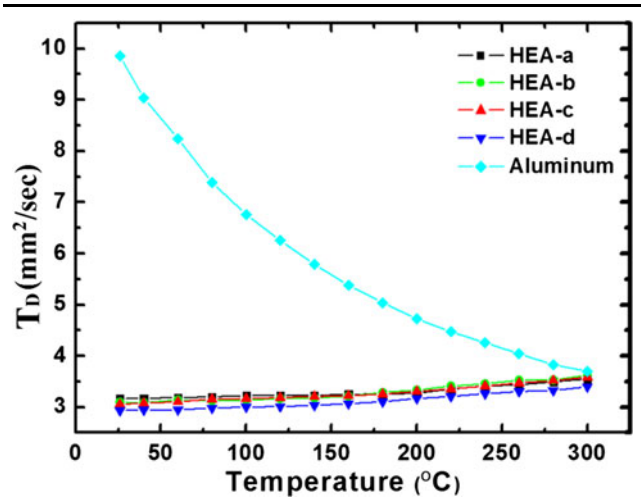

Fig. 4. Thermal diffusivities as a function of temperature for pure aluminum and HEA-a($Al_{0.3}CrFe_{1.5}MnNi_{0.5}$), HEA-b($Al_{0.5}CrFe_{1.5}MnNi_{0.5}$), HEA-c($Al_{0.3}CrFe_{1.5}MnNi_{0.5}Mo_{0.1}$), and HEA-d($Al_{0.5}CrFe_{1.5}MnNi_{0.5}Mo_{0.1}$).[32]

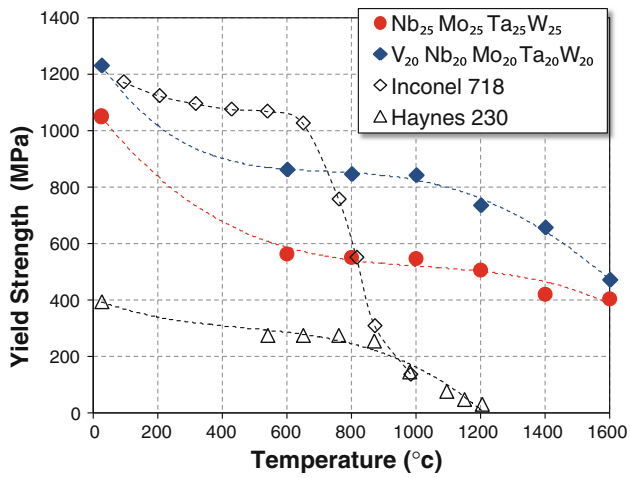

Fig. 5. The temperature dependence of the yield stress of $Nb_{25}Mo_{25}Ta_{25}W_{25}$ and $V_{20}Nb_{20}Mo_{20}Ta_{20}W_{20}$ HEAs and two superalloys, Inconel 718 and Haynes 230.[33]

strongly influence their microstructure and properties. Thus, it would become much easier for us to understand and explain the phenomena in HEAs through these four effects. In addition, four core effects are useful guidelines for one to design an HEA for specific purpose or application.

SEVERAL MISCONCEPTIONS ON HEAs

Several misconceptions about HEAs are as follows: (I) HEAs have low entropy and complex microstructure, (II) HEAs are hard and brittle, and (III) HEAs are expensive and difficult to fabricate. In the following sections, these misconceptions are clarified.

Low Entropy and Complex Microstructure

It should be clarified in the first place that mixing entropy is compared at the liquid solution or random solid-solution state. HEAs have a high mixing entropy at such states compared with those of conventional alloys. Why is high mixing entropy at such states emphasized? Figure 6 shows the phase evolution during solidification and cooling. If an alloy has a high mixing entropy, then simple solid-solution phases will form at high temperatures due to the large $T\Delta S_{mix}$. During subsequent cooling, mixing entropy become less important, and short-range ordering, long-range ordering, or even precipitation of second phases might occur. But a sluggish diffusion effect will yield fine precipitates or inhibit precipitation, which is welcomed for improving properties.[15] Conversely, if multielement alloys do not have a high mixing entropy at high temperatures, then intermetallic phases would form at high temperatures. In subsequent cooling, the microstructure would become even more complex. Such complex microstructures obviously become very difficult to understand and manipulate, and

