KINETIC PREDICTION OF COMPETITIVE PHASE FORMATION IN HIGH-ENTROPY ALLOYS UNDER VARYING COOLING RATES

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This study presents a kinetic approach for predicting the phase constitution of multicomponent high-entropy alloys processed under non-equilibrium conditions. Unlike conventional thermodynamic, atomic-size, and electronic parameters that neglect the time-dependent nature of solidification, the proposed approach evaluates the critical cooling rate required to suppress the nucleation of competing stable and metastable phases. This allows phase stability to be assessed according to the actual time available for nucleation rather than equilibrium considerations alone.

The key feature of the model is a structure-dependent viscosity parameter that captures the packing efficiency of different crystal lattices and influences atomic mobility near the solidification front. Incorporating this parameter makes it possible to distinguish between phases that are thermodynamically similar but differ in kinetic accessibility. The model is evaluated using 30 multicomponent alloys processed under near-equilibrium casting and rapid quenching. The results show that the phase exhibiting the highest kinetic stability becomes dominant, enabling stabilization of metastable states that are inaccessible under slow cooling. The proposed kinetic approach successfully explains the formation of single-phase solid solutions, ordered structures, and complex multiphase microstructures in cases where static parameters produce ambiguous or incorrect predictions.

Keywords: high-entropy alloys, kinetic prediction, phase selection, rapid quenching, nucleation kinetics, critical cooling rate.

Received 29.10.2025; Received in revised form 26.11.2025; Accepted 10.12.2025

1. Introduction

Since the introduction of the concept in 2004, high-entropy alloys (HEAs) have emerged as a promising class of metallic materials. Defined as multicomponent alloys containing five or more principal elements in near-equiatomic concentrations, HEAs exhibit a unique combination of 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 fundamental premise of the HEA concept is that high configurational entropy of mixing (ΔS_{mix}) stabilizes simple solid solution phases, such as face-centered cubic (FCC) or body-centered cubic (BCC) against the formation of brittle intermetallic compounds.

While early HEA research prioritized single-phase solid solutions driven by maximized entropy, recent studies demonstrate that multiphase structures often offer superior performance. Consequently, the design strategy has evolved towards non-equiatomic compositions. Studies show that non-equimolar alloys significantly expand the possibilities of improving the characteristics of HEAs, as they can consist of several phases with fundamentally different properties, such as plastic FCC phase and solid and brittle intermetallic phase. Substances that combine the properties of several different types of materials are of considerable scientific interest [11 – 13].

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 [14 – 16]. As such, rapid solidification offers a promising route for the fabrication of high-performance HEAs.

To date, numerous semi-empirical thermodynamic, electronic, and atomic-size parameters have been proposed to predict phase stability in HEAs, such as the valence electron concentration (VEC), mixing enthalpy (ΔH_{mix}), atomic size mismatch (δ), and others [1 – 4]. While these static parameters successfully categorize phases under near-equilibrium conditions, they inherently fail to account for the time factor during solidification. However, in non-equilibrium processing methods like rapid solidification, the final phase constitution is determined not only by thermodynamic stability but by the kinetic competition between nucleation rates of different phases. A phase with a lower thermodynamic stability but a lower kinetic barrier (lower viscosity or higher nucleation frequency) may form preferentially. In this context, the primary objective of the present study is to develop a kinetic model for predicting competitive phase selection in multicomponent alloys and to verify its reliability under non-equilibrium conditions. We propose a modified formalism to calculate the critical cooling rate required to suppress the nucleation of competing crystalline phases (FCC, BCC, and HCP). This approach allows identifying the phase with the highest kinetic stability against amorphization, which becomes the dominant structure during solidification.

2. Experimental details

High-purity (99.9%) elements were used to fabricate the multicomponent alloys studied in this work. First, bulk ingots were produced in a Tamman electric furnace under argon protection with a cooling rate of ~10^2 K/s. These ingots were then subjected to splat-quenching, where the molten droplets were ejected on to the inner wall of a hollow copper cylinder (R = 135 mm) rotating at ∼8000 rpm. The cooling rate for the films was derived to be ~ 10^6 K/s, determined from the film thickness, heat transfer coefficient, density, and heat capacity as described in references [14, 16].

