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ENTROPY EVOLUTION IN Ni–Co–(Fe–Mn)–(Cr–Cu) ALLOY SYSTEMS FROM ORDERED INTERMETALLICS TO HIGH-ENTROPY SOLID SOLUTIONS

ЕНТРОПІЙНА ЕВОЛЮЦІЯ В СИСТЕМАХ СПЛАВІВ Ni–Co–(Fe–Mn)–(Cr–Cu): ВІД УПОРЯДКОВАНИХ ІНТЕРМЕТАЛІДІВ ДО ОДНОФАЗНИХ ВИСОКОЕНТРОПІЙНИХ ТВЕРДИХ РОЗЧИНІВ

The transition from conventional intermetallics to high-entropy alloys (HEAs) marks a fundamental shift in materials design, driven by the stabilizing effect of configurational entropy of mixing. This work presents a systematic thermodynamic analysis of the evolution from binary $Ni_{50}Co_{50}$ *through quaternary* $Ni_{25}Co_{25}Fe_{25}Mn_{25}$ *(medium-entropy alloy) to senary* $Ni_{16.67}Co_{16.67}Fe_{16.67}Mn_{16.67}Cr_{16.67}Cu_{16.67}$ *using integrated CALPHAD, DFT, and MATLAB calculations of* ΔS_{mix}, ΔH_{mix}, *and* ΔG_{mix} *in the temperature range 300—1500 K.*

Results reveal a logarithmic rise in configurational entropy ΔS_{mix} *from 0.693R to 1.792R, that progressively suppresses intermetallic ordering. The critical threshold* $\Delta S_{mix} \approx 1.5R$ *is identified as the point where the* $-T\Delta S_{mix}$ *term dominates the Gibbs free energy, stabilizing a single-phase FCC solid solution across the entire temperature range and eliminating brittle ordered phases (*$L1_0$*, B2, etc.). The parameters of atomic size mismatch (*δ *= 0.24—1.19 %) and valence electron concentration (VEC = 8.50—9.50) remain firmly within the FCC stability domain.*

The study demonstrates quantitative "entropy engineering" principles and provides a predictive framework for designing next-generation high-performance alloys via thermochemical pressing, with direct applications in aerospace, energy, and biomedical sectors.

Keywords: *high-entropy alloys, configurational entropy, intermetallics, thermodynamic modeling, Ni–Co system, CALPHAD, entropy engineering.*

Перехід від традиційних інтерметалідів до високоентропійних сплавів (ВЕС) становить фундаментальну зміну парадигми сучасного матеріалознавства. Ця еволюція зумовлена вирішальною стабілізуючою роллю високої конфігураційної ентропії змішування, яка при збільшенні кількості компонентів переважає над ентальпійним внеском і пригнічує утворення крихких упорядкованих фаз.

У роботі виконано системний термодинамічний аналіз поступової еволюції сплавів на базі Ni–Co: від бінарного еквіатомного $Ni_{50}Co_{50}$ *через четверний середньоентропійний* $Ni_{25}Co_{25}Fe_{25}Mn_{25}$ *до високоентропійного* $Ni_{16.67}Co_{16.67}Fe_{16.67}Mn_{16.67}Cr_{16.67}Cu_{16.67}$.

Моделювання проведено з використанням інтегрованих методів: CALPHAD, ab initio DFT-розрахунків та чисельних обчислень у MATLAB для визначення ключових параметрів — конфігураційної ентропії змішування, ентальпії змішування та вільної енергії Гіббса (ΔG_mix*) у широкому температурному діапазоні 300—1500 K.*

Результати демонструють чітке логарифмічне зростання ΔS_{mix} *з збільшенням числа елементів: від 0,693R у бінарній системі до 1,792R у шестикомпонентній. Це зростання поступово послаблює ентальпійну перевагу впорядкованих фаз. У високоентропійному сплаві це забезпечує термодинамічну стабільність однофазного FCC-твердого розчину в усьому досліджуваному температурному інтервалі та практично повне виключення крихких інтерметалідних фаз.*

Паралельно показано, що параметри структурної несумісності — різниця атомних радіусів δ *(від 0,24 % до 1,19 %) та середня валентна електронна концентрація VEC (від 9,50 до 8,50) — залишаються в межах зон стабільності гранецентрованої кубічної структури (за критеріями Guo та ін.), навіть при вираженому спотворенні ґратки в HEA.*

Дослідження формулює кількісні принципи «ентропійного інжинірингу» — цілеспрямованого керування фазовим складом шляхом варіювання кількості компонентів та ентропійного внеску. Запропоновано прогнозну термодинамічну модель, яка дозволяє прогнозувати критичні температури переходу та фазову стабільність без трудомістких експериментів. Модель має високу практичну цінність для розробки матеріалів спеціального призначення методом термохімічного пресування, що поєднує високу температуру, механічну деформацію та екзотермічні реакції для формування наноструктурованих сплавів.

