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A second criterion for sigma phase formation in high-entropy alloys

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The presence of the sigma phase in high-entropy alloys significantly affects their mechanical properties. Therefore, control of sigma phase formation is crucial. Current understanding of the stability of the sigma phase is largely based on the valence electron concentration (VEC) criterion. Here, we show that VEC alone is insufficient to describe its stability. A second criterion for sigma phase formation based on alloy composition is proposed. A new parameter called paired sigma-forming element (PSFE) content is invented to quantify this criterion. If PSFE content is lower than the threshold value, the sigma phase will not form even if the VEC is correct.

Keywords: High-entropy Alloys, Sigma Phase, Alloy Design, Phase Stability, Intermetallic

High-entropy alloy (HEA) is a novel alloy design concept that has received significant attention in recent years.[1–3] It has been reported that HEAs can have high strength/hardness,[4–7] exceptional damage tolerance (at cryogenic temperatures),[8] outstanding wear resistance,[9] exceptional high-temperature strength,[10,11] very good structural and chemical stabilities at high temperatures,[12,13] and good corrosion resistance.[14,15]

The sigma phase is one of the most frequently seen intermetallic phases in HEAs. It can sometimes be found in as-cast alloys, but it often forms during annealing at 600–1,000°C.[6,16–19] The sigma phase is very hard and brittle, and its presence after annealing can significantly change the mechanical properties of the alloy. For example, the formation of a sigma phase matrix in $\text{Al}_5\text{Cr}_{32}\text{Fe}_{35}\text{Ni}_{22}\text{Ti}_6$ hardens the alloy from HV481 to HV950, but reduces its fracture toughness (K_{IC}) to $\sim 5 \text{ MNm}^{-3/2}$. [19] The sigma phase is also known to reduce the tensile ductility of HEAs.[20,21] However, the sigma phase can bring advantages in some cases. For example, alloys with high fractions of the sigma phase are known to be very resistant to thermal softening.[10] The sigma phase can also be used as a surface protection layer that has outstanding wear resistance, if its formation is controlled properly.[22] In any case because the existence of the sigma phase evidently affects the mechanical properties, predicting the existence of the sigma phase and

controlling their volume fraction become critical in the design of HEAs.

Because the formation mechanism of the sigma phase in HEAs and conventional alloys can be very different, conventional strategies to predict sigma phase formation do not work for HEAs. For example, PHACOMP [23,24] and new PHACOMP [25] are both strategies to predict sigma phase formation in superalloys. However, their premises—the sigma phase being precipitated from an face-centered cubic matrix with a known composition—apparently does not hold in many HEAs.[26] Very recently, the formation conditions of the sigma phase in HEAs have been discussed in some publications.[20,26] In particular, a criterion for sigma phase formation in HEAs was proposed.[26] The criterion states that HEAs containing Cr and V as A elements are prone to sigma phase formation if their valence electron concentrations (VECs) fall between 6.88 and 7.84. This criterion successfully predicts sigma phase formation in a number of HEAs.[20,27,28] However, the VEC criterion alone is insufficient to describe the complete picture of sigma phase formation in HEAs. For example, many binary alloys do not develop the sigma phase even though they have the ‘right’ VEC—their binary phase diagrams simply do not predict so. Similarly, if five elements that do not form any binary sigma phase between each other are chosen to form a HEA, it is unlikely that this

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HEA will form the sigma phase, even if its VEC is correct.

This argument is supported by the compositions of sigma phases in published HEA literatures. These sigma phases are typically rich in elements that form binary sigma phases with each other. For example, the sigma-phase-forming pairs in the $\text{Al}_{0.3}\text{CrFe}_{1.5}\text{MnNi}_{0.5}$ alloy [18] are Cr–Fe and Cr–Mn. Al and Ni do not form the sigma phase with other elements in the alloy. The composition of the sigma phase in this alloy is indeed very rich in Cr, Fe, and Mn—the concentrations of them in this sigma phase sum up to 94.8 at%. In other words, generally it is the elements which form binary sigma phases with each other that compose the sigma phases in HEAs. Thus, these elements can be regarded as the ‘raw material’ to produce the sigma phase. Without sufficient ‘raw material’, the sigma phase is unlikely to be formed even if the VEC is correct.

In this paper, we discuss the effect of the content of these ‘raw materials’ to the formation and volume fraction of the sigma phase in HEAs. A parameter called paired sigma-forming element (PSFE) content is proposed to evaluate the amount of raw material available in the alloy. A series of alloys with different PSFE contents is designed and fabricated to probe such effects.

