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# **Results in Physics**

journal homepage: www.elsevier.com/locate/rinp

# Body-centered cubic phase stability in cobalt-free refractory high-entropy alloys

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#### ARTICLE INFO

Keywords: Refractory high-entropy alloys Cobalt-free Phase formation Alloy design Radiation resistant

#### ABSTRACT

Cobalt-free refractory high-entropy alloys (RHEAs) are strong contenders for structural materials in nuclear reactors because they do not exhibit cobalt activity under irradiation. The mechanical properties and thermal stability of RHEAs are primarily attributed to the solid solution phase, which is essentially the body-centered cubic (BCC) phase. The BCC phase formation rules thus became the basic criterion in the compositional design of RHEAs. In this paper, the BCC phase formation rules in cobalt-free RHEAs were determined via the calculation of six semiempirical parameters, namely, the entropy of mixing, enthalpy of mixing, atomic size difference,  $\Omega$ -parameter, d-orbital energy level and valance electron concentration. The mixing enthalpy and atomic size differences are more effective than other semiempirical parameters for predicting BCC phase stability in cobalt-free RHEAs.

#### Introduction

Since the concept of equiatomic or near-equiatomic multicomponent alloys comprising four or more metallic elements was proposed, highentropy alloys (HEAs) have attracted significant interest [1-3]. Compared to those of conventional metallic materials such as steels [4,5], copper alloys [6,7], tungsten alloys [8] and niobium alloys [9], the superior comprehensive mechanical properties of HEAs [10-13], especially their stable properties under extreme environments [14–18], have made them one of the most promising structural materials for nextgeneration nuclear energy systems [14]. For instance, the disordered solid solution phase still remained in a CrFeCoNi alloy under 1250 keV electron irradiation for up to 1 dpa at 673 K, and no phase separation or decomposition was detected [19]. It was reported that the Al<sub>x</sub>CoCrFeNi alloy system exhibited significantly lower irradiation-induced volume swelling than did conventional materials under 3 MeV Au-ion irradiation [20]. However, cobalt activation due to neutron irradiation makes Co-containing HEAs unsuitable for nuclear engineering applications [21,22]. Refractory HEAs (RHEAs) are a type of HEA that contains multiple transition elements with high melting points, such as Nb, Mo, Ta, W, Hb, V, Zr and Ti, as their main components can meet high-temperature stability and Co-free requirements [23–25].

The mechanical properties of RHEAs can be optimized by adjusting the phase components and microstructures through the selection of alloy systems and changing alloying elements [26]. However, the final phase structures can often be detected only after manufacturing due to the complex composition of RHEAs, which undoubtedly adds to the significant cost of the study. During the last decade, several semiempirical phase formation rules, such as the entropy of mixing ( $\Delta S_{mix}$ ), enthalpy of mixing ( $\Delta H_{mix}$ ), atomic size difference ( $\delta$ ) and  $\Omega$  parameter, have been proposed to improve HEA design [27,28]. It is easy to obtain a solid solution phase in HEAs when  $12 \le \Delta S_{mix} \le 17.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, -15 \le$  $\Delta H_{mix} \leq 5 \text{ kJ} \cdot \text{mol}^{-1}, \delta \leq 6.6 \text{ and } \Omega \geq 1.1 \text{ [27,28]}.$  With the development of related research, new parameters related to valence electrons, such as the d-orbital energy level  $(\overline{Md})$  and valence electron concentration (VEC), have been proposed to further improve the phase formation rules [29,30]. These six parameters are effective at predicting the phase formation of some HEAs. Nevertheless, the feasibility of phase prediction

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https://doi.org/10.1016/j.rinp.2024.107688

Received 1 February 2024; Received in revised form 7 April 2024; Accepted 16 April 2024 Available online 17 April 2024

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for RHEAs still needs further study.

In this work, multicomponent systems of Co-free RHEAs reported in the literature were collected, and the corresponding parameters, including  $\Delta S_{mix}$ ,  $\Delta H_{mix}$ ,  $\Omega$ ,  $\delta$ ,  $\overline{\text{Md}}$  and *VEC*, were calculated. Solid solution phase formation rules for Co-free RHEAs were proposed based on composition design theory, which can be used for nuclear engineering applications. The effect of Al in Co-free RHEAs on BCC phase formation was studied.

#### Methods

#### Data collection

The various multicomponent systems of Co-free RHEAs were summarized by collecting alloy systems in previous reports [31–103]. The compositions of Co-free RHEAs and the calculated values of the six parameters  $\Delta S_{mix}$ ,  $\Delta H_{mix}$ ,  $\Omega$ ,  $\delta$ ,  $\overline{\text{Md}}$  and *VEC* are listed in Table. A1. The phase components of Co-free RHEAs were characterized under as-cast/ homogenized/recrystallized conditions.

#### Composition design theory

The four semiempirical parameters  $\Delta S_{mix}$ ,  $\Delta H_{mix}$ ,  $\Omega$ , and  $\delta$  are defined by the following equations [27,28,104]:

$$\Delta S_{mix} = -R \sum_{i=1}^{n} C_i \ln C_i \tag{1}$$

where  $C_i$  is the atomic fraction of the *i*-th element,  $R = 8.314 \text{ JK}^{-1} \cdot \text{mol}^{-1}$  is the gas constant, and

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{n} \Omega_{ij} C_i C_j$$
<sup>(2)</sup>

where the *i*-th element is distinct from the *j*-th element;  $\Omega = 4\Delta H_{AB}^{mix}$  is the enthalpy of mixing between the interacting elements *i* and *j*; and

$$\delta = \sqrt{\sum_{i=1, i \neq j}^{n} C_{i} (1 - r_{i}/\bar{r})^{2}},$$
(3)

where  $r_i$  is the atomic radius of the *i* th element and the average atomic radius  $\bar{r}$  is defined as  $\bar{r} = \sum_{i=1}^{n} c_i r_i$ .  $\Omega$  is a parameter that takes into account the combined effects of  $\Delta S_{mix}$  and  $\Delta H_{mix}$  and is expressed as follows:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|},\tag{4}$$

where  $T_m$  is the melting temperature of the multicomponent alloy. Two other d-electron-related parameters,  $\overline{\text{Md}}$  and *VEC*, were also adopted, which were proposed as [29,30,105]:

$$\overline{Md} = \sum_{i=1}^{n} C_i (Md)_i, \tag{5}$$

$$VEC = \sum_{i=1}^{n} C_i (VEC)_i,$$
(6)

where  $(Md)_i$  and  $(VEC)_i$  are the d-orbital energy level and VEC of the *i*-th element, respectively. It is important to note that the alloying elements M exhibit different Md values when considering the structures of various solvent elements X due to the influence of electronegativity and the atomic radius of both solute and solvent elements [106,107]. Therefore, the Md values of the alloying elements in FCC Ni, BCC Fe and BCC Cr are all considered to verify the feasibility of each structure in Co-free RHEAs; these values are listed in Table 1 [108,109].