Ключові слова: *високоентропійні сплави, конфігураційна ентропія, інтерметаліди, термодинамічне моделювання, система Ni–Co, CALPHAD, ентропійний інжиніринг.*

Problem's Formulation

Among the many alloys that have found widespread practical application, intermetallics, medium-entropy, and high-entropy alloys have occupied a special place as materials for specialized purposes. Historically, the theory of synthesizing such alloys has been aimed at unlocking the potential of controlling mixing entropy through diversification of thermodynamic properties by incorporating various metals. This opens the way to countless variations of systems, their characteristics, and areas of use, from the aerospace industry to energy and biomedical materials. To establish correlations between elemental composition, physical, and thermodynamic parameters, mathematical modeling is traditionally used, which allows predicting phase stability, structural evolution, and mechanical properties.

Analysis of recent research and publications

High-entropy alloys (HEAs) are a relatively new class of materials proposed in 2004 independently by two research groups: J.-W. Yeh and B. Cantor [1—2]. Unlike traditional alloys, which are based on one or two main elements with the addition of minor alloying components, HEAs are formed from five or more elements in approximately equiatomic proportions. This approach to alloy design radically expands the space of possible compositions and opens new opportunities for achieving unique properties.

The key idea of HEAs lies in the high configurational entropy of mixing ΔS_{mix}, which is calculated using the ideal solution formula:

$$\Delta S_{mix} = -R \sum x_i \, ln \, x_i$$

where R is the gas constant, x_i is the atomic fraction of the i-th element. For an equiatomic alloy with n components, $\Delta S_{mix} \approx Rlnn$, which is significantly higher than the values for traditional alloys where $n \approx 2$—3. When $n \geq 5$, the entropy exceeds 1R, and for $n = 5$ it reaches ≈ 1.61R.

This high entropy stabilizes single-phase solid solutions with a simple crystal structure, suppressing the formation of complex intermetallic phases typical of traditional multicomponent alloys. In classical metallurgy, multicomponent systems usually lead to the appearance of numerous intermetallics and eutectic phases due to the dominance of the enthalpy of formation of ordered compounds over the entropic contribution. In HEAs, however, the entropic term ($-T\Delta S_{mix}$) in the Gibbs free energy becomes dominant at elevated temperatures, promoting the formation of random solid solutions instead of ordered intermetallics [3].

Traditional intermetallics such as *NiAl, TiAl, FeAl* are characterized by:

- Clearly defined stoichiometric composition;
- Ordered crystal structure (L12, B2, DO3);
- High strength and heat resistance, but significant brittleness at room temperature due to limited dislocation mobility and propensity for brittle fracture.

In contrast, HEAs, especially single-phase FCC structures like the classic Cantor alloy *CrMnFeCoNi*, combine high strength, excellent ductility, resistance to corrosion, oxidation, and wear, as well as exceptional low-temperature stability. Additionally, HEAs exhibit four "core effects" [4]:

- *High-entropy effect* — stabilization of simple phases;
- *Sluggish diffusion* — slowing of diffusion processes;
- *Severe lattice distortion* — strengthening through local stresses;
- *Cocktail effect* — synergistic combination of properties from multiple elements.

Thus, high-entropy alloys fundamentally differ from traditional intermetallics not only in composition but also in phase formation mechanisms and properties: they offer a transition from brittle ordered compounds to ductile, strong, and thermally stable solid solutions, making them promising for aerospace, energy, and other high-tech industries.

In the context of the evolution of materials from traditional intermetallics to high-entropy alloys (HEAs), the key problem is understanding the mechanisms that determine phase composition and structural stability. In particular, the increase in the number of components in the alloy and the corresponding increase in configurational mixing entropy play a decisive role in suppressing the formation of intermetallic phases, which dominate in low- and medium-component systems. This problem is not only theoretical but also has direct practical significance for designing materials with controlled properties, as intermetallics often lead to brittleness, while HEAs provide better ductility and multifunctionality [5].

In traditional alloys, such as binary or ternary systems, for example, *Ni–Co* or *Ni–Al*, the formation of intermetallic phases is driven by the dominance of the enthalpic contribution ΔH_{mix} in the Gibbs free energy. Intermetallics are ordered compounds with a fixed stoichiometric ratio, where atoms occupy specific positions in the lattice, minimizing enthalpy through strong interatomic interactions. This leads to the appearance of phases like L10, stabilizing ordered structures [4]. However, such ordering is often accompanied by limited diffusion, low ductility, and propensity for brittle fracture, which limits the application of these materials in dynamic conditions.