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 [15]. 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 Profex and QualX2 software for phase identification [17, 18]. The accuracy of determining the lattice period was ±0.0002 nm.

3. Results and discussion

3.1. Kinetic modeling of critical cooling rates

To overcome the limitations of static semi-empirical criteria [19], we developed a kinetic approach to predict phase selection in multicomponent alloys. The core hypothesis is that under non-equilibrium cooling, the phase selection is governed by the competition between the nucleation rates of possible structures (FCC, BCC, HCP). The phase exhibiting the highest critical cooling rate (R_c), i.e., the phase that requires the fastest cooling to be suppressed is considered the kinetically dominant structure.

The calculation is based on the non-equilibrium nucleation formalism adapted from the work of Takeuchi and Inoue [20]. We modified the original equation to differentiate between crystalline phases by introducing structure-dependent parameters. The critical cooling rate for a specific phase is calculated as follows:

$$R_\mathrm{c} = Z\frac{k_\mathrm{B}T_\mathrm{m}^2}{a^3\eta(T_\mathrm{m})}\exp\left[f_1\left(\frac{\Delta H_\mathrm{mix} - T_\mathrm{m}\Delta S_\mathrm{mix}}{300R}\right) - f_2\left(\frac{T_\mathrm{m}S_\mathrm{xs}}{300R}\right)\right]F_\mathrm{GFA}, \tag{1}$$

where k_B is the Boltzmann constant, T_m is the average melting temperature of the alloy, a is the mean interatomic distance, and R is the gas constant, f_1 and f_2 – calibration coefficients proposed in [20] for adapting (1) to the final cooling temperature of the samples (300 K). The thermodynamic driving force is approximated using the mixing enthalpy (ΔH_mix) and the configurational entropy (ΔS_mix), including the excess entropy term (S_xs) calculated via the hard-sphere model [20]. F_GFA is a correction factor accounting for the glass-forming ability (GFA) index.

A key innovation of the proposed model is the evaluation of the melt viscosity, $\eta(T_\mathrm{m})$. We assume that short-range order clusters in the liquid phase possess a topology similar to the corresponding crystalline phase. Consequently, the effective viscosity for the nucleation of BCC, FCC or HCP phases differs due to the packing efficiency. The viscosity is estimated using a modified Arrhenius-type relation [21]:

$$\eta(T_\mathrm{m}) = P(C_v)\cdot\frac{hN_\mathrm{A}}{V_\mathrm{alloy}}\exp\left[\frac{\left\{RT\left(\sum\nolimits_{i=1}^{n}x_i\ \ln\eta_i\right) + RT\ \ln\left(\frac{V_\mathrm{c}}{hN_\mathrm{c}}\right)\right\} - 0{,}155\Delta H_\mathrm{mix}}{RT_\mathrm{m}}\right], \tag{2}$$

where $P(C_\mathrm{v})$ is the topological parameter that depends on the coefficient of variation of atomic radii C_v, h is the Planck constant, N_A is the Avogadro number, N_c and V_c is the effective number of atoms per unit cell and the volume of the unit cell of the alloy, x_i is the mole fraction, n is the number of elements in the alloy, and η_i is the viscosity of a separate element of the alloy with number i, determined by the Arrhenius equation

$$C_\mathrm{v} = \frac{1}{\bar{r}}\sum\nolimits_{i=1}^{n}\sqrt{\frac{(r_i - \bar{r})^2}{n}}, \tag{3}$$

where $\bar{r} = \sum_{i=1}^{n}x_i r_i$, r_i is the atomic radius of the i-th element, n is the number of elements in the alloy. The molar volume of the alloy is calculated from the molar volumes of the components V_m^i by the formula

$$V_\mathrm{alloy} = \sum\nolimits_{i=1}^{n}x_i V_m^i, \tag{4}$$

For the FCC/HCP phases, the standard topological parameter [21] was adopted:

$$P_\mathrm{FCC/HCP}(C_\mathrm{v}) = \left(1 + \varepsilon N_\mathrm{c}C_\mathrm{v}\right). \tag{5}$$

Here ε is the packing coefficient, which is 0.68 for BCC and 0.74 for FCC and HCP. N_c in BCC, FCC and HCP are 2, 4 and 6, respectively.