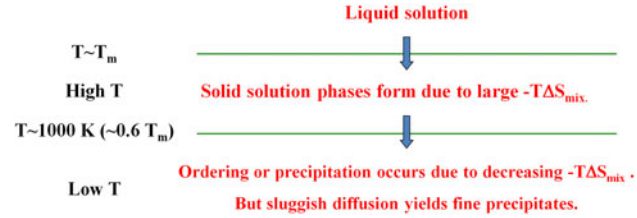

Fig. 6. Phase evolution during solidification and cooling of HEAs having a melting temperature around 1700 K.

they are very brittle to be used. Therefore, the fortune to avoid the complexity at low temperatures essentially comes from the high entropy effect, which is amplified by high temperatures to compete with mixing enthalpies of intermetallics.

Hard and Brittle by Nature

It is commonly held that highly alloyed conventional alloys are in general hard and brittle. However, this is not always true for HEAs. In fact, HEAs are like conventional alloys: Some are hard and brittle, while some are softer and ductile. In brief, fcc phases in HEAs in general possess lower hardness but excellent ductility.[28,36,37] They can be hot worked and cold worked easily. BCC phases in HEAs possess a higher hardness but lower ductility. They can be hot worked and warm worked, while some can be cold worked. As for the intermediate phases based on intermetallic compounds, they are also hard and can increase the alloy hardness by precipitation hardening or composite strengthening. If the overall hardness is high, then the slip deformation would become difficult and tend to become brittle. For such a case, hot forging or hot rolling is recommended to enhance the deformation and shaping. If the overall hardness is medium, then the slip deformation of the matrix is still possible. Cold working might be feasible. It should be mentioned that a high entropy effect tends to make all these phases become multielement solid solutions and to improve their mechanical properties. For fcc and bcc phases, solution hardening is known as a good strengthening mechanism to improve both strength and ductility. For intermetallic intermediate phases, multielement substitution will make their superlattices more disordered and enhance slip deformation and ductility.

Expensive and Difficult to Fabricate

Some elemental raw materials such as Zr, Ti, Co, and Ni for HEAs are more expensive than Mn, Fe, Al, and Cu. Hence, the overall material cost could be intermediate between the most expensive composing element and the cheapest element based on the rule of mixture. Therefore, HEAs might be cheaper than Ti alloys, Ni alloys, and Co alloys, depending on compositions. Like traditional alloys, HEAs could be fabricated by selecting suitable processes from ingot metallurgy, powder metallurgy, and coating

technology. The selection depends on the fabricability and purposes. For example, fcc-type HEAs could be hot forged and cold rolled. Tungsten carbides or cermets could use suitable HEAs as binders replacing Co or Ni. They are inevitably processed by powder metallurgy. In general, there are many conventional processes provided for fabricating HEAs.

ALLOY DESIGN STRATEGIES FOR HEAs

There are numerous combinations of compositions and processes to generate HEAs. The development of HEAs should be efficient rather than time and resource consuming. There are several routes to develop HEAs: (I) use combinatorial materials synthesis technique; (II) use computational materials science: ab initio simulation, molecular dynamics (MD), finite element, New PHACOMP, CALPHAD method, etc.; (III) use Taguchi method to optimize the properties; (IV) start from promising alloy systems; and (V) use alloy design principles of materials science. The following sections describe each route.

Use Combinatorial Materials Synthesis Technique

Over the last two decades, combinatorial chemistry has altered the drug-development process to discover new drugs.[38,39] By this encouragement, materials scientists also apply this methodology to accelerate the discovery of new compounds for high-T_c superconductors, luminescent materials, catalysts, and polymers.[40] They use thin-film technology to deposit substances sequentially in different amount layer by layer onto a gridded substrate and then to mix the elements and create a stable compound by heating. The physical properties of interest are then measured on each composition to find out the outstanding composition. Basically under little guidance to predict new materials, this is a very efficient trial-and-error method to discover new materials. Nowadays, laser-engineered net shaping (LENS) in the technology of rapid prototyping can fabricate HEAs in bulk form directly by injecting metal powders into the area focused with a high-powered laser beam. The stacking layer by layer could be changed in different compositions. For example, Al content can be varied from 0 to 3 segmentally in a grown $Al_xCoCrCuFeNi$ alloy rod.[41] Similarly, other elements could be varied to produce segmentally gradient rods. The analyses become more efficient on the gradient rods to generate data for further assessment.

