
STRUCTURE, PHASE TRANSFORMATIONS, AND DIFFUSION

Role of Various Parameters in the Formation of the Physicomechanical Properties of High-Entropy Alloys with BCC Lattices

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Abstract—An analysis of simple structures of the solid-solution non-ordered high-entropy alloys (HEAs) with a bcc crystal lattice has allowed us to determine the effect of various parameters on their physicomechanical properties. It was found that, as the hardness increases, the size mismatch results in a decrease in the modulus of elasticity; however, the normalized hardness characteristic increases. It has been found that, when the enthalpy of mixing of the bcc high-entropy alloys shifts to negative values, its effect on the hardness and modulus of elasticity is nonmonotonic. A formula for calculating the modulus of elasticity of high-entropy alloys with a bcc structure has been suggested that is based on the alloy composition and role of the most refractory metallic component.

Keywords: high-entropy alloys, size mismatch, enthalpy of mixing, lattice parameter, modulus of elasticity

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INTRODUCTION

As follows from the title of high-entropy alloys, they are among materials characterized by anomalously high values of configuration entropy of mixing, which are substantially higher than those of traditional multicomponent alloys. To form HEAs, the number of chemical elements should be no less than five and their concentrations should be 5–35 at % [1–3]. The large number of chemical elements results in the maximum increase in the configuration entropy of mixing of this alloy.

It is known that the values of enthalpy and entropy always compete in their effect in the formation of phases. The enthalpy of mixing plays role of the measure of long-range order. If the value of enthalpy of mixing is high enough to overcome the effect of entropy and is negative, backgrounds for the long-range ordering and formation of intermetallic compounds arise.

Thus, the high entropy increases the degree of disorder and decreases the free Gibbs energy. Different elements in this alloy are randomly distributed in the crystal lattice, and the tendencies to order and segregate is suppressed. In other words, the high entropy can favor the formation of non-ordered solid solution rather than intermetallic compounds or other ordered phases in the course of alloy solidification, i.e., the high entropy makes the formation of chemically ordered compounds less competitive. As a result, a

topologically simple structure of the non-ordered solid solution can form and dominate in a multicomponent alloy.

Numerous attempts to suggest simple parameters and criteria for the prognostication of phase composition of multicomponent alloys are available in the literature [3–6]. In part, these parameters have something in common with classical Hume-Rothery rules for the formation of substitutional solid solutions.

However, no definite information about criteria, which allow one to forecast the physicomechanical characteristics of solid-solution high-entropy alloys, is available in the literature. The aim of the present study is to search for criteria that allow one to predict the physicomechanical characteristics of high-entropy bcc solid-solution-based alloys.

EXPERIMENTAL

The alloys were prepared by arc melting in an argon atmosphere using a nonconsumable tungsten electrode and a water-cooled heart with a hole that has a hemisphere geometry; the mass of the ingots was 100 g. To homogenize the composition of ingots, they were remelted six to seven times with subsequent furnace cooling at a rate of 100–200 K/s.

The structure of alloys was studied by X-ray diffraction analysis (using a DRON-UM1 diffractometer and monochromatized $\text{CuK}\alpha$ radiation), scanning

Table 1. The composition of the high-entropy alloys based on bcc solid solutions and some of their experimental and calculated characteristics