For the BCC phase, to eliminate the discontinuity of the original model [21] at $C_\mathrm{v} \approx 0.06$, we developed a continuous tanh-based function:

$$P_\mathrm{BCC}(C_\mathrm{v}) = W_l(C_\mathrm{v}) \cdot \left[18.61 \left(C_\mathrm{v} + \frac{6,25 \cdot 10^{-5}}{C_\mathrm{v}^2} \right) \right] + W_h(C_\mathrm{v}) \cdot \left[0.895 + 0.1 \cdot C_\mathrm{v} \right], \tag{5}$$

where $W_\mathrm{l} = 0.5\left[1 - \tanh\left(500(C_\mathrm{v} - 0.05)\right)\right]$, $W_\mathrm{h} = 0.5\left[1 + \tanh\left(500(C_\mathrm{v} - 0.05)\right)\right]$.

This approach allows for smooth and physically consistent prediction of kinetic barriers for different lattice types.

It should be noted that the developed model focuses on evaluating the kinetic competition between fundamental crystalline lattices (BCC, FCC, and HCP). While it does not explicitly simulate complex intermetallic compounds such as Laves or σ-phases, the model implicitly accounts for the formation of common ordered superstructures (e.g., B2, $L1_2$) through their parent cubic symmetries and the strong thermodynamic interaction (ΔH_mix) included in the viscosity calculation. Consequently, a prediction of BCC dominance implies a kinetic preference for BCC-like structures, encompassing both disordered solid solutions (A2) and their ordered counterparts (B2).

The calculated parameters together with the results of X-ray diffraction analysis are presented in Table 1. The values of viscosity and R_c were calculated based on the nominal alloy compositions using data from [4, 22, 23]. Although elemental redistribution inevitably occurs during the growth of multiphase structures, the derived R_c values serve as a robust first-order approximation. They effectively identify the phase that kinetically dominates the initial nucleation stage under competitive solidification conditions, prior to subsequent diffusional stabilization.

Table 1

Values of calculated critical cooling rates R_c, predicted dominant phase and results of X-ray phase analysis of the investigated alloys

№	Alloy	R_c	Predicted dominant phase	Phase composition according to X-ray phase analysis
1	$AlCoCrFe_{0,87}Mn_{0,03}NiSi_{0,1}V$	BCC $9.519 \cdot 10^5$ K/s FCC $8.127 \cdot 10^5$ K/s HCP $7.6 \cdot 10^5$ K/s	BCC	As-cast: BCC (B2, *a*=0.2888 nm) SQ film: BCC (*a*=0.2882 nm)
2	$AlCoCrFe_{1,87}Mn_{0,03}NiSi_{0,1}V$	BCC $1.771 \cdot 10^6$ K/s FCC $1.640 \cdot 10^6$ K/s HCP $1.537 \cdot 10^6$ K/s	BCC	As-cast: BCC (B2, *a*=0.2882 nm) SQ film: BCC (*a*=0.2879 nm)
3	$Al_2CoCrFe_{0,87}Mn_{0,03}NiSi_{0,1}V$	BCC $8.046 \cdot 10^5$ K/s FCC $6.653 \cdot 10^5$ K/s HCP $6.171 \cdot 10^5$ K/s	BCC	As-cast: BCC (B2, *a*=0.2888 nm) SQ film: BCC (*a*=0.2887 nm)
4	$Al_2CoCrFe_{1,87}Mn_{0,03}NiSi_{0,1}V$	BCC $1.310 \cdot 10^6$ K/s FCC $1.087 \cdot 10^6$ K/s HCP $1.009 \cdot 10^6$ K/s	BCC	As-cast: BCC (B2, *a*=0.2886 nm) SQ film: BCC (*a*=0.2881 nm)
5	$Al_{0,7}CuFeNi$	BCC $1.764 \cdot 10^8$ K/s FCC $1.505 \cdot 10^8$ K/s HCP $1.407 \cdot 10^8$ K/s	BCC	As-cast: FCC (*a*=0.3622 nm) + BCC(*a*=0.2891nm) SQ film: FCC (*a*=0.3622 nm) + BCC (*a*=0.2879 nm)
6	$Al_{0,5}CuFeNi$	BCC $2.134 \cdot 10^8$ K/s FCC $2.608 \cdot 10^8$ K/s HCP $2.452 \cdot 10^8$ K/s	FCC	As-cast: FCC (*a*=0.3608 nm) SQ film: FCC (*a*=0.3616 nm)
7	$Al_{0,5}CuFeNiSi_{0,25}$	BCC $3.89 \cdot 10^7$ K/s FCC $3.344 \cdot 10^7$ K/s	BCC	As-cast: FCC (*a*=0.3626 nm) + BCC (*a*=0.2867 nm)