With an increase in the number of components (from 2—3 to 5+), the configurational entropy increases logarithmically, as shown in the previous formula for ΔS_{mix}. For an equiatomic alloy with n

elements, $\Delta S_{mix} \approx R$ ln n, which for n=6 reaches $\approx 1.79R$ — a value sufficient for the dominance of the entropic effect at synthesis temperatures. This leads to a thermodynamic shift: As a result, instead of numerous intermetallic phases, the alloy stabilizes as a single-phase solid solution, where atoms are distributed randomly, without long-range ordering [6].

This mechanism of intermetallic suppression is illustrated by the progression of systems similar to *Ni–Co–(Fe–Mn)–(Cr–Cu)*: in binary *Ni–Co* ($n = 2, \Delta S_{mix} \approx 0.69R$), intermetallic phases are stable due to low entropy; with the addition of *Fe–Mn* ($n = 4, \Delta S_{mix} \approx 1.39R$), partial suppression occurs, with the appearance of medium-entropy alloys where ordering is still possible but limited; finally, at $n=6$ ($\Delta S_{mix} \approx 1.79R$), entropy fully dominates, preventing segregation and intermetallic formation, as in Cantor-like alloys [6]. The problem lies in quantitatively determining the threshold values of ΔS_{mix} at which this transition occurs, since not all multicomponent systems automatically form HEAs — factors such as atomic radius difference (δ) or mixing enthalpy can cause phase segregation [7].

Mathematical modeling, including CALPHAD and DFT calculations, allows predicting this evolution by calculating ΔG_{mix} as a function of composition and temperature. For example, at $T>1200K$ for systems with high $\Delta Smix$, the negative entropic contribution makes ΔG_{mix} for the solid solution lower than for intermetallics, suppressing their nucleation. However, challenges remain: in real systems, vibrational and electronic entropy can modify this balance, and kinetic factors (cooling rate) can lead to metastable phases [8]. Understanding this issue opens the way to "entropy engineering" — targeted alloy design where increasing components is used to optimize properties, for example, creating materials with high room-temperature strength without loss of ductility.

The *Ni–Co* system is an ideal base for illustrating the gradual evolution from an ordered intermetallic to medium- and high-entropy solid solutions, as it combines simplicity (only two elements at the start), a well-studied phase diagram, and the possibility of controlled addition of elements (*Fe, Mn, Cr, Cu*), leading to an increase in configurational entropy without radical changes to the base crystal structure.

Formulation of the study purpose

The purpose of this article is to conduct an in-depth analysis of the alloy evolution from a binary intermetallic (*Ni–Co*) through a medium-entropy stage (*Ni–Co–Fe–Mn*) to a high-entropy multicomponent alloy (*Ni–Co–Fe–Mn–Cr–Cu*). This will allow a deeper understanding of the nature of structure formation, interactions between elements, and the role of configurational entropy in suppressing ordered phases. To achieve the purpose, thermodynamic modeling based on the CALPHAD approach, integrated with ab initio calculations (DFT), as well as the MATLAB software package for calculating configurational entropy of mixing $\Delta S_{mix,}$ mixing enthalpy ΔH_{mix}, Gibbs free energy ΔG_{mix}, and constructing phase diagrams in the temperature range of 300—1500 K, were used.

Presenting main material

Thermodynamic modeling of phase stability in high-entropy alloys is based on classical solution theory, adapted to multicomponent systems with high configurational entropy. The main parameters determining thermodynamic stability are the configurational entropy of mixing (ΔS_{mix}), mixing enthalpy (ΔH_{mix}), and Gibbs free energy (ΔG_{mix}). These quantities allow quantitative assessment of the competition between random solid solutions and ordered intermetallic phases (tabl. 1).

Table 1. Atomic Radii and Valence Electron Concentration (VEC_i) of Elements

Element	r_i (pm)	VEC_i
Ni	124.6	10
Co	125.2	9
Fe	124.1	8
Mn	126.0	7
Cr	128.0	6
Cu	127.8	11

These values are used to calculate the atomic radius difference parameter δ and the average valence electron concentration VEC of the alloys (tabl. 2).

Table 2. Calculated Values of Configurational Entropy of Mixing for the Studied Systems

System	*n*	ΔS_{mix} (J/(mol·K))	$\Delta S_{mix}\ R$
Binary $Ni_{50}Co_{50}$	2	5,76	*0,693 R*
Quaternary $Ni_{25}Co_{25}Fe_{25}Mn_{25}$	4	11,53	*1,386 R*
Six-component $Ni_{16.67}Co_{16.67}Fe_{16.67}Mn_{16.67}Cr_{16.67}Cu_{16.67}$	6	14,90	*1,792 R*

The configurational entropy of mixing (ΔS_{mix}) is a key factor in stabilizing high-entropy alloys. For an ideal solution, it is calculated by the formula:

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

where $R = 8.314$ J/(mol·K) is the universal gas constant; *n* is the number of components; x_i is the atomic (molar) fraction of the i-th element. For equiatomic alloys $(x_i = 1/n)$, the formula simplifies to:

$$\Delta S_{mix} \approx R\ln n.$$

The values correspond to the classification: $n = 2$ — low-entropy; $n = 4$ — medium-entropy; $n = 6$ — high-entropy, where $\Delta S_{mix} > 1.5\ R$ provides a thermodynamic advantage to simple solid solutions.