The alloys in the present study were prepared by vacuum arc melting. Raw materials with purities higher than 99.5% were placed in a water-cooled Cu mold and melted in Ar atmosphere. Melting was repeated for at least four times to ensure the liquid mixed well. The cast alloys were then aged at 700°C for 24 h to allow the formation of the sigma phase. The crystal structures of the alloys were identified using an X-ray diffractometer (BRUKER-D8 Discover). The X-ray used was Cu K_α radiation operated at 40 kV and 30 mA, and the scanning speed was 0.2–2°/min. Microstructure observations were conducted on a JOEL-5400 scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy capability. When the sigma phase was identified in the X-ray diffraction (XRD) pattern, its volume fraction was determined from SEM images using standard image analysis techniques.

First, we introduce the concept of PSFE. Binary sigma phases are formed between so-called *A* and *B* elements. In transition metals, *A* elements are group VB–VIIB elements and *B* elements are group VIIB–VIII elements. For example, when Mo serves as the *A* element, the corresponding sigma-forming *B* elements include Mn, Fe, and Co. If two composing elements in a multi-component alloy are known to form binary sigma phase, they are called the sigma-forming elements (SFEs) in that alloy. For instance, in the AlCoCrFeNi alloy, Cr is the only *A* element, and the corresponding *B* elements available in the alloy are Co and Fe. Therefore, Cr, Co, and Fe are the SFEs in AlCoCrFeNi . Note that although Al and Ni also form sigma phases (e.g. in

Nb–Al and V–Ni), their respective *A* elements (Nb and V) are not present in the alloy. Thus, they cannot be regarded as SFEs in this case.

The structure prototype of the sigma phase is $\text{Cr}_{50}\text{Fe}_{50}$ (Pearson symbol: tP30). Therefore, $A_{50}B_{50}$ is considered as the representative formula of the sigma phase. This means that it takes equal amount of *A* and *B* elements to form the sigma phase. Thus, the amount of ‘raw material’ in an alloy that can be used to form the sigma phase depends not on the content of SFE, but on the content of SFE that is *paired*. If an alloy contains 30 at% of *A* element, 50 at% of *B* element, and 20 at% of other elements that do not form the sigma phase with any other components, then the content of PSFE is 60 at%, i.e. 30 at% *A* and 30 at% of *B*. Note that although the content of *B* element is 50 at%, only 30 at% of *B* is *paired*, because there is only 30 at% of *A* element to pair with it. In short, one first identifies the SFEs in the alloy and determines the respective contents of *A* and *B* elements. Then, to obtain the content of PSFE, simply double the content of *A* or *B* element, whichever is smaller.

A total of 32 HEAs with different PSFE contents were designed and fabricated. Most of the alloys are designed specifically for this study, while some are taken from the literature.[10,29,30] Table 1 lists the notations, PSFE contents, compositions, VECs, and volume fractions of the sigma phase of the 32 alloys. A wide span of PSFE contents is included, ranging from 5 to 80 at%. The VEC values of all the alloys except one fall in the sigma-forming VEC range for Cr- and V-containing HEAs (6.88–7.84). The exception is alloy A25, which is taken from [30]. This alloy contains Mo, another known *A* element. It has been pointed out that alloys containing Mo can have different sigma-forming VEC ranges.[26]

The volume fractions of sigma phases in each alloy are plotted against their respective PSFE contents in Figure 1. The behavior of the alloys can be divided into three stages according to their PSFE contents. The first stage occurs when the PSFE content is low. At this stage, none of the alloys (A1–A7) develop the sigma phase. The XRD patterns of these alloys are shown in Figure 2. Indeed, in all these patterns, peaks corresponding to the sigma phase are not detected. The second stage is the intermediate stage. At this stage, the alloys may or may not develop the sigma phase, depending on their compositions. The third stage is the sigma-prone stage, which occurs at high PSFE contents. At this stage, all the alloys develop the sigma phase after annealing. The transition between the three stages occurs at two threshold PSFE contents. From Figure 1, the first threshold PSFE content (transition between stages I and II) is somewhere between 20 and 25 at%. The second threshold PSFE content (transition between stages II and III) is between 40 and 45 at%. The above results have important implications for the design of HEAs:

Table 1. Notations, PSFE contents (at%), compositions, VECs, and volume fractions of the sigma phase (%) of the 32 alloys used in this study.