Table 1

Mdvalues of the alloying elements in FCC Ni, BCC Fe and BCC C	Cr
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Alloying element	<i>Md</i> value in FCC Ni	<i>Md</i> value in BCC Fe	<i>Md</i> value in BCC Cr
Ti	2.271	2.497	2.87
V	1.543	1.61	1.998
Cr	1.142	1.059	1.301
Mn	0.957	0.854	0.752
Fe	0.858	0.825	0.694
Со	0.777	0.755	0.658
Ni	0.717	0.661	0.213
Cu	0.615	0.637	-0.346
Zr	2.944	3.074	3.359
Nb	2.117	2.335	2.662
Mo	1.55	1.663	1.968
Hf	3.02	3.159	4.518
Та	2.224	2.486	3.605
W	1.655	1.836	2.768
Al	1.9	1.034	1.034

#### Results

The individual parameter values of phases in RHEAs

The effects of parameters Md in FCC Ni, Md in BCC Fe, Md in BCC Cr, VEC,  $\Delta S_{mix}$ ,  $\Delta H_{mix}$ ,  $\Omega$  and  $\delta$  on the stability of various phases in Co-free RHEAs are clearly plotted in Fig. 1. All four phases, bulk metallic glass (BMG), intermetallic (IM), BCC and intermetallic mixed phase (BCC + IM) and the BCC phase, have different Md values for FCC Ni, BCC Fe and BCC Cr, respectively. Md in FCC Ni has the lowest values, and the highest values are in BCC Fe; Md in BCC Cr is between the former two. It can be clearly seen from Fig. 1a, b and c that Md for BMG and IM are relatively low, and the BCC + IM phase and BCC phase are distributed in wide ranges that almost cover the ranges of BMG and IM. Conversely, the VECs for BMG and IM had relatively greater values than did those for the BCC + IM phase and BCC phase. BMGs and IMs are prone to form when the VEC is greater than 5.67. However, describing the difference between these four phases in terms of  $\Delta S_{mix}$  is difficult because their ranges overlap. Like  $\overline{Md}$ ,  $\Delta H_{mix}$  is relatively high for the BCC phase and low for the BMG and IM phases. A clear phase boundary of -18.78 kJ·mol<sup>-1</sup> in terms of  $\Delta H_{mix}$  between the BMG and BCC phases can be observed in Fig. 1f. As the  $\Omega$  parameter is a function of  $\Delta S_{mix}$  and  $\Delta H_{mix}$ , BMG and IM are more stable when  $\Omega$  is lower than 1.65. It is noteworthy that the distribution range of the BCC phase is significantly different from that of the BMG and IM phases in terms of  $\delta$ . Only the BCC + IM phase forms when  $\delta$  is in the range of 7.63%—9.25%, and the BMG and IM phases form when  $\delta$  is greater than 9.25. As shown in Fig. 1,  $\Delta H_{mix}$ and  $\delta$  have the most significant effects on the formation of the solid solution phase and BMG. However, the distribution ranges of the BCC +IM phase and BCC phase of the BMG and IM phases always overlap and are difficult to distinguish. Further research is required for BMG and IM due to a lack of data.

#### Effect of various parameters on BCC-structured RHEAs

The excellent mechanical properties of RHEAs are mainly attributed to the solid solution phase, and the solid solution phase formation rules are critical for phase prediction in RHEAs [24,110]. Therefore, in the following sections, only the BCC + IM phase and BCC phase are discussed. It is noted that in Table. A1, a large number of RHEAs contain the nontransition metal Al. Al, as an extra element, can significantly impact the properties of RHEAs and is often used to adjust phase components and structure [111,112]. Therefore, there are two groups of Co-free RHEAs based on whether they contain Al.

The effects of the individual parameters on the solid solution phase stability in the two groups of Co-RHEAs are shown in Fig. 2. As shown in



Fig. 1. The effect of  $\overline{\text{Md}}$  for alloying elements in FCC Ni (a), BCC Fe (b) and BCC Cr (c), VEC (d),  $\Delta S_{mix}$  (e),  $\Delta H_{mix}$  (f),  $\Omega$  (g) and  $\delta$  (h) on phase stability in RHEAs.

Fig. 2a, b and c, Md in three different structures are unable to distinguish between the BCC phase and mixed phase of two groups of Co-free RHEAs. The distribution ranges of the mixed phase and BCC phase overlap with each other for both VEC and  $\Delta S_{mix}$ , irrespective of the presence of Al. In terms of  $\Delta H_{mix}$ , as illustrated in Fig. 2f, Al-containing RHEAs generally have more negative values than Al-free RHEAs, and the mixed phase of Al-containing RHEAs has even more negative values than the BCC phase. Notably, these two alloy systems contain the FCC structural element Ni, and the  $\Delta H_{mix}$  of RHEAs can reach a very negative value with the addition of Ni, thus forming a mixed phase. As  $|\Delta H_{mix}|$ increases and  $\Omega$  decreases, the inverse relationship between  $\Omega$  and  $\Delta H_{mix}$ is well established, as shown in Fig. 2g. Different distributions of  $\delta$  can be found between the mixed phase and the BCC phase within the two groups of RHEAs. The mixed phase had higher  $\delta$  values than did the BCC phase. However, it is still impossible to describe the solid solution formation rules for Co-free RHEAs when only one parameter is considered, regardless of the presence of Al.

Combined effect of parameters on BCC-structured RHEAs

Effect of the atomic size difference on the phase stability of Co-free RHEAs

Numerous studies have reported that  $\delta$  plays an important role in the phase prediction of HEAs [28,113,114]. It is important to note that  $\delta$  cannot be utilized as a single parameter for predicting phase formation. Therefore, the distributions of  $\delta$  superimposed on the valence electron-related parameters are plotted in Fig. 3. Interestingly, the BCC phase of the two Co-free RHEAs is distributed in the upper-right and lower-left regions of the  $\overline{Md}$  and  $\delta$  plots, as shown in Fig. 3a, b and c. Compared with the other two  $\overline{Md}$  plots, the BCC + IM phase in the Al-containing RHEAs is distributed in a region similar to that of the Al-free RHEAs when  $\overline{Md}$  is calculated based on FCC Ni, and the clear solid solution formation rules cannot be defined from the random distribution. For  $\overline{Md}$  in BCC Fe and Cr, the BCC + IM phase of the Al-containing RHEAs is distributed between these two regions, while the majority of the BCC + IM phase of the Al-free RHEAs is distributed between these two regions.



Fig. 2. Effect of  $\overline{Md}$  for FCC Ni (a), BCC Fe (b), BCC Cr (c), VEC (d),  $\Delta S_{mix}$  (e),  $\Delta H_{mix}$  (f),  $\Omega$  (g) and  $\delta$  (h) on the phase stability of BCC-structured RHEAs.

mainly consist of a combination of 3d, 4d and 5d transition metals, resulting in high  $\delta$  values. With the additions of high- $\overline{\text{Md}}$ -value elements, Hf and Zr, the Co-free RHEAs show high  $\overline{\text{Md}}$  values. However, if the  $\delta$  values of Al-free and Al-containing RHEAs exceed 7.63 % and 6.28 %, respectively, IM phases will form in Co-free RHEAs. The *VEC* in Fig. 3d displays a comparable distribution of the BCC phase in Al-free RHEAs, whereas a distinct two-part distribution is not found in Al-containing RHEAs with a BCC phase. Likewise, if the Co-free RHEAs contain low *VEC* elements such as Hf and Zr, they are located in the lower-right region. With the addition of the nontransition metal Al, the *VEC* values of Co-free RHEAs significantly decrease since Al has a lower *VEC* than transition metals.