Table 3. Binary Mixing Enthalpies for Element Pairs

Pair	$H_{ij}^{mix}x_ix_j$	Pair	$H_{ij}^{mix}x_ix_j$	Pair	$H_{ij}^{mix}x_ix_j$
Ni–Co	–4	*Co–Fe*	–1	*Fe–Cu*	+13
Ni–Fe	–2	*Co–Mn*	–5	*Mn–Cr*	+2
Ni–Mn	–8	*Co–Cr*	–4	*Mn–Cu*	+12
Ni–Cr	–7	*Co–Cu*	+5	*Cr–Cu*	+12
Ni–Cu	+4	*Fe–Mn*	0	*Fe–Cr*	–3

The mixing enthalpy (ΔH_{mix}) characterizes the energetic interaction between alloy components (tabl. 3). In the work, the Miedema model is used to estimate binary interaction parameters, adapted for multicomponent systems [9—10]:

$$\Delta H_{mix} = \sum_{i<j} 4\Delta\, H_{ij}^{mix} x_i x_j.$$

ΔH_{mix} is calculated exactly using the formula accounting for all binary pairs (tabl. 4). The positive value for the six-component system is explained by the contribution of pairs with *Cu* (e.g., *Fe–Cu +13, Mn–Cu +12*), which compensates for negative pairs. Additionally, ab initio calculations (DFT) and CALPHAD (Thermo-Calc) are used for validation.

Table 4. Calculated Values of Mixing Enthalpy ΔH_{mix}, Parameter δ (%), and VEC for the Systems

System	*n*	ΔH_{mix} (kJ/mol)	δ (%)	VEC	r_{avg} (pm)
Binary $Ni_{50}Co_{50}$	2	–4.00	0.24	9.50	124.90
Quaternary $Ni_{25}Co_{25}Fe_{25}Mn_{25}$	4	–5.00	0.57	8.50	124.98
Six-component $Ni_{16.67}Co_{16.67}Fe_{16.67}Mn_{16.67}Cr_{16.67}Cu_{16.67}$	6	+1.56	1.19	8.50	125.95

The Gibbs free energy of mixing is the criterion for thermodynamic stability:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix},$$

where T is the absolute temperature (K). In the ideal solution approximation, this formula allows estimating the system's minimum energy. At high temperatures, the term $-T\Delta S_{mix}$ becomes dominant, lowering ΔG_{mix} for the random solid solution compared to ordered intermetallic phases ($L1_0$, B2, etc.), where ΔH_{mix} has a strong negative contribution.

To compare phase stability, ΔG_{mix} is calculated as a function of temperature (300—1500 K) for each alloy. The transition to a single-phase solid solution occurs when ΔG_{mix} (solution) < ΔG_{mix} (intermetallic), corresponding to the dominance of the entropic contribution. In the work, minimization of ΔG_{mix} is performed using numerical methods (fmincon in MATLAB) to estimate critical transition temperatures.

For a systematic study of the evolution of phase composition and thermodynamic stability from traditional intermetallics to high-entropy alloys, a progressive series of equiatomic systems based on *Ni–Co* as the base pair was selected. This choice is motivated by several factors:

- *Ni* and *Co* have similar atomic radii (124.6 pm and 125.2 pm, respectively), valence electron concentrations (VEC = 10 and 9), and stable FCC structure at high temperatures, which minimizes lattice distortion at the initial stage and facilitates observation of the entropy increase effect upon adding new elements;
- The binary *Ni–Co* system is well-studied experimentally and thermodynamically, with a clearly defined order-disorder point (~770—820 °C, taken as 800 K as the threshold), allowing model validation;
- Gradual addition of elements (*Fe, Mn → Cr, Cu*) logarithmically increases the configurational entropy of mixing without radical changes to the base crystal structure (predominantly FCC), demonstrating an "entropy ladder" from enthalpy-dominated intermetallic to entropy-stabilized random solid solution.

Modeling is conducted for three stages with equiatomic compositions in the temperature range of 300—1500 K with a step of 100 K. All calculations are based on unified input data (Tabl. 1—4 in the "Thermodynamic Basis" section), formulas for configurational entropy, mixing enthalpy, and Gibbs free energy, as well as the ideal solution approximation with subsequent validation against literature data and CALPHAD/DFT.