Alloy notation	PSFE content	Composition	VEC	Volume fraction of σ
A1	5%	Co _{28.75} Fe _{31.25} Ni _{7.5} Ti ₃₀ V _{2.5}	7.16	0
A2	10%	Al _{16.5} Co _{22.5} Cr ₅ Fe _{12.5} Ni ₃₀ Ti _{13.5}	7.36	0
A3	10%	Al ₁₅ Cr ₅ Fe ₃₀ Ni ₃₀ Ti ₂₀	6.95	0
A4	15%	Al ₂₂ Co ₂₈ Ni _{31.75} Ti _{10.75} V _{7.5}	7.16	0
A5	15%	Co ₂₅ Fe ₂₅ Mn ₁₅ Ni ₁₅ Ti _{12.5} V _{7.5}	7.68	0
A6	20%	Co ₂₅ Fe ₂₅ Ni ₁₀ Ti ₃₀ V ₁₀	6.95	0
A7	20%	Al ₁₀ Co ₂₀ Cr ₁₀ Fe ₂₆ Mn ₁₄ Ni ₁₀ Ti ₁₀	7.16	0
A8	25%	Al _{17.5} Co ₂₄ Cr _{7.5} Fe ₂₂ Ni ₁₄ Ti ₁₀ V ₅	6.95	15
A9	25%	Al _{18.75} Co _{26.25} Cr _{6.25} Fe ₂₅ Ni _{17.5} V _{6.25}	7.36	0
A10	25%	Al ₁₅ Co _{24.375} Cr _{12.5} Fe _{21.875} Ni _{26.25}	7.77	0
A11	25%	Co _{15.625} Cr _{12.5} Fe _{15.625} Mn _{12.5} Ni _{18.750} Ti ₂₅	7.16	0
A12	25%	Al _{11.25} Co _{28.125} Fe _{6.875} Ni _{31.25} Ti ₁₀ V _{12.5}	7.57	0
A13	30%	Co ₂₅ Fe ₂₅ Mn _{17.5} Ni _{12.5} Ti ₅ V ₁₅	7.68	17
A14	30%	Al ₁₅ Co ₂₀ Cr ₁₅ Fe ₃₀ Mn ₂₀	6.95	0
A15	35%	Co ₃₅ Cr _{12.5} Mn ₃₀ Ti _{17.5} V ₅	6.95	0
A16	35%	Al ₂₀ Co _{18.75} Cr ₁₀ Fe _{13.75} Ni ₃₀ V _{7.5}	7.36	10
A17	40%	Al ₁₇ Co ₂₁ Cr ₂₀ Fe ₂₂ Ni ₂₀	7.36	40
A18	40%	Al _{6.7} Co _{23.3} Cr ₂₀ Fe _{21.7} Ni _{23.3} Ti ₅	7.77	0
A19	40%	Co ₂₀ Cr ₂₀ Fe ₂₀ Ni ₂₀ Zr ₂₀	7.40	21
A20	45%	Al ₁₀ Co _{26.25} Cr ₁₅ Fe ₅ Ni _{26.25} Ti ₁₀ V _{7.5}	7.36	17
A21	50%	Al ₁₀ Co _{33.75} Cr ₂₅ Ni _{21.25} Ti ₁₀	7.36	50
A22	50%	Al _{16.7} Co _{16.7} Cr _{16.7} Fe _{16.7} Mo _{8.3} Ni ₂₅	7.33	45
A23	60%	Al _{19.6} Co _{19.6} Cr _{19.6} Fe _{11.8} Mo _{9.8} Ni _{19.6}	7.02	55
A24	65%	Al _{16.9} Co _{16.9} Cr _{16.9} Fe _{16.9} Mo _{15.3} Ni _{16.9}	7.02	75
A25	67%	Co _{22.2} Cr _{22.2} Fe _{22.2} Mo _{11.1} Ni _{22.2}	8.00	15
A26	67%	Al ₈ Co ₁₃ Cr ₂₁ Fe ₁₅ Mo ₁₃ Ni ₃₀	7.65	20
A27	70%	Al ₅ Co ₄₁ Cr ₃₅ Fe ₉ Ni ₅ Ti ₅	7.36	56
A28	75%	Al _{5.66} Co _{18.87} Cr _{37.74} Fe _{18.87} Ni _{18.87}	7.53	44
A29	77%	Al _{15.4} Co _{15.4} Cr _{30.8} Fe _{15.4} Mo _{7.7} Ni _{15.4}	6.92	66
A30	80%	Co ₂₀ Cr ₂₀ Fe ₂₀ Ni ₂₀ Mo ₂₀	7.80	58
A31	80%	Co ₂₀ Cr ₂₀ Fe ₂₀ Ni ₂₀ V ₂₀	7.60	57
A32	80%	Co ₂₀ Cr ₄₀ Fe ₂₀ Ni ₂₀	7.80	5