		HCP $3.129\cdot10^{7}$ K/s		SQ film: FCC (a=0.3619 nm) + BCC (a=0.2863 nm)
8	$\mathrm{Al_{0,25}CuFeNiSi_{0,25}}$	BCC $5.194\cdot10^{7}$ K/s FCC $7.057\cdot10^{7}$ K/s HCP $6.671\cdot10^{7}$ K/s	FCC	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	$\mathrm{Al_{0,5}CoCuFeNi}$	BCC $8.553\cdot10^{7}$ K/s FCC $1.158\cdot10^{8}$ K/s HCP $1.094\cdot10^{8}$ K/s	FCC	As-cast: FCC (a=0.3600 nm) SQ film: FCC (a=0.3609 nm)
10	$\mathrm{AlCuFeMnSi_{0,5}}$	BCC $7.906\cdot10^{6}$ K/s FCC $6.478\cdot10^{6}$ K/s HCP $5.986\cdot10^{6}$ K/s	BCC	As-cast: BCC1 (B2, a=0.2881 nm) + BCC2 (B2, a=0.2919 nm) + BCC3 (B2, a=0.2945nm) SQ film: Ordered BCC1 (B2, a=0.2884 nm) + BCC2 (a=0.2919 nm)
11	$\mathrm{Al_{2,2}CrCuFeNi_{2}}$	BCC $1.817\cdot10^{7}$ K/s FCC $1.5\cdot10^{7}$ K/s HCP $1.39\cdot10^{7}$ K/s	BCC	As-cast: BCC (B2, a=0.2885 nm) SQ film: BCC (B2, a=0.2887 nm)
12	$\mathrm{Al_{4}CoCrCuFeNi}$	BCC $1.574\cdot10^{7}$ K/s FCC $1.29\cdot10^{7}$ K/s HCP $1.192\cdot10^{7}$ K/s	BCC	As-cast: BCC (B2, a=0.2919 nm) SQ film: BCC (B2, a=0.2916 nm)
13	$\mathrm{Al_{0,44}CuFeMnNi}$	BCC $6.914\cdot10^{7}$ K/s FCC $9.114\cdot10^{7}$ K/s HCP $8.587\cdot10^{7}$ K/s	FCC	As-cast: FCC (a=0.3645 nm) SQ film: FCC (a=0.3619 nm)
14	CuFeMnNi	BCC $3.57\cdot10^{8}$ K/s FCC $5.786\cdot10^{8}$ K/s HCP $5.536\cdot10^{8}$ K/s	FCC	As-cast: FCC (a=0.3641 nm) SQ film: FCC (a=0.3632 nm)
15	$\mathrm{CuFeMnNiSi_{0,25}}$	BCC $4.419\cdot10^{7}$ K/s FCC $6.282\cdot10^{7}$ K/s HCP $5.965\cdot10^{7}$ K/s	FCC	As-cast: FCC (a=0.3642 nm) SQ film: FCC (a=0.3634 nm)
16	$\mathrm{CuFeMnNiSi_{0,5}}$	BCC $9.748\cdot10^{6}$ K/s FCC $1.321\cdot10^{7}$ K/s HCP $1.248\cdot10^{7}$ K/s	FCC	As-cast: FCC1 (a=0.3660 nm) + FCC2 ($L1_2$, a=0.3620 nm) + FeSi + $\mathrm{FeSi_2}$ SQ film: FCC (a=0.3646 nm)
17	$\mathrm{CuFeNiSi_{0,5}}$	BCC $2.705\cdot10^{7}$ K/s FCC $4.776\cdot10^{7}$ K/s HCP $4.584\cdot10^{7}$ K/s	FCC	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	$\mathrm{Cu_{5}CrFeMnNiSi}$	BCC $8.406\cdot10^{7}$ K/s FCC $1.271\cdot10^{8}$ K/s HCP $1.212\cdot10^{8}$ K/s	FCC	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	$\mathrm{Cu_{5}AlCrFeMnNi}$	BCC $4.116\cdot10^{8}$ K/s FCC $5.699\cdot10^{8}$ K/s HCP $5.399\cdot10^{8}$ K/s	FCC	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	$\mathrm{Cu_{5}AlFeMnNiSi}$	BCC $5.423\ \cdot10^{7}$ K/s FCC $4.814\ \cdot10^{7}$ K/s HCP $4.509\ \cdot10^{7}$ K/s	BCC	As-cast: FCC (a=0.3658 nm)+BCC (B2, a=0.2832 nm) SQ film: BCC1 (B2, a=0.2834 nm) +BCC2 (B2, a=0.2894 nm) + FCC (a=0.3656 nm)
21	CoCrMnFeNiBe	BCC $1.217\cdot10^{7}$ K/s FCC $1.231\cdot10^{7}$ K/s HCP $1.155\cdot10^{7}$ K/s	FCC	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)
22	$\mathrm{Co_{19}Cr_{18}Mn_{21}Fe_{22}Ni_{20}}$	BCC $2.795\cdot10^{7}$ K/s FCC $4.618\cdot10^{7}$ K/s HCP $4.421\cdot10^{7}$ K/s	FCC	As-deposited film: fully amorphous phase Annealed film: FCC (a=0.3613 nm) + BCC B2 (FeCo, a=0.2857 nm) + MnO
23	$\mathrm{CoCr_{0,8}Cu_{0,64}FeNi}$	BCC $1.798\cdot10^{7}$ K/s FCC $2.637\cdot10^{8}$ K/s HCP $2.604\cdot10^{8}$ K/s	FCC	As-cast: FCC (a=0.3593 nm) SQ film: FCC (a=0.3589 nm)