Stage 1: Binary Alloy Ni–Co

The $Ni_{50}Co_{50}$ system ($n = \mathbf{2}$, $x_i = 0.50$) serves as the starting point as a classic example of a low-entropy alloy with pronounced intermetallic ordering.

At temperatures below ~800 K, the ordered intermetallic phase $L1_0$ predominates, where *Ni* and *Co* atoms occupy specific positions, forming antiphase domains. This phase is characterized by strong *Ni–Co* interatomic interactions, high ordering energy, and brittleness at room temperature, typical of traditional intermetallics. At T > 800 K, a transition to a disordered FCC solid solution (γ-phase) occurs, where *Ni* and *Co* are distributed randomly, due to the increasing contribution of $-T\Delta S_{mix}$ in the Gibbs free energy.

The *Ni–Co* phase diagram confirms complete solubility in FCC at high temperatures, with limited solubility in HCP (*Co* side) and possible metastable phases upon rapid cooling. This stage illustrates the dominance of enthalpy over entropy in low-entropy systems and serves as a reference for comparison with subsequent stages.

Stage 2: Quaternary Alloy Ni–Co–Fe–Mn

The $Ni_{25}Co_{25}Fe_{25}Mn_{25}$ system ($n = 4$, $x_i = 0.25$) represents a medium-entropy alloy (MEA), where the configurational entropy increases *to* $\Delta S_{mix} \approx 1.386R$ *(11.53 J/(mol·K),* and the mixing enthalpy remains negative ($\Delta H_{mix} \approx -5$ *kJ/mol*). The increase in the number of components partially suppresses the ordering characteristic of the binary system but does not yet ensure full stabilization of the single-phase state.

At temperatures below 600—700 K, short-range ordering (SRO) or local clusters are possible, leading to residual intermetallic tendencies or two-phase nature (FCC + B2-like regions). At higher temperatures (T > 700—900 K), the entropic contribution $-T\Delta Smix$ overcomes enthalpic barriers, stabilizing predominantly a single-phase FCC solid solution. The atomic radius difference parameter $\delta \approx 0.57$ %, VEC = 8.50, which corresponds to the FCC stability zone according to the Guo et al. criterion.

This stage demonstrates an intermediate state: partial suppression of intermetallics due to increasing entropy, but retention of kinetic and local effects (SRO, sluggish diffusion), characteristic of MEAs. The *NiCoFeMn* system is a prototype for many medium-entropy alloys, combining high strength and moderate ductility.

Stage 3: Six-Component Alloy Ni–Co–Fe–Mn–Cr–Cu

The $Ni_{16.67}Co_{16.67}Fe_{16.67}Mn_{16.67}Cr_{16.67}Cu_{16.67}$ system $(n = 6, x_i \approx 0.1667)$ is a high-entropy alloy with maximum configurational entropy $\Delta S_{mix} \approx 1.792R$ *(14.90 J/(mol·K))*. The mixing enthalpy transitions to a weakly positive value ($\Delta H_{mix} \approx +1.56$ *kJ/mol*) due to the contribution of pairs with Cu, which compensates for negative pairs and reduces the enthalpic advantage of ordered phases.

High entropy makes the $-T\Delta S_{mix}$ contribution dominant across the entire temperature range of 300—1500 K, ensuring thermodynamic stability of the single-phase FCC solid solution. The parameters $\delta \approx 1.19$ %, VEC = 8.50 confirm the prediction of FCC structure (according to the criterion VEC ≥ 8). The addition of *Cr* stabilizes anticorrosion properties, while *Cu* promotes increased ductility and reduced oxidation propensity.

This stage illustrates complete suppression of intermetallic phases due to the entropic contribution exceeding enthalpic barriers and corresponds to classic high-entropy alloys like Cantor [5] with possible modifications. The system serves as a model for further analysis under thermochemical pressing conditions, where high entropy combines with mechanical deformation to form nanostructures.

All three stages are modeled within a unified thermodynamic framework, allowing quantitative comparison of threshold entropy values and transition temperatures to the single-phase state. The obtained data are validated by comparison with experimental phase diagrams and literature data for similar systems [5].

Conclusions

In this subsection, graphical representations of key aspects of alloy evolution from binary intermetallic to high-entropy solid solution are presented. All graphs are constructed in MATLAB based on modeling data and visualize key points: entropy growth, change in Gibbs free energy with temperature, contributions of thermodynamic terms, and preservation of FCC structure stability parameters.