Composition	H_{IT} , GPa	E_r , GPa	\bar{E} , GPa	C_{cd} , electron per atom	a , nm	a_{ref} , nm	\bar{a} , nm	ΔH , kJ/mol	H_{IT}/E_r	$(\Delta a/a)$ average, %
TiZrVNbSn	3.4	57	88	4.2	0.3423	0.3294	0.3527	12.8	0.059	3.26
TiZrHfNbTa	3.8	88	103	4.4	0.3434	0.3302	0.3487	2.7	0.044	2.77
TiZrVNbHf	4.1	86	97	4.6	0.3358	0.3294	0.3431	0.16	0.049	3.45
TiZrHfNbRe	4.4	95	164	4.6	0.3306	0.3205	0.3464	−17	0.048	2.90
TiZrHfVNbTa	4.4	105	107	4.5	0.3348	0.3302	0.3413	1.12	0.045	3.56
TiZrNbVHfMo	4.8	110	135	4.7	0.3320	0.3160	0.3385	−2.8	0.045	3.13
TiZrVNbTaMo	4.6	115	147	4.8	0.3340	0.3160	0.3399	−1.8	0.043	2.99
TiZrVNbTa	4.3	117	113	4.6	0.3304	0.3302	0.3352	0.32	0.041	3.27
TiZrNbVHfTaW	5.3	120	140	4.7	0.3289	0.3168	0.3378	−3.3	0.046	3.34
TiZrVNbRe	6	169	173	5.2	0.3252	0.3205	0.3330	−16	0.039	2.94
AlTiVCrNbMo	6.8	178	171	4.7	0.3133	0.3160	0.3181	−8.8	0.038	2.94
FeCoNiAlCr	5.8	188	185	7.2	0.2871	0.2885	0.2984	−10.7	0.034	2.24
ReMoWNbTa	6.2	255	290	6.0	0.3288	0.3205	0.3228	−11	0.030	1.02

electron microscopy (using a Superprobe-733 electron microscope with a resolution of up to 7 nm), and Auger electron spectroscopy (using a JAMP-9500F spectrometer; the resolution is 8–10 nm (in local Auger-electron spectroscopy mode) and 2–4 μ m (in electron microprobe analysis mode)). The hardness H_{IT} and contact modulus of elasticity E_r were measured in accordance with International Standard (ISO 14577-1:2002(E)) using the automated microindentation method and a Mikron-gamma tester equipped with a Berkovich diamond indenter. The modulus of elasticity was calculated using Poisson's ratio for HEAs, which is equal to 0.33.

The theoretical lattice parameter and average atomic radius were calculated by a rule of mixture (Vegard's law [7]), i.e., $a_{calc} = \sum c_i a_i$ and $r_{calc} = \sum c_i r_i$, where c_i , a_i , and r_i are the concentration, lattice parameter, and atomic radius for i th atoms, respectively. This rule was used to calculate the theoretical electron concentration (number of valence electrons per atom); $x_{mixture} = \sum c_i x_i$ (x_i is the electron concentration for i th atoms in the alloy). The electron concentration for elements, atomic radii, and lattice parameters were taken from [8]. Some elements that comprise bcc HEAs do not have bcc crystal lattice. To calculate the average lattice parameter for these elements, their bcc lattice parameter was calculated using the expression $a_{calc} = 2.31r$, where r is the atomic radius of element. The a/r ratio for a bcc lattice is ~ 2.31 .

The size mismatch ($\Delta a/a$) was calculated by the expression

$$(\Delta a/a)_{av} = \sum c_i (a_i - a_{exp})/a_{exp}, \quad (1)$$

where a_i is the lattice parameter of i th atom and a_{exp} is the lattice parameter determined experimentally. The

enthalpy of mixing was calculated using the linear combination of interaction energies between pairs of atoms that are from the alloy composition

$$\Delta H_{mix} = \sum_{i=1, j \neq i}^n 4H_{ij}^{mix} C_i C_j, \quad (2)$$

where H_{ij}^{mix} is the enthalpy of mixing for i th and j th atoms, which was calculated in terms of Miedema model [9]. Data for H_{ij}^{mix} and subsequent calculations of ΔH were taken from [10].

RESULTS AND DISCUSSION

The characteristics of studied high-entropy alloys based on bcc solid solutions are shown in the Table 1, where H_{IT} is the hardness, E_r is the modulus of elasticity, \bar{E} is the calculated modulus of elasticity, C_{cd} is the number of electrons in the outer shell, a is the lattice parameter determined experimentally, a_{ref} is the lattice parameter of the most refractory element, \bar{a} is the calculated lattice parameter, $(\Delta a/a)$ is the size mismatch, and ΔH is the enthalpy of mixing.

In a number of works, the high characteristics of HEAs were related to the lattice distortion [11–13], and expressions for calculating the additional hardening of material at the expense of the size mismatch are suggested. As can be seen from the data given in Fig. 1, no common regularity of the effect of mismatch on the hardness of HEAs with a bcc structure is observed. A number of alloys can be indicated, which, as the size mismatch parameter increases, demonstrate a trend toward the increase in the hardness.