Use Computational Materials Science

New Phacomp was invented in 1984 using the d-electron concept to define the phase boundaries in terms of M_d (metal d-level), especially to define the critical M_d value of gamma phase and sigma phase boundary for predicting sigma phase formation in Ni-base superalloys.[42] Thermo-Calc software (Thermo-Calc Software, Stockholm, Sweden) is a computational tool for calculating phase diagrams. All these computations could save the experiments that are time consuming, difficult, or expensive. But the existing database for HEAs is still lacking in making predictions with accuracy and thus needs to be enriched in the future. For simple calculation and prediction, Guo et al.[43] found that the valence electron concentration (VEC) is the critical parameter controlling the phase stability for fcc (VEC ≥ 8) or bcc phase (VEC < 6.87). This criterion is useful to design some HEAs.

As for MD simulation, a many-body tight-binding potential model has been applied to study the effect of the number of elements and size difference on the amorphous structure of HEAs.[44,45] This is simply because this model treats the interatomic forces existing between any two unlike atoms as the geometric average of their bonding forces in their respective pure lattices, and thus it treats the systems as ideal solutions (i.e., the mixing enthalpy is zero). In other words, such MD simulation rules out the effect of actual bonding energy between unlike atoms and only investigates the effects from the number of elements and the atomic size. The alloys simulated were from traditional binary alloys to HEAs by adding one element in sequence. For example, Fig. 7 shows the initial radial distribution function curves of the alloys at 300 K before the system was heated.[44] Thus, we can see that the patterns of two-element to four-element alloys have well-defined peaks which indicate an ordered structure. However, the five-element alloy and six-element alloy containing large-sized Zr have lower and broader peaks, which confirm an amorphous structure. Virtually, this trend apparently shows that the amorphization is enhanced by the number of elements and large atomic size difference. When heated up to the molten state at 2200 K, the patterns typically depict a liquid structure as shown in Fig. 8a. Moreover, as the number of elements increases, peaks become broader and distance between peaks also become larger, which indicates that the liquid structure becomes more disordered. In the melt-quenched state, five-element and six-element alloys exhibit liquid-like solid structure as shown in Fig. 8b. But, two- to four-element alloys display an amorphous structure because there is a splitting in their second peaks, which indicates that the structure is more ordered than the liquid structure. This again shows an increased number of elements, and thus a large atomic size difference could enhance the amorphization. In fact, the shape and evolution of radial distribution function curves could be explained from the close-packed hard ball model as shown in Fig. 9. The splitting of the second peaks indicates that the second nearest-neighbor shell is not fully merged with the third shell due to the insufficiency in the degree of disorder. By the

hard ball model, the number of atoms and distance for each shell are shown in the second and third rows of Table V, respectively. Under a random occupation of sites by different atoms, the fluctuation range caused by the atomic size difference can be used to judge the merging of peaks. If the atomic size difference makes the atomic fluctuation range in the second and third shells larger than 7.2%, then the second and third shells or peaks are expected to merge into each other. It can be seen from Table VI that only 5- and 6-element alloys with deviation over 10% can fit this requirement. Because the deviation between 4th and 5th shell is 6.2%, all the alloys can have merging of the 4th and 5th peaks. Therefore, the judgment of peak merging by the atomic size difference is consistent with the radial distribution function calculated by MD simulation.

Besides MD simulation, ab initio calculation from the electron level or directly from the first principles of quantum mechanics is also powerful to predict materials behavior and properties. However, ab initio calculations require a large amount of numerical computation. The computing time increases rapidly as the number of atoms increases.

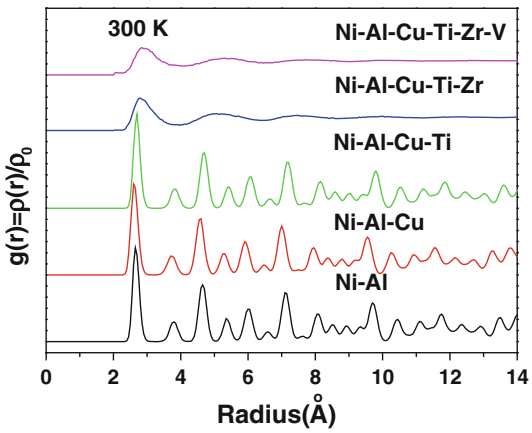

Fig. 7. The radial distribution functions obtained at 300 K for Ni-Al to Ni-Al-Cu-Ti-Zr-V equimolar alloys by MD simulation.

