EXPERIMENTAL VALIDATION OF SEMI-EMPIRICAL PARAMETERS FOR PHASE PREDICTION IN RAPID-QUENCHED AND AS-CAST HIGH-ENTROPY ALLOYS

O. I. Kushnerov[1]*, S. I. Ryabtsev[1], P. O. Galagan[1], V. F. Bashev[2]

[1]Oles Honchar Dnipro National University, Dnipro, Ukraine
[2]Dniprovsky State Technical University, Kamianske, Ukraine
**e-mail: kushnrv@gmail.com*

Predicting phase formation in high-entropy alloys remains a significant challenge due to the complex interplay of thermodynamic, atomic size, electronic, and kinetic factors. Nowadays, various empirical and semi-empirical criteria are proposed with this end in view, relying on parameters such as atomic size difference, mixing enthalpy and entropy, valence electron concentration, electronegativity difference, and electron-to-atom ratios. This study evaluates several widely used criteria by comparing their phase predictions with actual phase compositions observed experimentally in 29 high-entropy alloys produced by casting and rapid quenching. Results show that while many criteria capture general trends, none are universally accurate. Electronic criteria based on valence electron concentration and related parameters generally predict crystal structures well for 3d transition metal-based alloys but are less reliable for alloys containing non-transition elements or oxidized phases. Thermodynamic and atomic size-based criteria frequently fail to predict intermetallic and amorphous phase formation accurately. Increased cooling rates suppress intermetallic compounds and favor metastable phases, including amorphous structures; however, some criteria only partially capture this behavior. Discrepancies between predictions and observations are linked to temperature dependence of criteria, kinetic constraints, nanoscale phase inclusions, and alloy-specific chemical effects.

Keywords: high-entropy alloy, phase composition, rapid quenching, semi-empirical parameters, microstructure prediction.

Received 10.09.2025; Received in revised form 05.10.2025; Accepted 14.11.2025

1. Introduction

High-entropy alloys (HEAs) represent a novel class of metallic materials composed of multiple principal elements in equiatomic or near-equiatomic proportions. Due to their exceptional mechanical, thermal, and chemical properties, HEAs attract significant interest in materials science and engineering [1–4]. Unlike conventional alloys, which are typically based on one or two dominant elements, HEAs exhibit high configurational entropy, which promotes the formation of simple solid solution phases – typically face-centered cubic (FCC), body-centered cubic (BCC), or hexagonal close-packed (HCP) structures.

Some researchers argue that only equiatomic alloys forming single-phase FCC or BCC solid solutions should be strictly defined as HEAs. In contrast, alloys with non-equiatomic compositions or those containing ordered phases and intermetallics are often referred to as complex concentrated alloys (CCAs) or multi-principal element alloys (MPEAs) [4].

HEAs are known for their outstanding properties, including high strength, excellent performance at elevated temperatures, good ductility and toughness at low temperatures, enhanced corrosion and oxidation resistance, and in some cases, shape memory behavior [1–10]. The vast compositional space of HEAs enabled by the combination of elements from different regions of the periodic table offers huge potential for the development of new materials with tailored functionalities.

Various synthesis methods are available for producing HEAs, including arc melting, powder metallurgy, mechanical alloying, additive manufacturing, and thin film deposition. Among these, rapid solidification – achieved by cooling rates exceeding 10^4 K/s – stands out as a powerful technique for refining microstructure and enhancing properties. It enables the formation of metastable phases such as nanocrystalline and amorphous states, which often exhibit superior physical and mechanical characteristics [11–14]. As such, rapid solidification offers a promising route for the fabrication of high-performance HEAs.

The prediction of phase formation in HEAs remains a key challenge in materials science. Over the past decade, numerous empirical and semi-empirical criteria have been proposed based on parameters such as atomic size difference, mixing enthalpy and entropy, valence electron concentration, and others.

These criteria aim to predict whether a given alloy composition will form a solid solution, intermetallic compound, or amorphous phase. However, their reliability remains under debate, highlighting the need for systematic experimental validation. This work presents an experimental assessment of several widely used criteria by comparing their predictions with the actual phase compositions observed in selected HEAs. The peculiarity of the work is that the alloys are obtained both by casting and by rapid quenching.

2. Experimental details

All high-entropy alloys studied in this work were synthesized from pure (99.9%) elements in the required proportion by casting under an argon atmosphere using a Tamman high-temperature electric furnace.