The effects of  $\delta$  superimposed on  $\Delta S_{mix}$ ,  $\Delta H_{mix}$  and  $\Omega$  are shown in Fig. 4. Like for the effect of a single  $\Delta S_{mix}$ , the  $\Delta S_{mix} - \delta$  plot still displays a random distribution of phase stability. The mixed and BCC phases are divided into four parts based on whether the Co-free RHEAs contained Al when  $\Delta H_{mix}$  and  $\delta$  are combined. Co-free RHEAs without Al are prone to form a solid solution phase when  $-6.50 \leq \Delta H_{mix} \leq 2.72 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\delta \leq 7.63 \%$ , and the range is changed to  $-16.84 \leq \Delta H_{mix} \leq -3.99$ 

kJ·mol<sup>-1</sup> and  $\delta \leq 6.28$  % with the addition of Al. Although there is some overlap between these four regions, it is possible to describe simple rules for the formation of solid solution phases in Co-free RHEAs. The two mixed-phase multicomponent alloys without Al located in the Alcontaining RHEAs region result from the addition of the FCC structural element Ni, as mentioned earlier. The solid solution phase formation rules for  $\Omega$  can also be described as  $\Omega \geq 5.40$  and  $1.19 \leq \Omega \leq 8.81$  for Al-free and Al-containing RHEAs, respectively.

# Effect of valence electron-related parameters on the phase stability of Co-free RHEAs

The parameters  $\overline{\text{Md}}$  and *VEC*, which are both related to valence electrons, may be correlated in predicting HEA phases. Fig. 5 is generated by superimposing *VEC* and  $\overline{\text{Md}}$  on three structures. The mixed phase in Al-free RHEAs exhibits a greater  $\overline{\text{Md}}$  in FCC Ni than in the solid solution phase in Al-free RHEAs and the phases in Al-containing RHEAs. The difference between the solid solution phase in Al-free RHEAs and the phases in Al-containing RHEAs and the phases in Al-containing RHEAs is difficult to describe. The  $\overline{\text{Md}}$  in FCC Ni, BCC Fe and BCC Cr exhibit a convergent negative correlation with



Fig. 3. The distribution of  $\delta$  superimposed  $\overline{Md}$  for FCC Ni (a), BCC Fe (b), BCC Cr (c) and VEC (d) in BCC-structured RHEAs.



**Fig. 4.** The distribution of  $\delta$  superimposed on  $\Delta S_{mix}$ ,  $\Delta H_{mix}$  and  $\Omega$  in BCC-structured RHEAs.

*VEC*. In addition, Al-containing and Al-free RHEAs are distributed in parallel in the  $\overline{\text{Md}}$  – *VEC* plots. It is indicated that Al-containing RHEAs have lower  $\overline{\text{Md}}$  in BCC Fe and BCC Cr with comparable *VEC* values. The linear correlation of the phase distribution becomes increasingly divergent as FCC Ni changes to BCC Cr. Nevertheless, the mixed phase and BCC phase are difficult to distinguish in both the Al-free and Al-containing RHEAs from  $\overline{\text{Md}}$  (in the BCC Fe and BCC Cr) – *VEC* plots. This emphasizes the significance of selecting an appropriate  $\overline{\text{Md}}$  structure for predicting phases in Co-free RHEAs.

#### Discussion

### Effect of $\Delta H_{mix}$ and $\delta$ on the stability of solid solution phases

According to the study by Guo et al., a two-dimensional  $\Delta H_{mix} - \delta$  plot is essential for distinguishing between solid solution phases and amorphous phases in HEAs [115]. Singh et al. [104] noted the limitations of phase formation prediction based on the entropy of mixing; instead, the significance of the enthalpy of mixing and atomic size differences in the interpretation of disordered solid solution phase formation was emphasized. In the present study, the enthalpy of mixing and atomic size differences were also the most important parameters for



Fig. 5. Effect of Md for FCC Ni (a), BCC Fe (b) and BCC Cr (c) on VEC.

determining BCC phase formation in Co-free RHEAs. The enthalpy of mixing  $\Delta H_{mix}$  is the miscibility of equimolar elements in binary liquid alloys [116]. Theoretically, the closer H is to 0, the more the atoms tend to be distributed in a disordered manner, favoring the formation of solid solution phases; conversely, the more negative H is, the stronger the bonding between the two elements is, favoring the formation of intermetallic phases. Since Zhang et al. [28] proposed the  $\Delta H_{mix}$  range of -15to 5  $kJ \cdot mol^{-1}$  for solid solution formation rules in HEAs, it has been extended to -22 to 7 kJ·mol<sup>-1</sup> through the expansion of multicomponent alloy databases [117]. The criterion of  $\Delta H_{mix} \ge -16.25 \text{ kJ} \cdot \text{mol}^{-1}$  for solid solution phases in lightweight HEAs was defined by Feng et al. [118] and verified by an Al<sub>x</sub>CrFeMnTi<sub>y</sub> alloy system. Furthermore, through the study of 16 RHEAs, Gao et al. [57] revealed that both the sign and absolute value of  $\Delta H_{mix}^{BCC}$  are not necessarily in accordance with  $\Delta H_{mix}^{liq}$ . which is calculated by the Miedema model. In general, the range of  $\Delta H_{mix}$  for solid solution phase formation in HEAs is sensitive to the alloy system and component, and the value of  $\Delta H_{mix}$  may change with the addition of FCC, BCC or HCP structural elements. Therefore, in this work, the solid solution phase formation rules in Co-free RHEAs considering the presence or absence of the nontransition element Al were considered. Two distinctly different  $\Delta H_{mix}$  ranges for solid solution phase formation in Co-free RHEAs are proposed: -6.24 - -2.72  $kJ \cdot mol^{-1}$  and  $-16.84 - 3.99 kJ \cdot mol^{-1}$  for Co-free RHEAs without and with the addition of Al, respectively. Notably, the Al-containing RHEAs Al<sub>5</sub>(TiZrHfNb)<sub>95</sub> and Al<sub>3</sub>(TiZrHfNb)<sub>97</sub> are listed in Table. A1, have larger  $\Delta H_{mix}$  values than the upper limit of BCC phase formation rules proposed in this work, which are -3.97 and -1.46 kJ·mol<sup>-1</sup>, respectively. This is because the limits are defined by as-cast Co-free RHEAs, whereas these two alloys are in the recrystallized state. The as-homogenized/ recrystallized Co-free RHEAs were added to show more information.

The Hume-Rothery rules state that small atomic size differences between constituent elements are one of the necessary conditions for the formation of solid solution phases in binary alloys [119]. As HEAs lack dominant elements, each constituent element can be regarded as a solute in relation to the others. The disorder in the distribution of solute atoms among solvent atoms is disrupted by large differences in atomic size. This causes lattice distortions and introduces strain energy, which reduces the stability of the solid solution phase. In addition, significant lattice distortions can impede atomic diffusion during solidification, resulting in the formation of intermetallic phases and potentially amorphous phases. The geometric factor  $\delta$  is a widely used parameter for representing the atomic size differences among the constituent elements in HEAs. Generally, excess  $\delta$  inhibits atomic diffusion and the formation of disordered solid solution phases, resulting in the generation of intermetallic compounds in HEAs [27,117,120]. Therefore, the mixed phases in Co-free RHEAs exhibit higher  $\delta$  values than solid solution phases as shown in Fig. 4b. It was initially proposed by summarizing multicomponent alloys from the literature that disordered solid solution phases are more stable in HEAs when  $\delta \leq 6.5 \%$  [28]. Subsequently, Zhang et al. [27] extended the upper limit of  $\delta$  to 6.6 % with the development of new multicomponent HEAs. Guo et al. [117] reported that solid soliton phases can still form in HEAs even when  $\delta$  is as high as 8.5 %, which is based on the data from amorphous phase and solid solution phase alloy systems. The phase formation rules in HEAs should be promptly revised due to the rapid development of new multicomponent HEA systems. The values of  $\delta$  are also affected by the alloy components and should be discussed separately for different alloy systems. Therefore, this work proposes  $\delta$  limits of 6.28 % and 7.63 % for the formation of solid solution phases in Co-free RHEAs with and without the addition of Al, respectively. The next section will explore the reasons for the different  $\delta$  limits. Although many other parameters, such as  $\gamma$  [121],  $\Lambda$ [122],  $\Delta \gamma$  [123] and  $\phi$  [124], have been proposed to predict the phase of HEAs, the six parameters  $\Delta S_{mix}$ ,  $\Delta H_{mix}$ ,  $\Omega$ ,  $\delta$ ,  $\overline{Md}$  and VEC are the most widely used parameters in current research.