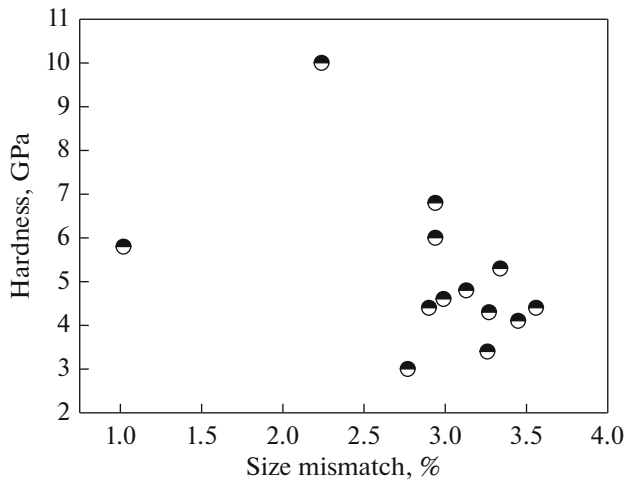


Fig. 1. Effect of size mismatch on hardness of bcc solid-solution-based high-entropy alloys.

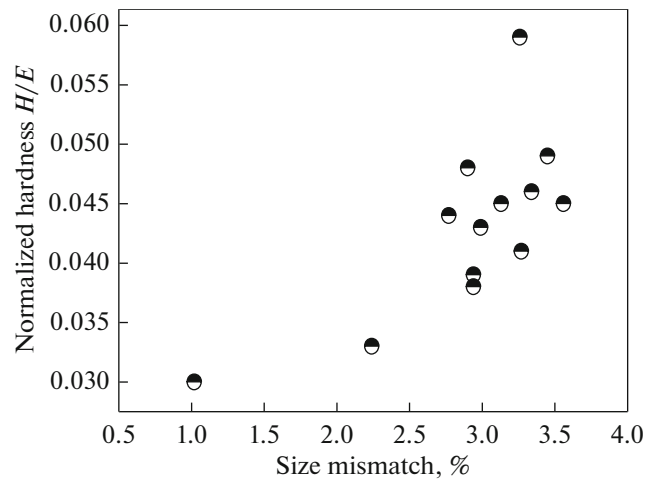


Fig. 2. Effect of size mismatch on normalized hardness of bcc solid-solution high-entropy alloys.

At the same time, a number of HEAs with the bcc crystal lattice demonstrate a decrease in hardness as the lattice distortion increases (see Fig. 1). However, as the size mismatch in HEAs with the bcc crystal lattice increases, the normalized hardness (H_{IT}/E_r) demonstrates the trend toward the increase (Fig. 2).

We may assume that the effect of size mismatch on the properties of HEAs demonstrates two tendencies, i.e., (1) the size mismatch in HEAs increases the non-conservative elastic movement of dislocation concentrated areas, which results in the increase in the hardness, and (2) the size mismatch in HEAs leads to weakening bonds between neighboring atoms at the expense of increase in the lattice parameter, which results in the decrease in the modulus of elasticity.

At the same time, their ratio H_{IT}/E_r demonstrates the trend toward the increase. This is confirmed by data given in Fig. 2.

For many solid-solution HEAs, the normalized hardness reaches 0.04 and more. According to data of [14, 15], the grain size of solid solutions characterized by a normalized hardness of more than 0.04 is 100 nm and less. Pure metals, such as titanium and iron in the nanostructured state demonstrate a high yield strength (800–1100 MPa), but low plasticity. Solid-solution HEAs with a bcc crystal lattice are characterized by a yield strength of 1100 MPa; in this case, they can be deformed at room temperature [16, 17]. The combination of these strength and plasticity characteristics of HEAs is related to their cluster structure [18, 19].

The enthalpy of mixing demonstrates a slightly different effect on the hardness and modulus of elasticity of high-entropy alloys with a bcc crystal lattice (Fig. 3). It can be seen from the data given in Fig. 3 that, as the enthalpy of mixing shifts to negative values to -10 kJ/mol, the hardness and modulus of elasticity increase. The further decrease in the enthalpy of mix-

ing is accompanied by the decrease in hardness and modulus of elasticity of HEAs based on bcc solid solutions.