To achieve compositional homogeneity, alloys were remelted three times and then cast into a copper mold to obtain a cylindrical ingot with a diameter of 10 mm. The cooling rate of the as-cast ingots was ~10^2 K/s. The ingots were then cut into slices, which were used to study the microstructure and phase composition of the alloy. After that the ingots were remelted and quenched into films using a splat-quenching technique, which involved the collision of molten droplets onto the inner surface of a hollow copper cylinder with a radius R=135 mm rotating at ~8000 rpm. The cooling rate of the films was calculated from the film thickness [11, 14]. The following equation was used:

$$V = \frac{\alpha}{c\rho\delta}\left(T - T_0\right), \tag{1}$$

where V is the cooling rate, α is the heat transfer coefficient, ρ is the film density, c is the heat capacity of the film, T is the film temperature, T_0 is the ambient temperature, and δ is the film thickness. Considering that the splat-quenched (SQ) films had a thickness of ~40 μm, the cooling rate was estimated to be ~10^6 K/s.

The high-entropy films $Co_{19}Cr_{18}Fe_{22}Mn_{21}Ni_{20}$ (in at. %) were synthesized by the modernized method of three-electrode ion-plasma sputtering of composite targets [12, 13]. The cooling rate, which relates to the relaxation time of individual atoms on the substrate, was in this case theoretically evaluated to be 10^{12} – 10^{14} K/s. Sputtering was carried out on the sitall substrates, as well as on a fresh cleavage of NaCl single crystals.

The as-deposited HEA film thickness was estimated to be ~ 110 nm. Films deposited on single-crystal substrates after the dissolution of the salt were used for structural studies by X-ray diffraction analysis (XRD) (with a photographic registration, in a Debye camera on the URS-2.0 diffractometer in filtered Co Kα radiation). The Debye–Scherrer photographs were then subjected to digital microphotometry. The crystal structures of the as-cast and splat-quenched (SQ) samples were characterized by X-ray diffraction using a DRON-2.0 diffractometer with monochromatized Cu Kα radiation. The XRD patterns were analyzed using the QualX2 software for qualitative phase identification [15].

3. Results and discussion

3.1. Fundamental thermodynamic, electronic, and atomic-size parameters of multicomponent high-entropy alloys

There are two main parameters by which high-entropy alloys are usually characterized. This is the entropy of mixing ΔS_{mix} and the enthalpy of mixing ΔH_{mix}. However, to predict the phase composition of HEAs, some additional parameters were proposed [1-4]. These parameters include in particular the valence electron concentration (VEC), the thermodynamic parameter Ω, which takes into account the melting temperature, mixing entropy and the mixing enthalpy. The important parameter is an atomic-size difference between alloy components which is denoted as δr. Let's take a closer look at the above parameters and some others.

The basic principle of HEAs is the stabilization of solution phases by the significantly higher configurational entropy of mixing ΔS_{mix} compared to conventional alloys. The configurational entropy of mixing during the formation of regular solution alloy can be determined as

$$\Delta S_{\mathrm{mix}} = -R\sum_{i=1}^{n} c_i \ln c_i \,, \tag{2}$$

c_i is atomic fraction of the i-th component, R is the universal gas constant. Increasing the entropy of mixing decreases the Gibbs free energy of the alloy and improves the stability of the solid solution. For the alloy where n is the number of components, the maximum mixing entropy is when they are mixed in equal atomic fractions. Usually in HEAs value of ΔS_{mix} is in the range of 12 – 19 J/(mol·K).

According to [16], the Ω parameter can be used to estimate the phase composition of HEA.

$$\Omega = \frac{T_{\mathrm{m}}\Delta S_{\mathrm{mix}}}{\left|\Delta H_{\mathrm{mix}}\right|} \,, \tag{3}$$

where T_{m} is the average melting temperature of alloy and ΔH_{mix} is the enthalpy of mixing

$$T_{\mathrm{m}} = \sum_{i=1}^{n} c_i (T_{\mathrm{m}})_i \,, \tag{4}$$

$$\Delta H_{\mathrm{mix}} = \sum_{i=1, i\neq j}^{n} \omega_{ij} c_i c_j \,, \tag{5}$$

where the regular melt-interaction parameter between i-th and j-th elements $\omega_{ij} = 4\Delta H_{\mathrm{mix}}^{AB}$, and $\Delta H_{\mathrm{mix}}^{AB}$ is mixing enthalpy of binary liquid AB alloy. Alloy components should not have large atomic-size difference, which is described by the parameter

$$\delta r = 100\sqrt{\sum_{i=1}^{n} c_i \left(1 - {r_i}/{\bar{r}}\right)^2} \,, \tag{6}$$

where $\bar{r} = \sum_{i=1}^{n} c_i r_i$, r_i is the atomic radius of the i-th element.