#### Effect of the nontransition metal Al on the phase stability of RHEAs

Although pure aluminum has an FCC structure, Al is an important BCC phase tuning element for HEAs due to its BCC stabilizing nature and high solubility in Ti, Hf and Zr. According to previous reports, the phase components of CoCrCuFeNi alloys transition from a single FCC phase to a mixture of FCC and BCC phases and eventually transform into a BCC phase when the Al content reaches 2.8 at. % [125]. Guo et al. [29] proposed a correlation between VEC and the phase stability of HEAs in which  $VEC \leq 6.87$  favors the formation of the BCC phase, and FCC is more stable when  $VEC \ge 8.0$ . The VEC values for the HEAs decreased from more than 8.0 to less than 6.87 with the addition of Al, resulting in a transition from the FCC phase to the BCC phase, as Al has the lowest VEC value compared to that of transition metals. The IM phase can be induced into Co-free RHEAs with the addition of Al due to the strong interaction between Al and constitutive elements of Co-free RHEAs, such as Ti and Zr [38,42,126]. It was found that C14Laves and IM phases are induced into the Al<sub>x</sub>NbTiVZr alloy with a higher Al content, and the volume fraction of the second phases is proportional to the Al content [38]. The large negative enthalpy of mixing leads to the aggregation of atoms in RHEAs, resulting in the formation of an ordered solid solution or IM phase [127]. This is exemplified by the large negative  $\Delta H_{AB}^{mix}$  between Al and the other elements [128]. As illustrated in Fig. 5b, the addition of Al results in a decrease in the formation range for the  $\Delta H_{mix}$ of BCC phases from -6.24 - 2.72 kJ·mol<sup>-1</sup> to -16.84 - -3.99 kJ·mol<sup>-1</sup>. The Al-containing RHEAs exhibits overall larger negative  $\Delta H_{mix}$  values than did the Al-free RHEAs, which can be explained by

orbital hybridization. The electrons in the *p*-orbitals of Al easily transfer to the partially filled *d*-orbitals of the constitutive elements due to the high electron density of the p-orbitals and the high Fermi level of Al [102,129]. The hybrid *pd*-orbitals between Al and the constitutive elements cause the Al-X (X is a constitutive element) bonds to be shorter and stronger than the bonds among the constitutive elements. Therefore, Al-containing RHEAs have a more negative  $\Delta H_{mix}$  than Al-free RHEAs. Although Al and some refractory elements, such as Nb, Ti and Ta, have similar atomic sizes, the  $\delta$  limit for BCC phase stability in Al-containing RHEAs is 6.28 %, which is lower than the  $\delta$  limit of 7.63 % in Al-free RHEAs due to the large negative enthalpy of mixing. According to the solid solution formation rules proposed by Zhang et al. [28], the  $\Delta H_{mix}$ values of BCC phase formation rules in Al-free RHEAs are in the range of  $-15 \leq \Delta H_{mix} \leq 5 \text{ kJ} \cdot \text{mol}^{-1}$ , whereas the BCC phases in Al-containing RHEAs remain stable even when the  $\Delta H_{mix}$  values are lower than this range. In contrast, the tolerance range of  $\delta$  values for BCC phase stabilization in Al-free RHEAs is extended to 7.63 %, while the  $\delta$  limit of 6.28 % for BCC phase formation in Al-containing RHEAs is in the range proposed by Zhang et al., which is  $\delta \le 6.6$  %. Therefore, the sensitivity of the BCC phase stability of Co-free RHEAs to  $\Delta H_{mix}$  and  $\delta$  is likely determined by the presence or absence of Al. As Al is added, Co-free RHEAs become more sensitive to the values of  $\delta$  than to the values of  $\Delta H_{mix}$ . Accordingly, it is necessary to consider alloying systems with or without Al separately and select appropriate parameters when predicting the phase of Co-free RHEAs.

#### Conclusions

In the present study, the semiempirical parameters  $\overline{\text{Md}}$ , VEC,  $\Delta S_{mixo}$  $\Delta H_{mixo}$   $\Omega$  and  $\delta$  of multicomponent Co-free RHEAs were carefully calculated to determine the solid solution phase formation rules, taking into account the effect of Al. The following conclusions were reached:

- (1) The parameters  $\Delta H_{mix}$  and  $\delta$  are more effective at distinguishing the BCC phase and BCC + IM mixed phase stabilities in Co-free RHEAs than are other semiempirical parameters.
- (2) A clear difference in the  $\Delta H_{mix} \delta$  plot was observed for the Cofree RHEAs depending on the presence or absence of Al. The Alcontaining RHEAs exhibited overall larger negative  $\Delta H_{mix}$  values than did the Al-free RHEAs. The mixed phases in Co-free RHEAs exhibit higher  $\delta$  values than solid solution phases.
- (3) The solid solution phases in Co-free RHEAs without the addition of Al simultaneously occur when  $-6.24 \le \Delta H_{mix} \le 2.72 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\delta \le 7.63$  %. For Co-free RHEAs with the addition of Al, solid

solution phases are prone to form when  $-16.84 \le \Delta H_{mix} \le -3.99$  kJ·mol<sup>-1</sup> and  $\delta \le 6.28$  %.

#### CRediT authorship contribution statement

Yulin Li: Writing – original draft, Visualization, Investigation, Formal analysis. Łukasz Kurpaska: Writing – review & editing. Eryang Lu: Writing – review & editing, Formal analysis. Zonghan Xie: Writing – review & editing. Hyoung Seop Kim: Writing – review & editing. Wenyi Huo: Writing – review & editing, Writing – original draft, Supervision, Methodology, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgments

This research is part of the project No. 2021/43/P/ST5/

02663 co-funded by the National Science Centre and the European Union Framework Programme for Research and Innovation Horizon 2020 under the Marie Skłodowska-Curie grant agreement No. 945339. For the purpose of Open Access, the author has applied a CC-BY public copyright licence to any Author Accepted Manuscript (AAM) version arising from this submission. We also acknowledge support from the European Union Horizon 2020 research and innovation program under grant agreement no. 857470, the European Regional Development Fund via the Foundation for Polish Science International Research Agenda PLUS program grant No. MAB PLUS/2018/8, and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (NRF-2021R1A2C3006662, NRF-2022R1A5A1030054). The publication was created within the framework of the project of the Minister of Science and Higher Education "Support for the activities of Centres of Excellence established in Poland under Horizon 2020" under contract no. MEiN/2023/DIR/3795. Z. Xie acknowledges the support provided by the Australian Research Council Discovery Projects, Australia.