24	$CoCrCuFeNiSn_{0,5}$	BCC $7.031\cdot10^7$ K/s FCC $5.557\cdot10^7$ K/s HCP $5.062\cdot10^7$ K/s	BCC	As-cast: FCC (a=0.3586 nm) + BCC (B2, a=0.2979 nm) SQ film: FCC (a=0.3588 nm) + BCC (B2, a=0.2974 nm)
25	CoCrCuFeNiSn	BCC $4.251\cdot10^7$ K/s FCC $3.201\cdot10^7$ K/s HCP $2.864\cdot10^7$ K/s	BCC	As-cast: FCC (a=0.3600 nm) + BCC (B2, a=0.2981 nm) SQ film: FCC (a=0.3600 nm) + BCC (B2, a=0.2987 nm)
26	$Co_4Fe_2AlMn_{1,5}Bi_{0,5}$	BCC $4.58\cdot10^7$ K/s FCC $3.698\cdot10^7$ K/s HCP $3.396\cdot10^7$ K/s	BCC	As-cast: BCC (B2, a=0.2889 nm) + FCC (a=0.3613 nm) SQ film: (BCC, a=0.2895 nm)
27	$Fe_5CoCuMnNiSi$	BCC $1.347\cdot10^7$ K/s FCC $2.063\cdot10^7$ K/s HCP $1.968\cdot10^7$ K/s	FCC	As-cast: FCC (a = 0.3610 nm) SQ film: FCC (a = 0.3601nm)
28	$Fe_5CrCuMnNiSi$	BCC $1.387\cdot10^7$ K/s FCC $2.124\cdot10^7$ K/s HCP $2.027\cdot10^7$ K/s	FCC	As-cast: FCC1 (a = 0.3656 nm) + FCC2 (a = 0.3607 nm) + BCC (a = 0.2810 nm) SQ film: FCC (a = 0.3615 nm)
29	$FeCo_{0,854}Nb_{0,146}NiB_{0,7}Si_{0,3}$	BCC $3.854\cdot10^2$ K/s FCC $2.682\cdot10^2$ K/s HCP $2.336\cdot10^2$ K/s	BCC	As-cast: FCC (a=0.3574 nm) +Fe_2B SQ film: fully amorphous phase Annealed: FCC a=0.3527 nm) + Fe_xNi_{23}-xB_6 + Fe_3Si
30	$FeB_{0,7}CoBeNiSi_{0,3}$	BCC $1.04\cdot10^4$ K/s FCC $7.504\cdot10^3$ K/s HCP $6.616\cdot10^3$ K/s	BCC	As-cast: BCC (B2, a=0.2655 nm) + (Fe, Ni, $Co)_2B$ SQ film: BCC (B2, a=0.2653 nm) + (Fe, Ni, $Co)_2B$