as long as the PSFE content of an alloy is 20 at% or lower, it will not develop the sigma phase even if its VEC value falls in the sigma-forming region. In other words, there is a threshold PSFE content below which sigma phase formation is suppressed. This provides an additional dimension (other than adjusting the VEC) to design sigma-free HEAs. Additionally, as long as the PSFE content does not exceed 40 at%, the alloy may still remain sigma-free. However, the factor that controls sigma phase formation at the second stage is still unclear.

In addition to the existence of the three different stages, it is also important to observe how the PSFE content affects the volume fraction of the sigma phase. This is also seen in Figure 1. The trend is somewhat counterintuitive—higher PSFE contents do not necessarily lead to higher sigma phase volume fractions. For example, CoCr₂FeNi (A32) has a high PSFE content of 80 at% but it contains only 5 vol% of the sigma phase. In contrast, the PSFE content of Al₁₀Co_{33.75}Cr₂₅Ni_{21.25}Ti₁₀ (A21) is only 50 at%, but it contains 50 vol% of the sigma phase. However, the PSFE content does affect the distribution of the sigma phase volume fraction, particularly its maximum value. This can be seen by delineating the distribution areas

of data points in stages II and III, which are shown as trapeziums in Figure 1. Both trapeziums have a larger height on the right side, which demonstrates that the maximum volume fraction of the sigma phase increases with the PSFE content.

The existence of threshold PSFE content for sigma phase formation is not unreasonable. Firstly, the sigma phases in the present study are formed between (Cr, V, Mo) and (Mn, Fe, Co, Ni). Sigma phases of these compositions typically have small negative, sometime even positive, enthalpies of formation. For example, the formation enthalpies of CrFe, Mo₃Co₂, and VFe are 4, −4, and −8 kJ (mole of atoms)^{−1}, respectively.[31] This suggests that these sigma phases are not very energetically competitive compared with other intermetallic phases. Secondly, the higher configurational entropy in HEA is known to increase the solubility of composing elements in the phases.[1] Therefore, when the PSFE content is sufficiently low, the SFES can stay in existing phases without exceeding their solubility limits. In that case, no sigma phase will be formed.

The increase in the maximum sigma phase volume fraction with increasing PSFE content is also not unexpected. As mentioned previously, PSFEs can be

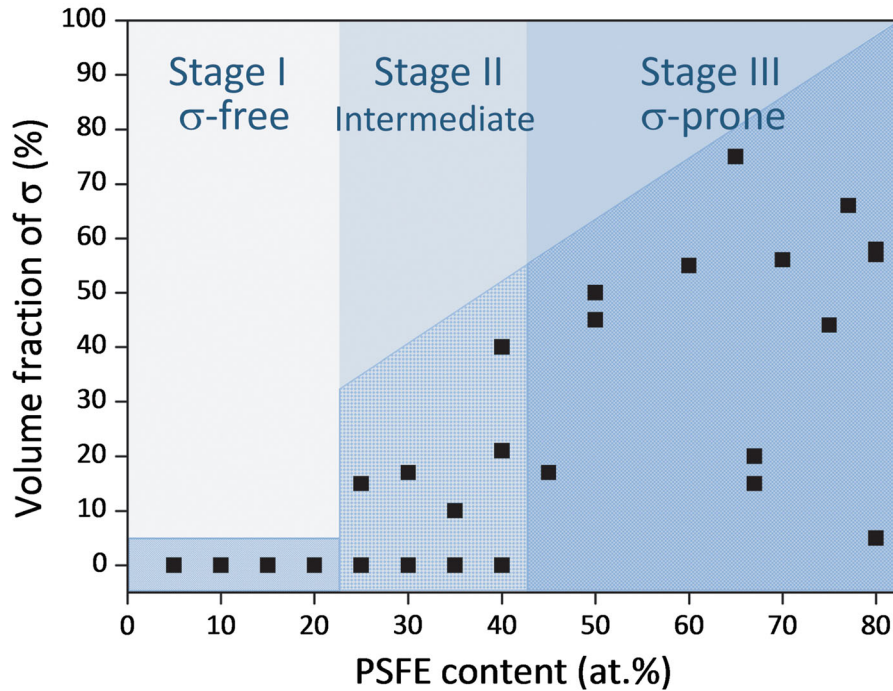


Figure 1. The PSFE contents and sigma phase volume fractions of the 32 alloys used in this study. The behaviors of the alloys can be divided into three stages based on the PSFE content.