#### Appendix

Table A1

Compositions of Co-free RHEAs and the parameters  $\Delta S_{mix}$ ,  $\Delta H_{mix}$ ,  $\Omega$ ,  $\delta$ ,  $\overline{Md}$ , VEC, phases and state. Note: the intermetallic phases are denoted as IM.

Materials	$\Delta S_{mix}$	$\Delta H_{mix}$	Ω	δ	Md		VEC	Phase	State	Ref.	
	(J·K- 1∙mol <sup>-1</sup> )	(kJ·mol <sup>1</sup> )			<i>M</i> in FCC Ni	<i>M</i> in BCC Fe	<i>M</i> in BCC Cr				
Al <sub>0.25</sub> CrNbTiVZr	14.34	-8.49	3.67	8.46	1.998	2.064	2.371	4.71	BCC + IM	as- homogenized	[31]
Al <sub>0-25</sub> HfNbTiZr	12.71	-5.04	5.67	4.92	2.548	2.664	3.216	4.18	BCC	as-cast	[32]
Al <sub>0-25</sub> NbTaTiV	12.71	-4.82	6.45	3.82	2.031	2.162	2.681	4.65	BCC	as-cast	[33]
Al <sub>0-3</sub> HfNbTaTiZr	14.43	-3.99	8.81	4.97	2.480	2.615	3.269	4.32	BCC	as-cast	[102]
Al <sub>0.3</sub> NbTa <sub>0.8</sub> Ti <sub>1.4</sub> V <sub>0.2</sub> Zr <sub>1.3</sub>	13.46	-4.86	6.41	5.30	2.356	2.490	2.928	4.34	BCC	as-cast	[34]
Al <sub>0.3</sub> NbTaTi <sub>1.4</sub> Zr <sub>1.3</sub>	12.63	-4.41	6.76	4.83	2.384	2.525	2.992	4.34	BCC	as-cast	[34]
Al <sub>0.4</sub> Hf <sub>0.6</sub> NbTaTiZr	14.50	-6.33	5.49	4.93	2.426	2.540	3.124	4.32	BCC	as-cast	[103]
Al <sub>0.5</sub> Cr <sub>0.5</sub> MoNbTiZr	14.53	-11.84	2.77	7.03	2.081	2.123	2.405	4.70	BCC +	as-	[35]
									IM	homogenized	
Al <sub>0.5</sub> Cr <sub>1.5</sub> NbTiZr	12.95	-13.84	1.97	8.87	1.999	2.002	2.272	4.70	BCC +	as-	[35]
									IM	homogenized	

(continued on next page)