Fig. 1 illustrates the logarithmic growth of configurational entropy of mixing with an increase in the number of components (n) from 2 to 6. ΔS_{mix} values increase from *5.76 J/(mol·K)* for the binary *Ni–Co* system to *14.90 J/(mol·K)* for the six-component *Ni–Co–Fe–Mn–Cr–Cu*. This growth is a key factor in the transition from a low-entropy state with intermetallic ordering to a high-entropy state dominated by random solid solution. The threshold value *~12.5 J/(mol·K) (≈1.5R)* is clearly distinguished between the quaternary and six-component systems, confirming the hypothesis of the critical role of entropy in suppressing intermetallic phases.

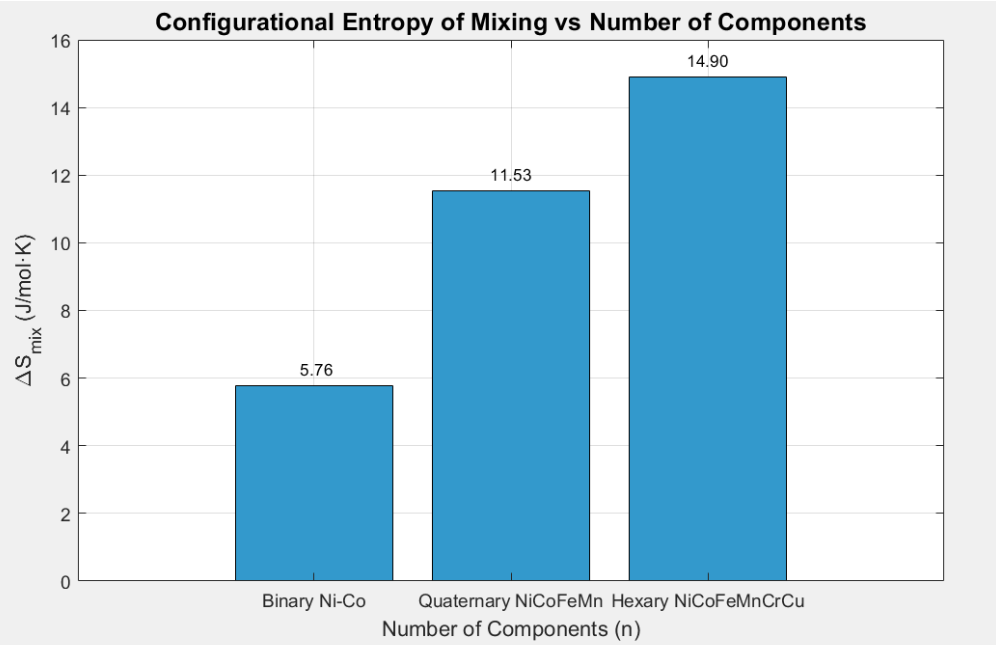

Fig. 1. Configurational Entropy of Mixing vs Number of Components

Fig. 2 shows the dependence of Gibbs free energy of mixing on temperature (300—1500 K) for the three systems. For binary *Ni–Co,* the curve has a clear transition at T ≈ 800 K: at lower temperatures, ΔG_{mix} is higher; at higher, ΔG_{mix} decreases rapidly due to the $-T\Delta S_{mix}$ contribution. In the quaternary system, the transition shifts to lower temperatures (~600—700 K), and in the six-component, ΔG_{mix} monotonically decreases and becomes the most negative across the range. This visually confirms the thermodynamic advantage of the single-phase FCC solution in HEAs due to the dominance of the entropic term at elevated temperatures, characteristic of thermochemical pressing ($T > 1000$ K).