The other useful parameter is the valence electron concentration, which has been proven useful in determining the phase stability of high entropy alloys [17]. VEC is defined by:

$$\mathrm{VEC} = \sum_{i=1}^{n} c_i (\mathrm{VEC})_i \tag{7}$$

where $(\mathrm{VEC})_i$ is the valence electron concentration (including the *d*-electrons) of the *i*-th element.

The parameter *e/a* is also used – the number of free valence electrons per atom:

$$e/a = \sum_{i=1}^{n} c_i z_i , \tag{8}$$

where z_i is the number of free valence electrons for the *i*-th element.

The electronegativity mismatch between alloy elements also was considered as one of the parameters that allows us to predict HEAs structure. In [18], the electronegativity mismatch was determined on the Allen scale:

$$\delta\chi^{\mathrm{A}} = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{\chi_i^{\mathrm{A}}}{\chi^{\mathrm{A}}}\right)^2} , \tag{9}$$

$$\chi^{\mathrm{A}} = \sum_{i=1}^{n} c_i \chi_i^{\mathrm{A}} \tag{10}$$

where χ^{A} is the average Allen electronegativity for the alloy and χ_i^{A} is electronegativity for the *i*-th element.

In [19], the parameter Λ was suggested, which is determined by the following formula:

$$\Lambda = \frac{\Delta S_{\mathrm{mix}}}{\delta r^2} . \tag{11}$$

In [20, 21] a parameter was proposed $\varphi(\xi)$ that was supposed to be the only criterion, which considers as competition between mixing enthalpy ΔH_{mix} , mixing entropy ΔS_{mix} and the excess configurational entropy ΔS_{xs} , which describes the deviation from the randomness of the ideal solid solution. If a large atom occupies a certain atomic site, then the surroundings sites will be compressed; thus, it is more likely that a small atom occupies those compressed sites than a large one, in opposition to the ideal solid solution conceptualization. According to the model of rigid spheres of Mansoori et al. [22], ΔS_{xs} is a function of the composition, the atomic radii, and the packing factor (ξ) (which takes a value of 0.68 for BCC structures and 0.74 for FCC structures). Then $\varphi(\xi)$ can be calculated according to the following formula

$$\varphi(\xi) = \frac{\Delta S_{\mathrm{mix}} - \Delta H_{\mathrm{mix}} / T_{\mathrm{m}}}{\left|\Delta S_{\mathrm{xs}}(\xi)\right|} . \tag{12}$$

Recently it has been established that the difference in atomic sizes affects the topological instability of atomic packing [7]. It was suggested that atoms with the maximum and minimum radii play a crucial role in determining the stability of the packing in high-entropy alloys. The solid angles of packing for the atoms with the smallest ω_S and highest ω_L sizes were chosen [7] to describe the effects of the atomic packing in HEAs quantitatively:

$$\omega_S = 1 - \sqrt{\frac{(r_S + \bar{r})^2 - \bar{r}^2}{(r_S + \bar{r})^2}}\ , \tag{13}$$

$$\omega_L = 1 - \sqrt{\frac{(r_L + \bar{r})^2 - \bar{r}^2}{(r_L + \bar{r})^2}}\ . \tag{14}$$

Here r_S and r_L are the atomic radii of the smallest and largest atoms respectively, $\bar{r} = \sum_{i=1}^{n} c_i r_i$, r_i is the atomic radius, c_i is atomic fraction of the *i*-th component.

Then, the normalized parameter of packing state was defined as the ratio between the solid angles for the atoms with the smallest and largest sizes.

$$\gamma = \frac{\omega_S}{\omega_L}\ . \tag{15}$$

In [24, 25], a simple and comparative method was proposed to establish the temperature, at which the intermetallic phases would be more stable than the solid solution. It was postulated that the parameter η allows to predict the appearance of these phases in the alloy structure at a certain temperature:

$$\eta(T) = \frac{T\Delta S_{\text{mix}}}{\left|\min\left\{\Delta H_{ij}^{\text{IM}}\right\}\right|}\ ;\ i, j = 1,...n\ . \tag{16}$$

Here $\min\left\{\Delta H_{ij}^{\text{IM}}\right\}$ corresponds to the most negative value among the enthalpies $\Delta H_{ij}^{\text{IM}}$ of the intermetallic compound formation of all the possible binary pairs of elements.