# Table A1 (continued)

Materials	$\Delta S_{mix}$	$\Delta H_{mix}$	Ω	δ	Md			VEC	Phase	State	Ref.
	(J·K- 1∙mol <sup>-1</sup> )	(kJ∙mol <sup>-</sup> <sup>1</sup> )			<i>M</i> in FCC Ni	<i>M</i> in BCC Fe	<i>M</i> in BCC Cr				
Al <sub>0.5</sub> CrMo <sub>0.5</sub> NbTiZr	14.53	-12.84	2.47	8.03	2.040	2.063	2.339	4.70	BCC +	as-	[35]
									IM	homogenized	
Al <sub>0.5</sub> CrNb <sub>0.5</sub> TiV	12.97	-11.63	2.27	6.28	1.741	1.713	2.004	4.75	BCC	as-cast	[36]
Al <sub>0.5</sub> CrNbTiVZr	14.70	-11.64	2.68	8.26	1.994	2.017	2.310	4.64	BCC + IM	as- homogenized	[31]
Ala -HfNbTaTiZr	14 70	-7.67	4 56	4 95	2 459	2 558	3 187	4 27	BCC	as-cast	[102]
Ala HfNbTiZr	13.15	-10.96	2.61	4.95	2.435	2.556	3.095	4 11	BCC	as-cast	[32]
Al Mo NET 7	13.15 12.0E	10.90	2.01	F 90	2.312	2.374	3.093	4.11	DCC I	as-cast	[32]
A10.510101.51001121	12.95	-10.84	2.70	5.60	2.121	2.104	2.472	4.70	DCC +	do- homogonizod	[33]
Al Mb Ti VZr	10.00	11.04	2.22	6 20	2 200	0.072	2 590	4 20	IIVI PCC	noniogenizeu	[97]
Alo.5ND0.5112VZr	12.23	-11.04	2.22	0.28	2.208	2.2/3	2.589	4.20	BCC	as-cast	[37]
Al <sub>0.5</sub> ND1a <sub>0.8</sub> 11 <sub>1.5</sub> V <sub>0.2</sub> Zr	13.78	-8.62	3.62	4.93	2.301	2.396	2.825	4.30	BCC	as-cast	[34]
Al <sub>0.5</sub> NDTa11V	13.15	-8.40	3.70	3.73	2.023	2.099	2.589	4.56	BCC	as-cast	[33]
Al <sub>0.5</sub> NDTiVZr	13.15	-10.86	2.55	6.66	2.183	2.230	2.535	4.33	BCC + IM	as-cast	[38]
Ale ==HfNbTaTiZr	14.85	-11 55	2.98	4 92	2 435	2 492	3 094	4 22	BCC	as-cast	[102]
Al HfNbTiZr	12.22	15.65	1.90	4.06	2.100	2.192	2.096	4.05	BCC	as cast	[20]
Al Cr NhTi7r	13.33 12.0E	-13.05	1.00	4.90 6.40	2.479	1.007	2.900	4.05	DCC I	as-cast	[32]
AI1.5GI0.5INDTIZI	12.95	-24.40	0.99	0.49	2.131	1.997	2.219	4.10	DCC +	do- homogonizod	[33]
Al Mo MbT:7-	10.05	22.00	1.00	F 02	2.204	2.059	2.205	4 1 0	IIVI DCC	nomogenized	[0]]1
A11.51000.510011ZF	12.95	-23.00	1.09	5.05	2.204	2.058	2.285	4.10	BCC +	as-	[35]
	40.05								IM	homogenized	50.03
Al <sub>1.5</sub> NbTiVZr	13.25	-21.55	1.16	6.06	2.132	2.012	2.262	4.09	BCC +	as-cast	[38]
									IM		
Al <sub>12</sub> (TiZrHfNb) <sub>88</sub>	13.19	-11.90	2.40	4.95	2.505	2.558	3.074	4.10	BCC	as-	[39]
										recrystallized	
Al <sub>20</sub> Mo <sub>10</sub> Nb <sub>20</sub> Ti <sub>30</sub> V <sub>20</sub>	12.95	-14.16	1.87	3.86	1.948	1.911	2.197	4.40	BCC	as-cast	[41]
Al <sub>3</sub> (TiZrHfNb)97	12.30	-1.46	19.29	4.89	2.567	2.714	3.283	4.21	BCC	as-	[39]
30 751										recrystallized	
Al_(TiZrHfNb)or	12.60	-3.97	7 18	4 93	2 554	2 680	3 236	419	BCC	25-	[30]
115(112111110)95	12.00	-3.57	7.10	4.55	2.554	2.000	3.230	7.19	DCC	recrustallized	[35]
A1 (T:7-HANK)	10.00	6.97	4 50	4.02	2 5 40	2645	2 100	416	DCC	recrystanizeu	[20]
$AI_7(11ZrHfND)_{93}$	12.83	-6.37	4.50	4.93	2.540	2.645	3.190	4.16	BCC	as-	[39]
										recrystallized	
AlCr <sub>0.5</sub> Mo <sub>0.5</sub> NbTiZr	14.53	-18.32	1.63	6.78	2.116	2.060	2.312	4.40	BCC +	as-	[35]
									IM	homogenized	
AlCr <sub>0.5</sub> NbTa <sub>0.5</sub> Ti <sub>3.5</sub>	10.84	-13.85	1.59	3.85	2.100	2.136	2.491	4.23	BCC	as-cast	[40]
AlCr <sub>0.5</sub> NbTaTi <sub>3</sub>	11.79	-13.30	1.89	3.81	2.096	2.135	2.548	4.31	BCC	as-cast	[40]
AlCr <sub>0.5</sub> NbTi <sub>4</sub>	8.91	-14.44	1.19	3.87	2.103	2.136	2.435	4.15	BCC	as-cast	[40]
AlCrMoNbTi	13.38	-13.60	2.11	5.49	1.796	1.718	1.967	4.80	BCC	as-cast	[42]
AlCrMoTaTi	13.38	-13.76	2.19	5.50	1.817	1.748	2.156	4.80	BCC +	as-	[43]
									IM	homogenized	1.001
AlCrMoTiW	13 38	-10.08	3.09	5 32	1 704	1 618	1 988	5.00	BCC	as-cast	[44]
AlCrNbTiV7r	14.00	16.00	1.84	7.01	1.086	1.015	2 204	4 50	BCC	26	[21]
AIGINDIIVZI	14.90	-10.55	1.04	7.91	1.900	1.935	2.204	4.50		do-	[31]
110 NI 77	10.00	10 50	1.07	<b>-</b> 04	0.075	0.000	0.045	4 40	IIVI DOG	nomogenized	1051
AlCrND11Zr	13.38	-19.52	1.36	7.84	2.075	2.000	2.245	4.40	BCC +	as-	[35]
									IM	homogenized	
AlCrNi <sub>1.5</sub> NbTi <sub>3.52</sub> V	13.64	-23.82	1.11	6.69	1.748	1.754	1.931	5.33	BCC +	as-cast	[45]
									IM		
AlCuHfNiTiZr	14.90	-34.11	0.77	9.43	1.911	1.844	1.941	6.00	IM	as-cast	[46]
AlFeNiTiVZr	14.90	-31.33	0.85	9.34	1.706	1.617	1.695	5.67	BMG	as-cast	[47]
AlHfNbTaTiZr	14.90	-15.11	2.23	4.89	2.413	2.431	3.008	4.17	BCC	as-cast	[102]
AlHfNbTiZr	13.38	-19.36	1.42	4.96	2.450	2.420	2.889	4.00	BCC +	as-cast	[32]
									IM		
AlMoo sNbTao sTiZr	14.53	-16.84	1.87	5.03	2 224	2 203	2.542	4.30	BCC	as-cast	[103]
AlMoNhTiZr	13 38	-17.12	1.66	5 45	2 1 5 6	2 1 2 1	2 379	4 40	BCC +	25-	[35]
	10.00	17.12	1.00	0.10	2.100	2.121	2.07 5	1.10	IM	homogenized	[00]
AlNIA To Ti Zr	10 51	15 10	1 77	2 16	0.010	0.010	2 562	4 20	PCC	nomogenizeu	[94]
AIND1.5180.5111.5210.5	12.51	-15.12	1.//	5.40	2.213	2.212	2.503	4.20	BCC .	as-cast	[34]
$AIND_{1.5}Ia_{0.5}II_{3}Zr_{4}$	11.58	-10.48	2.32	5.16	2.478	2.557	2.888	4.10	BCC +	as-	[48]
									IM	homogenized	
AlNbNiTaTiW	14.90	-22.89	1.56	5.17	1.814	1.808	2.192	5.50	BCC +	as-cast	[49]
									IM		
AlNbTaTiV	13.38	-13.44	2.21	3.55	2.011	1.992	2.434	4.40	BCC	as-cast	[33]
AlNbTaTiZr	13.38	-16.16	1.83	4.54	2.291	2.285	2.706	4.20	BCC +	as-cast	[50]
									IM		
AlNbTiV	11.53	-16.25	1.38	3.94	1.958	1.869	2.141	4.25	BCC	as-cast	[51]
AlNbTiVZr	13.38	-17 44	1.52	6.33	2.155	2.110	2.385	4.20	BCC +	as-cast	[38]
	10.00	27.111		5.00					IM		[00]
AINIBTIV7r.	12.15	17 10	1 5 1	E 60	2.067	2 002	2 276	4 22	PCC	00	[50]
11110111210.5	13.15	-1/.19	1.51	5.00	2.007	2.003	2.2/0	4.22		do-	[32]
A 1811-17177	11 50	01 50	1.04	4.01	0.000	0.005	0.401	4.00	IIVI DOC	nomogenized	1003
AINDTIZ	11.53	-21.50	1.04	4.81	2.308	2.235	2.481	4.00	RCC +	as-cast	[53]
									IM		
Cr <sub>0.1</sub> Hf <sub>0.5</sub> Mo <sub>0.5</sub> NbTiZr	13.60	-0.96	33.53	6.21	2.373	2.542	2.991	4.54	BCC +	as-	[54]
									IM	homogenized	
Cr <sub>0.3</sub> Hf <sub>0.2</sub> NbTaZr	12.04	0.02	1,636.74	7.05	2.352	2.527	3.120	4.74	BCC +	as-cast	[55]
									IM		

(continued on next page)