Use Taguchi Method

The Taguchi method is helpful to us in designing a minimum number of experiments to investigate how different parameters affect the product quality or performance and then to find the combination of parameters for optimum performance.[46] The experimental design uses orthogonal arrays to organize the parameters that affect the performance and the levels at which the parameters vary. This saves time and resources without doing a lot of experiments. Similarly, the Taguchi method could be applied to an HEA system to observe those compositions that display better properties and performance. For example, with an aim to optimize hardness, toughness, and oxidation resistance for plasma spray coatings on elevated-temperature components, the best compositions based on a promising HEA system could be obtained. One of the best compositions from this method is the nonequal-mole alloy Al-Co-Cr-Fe-Ni-Si-Ti, which has been successfully deposited on 304 stainless steels by plasma spray as shown in Fig. 10. Thus, it displays good performance with a high hardness of Hv 880, good fracture toughness, and oxidation resistance similar to that of well-known NiCrAlY coatings.

Start from Promising Alloy Systems

We might start HEA research from promising alloy systems. For each system, equal and nonequal-mole alloys could be systematically studied. Figure 11 shows an example of a six-element Al-Co-Cr-Fe-Mo-Ni system,[23,29,47–49] which is thought to be an interesting and promising system because Co, Cr, Fe, and Ni are the bases for superalloys, Al is critical to increase oxidation resistance at high temperatures, and Al and Mo are important elements to increase the temperature capability. Because there are lots of compositions in this six-element system, a strategy was used to reduce the number of compositions investigated and effectively understand the system in a whole view. Figure 11 shows a center alloy base in which five elements are in equal mole and Mo is in

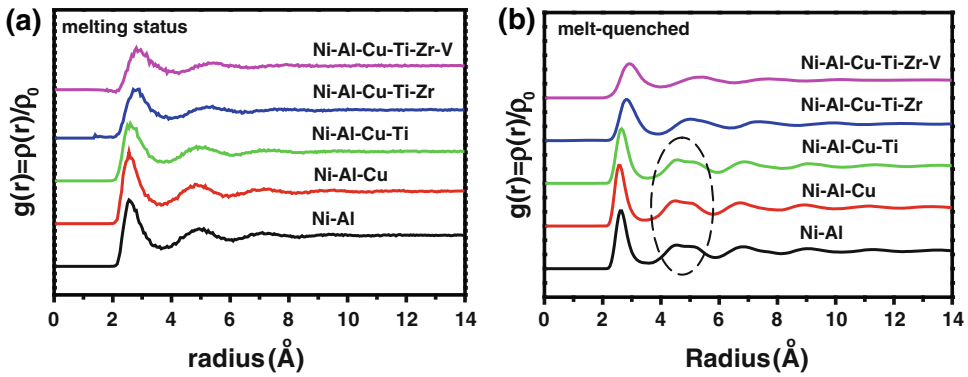

Fig. 8. The radial distribution functions obtained (a) at the melt state of 2200 K, and (b) at the quenched state for Ni-Al to Ni-Al-Cu-Ti-Zr-V equimolar alloys by MD simulation.

half amount because of its high cost. Then Al, Co, Cr, Fe, and Ni contents were varied from 0 to 2 in molar ratio, respectively, except Mo between 0 and 0.9. Thus, the center alloy with half Mo is positioned at the zone center of this alloy system. By this strategy, it is expected that we can easily understand and estimate the data for any other compositions such as X and Y from their neighboring data. Table VII shows the constituent phases of all alloys. In summary, Al can enhance bcc phase but inhibit σ phase; Co and Ni enhance fcc phase; Cr and Mo enhance σ phase; and Fe inhibits σ phase (also judged by the relative peak intensities of different phases from XRD patterns). Figure 12 shows hot hardness as a function of temperature for Fe and Mo. The plots for Al, Co, Fe, and Ni are not shown but are similar in trend to Fig. 12.[23,29,47–49] For each element's variation, three curves of superalloys IN718, IN718H, and T-800 are compared. T-800 has much higher hardness in lower temperature range but rapid softening at temperatures above 800 K. Precipitation hardened IN718 has medium hardness. Nonhardened IN718 has the lowest hardness but becomes hardened at temperatures above 900 K. It is interesting to see all these three commercial alloys approach the same hardness at 1100 K and soften at the same rate. In contrast, HEAs have a lower softening rate. Although some HEAs have lower hardness values than T-800 in a lower temperature range, a lower softening rate allows them to maintain much higher hardness than T-800 at temperatures above 1000 K. It is noted that among these data, some HEAs have a hardness around Hv 300–400 (or Rockwell hardness 30–40) at 1000°C.