In [26], a new approach for the phase selection in HEAs, which takes into account both enthalpy and entropy terms of the competing phases, was proposed. If the enthalpy ΔH_{IM} and the entropy ΔS_{IM} of formation for intermetallic compounds are related with mixing ones

$$\Delta H_{\text{IM}} = k_1 \Delta H_{\text{mix}}\ , \tag{17}$$

$$\Delta S_{\text{IM}} = k_2 \Delta S_{\text{mix}}\ , \tag{18}$$

then the thermodynamic condition for the formation of a solid solution phase at a temperature *T* from the Gibbs equation [26] is

$$\Delta H_{\text{mix}} - T\Delta S_{\text{mix}} < \Delta H_{\text{IM}} - T\Delta S_{\text{IM}}\ . \tag{19}$$

Here $\Delta H_{\text{IM}} = \sum_{i=1}^{n} \sum_{j>i}^{n} 4\Delta H_{ij}^{\text{IM}} c_i c_j$, $\Delta H_{ij}^{\text{IM}}$ are enthalpies of binary intermetallics formation.

Thus, by considering the parameter

$$k^{\mathrm{cr}}(T) = 1 - \frac{T\Delta S_{\mathrm{mix}}}{\Delta H_{\mathrm{mix}}}\left(1 - k_2\right), \tag{20}$$

the condition for suppression of IM phases at a temperature T can be defined as $k^{\mathrm{cr}}(T) > k_1$ for HEAs with negative values of ΔH_{mix} and $k^{\mathrm{cr}}(T) < k_1$ for HEAs with positive values of ΔH_{mix}.

We calculated all the above parameters for a set of high-entropy alloys that we had studied experimentally. The calculations were based on data from [4, 27]. High-Entropy Alloys Predicting Software (HEAPS) [28] was also used. Calculated parameters, together with the results of X-ray diffraction analysis, are presented in Table 1.

Table 1

Electronic, thermodynamic, atomic-size parameters and phase composition of the investigated alloys

№	Alloy	T_{m}, K	ΔS_{mix}, J/(mol·K)	ΔH_{mix}, kJ/mol	δr, %	VEC	γ	Ω	Λ, J/(mol·K)	φ(BCC)/ φ(FCC)	$\delta\chi^{A}$, %	η	e/a	Δk	Phase composition
1	$\mathrm{AlCoCrFe_{0,87}Mn_{0,03}NiSi_{0,1}V}$	1764	15.53	-17.05	5.48	6.76	1.262	1.61	0.517	8.54/ 5.28	7.606	0.153	2.03	-1.88	As-cast: BCC + B2 (*a*=0.2888 nm) SQ film: BCC (*a*=0.2882 nm)
2	$\mathrm{AlCoCrFe_{1,87}Mn_{0,03}NiSi_{0,1}V}$	1770	15.19	-14.61	5.26	6.94	1.263	1.84	0.549	10.9/ 6.76	7.179	0.15	2.03	-2.19	As-cast: BCC + B2 (*a*=0.2882 nm) SQ film: BCC (*a*=0.2879 nm)
3	$\mathrm{Al_2CoCrFe_{0,87}Mn_{0,03}NiSi_{0,1}V}$	1645	15.07	-18.98	6.3	6.22	1.261	1.31	0.38	3.97/ 2.46	7.457	0.139	2.17	-2.62	As-cast: BCC + B2 (*a*=0.2888 nm) SQ film: BCC (*a*=0.2887 nm)
4	$\mathrm{Al_2CoCrFe_{1,87}Mn_{0,03}NiSi_{0,1}V}$	1666	14.98	-16.81	6.17	6.45	1.261	1.48	0.393	5.67/ 3.51	7.168	0.139	2.15	-3.04	As-cast: BCC + B2 (*a*=0.2886 nm) SQ film: BCC (*a*=0.2881 nm)
5	$\mathrm{Al_{0,7}CuFeNi}$	1500	11.44	-2.57	5.49	8.41	1.169	6.67	0.379	14.0/ 8.66	5.341	0.138	1.92	-14.6	As-cast: FCC (*a*=0.3622 nm)+BCC (*a*=0.2891 nm) SQ film: FCC (*a*=0.3622 nm)+BCC (*a*=0.2879 nm)
6	$\mathrm{Al_{0,5}CuFeNi}$	1532	11.24	-0.65	4.97	8.71	1.169	26.37	0.455	18.8/ 11.64	4.816	0.139	1.86	-46.6	As-cast: FCC (*a*=0.3608