# Table A1 (continued)

Materials	$\Delta S_{mix}$	$\Delta H_{mix}$	Ω	Ωδ	Md			VEC	Phase	State	Ref.
	(J·K- 1∙mol <sup>-1</sup> )	(kJ·mol⁻ ¹)			<i>M</i> in FCC Ni	<i>M</i> in BCC Fe	<i>M</i> in BCC Cr				
Cr <sub>0.5</sub> Hf <sub>0.2</sub> NbTaZr	12.38	-1.61	20.32	7.73	2.286	2.448	3.022	4.81	BCC +	as-cast	[55]
Cr <sub>0.5</sub> Mo <sub>1.5</sub> NbTiZr	12.95	-4.96	6.40	7.25	2.046	2.186	2.499	5.00	BCC + IM	as- homogenized	[35]
Cr0.5MoNbTaVW	14.70	-4.83	8.81	4.10	1.756	1.902	2.482	5.45	BCC	as-cast	[56]
Cr <sub>0.75</sub> Hf <sub>0.2</sub> NbTaZr	12.55	-3.19	10.26	8.35	2.214	2.360	2.913	4.89	BCC + IM	as-cast	[55]
Cr <sub>1.5</sub> Mo <sub>0.5</sub> NbTiZr	12.95	-6.56	4.55	8.98	1.964	2.065	2.365	5.00	BCC +	as- homogenized	[35]
Cr₂MoNbTaVW	14.53	-4.82	8.26	5.22	1.625	1.721	2.229	5.57	BCC	as-cast	[56]
CrHf <sub>0.2</sub> NbTaZr	12.57	-4.40	7.38	8.78	2.150	2.282	2.817	4.95	BCC + IM	as-cast	[55]
CrHfMoNbTaTiVWZr	18.27	-4.84	9.89	7.63	2.052	2.191	2.783	5.00	BCC	as-cast	[57]
CrMoNbTaV	13.38	-4.64	7.67	5.09	1.715	1.831	2.307	5.40	BCC	as-cast	[58]
CrMoNbTaVW	14.90	-4.89	8.63	4.65	1.705	1.832	2.384	5.50	BCC	as-cast	[56]
CrMoNbTaW	13.38	-6.24	6.35	4.82	1.738	1.876	2.461	5.60	BCC	as-cast	[59]
CrMoNbTiZr	13.38	-5.76	5.53	8.19	2.005	2.126	2.432	5.00	BCC + IM	as- homogenized	[35]
CrMoTaTi	11.53	-5.50	5.40	5.92	1.797	1.926	2.436	5.25	BCC	as-cast	[60]
CrMoVW	11.53	-0.50	63.13	3.59	1.473	1.542	2.009	5.75	BCC	as-cast	[61]
CrNbTa <sub>0.25</sub> TiZr	12.71	-4.60	6.39	8.51	2.125	2.256	2.610	4.76	BCC +	as-cast	[62]
CrNbTaTi	11.53	-4.50	6.51	6.02	1.939	2.094	2.610	5.00	IM BCC	as-cast	[60]
CrNbTaTiZr	13.38	-3.68	8.94	7.85	2.140	2.290	2.759	4.80	BCC +	as-cast	[50]
CrNbTiVZr	13.38	-4.64	6.45	8.67	2.003	2.115	2.438	4.80	BCC +	as-	[63]
CrNbTiZr	11.53	-5.00	5.19	8.77	2.119	2.241	2.548	4.75	IM BCC +	homogenized as-	[63]
0	11 50	4.50	6.14	6.00	1 705	1.010	0.444	5.00	IM	homogenized	
Crially	11.53	-4.50	6.14	6.28	1.795	1.913	2.444	5.00	IM	as-cast	[65]
CuFeHfTiZr	13.38	-15.84	1.65	10.41	1.942	2.038	2.219	6.20	IM	as-cast	[66]
CuFeNiTiVZr	14.90	-18.78	1.47	9.74	1.491	1.551	1.465	7.00	BMG	as-cast	[47]
CuHfNiTiZr	13.38	-27.36	0.94	10.32	1.913	2.006	2.123	6.60	BMG	as-cast	[66]
CUNDNiTiZr	13.38	-21.28	1.25	9.25	1.733	1.841	1.752	6.80	BMG	as-cast	[67]
FeMON111VZr	14.90	-19.78	1.59	9.29	1.64/	1.722	1.850	6.17	BMG	as-cast	[47]
$HI_{0.25}NDIAW_{0.5}$	10.51	-3.44	9.40	3.62	2.154	2.374	3.193	5.09	BCC	as-cast	[60]
H10.5IND0.5120.5111.5Zr	12.42	1.88	15.4Z	4.79	2.508	2.702	3.204	4.25	BCC	as-cast	[09]
	12.00	0.00	N/A	0.42	2.301	2.471	2.912	4.50	IM	homogenized	[31]
$Hf_{18.49}Mo_{8.97}ND_{12.7}Ia_{0.19}II_{32.07}Zr_{27.58}$	12.66	-0.32	90.14	5.45	2.511	2.683	3.204	4.31	BCC	as-cast	[70]
HI <sub>20.39</sub> MO <sub>5.57</sub> ND <sub>12.05</sub> I a <sub>0.80</sub> II <sub>32.61</sub> Zr <sub>28.58</sub>	12.49	0.29	97.28	5.20	2.55/	2./31	3.276	4.24	BCC	as-cast	[70]
$H_{23}ND_{22}H_{37}V_{15}VV_3$	11.88	-0.05	529.98 20 60	5.03	2.282	2.401	3.009	4.43	BCC	as-cast	[/1]
H128.331401.551006.74146.741128.332128.33	12.4/	1.01	28.08	4.74	2.049	2.823	3.497	4.17	BCC	as-cast	[70]
HfMoo orNbTaTi7r	9.23 14.34	1.40	23 35	5.27	2.212	2.438	3 334	4.00	BCC	as-cast	[72]
HfMoo NbTaTiZr	14.70	0.60	63.15	5.47	2.427	2.615	3 272	4.55	BCC	as-cast	[73]
HfMoo.75NbTaTiZr	14.85	-0.21	180.43	5.65	2.389	2.574	3.216	4.61	BCC	as-cast	[73]
HfMoNbTaTi	13.38	-1.44	24.87	4.86	2.236	2.428	3.125	4.80	BCC +	as-cast	[74]
110 4 - NIL TT- TT1 TA172.	17.00	0.44	10.75	6.60	0.166	0.000	2.000	4.00	IM		[57]
HIMONDIAIIV WZF	17.29	-3.44	12.75	0.00	2.100	2.333	2.969	4.00	BCC	as-cast	[3/]
	16.18	-1.47	27.03	6.00	2.230	2.403	2.997	4.71	BCC	as-cast	[37]
HIMONDTATIVE HfMoNbTati7r	14 90	-0.89	43 32	5.78	2.234	2.430	3.107	4.60	BCC	as-cast	[75]
HfMoNbTaW	13 38	-4.64	8 73	5.43	2.334	2.330	3 104	5 20	BCC	as-cast	[70]
HfMoNbTiZr	13 38	-1.60	20.44	6.10	2.110	2.290	3.075	4 60	BCC	as-cast	[35]
HfMoTaTiVZr	14.90	-2.33	15.90	7.15	2.259	2.415	3.053	4.67	BCC	as-cast	[57]
HfMoTaTiZr	13.38	-1.92	17.79	6.08	2.402	2.576	3 264	4.60	BCC	as-cast	[76]
HfNb <sub>0.18</sub> Ta <sub>0.18</sub> Ti <sub>1.27</sub> Zr	11.44	0.97	26.50	4.48	2.653	2.830	3.485	4.10	BCC +	as-cast	[78]
HfNbTaTiV	13.38	0.64	52,98	5.79	2.235	2.417	3.131	4.60	IM BCC	as-cast	[79]
HfNbTaTiVZr	14.90	0.44	82.67	6.59	2.353	2.527	3.169	4.50	BCC	as-cast	[80]
HfNbTaTiWZr	14.90	-2.11	19,18	5.71	2.372	2.565	3.297	4.67	BCC	as-cast	[75]
HfNbTaTiZr	13.38	2.72	12.41	4.98	2.515	2.710	3.403	4.40	BCC	as-cast	[81]
HfNbTiVZr	13.38	0.16	192.48	7.05	2.379	2.535	3.081	4.40	BCC	as-cast	[82]
HfNbTiZr	11.53	2.50	10.75	4.86	2.588	2.766	3.352	4.25	BCC	as-	[83]
LIFTO TI V 7-	11.60	0.62	20.07	EOF	2 404	2666	2 262	415	PCC	homogenized	[0.4]
$\pi_{1140,2112} V_{0.5LT}$	11.00	-0.03	39.9/	5.95	2.494	2.000	3.203	4.15	BCC	as-cast	[04]
MO(NhTaTi7r)	12.9/	-0.25	123.44	5.72	2.404	2.579	3.034	4.50	BCC	as-cast	[06] [0=1
$Mo_{10}(1001a1121)90$	13.00	-0.27	240.30 30 16	5.22	2.303	2.303	2 951	4.05	BCC	as-cast	[00] [85]
$M_{0-15}(1011a1121)_{85}$ $M_{0-r}(NbTaTiZr)_{-r}$	12.51	-0.07	25.40	5.55	2.203	2.730 2.551	2.551	4.73	BCC	as-cast	[85]
MoNb1.3TaTiW0.4	12.00	-4.09	8.86	2.57	2.013	2.216	2.768	5.09	BCC	as-cast	[86]
		1.09	0.00	2.07	2.010	2.210	00	5.05	200		[00]