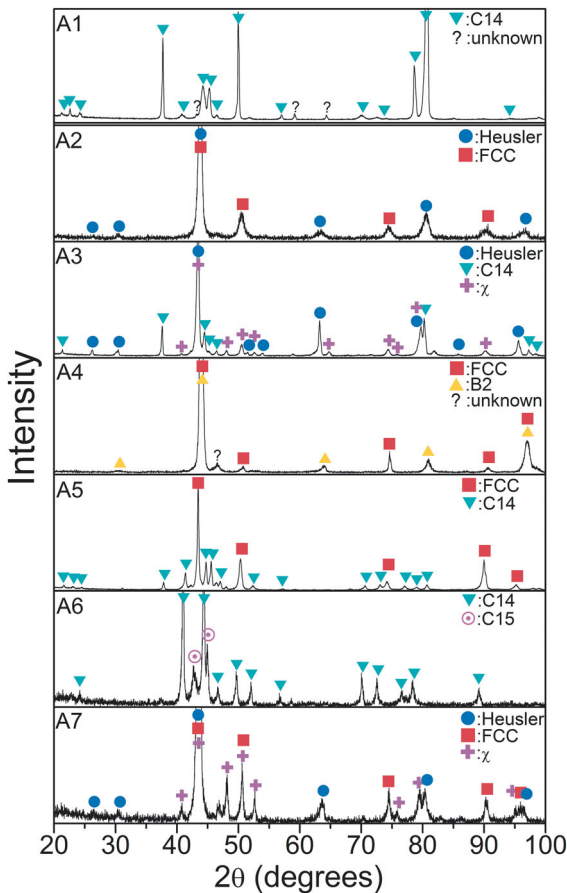


Figure 2. XRD patterns of alloys A1–A7. No sigma phase is detected in these alloys despite their ‘correct’ VEC.

regarded as the ‘raw material’ to form the sigma phase. Once all the raw materials are consumed, sigma phase formation cannot proceed. Thus, the maximum amount of sigma phase attainable in an alloy should certainly be proportional to the raw material available in that alloy, i.e. the PSFE content. The roughly linear relationship between the two clearly supports this argument. It should be noted, however, that a higher PSFE content does not always translate to a higher sigma phase volume fraction. This is because the type of phases present in an alloy and their respective volume fraction are the result of a rather complex competition among all possible phases. The volume fraction of the sigma phase depends not only on the composition of the sigma phase, but also on the composition of other co-existing phases. Because the situation (type of existing phases and their compositions) differs in each alloy, the volume fraction of the sigma phase can also vary significantly. If other phases are more competitive, the volume fraction of the sigma phase can be evidently lowered. In other words, having a sufficient amount of raw material for the sigma phase does not mean that these raw materials will all be used to produce the sigma phase.

Although the VEC criterion provides useful guideline to the existence of the sigma phase, it alone is insufficient to describe the complete picture of sigma phase formation in HEAs. If the content of PSFE is low, no sigma phase will be observed even if the VEC is correct—Figure 1 has clearly demonstrated this. The effect of PSFE content is therefore as important as that

of the VEC value, and is a necessary factor for reliable predictions of sigma phase formation. Thus, PSFE content should be regarded as the second criterion for sigma phase formation in HEAs. The two criteria are complementary to each other, and the sigma phase will form only if *both* criteria are satisfied. The effect of PSFE content was not observed in previous literatures regarding sigma phase formation because the PSFE contents in many HEAs exceed 40 at%. This is because Cr, Fe, and Co are among the most frequently used elements in HEAs, but any quinary equimolar HEA that contains (Cr, Fe) or (Cr, Co) has a PSFE content of 40 at%. In deriving the VEC criterion, 15 out of the 18 alloys used have PSFE contents ≥ 40 at%.[26] In particular, all the alloys that fall within the sigma-forming VEC range have PSFE contents ≥ 40 at%. Therefore, the PSFE content criterion is automatically satisfied and its effect is hidden.