															nm)
															SQ film: FCC (*a*=0.3616 nm)
7	$Al_{0,5}CuFeNiSi_{0,25}$	1543	12.53	-7.93	5.44	8.4	1.264	2.44	0.423	10.9/ 6.73	4.874	0.108	2	-3.96	As-cast: FCC (*a*=0.3626 nm)+BCC (*a*=0.2867 nm)
															SQ film: FCC (*a*=0.3619 nm)+BCC (*a*=0.2863 nm)
8	$Al_{0,25}CuFeNiSi_{0,25}$	1586	12.06	-5.94	4.47	8.79	1.265	3.22	0.604	18.2/ 11.2	3.905	0.107	1.93	-3.13	As-cast: FCC (*a*=0.3604 nm)+BCC (*a*=0.2844 nm)
															SQ film: FCC (*a*=0.3602 nm)+BCC (*a*=0.2844 nm)
9	$Al_{0,5}CoCuFeNi$	1585	13.15	-1.28	4.51	8.78	1.17	16.23	0.647	25.9/ 16.02	4.287	0.119	1.89	-24.5	As-cast: FCC (*a*=0.36 nm)
															SQ film: FCC (*a*=0.3609 nm)
10	$AlCuFeMnSi_{0,5}$	1437	13.15	-14.42	6.7	6.89	1.261	1.31	0.293	3.17/ 1.96	5.618	0.105	2.22	-2.61	As-cast: Ordered: BCC1 (B2, *a*=0.2881 nm) + BCC2 (B2, *a*=0.2919 nm) + BCC3 (B2, *a*=0.2945 nm)
															SQ film: Ordered BCC BCC1 (B2, *a*=0.2884 nm) + BCC2 (*a*=0.2912 nm)
11	$Al_{2,2}CrCuFeNi_2$	1508	12.81	-10.12	6.39	7.17	1.168	1.91	0.314	6.61/ 4.09	6.714	0.1545	2.03	-3.61	As-cast: Ordered BCC (B2, *a*=0.2885 nm)
															SQ film: Ordered BCC (B2, *a*=0.2887 nm)
12	$Al_4CoCrCuFeNi$	1397	13.15	-11.46	6.7	6.22	1.166	1.59	0.293	4.99/ 3.09	6.625	0.105	2.22	-5.48	As-cast: Ordered BCC (B2, *a*=0.2919 nm)
															SQ film: Ordered BCC (B2, *a*=0.2916 nm)
13	$Al_{0,44}CuFeMnNi$	1538	13.07	-2.5	4.76	8.41	1.169	8.04	0.577	22.2/ 13.8	4.357	0.162	1.87	-5.7	As-cast: FCC (*a*=0.3645

															nm) SQ film: FCC (*a*=0.3619 nm)
14	CuFeMnNi	1604	11.53	2.75	3.4	9	1.095	6.72	0.996	37.7/ 23.3	2.72	1.619	1.75	-0.61	As-cast: FCC (*a*=0.3641 nm) SQ film: FCC (*a*=0.3632 nm)
15	CuFeMnNi$Si_{0,25}$	1609	12.71	-5.26	4.05	8.71	1.184	3.89	0.773	25.9/ 16.04	2.929	0.384	1.88	0.46	As-cast: FCC (*a*=0.3642 nm) SQ film: FCC (*a*=0.3634 nm)
16	CuFeMnNi$Si_{0,5}$	1613	13.15	-11.56	4.5	8.44	1.184	1.84	0.648	13.4/ 8.29	3.073	0.4	2	0.24	As-cast: FCC1 (*a*=0.3660 nm)+ FCC2 ($L1_2$, *a*=0.3620 nm)+ FeSi + $FeSi_2$ SQ film: FCC (*a*=0.3646 nm)
17	CuFeNi$Si_{0,5}$	1640	11.24	-10.45	3.13	8.86	1.116	1.76	1.15	23.0/ 14.3	2.193	0.348	2	-0.12	As-cast: FCC (*a*=0.3635 nm)+BCC (*a*=0.2801 nm) SQ film: FCC (*a*=0.3586 nm)+BCC (*a*=0.2801 nm)
18	Cu_5CrFeMnNiSi	1572	12.45	-4.12	3.69	9	1.184	4.75	0.913	33.1/ 20.4	3.953	0.369	1.6	1.48	As-cast: FCC (*a*=0.3645 nm) + BCC1 (B2, *a*=0.2827 nm) + BCC2 (*a*=0.2886 nm) SQ film: FCC (*a*=0.3649 nm) + BCC1 (*a*=0.2823 nm) + BCC2 (*a*=0.2889 nm)
19	Cu_5AlCrFeMnNi	1496	12.45	3.28	4.27	8.9	1.169	5.68	0.683	24.4/ 15.1	4.974	0.15	1.5	2.13	As-cast: FCC (*a*=0.3674 nm)+BCC (*a*=0.2881 nm) SQ film: FCC (*a*=0.3677 nm)+BCC (*a*=0.2896 nm)
20	CoCrMnFeNiBe	1761	14.9	-6.11	5.16	7	1.213	4.29	0.558	19.6/ 12.1	6.011	0.583	1.5	-0.58	As-cast: FCC (*a*=0.3598 nm)+ BCC (*a*=0.2872