## Table A1 (continued)

Materials	$\Delta S_{mix}$	$\Delta H_{mix}$	Ω	δ	Md			VEC	Phase	State	Ref.
	(J·K- 1·mol <sup>-1</sup> )	(kJ·mol <sup>-</sup> <sup>1</sup> )			M in FCC	M in BCC	M in BCC				
					Ni	Fe	Cr				
MoNbTa <sub>0·3</sub> V	10.84	-3.23	8.96	3.45	1.781	1.925	2.336	5.30	BCC	as-cast	[87]
MoNbTa <sub>0.5</sub> V	11.24	-3.27	9.32	3.48	1.806	1.957	2.409	5.29	BCC	as-cast	[87]
MoNbTa <sub>0.7</sub> V	11.44	-3.27	9.57	3.48	1.829	1.986	2.473	5.27	BCC	as-cast	[87]
MoNbTaTi <sub>0.25</sub> W	12.71	-6.15	6.38	2.49	1.909	2.105	2.758	5.41	BCC	as-cast	[88]
MoNbTaTi <sub>0.5</sub> W	13.15	-5.83	6.82	2.61	1.929	2.126	2.764	5.33	BCC	as-cast	[88]
MoNbTaTi <sub>0.5</sub> Zr	13.15	-2.07	16.95	5.75	2.216	2.401	2.895	4.89	BCC	as-cast	[89]
MoNbTaTi <sub>0.75</sub> W	13.33	-5.54	7.14	2.66	1.947	2.146	2.770	5.26	BCC	as-cast	[88]
MoNbTaTi <sub>1.5</sub> Zr	13.25	-1.52	22.15	5.20	2.226	2.419	2.891	4.73	BCC	as-cast	[89]
MoNbTaTi <sub>2</sub> Zr	12.98	-1.33	24.24	4.98	2.230	2.425	2.889	4.67	BCC	as-cast	[89]
MoNbTaTiV	13.38	-2.56	13.65	3.78	1.941	2.118	2.621	5.00	BCC	as-cast	[90]
MoNbTaTiVW	14.90	-4.22	9.85	3.58	1.893	2.071	2.645	5.17	BCC	as-cast	[91]
MoNbTaTiVZr	14.90	-2.11	17.86	6.24	2.108	2.278	2.744	4.83	BCC	as-cast	[92]
MoNbTaTiW	13.38	-5.28	7.39	2.77	1.963	2.163	2.775	5.20	BCC	as-cast	[88]
MoNbTaTiZr	13.38	-1.76	19.77	5.45	2.221	2.411	2.893	4.80	BCC	as-cast	[85]
MoNbTaV	11.53	-3.25	9.86	3.46	1.859	2.024	2.558	5.25	BCC	as-cast	[93]
MoNbTaVo as	10.69	-4.36	7.16	2.77	1.931	2.119	2.688	5.31	BCC	as-cast	[94]
MoNbTaVor	11.24	-3.92	8 22	3.11	1.904	2.083	2.638	5 29	BCC	as-cast	[94]
MoNbTaVo 75	11.21	-3.56	9.09	3 32	1.880	2.000	2.596	5 27	BCC	as-cast	[94]
MoNbTaVW	13 38	-4 64	8 54	3.15	1.818	1 986	2.600	5 40	BCC	as-cast	[95]
MoNbTaW	11.53	-6.50	5.60	2 32	1.887	2 080	2.000	5 50	BCC	as-cast	[95]
MoNbTaW7r	13.38	-5.44	7.26	6.06	2.008	2.000	2.701	5 20	BCC	as-cast	[96]
MoNbTaWZro 4	12.00	-6.38	5.99	3 21	1 012	2.279	2.072	5.46	BCC	as-cast	[96]
MoNbTaWZr.	12.20	6.14	6.44	4 3 2	1.912	2.104	2.700	5.40	BCC	as-cast	[06]
MoNbTaWZr.	12.05	5.03	6 75	5.02	2.004	2.149	2.795	5.33	BCC	as-cast	[06]
MoNDTAWZI0.5	11 52	-3.95	10.24	1.05	1.004	2.190	2.010	5.55 E 00	PCC	as-cast	[90]
MoNDTIV	11.55	-2.75	11.24	4.00	2 1 2 1	2.020	2.373	3.00 4.76	BCC	as-cast	[97]
MoNDTIV 0.2521	12.71	-2.00	11.79	6 55	2.101	2.340	2.073	4.70	PCC	as-cast	[90]
MoNDTIV 7.	14.05	-2.07	0.24	6.47	2.143	2.303	2.033	F.00	PCC	as-cast	[90]
MoNDTIV 7.	14.00	-2.70	0.24	6.00	2.114	2.209	2.002	4.00	BCC BCC	as-cast	[90]
MoNINTIV 1.521	13.23	-2.71	11.33	0.99	2.030	2.179	2.319	4.02	DCC	ds-Cast	[90]
MONDITV <sub>2</sub> Zr	12.98	-2.67	11.42	7.00	1.995	2.132	2.470	4.83	DCC	as-cast	[98]
MONDITY 3ZF	12.20	-2.53	11.20	7.04	1.930	2.057	2.408	4.80	DCC	as-cast	[98]
MONDIIVZr MoNhT:7r	14.90	-2.72	8.50	0.53	2.085	2.230	2.5/1	5.00	BCC	as-cast	[98]
MoNDIE	11.55	-2.50	7.66	5.98	2.221	2.392	2.715	4.75	BCC	as-cast	[98]
MONDV	9.13	-3.11	7.66	3.39	1./3/	1.869	2.209	5.33	BCC	as-cast	[87]
MolavwZr	13.38	-4.80	7.91	7.09	1.983	2.134	2.740	5.20	BCC +	as-cast	[99]
	10.50	0.11	000.01		0.110	0.001	0 700	1.00	IM		[100]
ND <sub>0.25</sub> Ta <sub>0.1</sub> Ti <sub>0.3</sub> V <sub>0.25</sub> Zr <sub>0.1</sub>	12.59	-0.11	269.91	5.66	2.113	2.291	2.722	4.60	BCC	as-cast	[100]
Nb <sub>0.5</sub> 11V <sub>0.5</sub> Zr	11.05	-0.11	216.75	6.77	2.348	2.515	2.853	4.33	BCC	as-	[101]
										homogenized	50.03
NbTaTiV	11.53	-0.25	117.15	3.92	2.039	2.232	2.784	4.75	BCC	as-cast	[33]
NbTaTiVZr	13.38	0.32	102.80	6.34	2.220	2.400	2.899	4.60	BCC	as-cast	[57]
NDTaTiW	11.53	-4.50	7.48	2.41	2.067	2.289	2.976	5.00	BCC	as-cast	[60]
NDTaTiZr	11.53	2.50	11.65	4.83	2.389	2.598	3.124	4.50	BCC	as-cast	[85]
NbTi <sub>2</sub> VZr	11.08	-0.16	151.50	6.28	2.229	2.403	2.752	4.40	BCC	as-cast	[37]
NbTiV <sub>2</sub> Zr	11.08	-1.28	19.36	7.46	2.084	2.225	2.577	4.60	BCC	as-	[63]
										homogenized	
NbTiVZr	11.53	-0.25	103.75	7.03	2.219	2.379	2.722	4.50	BCC	as-cast	[64]

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