Finally, it should be noted that the elements involved in the present study include Al, Co, Cr, Fe, Mn, Mo, Ni, Ti, V, and Zr. If the alloys of interest have very different composing elements, they may have different threshold PSFE contents between the three stages.

In summary, the effect of PSFE content on sigma phase formation is probed in a series of HEAs that has the correct VEC for sigma phase formation. Three stages are identified based on the PSFE content of the alloys. Below the first threshold PSFE content (somewhere between 20 and 25 at%), the sigma phase is not observed even if the VEC of the alloy is between 6.88 and 7.84. Above the second threshold PSFE content (somewhere between 40 and 45 at%), the sigma phase appears in all alloys after annealing. In between the two threshold values, the sigma phase may or may not develop in the alloy. The effect of PSFE content on sigma phase formation is significant, and should therefore be regarded as the second criterion of sigma phase formation. The two criteria are complementary to each other, and the sigma phase will form only if *both* criteria are satisfied. It is also noticed that alloys with higher PSFE contents do not necessarily contain higher volume fractions of the sigma phase. However, the maximum volume fraction of the sigma phase do increase with the PSFE content.

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References

- [1] Yeh JW, Chen SK, Lin SJ, et al. Nanostructured high-entropy alloys with multiple principal elements: novel

- alloy design concepts and outcomes. *Adv Eng Mater.* 2004;6:299–303.
- [2] Tsai MH, Yeh JW. High-entropy alloys: a critical review. *Mater Res Lett.* 2014;2:107–123.
- [3] Zhang Y, Zuo TT, Tang Z, et al. Microstructures and properties of high-entropy alloys. *Prog Mater Sci.* 2014;61:1–93.
- [4] Tong CJ, Chen MR, Chen SK, et al. Mechanical performance of the $\text{Al}_x\text{CoCrCuFeNi}$ high-entropy alloy system with multiprincipal elements. *Metall Mater Trans A.* 2005;36A:1263–1271.
- [5] Zhou YJ, Zhang Y, Wang YL, Chen GL. Solid solution alloys of AlCoCrFeNiTi_x with excellent room-temperature mechanical properties. *Appl Phys Lett.* 2007;90:181904.
- [6] Chen ST, Tang WY, Kuo YF, et al. Microstructure and properties of age-hardenable $\text{Al}_x\text{CrFe}_{1.5}\text{MnNi}_{0.5}$ alloys. *Mater Sci Eng A.* 2010;527:5818–5825.
- [7] He JY, Wang H, Huang HL, et al. A precipitation-hardened high-entropy alloy with outstanding tensile properties. *Acta Mater.* 2016;102:187–196.
- [8] Gludovatz B, Hohenwarter A, Catoor D, Chang EH, George EP, Ritchie RO. A fracture-resistant high-entropy alloy for cryogenic applications. *Science.* 2014;345:1153–1158.
- [9] Chuang MH, Tsai MH, Wang WR, Lin SJ, Yeh JW. Microstructure and wear behavior of $\text{Al}_x\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_y$ high-entropy alloys. *Acta Mater.* 2011;59:6308–6317.
- [10] Hsu CY, Juan CC, Wang WR, Sheu TS, Yeh JW, Chen SK. On the superior hot hardness and softening resistance of $\text{AlCoCr}_x\text{FeMo}_{0.5}\text{Ni}$ high-entropy alloys. *Mater Sci Eng A.* 2011;528:3581–3588.
- [11] Senkov ON, Wilks GB, Scott JM, Miracle DB. Mechanical properties of $\text{Nb}_{25}\text{Mo}_{25}\text{Ta}_{25}\text{W}_{25}$ and $\text{V}_{20}\text{Nb}_{20}\text{Mo}_{20}\text{Ta}_{20}\text{W}_{20}$ refractory high entropy alloys. *Intermetallics.* 2011;19:698–706.
- [12] Tsai MH, Wang CW, Tsai CW, et al. Thermal stability and performance of NbSiTaTiZr high-entropy alloy barrier for copper metallization. *J Electrochem Soc.* 2011;158:H1161–H1165.
- [13] Liu WH, Wu Y, He JY, Nieh TG, Lu ZP. Grain growth and the Hall-Petch relationship in a high-entropy FeCrNiCoMn alloy. *Scr Mater.* 2013;68:526–529.
- [14] Chou YL, Wang YC, Yeh JW, Shih HC. Pitting corrosion of the high-entropy alloy $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}\text{Mo}_{0.1}$ in chloride-containing sulphate solutions. *Corros Sci.* 2010;52:3481–3491.
- [15] Kao YF, Lee TD, Chen SK, Chang YS. Electrochemical passive properties of $\text{Al}_x\text{CoCrFeNi}$ ($x = 0, 0.25, 0.50, 1.00$) alloys in sulfuric acids. *Corros Sci.* 2010;52:1026–1034.
- [16] Ren B, Liu ZX, Cai B, Wang MX, Shi L. Aging behavior of a $\text{CuCr}_2\text{Fe}_2\text{NiMn}$ high-entropy alloy. *Mater Des.* 2012;33:121–126.
- [17] Ng C, Guo S, Luan J, Shi S, Liu CT. Entropy-driven phase stability and slow diffusion kinetics in an $\text{Al}_{0.5}\text{CoCrCuFeNi}$ high entropy alloy. *Intermetallics.* 2012;31:165–172.
- [18] Tsai MH, Yuan H, Cheng G, et al. Significant hardening due to the formation of a sigma phase matrix in a high entropy alloy. *Intermetallics.* 2013;33:81–86.
- [19] Lin CW, Tsai MH, Tsai CW, Yeh JW, Chen SK. Microstructure and aging behaviour of $\text{Al}_5\text{Cr}_{32}\text{Fe}_{35}\text{Ni}_{22}\text{Ti}_6$ high entropy alloy. *Mater Sci Technol.* 2015;31:1165–1170.