															nm)+BCC B2 (BeNi(Co), *a*=0.2616 nm)
															SQ film: FCC (*a*=0.3579 nm)+ BCC (*a*=0.2872 nm)+BCC B2 (BeNi(Co), *a*=0.2610 nm)
21	$Co_{19}Cr_{18}Mn_{21}Fe_{22}Ni_{20}$	1791	13.36	-4.07	3.33	8.02	1.096	5.88	1.203	43.8/ 27.1	4.324	2.11	1.82	1.96	As-deposited film: fully amorphous phase
															Annealed film: FCC (*a*=0.3613 nm)+ BCC B2 (FeCo, *a*=0.2857 nm)+MnO
22	$CoCr_{0,8}Cu_{0,64}FeNi$	1784	13.26	1.68	0.92	8.75	1.032	14.11	15.59	645/ 399	4.344	2.53	1.68	-3.5	As-cast: FCC (*a*=0.3593 nm)
															SQ film: FCC (*a*=0.3589 nm)
23	$CoCrCuFeNiSn_{0,5}$	1654	14.7	4.23	8.26	8.36	1.348	5.75	0.216	7.23/ 4.47	4.899	0.884	1.45	-0.69	As-cast: FCC (*a*=0.3586 nm)+ BCC (B2, CsCl-type, *a*=0.2979 nm)
															SQ film: FCC (*a*=0.3588 nm)+ BCC (B2, CsCl-type, *a*=0.2974 nm)
24	CoCrCuFeNiSn	1558	14.9	4.89	10.44	8	1.344	4.75	0.137	4.55/ 2.81	5.139	0.842	1.33	-0.05	As-cast: FCC (*a*=0.3600 nm)+ BCC (B2, CsCl-type, *a*=0.2981 nm)
															SQ film: FCC (*a*=0.3600 nm)+ BCC (B2, CsCl-type, *a*=0.2987 nm)
25	$Co_4Fe_2AlMn_{1,5}Bi_{0,5}$	1575	11.62	-5.1	7.33	7.56	1.326	3.59	0.216	6.64/ 4.10	4.84	0.104	2	-7.19	As-cast: BCC (B2, *a*=0.2889 nm) + FCC (*a*=0.3613 nm)
															SQ film: (BCC, *a*=0.2882 nm)
26	$Fe_5CoCuMnNiSi$	1712	12.45	-10.64	3.63	8.1	1.185	2	0.943	21.3/ 13.1	2.55	0.169	2.1	-0.18	As-cast: FCC (*a* = 0.361nm)

															SQ film: FCC (a = 0.3601nm)
27	Fe_5CrCuMn NiSi	1753	12.45	-10.36	3.63	7.8	1.185	2.11	0.943	22.3/ 13.8	3.84	0.41	2	0.29	As-cast:FCC1 (a = 0.3656 nm) + FCC2 (a = 0.3607 nm) + BCC (a = 0.281 nm)
															SQ film: FCC (a = 0.3615 nm)
28	Fe$Co_{0,854}$ $Nb_{0,146}$Ni$B_{0,7}$ $Si_{0,3}$	1900	13.66	-26.3	14.29	7.43	1.785	0.99	0.067	-0.05 / -0.03	6.563	0.053	2.29	-1.2	As-cast: FCC (a=0.3574 nm) +Fe_2B
															SQ film: fully amorphous phase
															Annealed: FCC (a=0.3527 нм) + $Fe_xNi_{23-x}B_6$ + Fe_3Si
29	Fe$B_{0,7}$CoBe Ni$Si_{0,3}$	1803	14.4	-17.3	12.47	6.46	1.538	1.5	0.093	1.66/ 1.03	7.838	0.053	1.86	-4.08	As-cast: BCC (B2, a=0.2655 nm)+(Fe, Ni, Co)$_2$B
															SQ film: BCC (B2, a=0.2653 nm)+(Fe, Ni, Co)$_2$B