As a result, this alloy system provides a wide range of hardness and displays excellent softening resistance and oxidation resistance. Thus, they

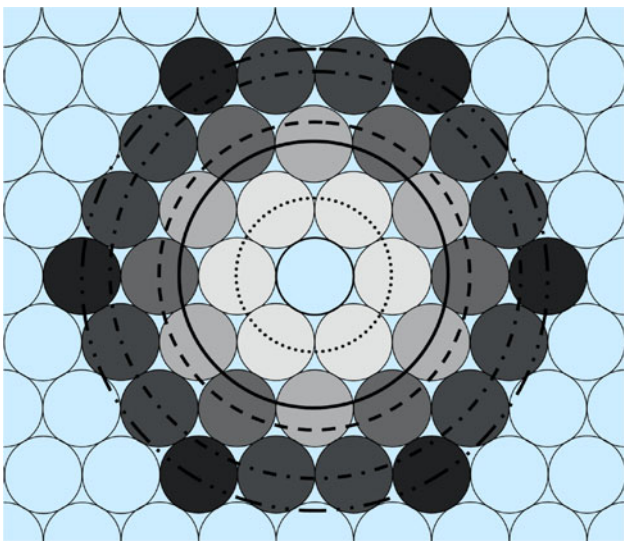

Fig. 9. Hard ball model showing shells from the first to the fifth.

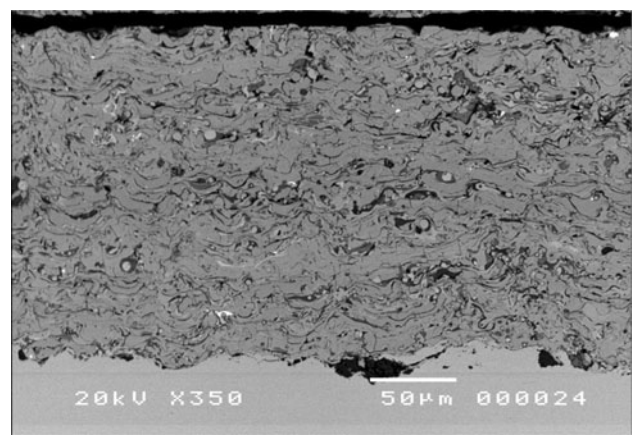

Fig. 10. Typical layer structure of nonequal-mole alloy Al-Co-Cr-Fe-Ni-Si-Ti deposited on 304 stainless steels obtained by plasma spray.

Table V. The number of atoms and distance for each shell in the hard ball model with an atomic size of r

	1st shell	2nd shell	3rd shell	4th shell	5th shell
Number of atoms	6	6	6	12	6
Distance (shell radius)	2r	3.46*r*	4*r*	5.29*r*	6*r*
Mean Distance of two close shells		3.73*r*		5.65*r*	
Deviation from mean		−7.2%	+7.2%	−6.2%	+6.2%

Table VI. The merging and atomic size difference for NiAl to NiAlCuTiZrV equimolar alloys based on hard ball model

Alloys	NiAl	NiAlCu	NiAlCuTi	NiAlCuTiZr	NiAlCuTiZrV
Atomic size deviation	±6.7%	−5.3%, + 8.3%	±7.8%	−11%, + 14%	−10.4%, + 14.7%
Deviation of 2nd and 3rd shells	±7.2% Partially merged	±7.2% Partially merged	±7.2% Partially merged	±7.2% Merged	±7.2% Merged
Deviation of 4th and 5th shells	±6.2% Merged	±6.2% Merged	±6.2% Merged	±6.2% Merged	±6.2% Merged