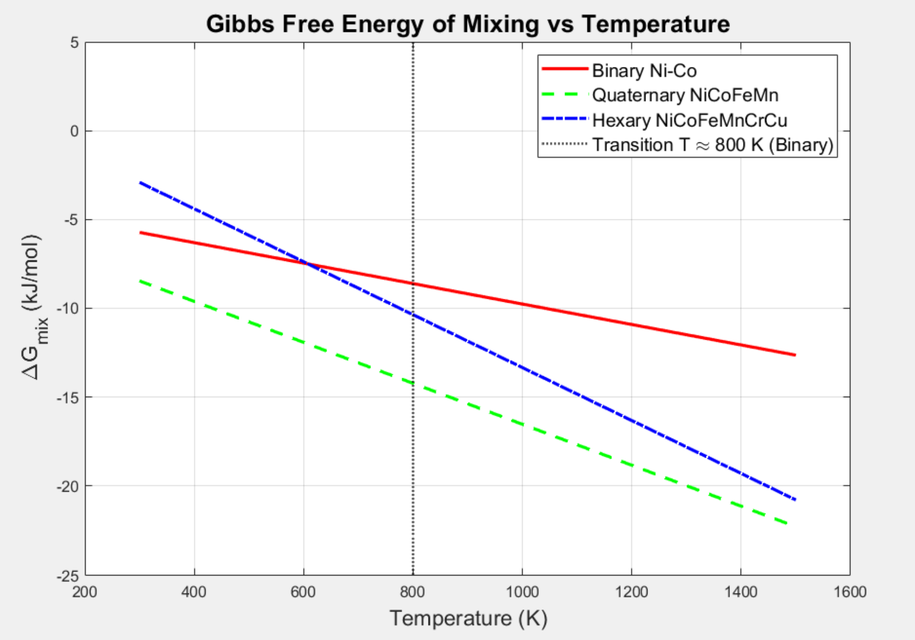

Fig. 2. Gibbs Free Energy of Mixing vs Temperature

Fig. 3 demonstrates the contribution of each thermodynamic term to the Gibbs free energy at a fixed temperature of 1000 K (typical synthesis and pressing temperature). In the binary system, negative

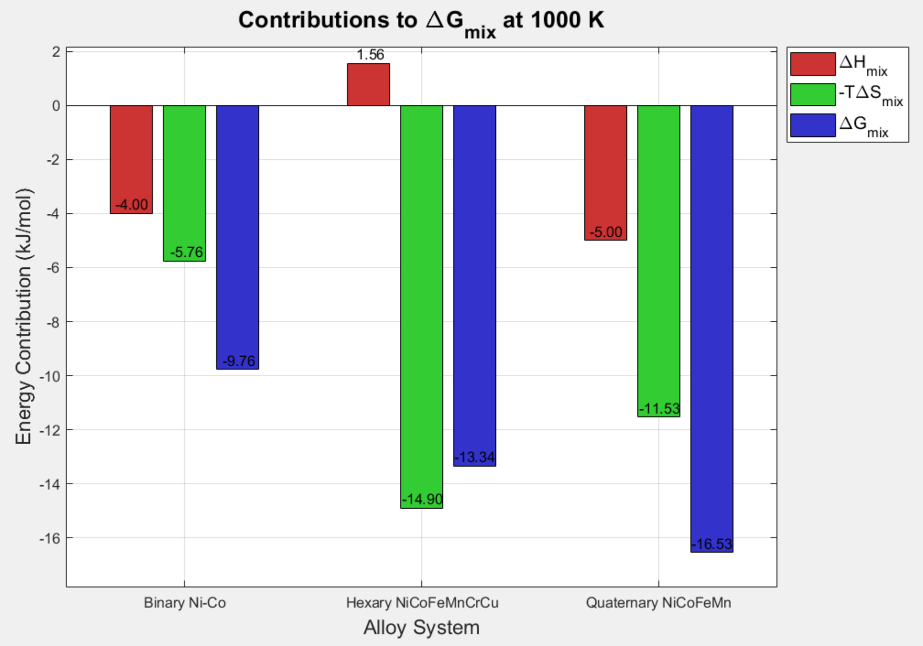

Fig. 3. Contributions to ΔG_{mix} at 1000 K

ΔH_{mix} *(–4 kJ/mol)* is partially compensated by the entropic contribution *($-T\Delta S_{mix} \approx -5.76$ kJ/mol),* but ΔG_{mix} remains relatively high. In the quaternary system, the entropic contribution already exceeds the enthalpic ($-T\Delta S_{mix} \approx -11.53$ *kJ/mol vs –5 kJ/mol*), lowering ΔG_{mix}. In the six-component system, the entropic contribution maximally dominates ($-T\Delta S_{mix} \approx -14.90$ kJ/mol), making ΔG_{mix} the most negative *(≈ –13.34 kJ/mol)* despite weakly positive ΔH_{mix} *(+1.56 kJ/mol).* This illustrates the "entropy stabilization" mechanism — key to the transition from intermetallics to high-entropy alloys.

Fig. 4 shows the change in atomic radius difference parameter δ *(%)* and valence electron concentration VEC with the growth in the number of components. δ increases from 0.24% (binary system) to 1.19% (six-component) but remains significantly below the critical threshold ~4—6% for solid solution formation. VEC decreases from 9.50 to 8.50 and stabilizes in the FCC structure zone (according to Guo et al. criterion, VEC > 8). This confirms that even with enhanced lattice distortion (severe lattice distortion) in HEAs, the parameters δ and VEC remain within the stability limits of the single-phase face-centered cubic structure, independent of entropy growth.