3.2. Criteria for predicting the phase composition of multicomponent high-entropy alloys

A significant number of works have been devoted to determining the ranges of parameters, within which the formation of certain phases in the structure of HEAs is expected [1-4]. However, their results cannot currently be considered universal, since each study was based on experimental data obtained for a limited number of alloys. Despite possible inaccuracies in the numerical values determining the predicted intervals of existence of certain phases, a number of criteria have been formulated that, taken together, allow the phase composition of multicomponent high-entropy alloys to be predicted. Let's consider these criteria, comparing their predictions with the data in Table 1:

1. According to the authors of [29], only simple solid solutions are observed in the structure of HEAs, for which $0.5\% \leq \delta r \leq 6.5\%$ and -17.5 kJ/mol < ΔH_{mix} < 5 kJ/mol. According to our research, this criterion is not sufficient and is not met for alloys 1, 2, 4, 10-12, 16, 18-20. At the same time, with an increase in the cooling rate of the alloy, the formation of intermetallic compounds becomes difficult, and for alloys 1, 2, 4, 16 this criterion begins to be fulfilled.
2. According to [16], the HEA alloys for which $\Omega \geq 1.1$ and $\delta r \leq 6.6$ % can form solid solutions without intermetallic compounds and amorphous phases. However, simple (not ordered) solid solutions are formed if -15 kJ/mol < ΔH_{mix} < 5 kJ/mol and $\delta r \leq 4.6$ %. Such

criterion is much more suitable, it is not fulfilled only for annealed film 21, which can be explained by the formation of oxides and the decomposition of metastable phases

3. In the study [30], it was shown that simple solid solutions are formed when -11.6 kJ/mol < ΔH_{mix} < 3.21 kJ/mol and $\delta r < 6.6\%$, that is consistent with [48, 53, 55]. At the same time, the authors found that amorphous phases tend to form when $\Delta H_{\mathrm{mix}} \leq -12.21$ kJ/mol and $\delta < 6.4\%$. However, intermetallic phases were also found in some alloys even when these conditions were met. According to our data, this criterion, like criterion 1, is not always met. Deviations are observed specifically in the formation of intermetallic compounds. Formation of the amorphous phase is correctly predicted only in the rapidly quenched alloy 28, but not in alloy 29.

4. As pointed out in [23], the Hume–Rothery rule of 15% of the atomic size difference in binary alloys corresponds to a critical value of packing misfitting of $\gamma = 1.167$. The critical value of $\gamma = 1.175$ can distinguish the simple solid solution alloys and alloys with intermetallic compounds [23]. This criterion is generally fulfilled, however, for alloys 7, 8, 26, 27 the predicted intermetallic compounds are not observed, which can be explained by the formation of a multiphase structure of simple solid solutions. At the same time, for alloys 11, 12, for which γ is slightly below the critical value, the formation of intermetallic compounds still occurs.

5. According to [18], the formation of simple solid solutions in HEAs is likely when $1\% \leq \delta r \leq 6\%$ and $1\% \leq \delta\chi^{\mathrm{A}} \leq 6\%$. Alloys that do not meet these conditions are likely to form intermetallic compounds. According to our data, this criterion is not always fulfilled, in particular, the formation of intermetallic compounds is observed in alloys 16, 18, 21, and 23. At the same time, an increase in the cooling rate contributes to the suppression of intermetallic formation.

6. In [19], the phase composition of HEAs was predicted using a single parameter Λ. If $\Lambda \geq 0.96$ J/(mol·K), only a single-phase simple disordered solid solution should form. If 0.24 J/(mol·K) < Λ < 0.96 J/(mol·K), a multiphase structure with several solid solutions is expected. When $\Lambda \leq 0.24$ J/(mol·K), intermetallic phases should form. According to our data, this criterion is highly inaccurate. In particular, it is not satisfied for alloys 1, 2, 3, 4, 10, 11, 12, 16, 17, 18, 21, 25, and 27, where either the formation of intermetallic compounds or a multiphase structure is observed. Moreover, increasing the cooling rate does not lead to any significant improvement.

7. Another criterion was proposed in [20, 21]. According to this study, a single-phase structure consisting of a simple disordered solid solution is expected when the parameter $\varphi \geq 20$. This criterion is not satisfied for alloys 17, 18, 19, 20, and 27. Moreover, even for those alloys where the criterion is met, the prediction of the structure type (FCC or BCC) is generally inaccurate.

8. In [24, 25], it is argued that a single-phase structure, representing a simple disordered solid solution, will form under the condition that $\eta > 1$ and $\min\left\{\Delta H_{ij}^{\mathrm{ic}}\right\} < 3.71$ J/(mol·K). In contrast, intermetallic phases are expected to form in HEAs when $\eta < 1$, regardless of the value of $\min\left\{\Delta H_{ij}^{\mathrm{ic}}\right\}$. For most of the alloys we studied, this criterion predicts the formation of intermetallic phases, whereas experimentally they are observed quite rarely. This may be explained by the fact that, in many HEAs, the formation of intermetallics occurs only at the level of nanoscale inclusions, which are not always detectable experimentally.