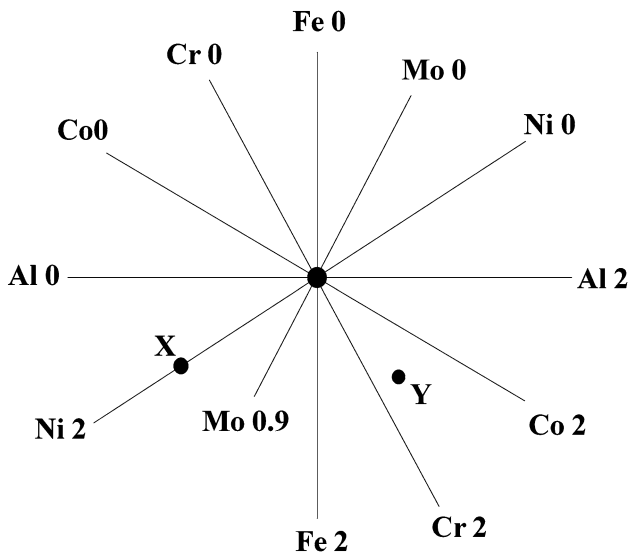

Fig. 11. Content variation lines of all elements passing through the center alloy $AlCoCrFeNiMo_{0.5}$, in which Al, Co, Cr, Fe, and Ni contents are varied from 0 to 2 in molar ratio, but Mo is from 0 to 0.9.

might find applications in different environments. Furthermore, based on these data, where there are some specific industrial applications requiring improved properties, some of these compositions studied might be considered or modified. Similarly, this route could be applied to other promising alloy systems. In other words, the systematic study of a system with compositions centered at equal-mole alloy or near-equal-mole alloy could provide a very valuable database.

Use Alloy Design Principles of Materials Science

Using principles of materials science to design and research new materials is the most basic route to develop HEAs. This route needs better understanding on the features of elements such as melting point, atomic size, crystal structure, valence electron, electronegativity, density, elastic constants, interactions in unlike atom pairs, thermodynamics and kinetics, microstructure and properties relationship, and four core effects of HEAs. In fact, most HEA researchers have used such principles to develop new HEAs for desired properties from the beginning. This route is convincing and would become more effective with increased accumulation of data, knowledge, and experiences on HEAs. For example, when you examine an equimolar alloy system such as AlCoCrFeNiMnSi and TiCoCrFeNiMnB for high strength and moderate toughness, you might find their microstructures containing several solid-solution phases and also their high hardness but poor ductility. For such cases, you could further use scanning electron microscope with energy dispersive spectrometer or electron microprobe analyzer to analyze each phase composition and use a microhardness tester to measure the microhardness. Thereafter, you could select the phase preferred for your purpose and property requirement as well as prepare the second alloy according to its composition. The monolithic phase displaying high strength and moderate ductility could be obtained because those brittle phases have been excluded. It should be mentioned that by the Gibbs phase rule, the degree of freedom in composition is high. So, you can further adjust the concentration of each element to improve some properties but still maintain the simple phase. Apparently, promising HEAs with better performance usually have nonequal-mole compositions. Equal-mole HEAs are in general the beginning points for understanding new alloy systems. Fine tuning of composition and process are always necessary to achieve aimed properties just like the historical development of high-performance traditional alloys.

FUTURE TRENDS OF HEAs

Although over 400 HEA papers have been published up to now, the understanding of the whole HEA world is still at the infant stage. However, several future trends can be pointed out at this stage:

1. More fundamental and basic science studies are required. Because materials science and solid-state physics are mainly based on the research on conventional materials with one or two principal elements, what happens in HEAs would be interesting in many aspects and become valuable academic issues. In the whole-solute matrix, different contributions to mixing entropy, mutual interactions in unlike atomic pairs, short range order, lattice distortion, electrical and thermal conductivity, vacancy concentration, diffusion coefficients, dislocation energy, staking fault energy, grain boundary energy, slip, twinning, strengthening, toughening, creep, wear, corrosion, and oxidation are all needed to be understood with their mechanisms and theories. Whether they are a simple extension from that of conventional alloys or not is still curious for scientists.
2. More research on promising alloy systems for better mechanical, chemical, and physical properties is required. This is in response to the endless requirements in the improvements of existing materials. Better performances will bring cost, energy, and resource savings for us.
3. More research on the performance challenges unattainable by traditional alloys or materials is required, such as room-temperature superconductors, alloys exceeding the performance and temperature capability of superalloys, and tools with very high hot hardness and long lifespan.
4. More research on high-entropy nitrides, carbides, oxides, and their combinations is required. A certain amount of such research[50–53] has indicated that four core effects of HEAs also hold