3.2. Experimental validation of the kinetic model

The comparison of calculated critical cooling rate R_c values with experimental data for the 30 investigated alloys (Table 1) reveals that the kinetic model effectively categorizes them into distinct behavioral groups based on the magnitude of the nucleation barrier. For systems where one crystalline phase exhibits a decisive kinetic advantage, the model accurately predicts the formation of a single-phase structure. Specifically, for alloys 1 – 4 and 10 – 12, which contain strong body-centered cubic stabilizers such as Al, Cr, and V, the calculated critical cooling rates for the BCC are significantly higher than those for the FCC. This kinetic dominance results in the formation of BCC or ordered B2 structures, which is consistent with the experimental X-ray diffraction data. Conversely, for alloys 6, 9, 13 – 16, 23, and 27, which are based on 3d-transition metals with lower Al content, the model predicts an undeniable kinetic preference for the FCC lattice. This correctly forecasts the single-phase FCC solid solutions observed in these alloys.

In cases where the calculated R_c for the BCC and FCC phases are of the same order of magnitude, thermodynamic driving forces for segregation become significant. This applies to a large group of compositions, specifically alloys 5, 7, 8, 17–19, 21, 24, 25, and 28. For these compositions, the lack of a clear kinetic winner combined with the presence of segregating elements leads to the formation of multiphase structures containing precipitates or dual-phase mixtures, explaining why simple single-phase thermodynamic, electronic, and atomic-size criteria fail for this group.

Alloys 20 and 26 provide the most compelling experimental validation of the kinetic approach, demonstrating the transition from thermodynamic to kinetic control. For these alloys, the model predicts a slight kinetic preference for the BCC phase despite the high thermodynamic stability of the FCC phase. Consequently, in the as-cast state produced by slow cooling, thermodynamic factors prevail, leading to FCC-containing multiphase structures. However, in the melt-spun state produced by rapid cooling, the system follows the path of least kinetic resistance, freezing into the BCC or B2 phase as predicted by the calculations.

Finally, the model successfully quantifies the glass-forming ability for alloys 22, 29, and 30. For alloy 22, the high calculated R_c explains why amorphization is achieved only under extreme vapor deposition rates. For alloys 29 and 30, which contain metalloids and Be, the model yields extremely low critical cooling rates, indicating high intrinsic GFA. This aligns with the easy formation of amorphous SQ films in these systems, whereas crystalline phases appear only under equilibrium conditions. By grouping all 30 alloys based on their R_c, the proposed model provides a unified framework that correctly predicts phase selection across the entire spectrum from stable solid solutions to competitive multiphase systems and metallic glasses.

4. Conclusions

1. A new kinetic approach for predicting phase selection in high-entropy alloys has been developed. The model calculates the critical cooling rate R_c for competing phases based on a modified nucleation theory. A key feature of the proposed method is the introduction of a structure-dependent viscosity term, which differentiates kinetic barriers based on the topological packing efficiency of the specific crystal lattice.
2. The predictive accuracy of the model was verified against experimental data for 30 multicomponent alloys processed under different cooling regimes. The analysis confirms that the phase exhibiting the highest R_c becomes kinetically dominant. The model correctly predicts the primary solidification phase in most of the investigated cases, demonstrating superior reliability compared to static for non-equilibrium conditions.
3. The model provides a physical explanation for the diversity of microstructures in HEAs.
4. It was established that in systems with a large difference in critical rates, a single-phase structure is formed even under rapid cooling. Conversely, in systems where R_c values for FCC and BCC phases are close, a multiphase structure is formed due to competitive nucleation and subsequent decomposition.
5. Unlike thermodynamic criteria, the developed kinetic model allows for a quantitative assessment of glass-forming ability. The calculated R_c values successfully distinguish between alloys with high intrinsic GFA (which easily amorphize at moderate cooling rates) and those requiring extreme cooling rates to suppress crystallization, providing a unified tool for designing both crystalline and amorphous high-entropy materials.

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