The modulus of elasticity demonstrates a similar nonmonotonic dependence on the average electron concentration (Fig. 4). As the average electron concentration increases to 6 electrons per atom, the increase in the modulus of elasticity is observed; if the average electron concentration is above this value, the modulus of elasticity decreases.

The authors of work [11] showed that the lattice parameter of HEAs is formed based on that of the most refractory metal, while the modulus of elasticity of the alloy depends on the fact that its lattice parameters is higher or lower than that of the most refractory metal comprising the alloy. The data given in the table and in Fig. 5 show that, when the lattice parameter of the most refractory metal in the HEA is close to that of

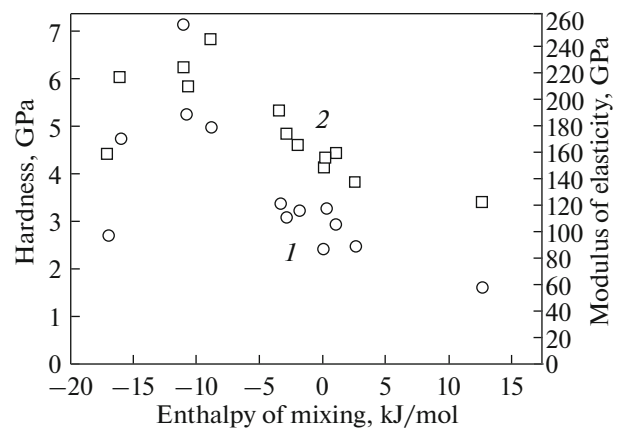


Fig. 3. Effect of enthalpy of mixing on (1) hardness and (2) modulus of elasticity of bcc solid-solution-based high-entropy alloys: (○) hardness and (□) modulus of elasticity.

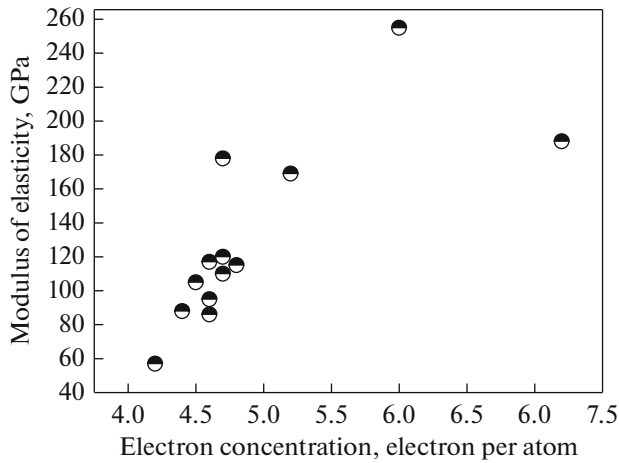


Fig. 4. Effect of average electron concentration of bcc solid-solution-based high-entropy alloys on modulus of elasticity.

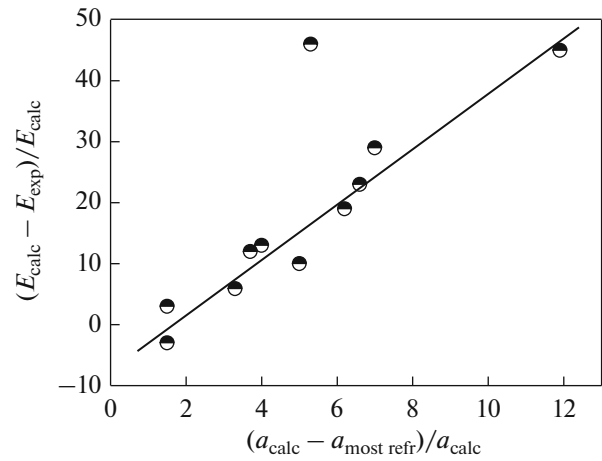


Fig. 5. Effect of lattice parameter of most refractory metal in bcc solid solutions on the characteristic modulus of elasticity.