Table VII. The constituent phases of all Al-Co-Cr-Fe-Mo-Ni alloys centered at $AlCoCrFeMo_{0.5}Ni$ alloy

	0	0.5	1.0	1.5	2.0
Al_u	fcc + σ	fcc + σ	B2 + σ	B2 + σ	B2 + bcc
Co_v	B2 + σ	B2 + σ	B2 + σ	B2 + σ	B2 + fcc + σ
Cr_w	B2 + σ	B2 + σ	B2 + σ	B2 + σ	B2 + σ
Fe_x	–	Fe-0.6 B2 + σ	B2 + σ	B2 + σ	B2 + σ
Mo_y	bcc + B2	B2 + σ	Mo-0.9 B2 + σ	–	–
Ni_z	B2 + σ	B2 + σ	B2 + σ	B2 + fcc + σ	B2 + fcc + σ

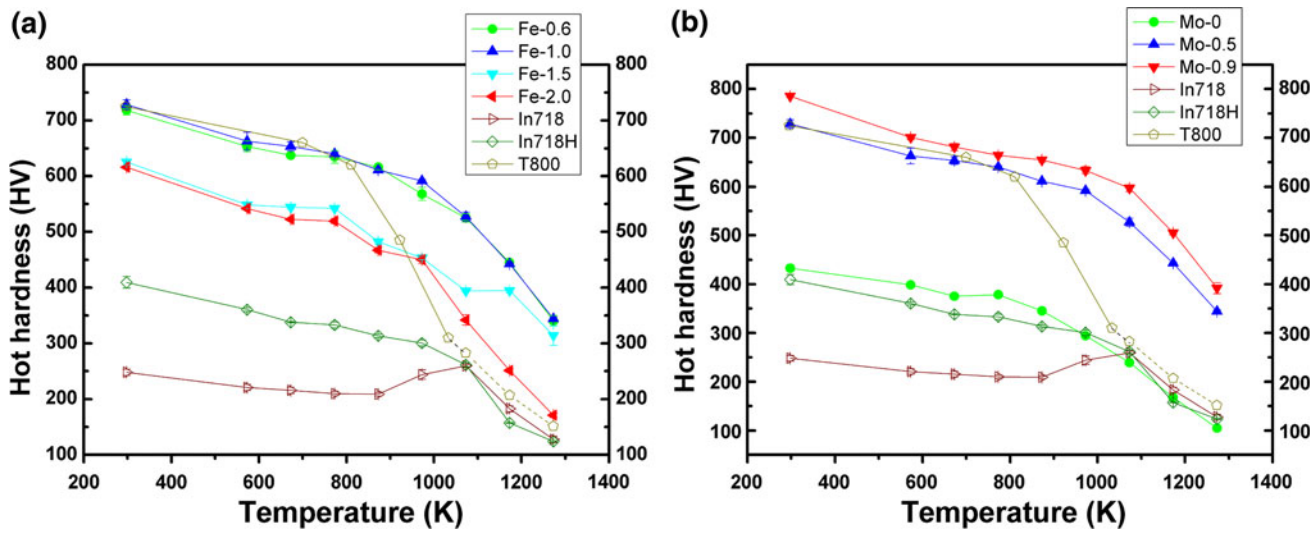

Fig. 12. Hot hardness (H) as a function of temperature for (a) $AlCoCrFe_xMo_{0.5}Ni$ alloys and (b) $AlCoCrFeMo_yNi$ alloys. Comparing alloys are Ni-based superalloys of IN718 (as received) and IN718H (precipitation hardened), and Co-based superalloy of Tribaloy T-800 (data are obtained from Stellite Company website).

true in such high-entropy ceramics (HECs), and many promising properties are obtained for diffusion barriers, hard coatings, and functional coatings.

5. Assessments of the existing database to find possible applications are required. It is believed that HEAs or HECs could solve many bottlenecks encountered by conventional materials. So, do not forget to correlate HEAs and HEC data with industrial applications and exploit their promising properties. By this effort, one might get closer to use or modify HEAs and HECs to fit the application requirements.

CONCLUSIONS

1. High-entropy materials have four core effects: high entropy, sluggish diffusion, severe lattice distortion, and cocktail effects, and could provide a wide spectrum of properties.
2. Like traditional alloys, HEAs have potential applications in different fields and might replace traditional materials.
3. Basic science, new HEAs, new HECs, and new applications are awaiting further research.

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