- [20] Stepanov ND, Shaysultanov DG, Salishchev GA, et al. Effect of V content on microstructure and mechanical properties of the CoCrFeMnNiV_x high entropy alloys. *J Alloys Compd.* 2015;628:170–185.
- [21] Zaddach AJ, Scattergood RO, Koch CC. Tensile properties of low-stacking fault energy high-entropy alloys. *Mater Sci Technol.* 2015;636:373–378.
- [22] Chuang MH, Tsai MH, Tsai CW, et al. Intrinsic surface hardening and precipitation kinetics of Al_{0.3}CrFe_{1.5}MnNi_{0.5} multi-component alloy. *J Alloys Compd.* 2013;551:12–18.
- [23] Boesch WJ, Slaney JS. Preventing sigma phase embrittlement in nickel-base superalloys. *Metals Progress.* 1964;86:109–111.
- [24] Sims CT, Stoloff NS, Hagel WC. *Superalloys II*. New York: John Wiley & Sons; 1987.
- [25] Morinaga M, Yukawa N, Adachi H, Ezaki H. New PHA-COMP and its applications to alloy design. In: Gell M, Kortovich CS, Bricknell RH, Kent WB, Radavich JF, editors. *Superalloys 1984*. Warrendale, PA: Metallurgical Society of AIME; 1984. p. 523–532.
- [26] Tsai MH, Tsai KY, Tsai CW, Lee C, Juan CC, Yeh JW. Criterion for sigma phase formation in Cr- and V-containing high-entropy alloys. *Mater Res Lett.* 2013;1:207–212.
- [27] Singh AK, Kumar N, Dwivedi A, Subramaniam A. A geometrical parameter for the formation of disordered solid solutions in multi-component alloys. *Intermetallics.* 2014;53:112–119.
- [28] Zhang C, Wu GF, Dai PQ. Phase transformation and aging behavior of Al_{0.5}CoCrFeNiSi_{0.2} high-entropy alloy. *J Mater Eng Perform.* 2015;24:1918–1925.
- [29] Hsu CY, Sheu TS, Yeh JW, Chen SK. Effect of iron content on wear behavior of AlCoCrFe_xMo_{0.5}Ni high-entropy alloys. *Wear.* 2010;268:653–659.
- [30] Hsu CY, Juan CC, Sheu TS, Chen SK, Yeh JW. Effect of aluminum content on microstructure and mechanical properties of Al (x) CoCrFeMo_{0.5}Ni high-entropy alloys. *JOM.* 2013;65:1840–1847.
- [31] de Boer FR, Boom R, Mattens WCM, Miedema AR, Niessen AK. *Cohesion in metals: transition metal alloys*. Amsterdam: Elsevier Science Publishers B.V.; 1988.