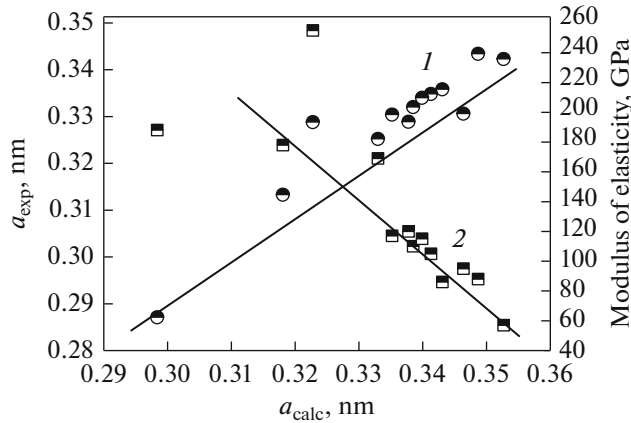


Fig. 6. Correlations between calculated lattice parameter and (1) experimental lattice parameter and (2) modulus of elasticity of bcc solid solutions.

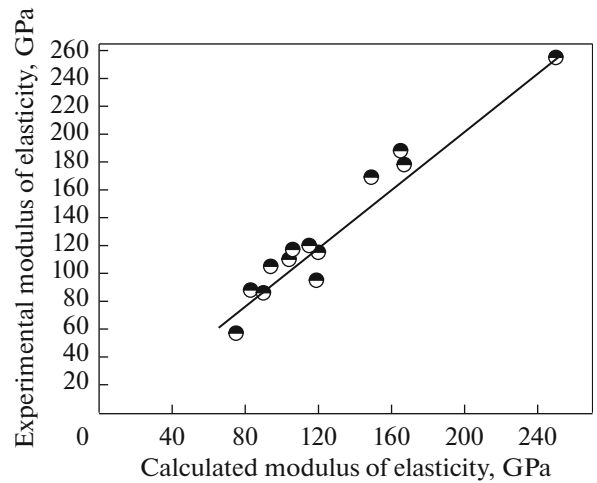


Fig. 7. Correlation between experimental and calculated (by Eq. (3)) modules of elasticity of bcc solid-solution-based HEAs.

the alloy, the modulus of elasticity is close to the calculated one.

For the majority of cases, the lattice parameter of the most refractory metal of HEA is lower than that of the alloy; therefore, the modulus of elasticity of HEA is substantially lower than the calculated modulus of elasticity.

At the same time, as can be seen from Fig. 6, the calculated lattice parameter of HEA with the bcc crystal lattice is proportional to the calculated lattice parameter (Fig. 6, curve 1). This allows us to calculate the modulus of elasticity of HEA with the bcc crystal lattice using the alloy composition and expression

$$\begin{aligned} E_{\text{composition}} &= \bar{E}[1 - \{3.6(|\bar{r} - r_{\text{most refr. metal}}|/\bar{r})\}] \\ &= \bar{E}[1 - \{3.6(|\bar{a} - a_{\text{most refr. metal}}|/\bar{a})\}]. \end{aligned} \quad (3)$$

Figure 7 shows the experimentally determined modules of elasticity of bcc solid-solution HEAs, which are given in comparison with those calculated by Eq. (3).

An analysis of the reported results indicates that some parameters of solid-solution HEAs directly are related to their physicomechanical properties. This allows us to preliminarily optimize the composition of HEA to reach given physicomechanical properties. In particular, the average electron concentration determines the phase composition of the alloy. A comparison of the lattice parameter of the most refractory metal with the calculated parameters allows us to determine the expected value of the modulus of elasticity of composition. The values of lattice distortion and the enthalpy of mixing allow one to judge the level

of the strength characteristics. The specific weight of assumed composition can also be calculated.

CONCLUSIONS

(1) It has been confirmed that the size mismatch in HEAs based on bcc solid solutions nonmonotonically affects their hardness and decreases the modulus of elasticity. In this case, the normalized hardness increases.

(2) It was found that, as the enthalpy of mixing shifts to negative values, its effect on the hardness and modulus of elasticity is nonmonotonic.

(3) An expression for calculating the modulus of elasticity of HEA based on a bcc solid solution has been suggested, which is based on the role of most refractory metal in the composition.

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