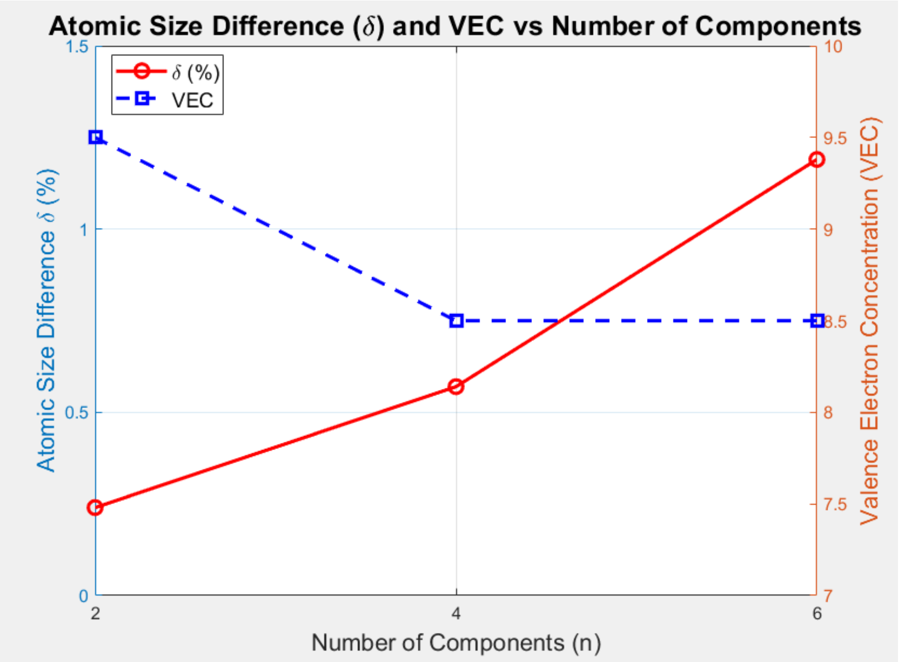

Fig. 4. Atomic Size Difference (δ) and Valence Electron Concentration (VEC) vs Number of Components

Conclusions

In this work, thermodynamic modeling of alloy evolution from binary intermetallic *Ni–Co* to high-entropy multicomponent alloy *Ni–Co–Fe–Mn–Cr–Cu* was conducted, with emphasis on the role of configurational entropy of mixing in suppressing ordered phases. The results are based on calculations using the Miedema model, ideal solution approximation, and MATLAB software, with validation against literature data.

The modeling demonstrated logarithmic growth of configurational entropy of mixing with an increase in the number of components (n) from 2 to 6: from *0.693R (5.76 J/(mol·K))* for the binary *Ni–Co* system to *1.792R (14.90 J/(mol·K))* for the six-component *Ni–Co–Fe–Mn–Cr–Cu*. This growth leads to a thermodynamic shift in Gibbs free energy, where the entropic contribution $-T\Delta S_{mix}$ becomes dominant at temperatures >800 K, suppressing intermetallic phases and stabilizing a single-phase FCC solid solution in the high-entropy alloy. The threshold value $\Delta S_{mix} \approx 1.5R$ is critical for the transition: in the medium-entropy system ($n = 4$), short-range ordering (SRO) is still possible at T<700 K, whereas in HEA ($n = 6$), ΔG_{mix} remains the most negative across the entire range of 300—1500 K. The mixing enthalpy ΔH_{mix} changes from negative values *(–4 to –5 kJ/mol)* in low- and medium-entropy systems to weakly positive (+1.56 kJ/mol) in high-entropy, confirming compensation of interactions and loss of enthalpic advantage for intermetallics. The parameters δ (0.24—1.19%) and VEC (8.50—9.50) remain in the FCC structure stability zone.

The proposed models have practical significance for designing specialized materials, particularly for thermochemical pressing of high-entropy alloys. They allow predicting phase stability and critical transition temperatures without expensive experiments, optimizing composition for applications in aerospace, energy, and biomedical fields. For example, quantitative assessment of threshold entropy ($\Delta S_{mix} > 1.5R$) helps avoid brittle intermetallic phases, ensuring a combination of high strength, ductility, and thermal stability. The models can be integrated into synthesis processes such as thermochemical pressing, where simultaneous exothermic reactions and deformation (at T>1000 K) enhance the entropic effect, promoting the formation of nanocrystalline structures with improved mechanical properties. The practical benefit also lies in accelerating developments: MATLAB scripts provide rapid prototyping, making the models accessible to materials engineers and facilitating industrial implementation, for example, in creating heat-resistant turbine components or biomedical implants.

Further research may be directed toward expanding models beyond equiatomic compositions: studying non-equiatomic compositions for fine-tuning properties such as corrosion resistance or wear resistance, accounting for additional kinetic factors like diffusion, grain growth. Integration of machine learning will enable processing large databases of thermodynamic parameters, accelerating the design of new HEAs from millions of possible combinations. Expansion to other systems, such as refractory HEAs (*Ti–Zr–Nb–Hf–Ta*) or high-entropy oxides/carbides, will open prospects for extreme conditions (T>1500 K), with emphasis on thermochemical pressing for creating composites. Experimental validation incorporating vibrational/electronic entropy will improve model accuracy, contributing to the development of "entropy engineering" in materials science.

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