9. Another criterion was proposed in [26]. The authors established that a single-phase structure representing a simple disordered solid solution is expected to form if the following

conditions are met: $k_2 = 0{,}6$, $\Delta k(T) > 0$ (i.e. $k_1^{\mathrm{cr}}(T) > k_1$) and $\Delta H_{\mathrm{mix}} < 0$. However, this criterion has a limitation: an ordered solid solution of the B2 structural type may also form under these same conditions. As in the previous case, the phase compositions predicted using this criterion differ significantly from those observed experimentally. This may be due to the fact that the criterion is temperature-dependent, and its values were determined at the average melting temperature of the alloy, whereas in the experiment, phase formation may begin at higher temperatures.

All the previously discussed criteria focused on predicting the phase composition of HEAs, determining whether a simple disordered solid solution, an intermetallic compound, or an amorphous phase is likely to form. However, there also exist criteria that specify the type of crystal structure that may form during the solidification of HEAs:

10. As pointed in [17] at VEC ≥8.0, sole FCC phase exists in alloy; at 6.87 ≤ VEC < 8.0, mixed FCC and BCC phases coexist; and sole BCC phase exists at VEC < 6.87. At the same time, other relationships are given in [31]: the formation of solid solution with an FCC structure should be expected at VEC > 8.2; solid solutions with a BCC structure are formed at 4.25 < VEC < 7.2; at 7.2 < VEC < 8.2, two-phase solid solutions with BCC and FCC crystal lattices are expected to be formed; and at VEC < 4.25, an HCP crystal lattice is expected. This criterion is generally fulfilled for alloys based on 3d transition metals, with the exception of alloys 5, 7, 8, 10, 18, 19, 21, 23, 25 (SQ film), and 28. The alloys for which the criterion is not satisfied contain non-transition elements such as Sn, Bi, and Si. But obviously, it must be assumed that the exact boundaries of the valence electron concentration range, in which the formation of two-phase solid solutions based on the FCC and BCC lattices is expected, are specific to each alloy system.

11. A similar criterion was also proposed in [18], where, in addition to the VEC parameter, the e/a ratio was used. According to the [18], FCC solid solutions are stable within the region defined by VEC > 7.5 and 1.6 < e/a < 1.8, whereas BCC solid solutions are more likely to form when VEC < 7.5 and 1.8 < e/a < 2.3 . This criterion is generally fulfilled, except for the Si-containing alloy 18, and the oxidized film of alloy 21. Additionally, it does not account for multiphase structures and does not always predict the formation of intermetallic compounds.

12. The prediction of the lattice type of a simple disordered solid solution formed in HEAs can also be carried out using the criterion proposed in [20, 21]. According to the authors, if the parameter $\varphi \geq 20$, a simple solid solution with an FCC-type lattice is expected to form when 7.5 < VEC < 9.5; a BCC-type lattice is predicted if 4.3 < VEC < 5.7; and an HCP-type lattice may form if 2.6 < VEC < 3. As in the previous case, this criterion is generally fulfilled, except for alloys 17, 18, 19, and 27, which contains non-transition elements such as Si and the oxidized film of alloy 21.

4. Conclusions

1. Predicting phase formation in high-entropy alloys (HEAs) remains challenging due to limited universality of existing empirical criteria, often based on narrow alloy datasets.
2. Thermodynamic and atomic size-based criteria partially describe phase stability but often fail to reliably predict intermetallic, multiphase, and amorphous structures.
3. Electronic criteria based on Allen electronegativity difference and e/a ratio provide useful guidance but have limited accuracy for alloys with non-transition elements or oxidation. Valence electron concentration (VEC)-based criteria generally predict crystal structures (FCC, BCC) well for 3d transition metal-based alloys but less so for complex compositions.

4. Cooling rate and kinetic factors strongly influence phase formation, often suppressing intermetallic compounds and enabling metastable phases, including amorphous phases; however, some criteria only partially predict amorphous phase formation, as confirmed by experimental deviations.
5. Deviations between predicted and experimental phases arise from temperature dependence of parameters, nanoscale phases inclusions below detection limits, oxidation, and kinetic constraints.
6. Reliable phase prediction in HEAs requires integrating thermodynamic, electronic, atomic size parameters with kinetic considerations and systematic experimental validation under diverse processing conditions.

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