

Stable HCP high-entropy alloys identified by knowledge-based screening and valence electron concentration criteria

Hiroshi Mizuseki^{a,*}, Ryoji Sahara^b, Kenta Hongo^{c,*}

^a Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea

^b National Institute for Materials Science (NIMS), Tsukuba 305-0047, Japan

^c Research Center for Advanced Computing Infrastructure, JAIST, Asahidai 1-1, Nomi, Ishikawa 923-1292, Japan

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ABSTRACT

Although extensive research has been conducted on High-Entropy Alloys (HEAs) with face-centered cubic (FCC) and body-centered cubic (BCC) structures, the formation conditions and stability of HEAs with hexagonal close-packed (HCP) structures remain less explored compared to their cubic counterparts. Comprehensive exploration of HEAs requires efficient and reliable methods to assess structural stability across a vast compositional space comprising multiple metallic elements. In this study, we investigated 40,920 equimolar quaternary alloys, generated by selecting arbitrary combinations of four elements from a pool of 33. Metallurgical screening was performed based on criteria including atomic radius and electronegativity differences among constituent elements, enthalpy–entropy competition, and mixing enthalpy calculated using the semi-empirical Miedema model. This screening identified 1005 compositions with the potential to form random solid solutions (RSS). For these candidates, first-principles calculations were conducted to evaluate the RSS formation energies for FCC, BCC, and HCP structures, thereby determining the most stable crystal structure for each composition. The results revealed a clear correlation between valence electron concentration (VEC) and the distribution of crystal structures. Notably, HCP structures were frequently observed not only in the intermediate VEC range between those favoring BCC and FCC, but also in low-VEC regions around 3 and high-VEC regions exceeding 10. This trend closely mirrors the VEC-dependent structural preferences of individual 4d and 5d transition metals, suggesting that the intrinsic crystal structures of constituent elements may be preserved in HEAs. Our findings provide a systematic dataset of HCP stability within the VEC framework and offer a baseline for the development of multicomponent alloys.

1. Introduction

High-Entropy Alloys (HEAs) are a class of materials formed by mixing multiple principal elements in nearly equiatomic ratios. These alloys exhibit exceptional mechanical and physicochemical properties that are often unattainable through conventional alloy design strategies [1–5]. In particular, their high strength, corrosion resistance, and thermal stability make them promising candidates for applications in aerospace, energy, and biomedical fields [6–8]. More recently, HEAs have garnered attention as sustainable catalytic materials that do not rely on precious metals [9,10]. While high-throughput computational studies have successfully mapped the stability of face-centered cubic (FCC) and body-centered cubic (BCC) structures [11–13], hexagonal close-packed (HCP) structures have been significantly less explored [14]. Despite

their potential, a systematic understanding of HCP formation conditions remains a notable knowledge gap in HEA research.

Valence Electron Concentration (VEC) is a widely adopted criterion for predicting crystal structures in HEAs [15]; typically, FCC is favored at high VEC and BCC at low VEC. However, this conventional framework primarily focuses on the competition between FCC and BCC, leaving the stability regions of HCP phases—especially in non-traditional VEC ranges—unclear. Takeuchi and Wada [16] further explored HEA crystal structure classification using both VEC and the average period of constituent elements in the periodic table. Moreover, VEC-dependent structural stability has been observed in binary alloys through both experimental and theoretical studies [17–20], and more recently, VEC has also been suggested as a relevant indicator for the stability of semi-ordered phases in HEAs [21,22]. Interestingly, among 4d and 5d

* Corresponding authors.

E-mail addresses: mizuseki@kist.re.kr (H. Mizuseki), hongo@jaist.ac.jp (K. Hongo).

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transition metals, which are less influenced by magnetic effects, elements within the same group exhibit the same crystal structure. This intrinsic structural tendency may serve as a useful indicator for predicting phase stability in HEAs based on VEC. However, it remains to be determined whether these elemental trends can be generalized to predict HCP stability across a broad compositional space.

The objective of this study is to systematically map the VEC-dependent stability of HCP phases relative to FCC and BCC structures. Using a combination of metallurgical screening and high-throughput first-principles calculations, we evaluated 1005 equiatomic quaternary compositions selected from a pool of 33 elements. By analyzing the resulting phase stability map, we aim to identify the specific VEC regions where HCP structures become competitive and clarify the extent to which the structural preferences of constituent elements are preserved in complex multicomponent systems.

2. Computational methods

To systematically explore equiatomic quaternary HEAs, we developed a metallurgy-informed screening framework. A total of 33 elements were selected as candidate constituents: Mg, Al, P, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Lu, Hf, Ta, W, Re, Os, Ir, Pt, and Au. By combining any four of these elements, 40,920 possible equiatomic quaternary alloys can be generated. Since performing first-principles calculations for all compositions is computationally prohibitive, we applied a series of metallurgical criteria to efficiently narrow down the candidate space to those compositions most likely to form solid solutions.

2.1. Screening based on atomic radius differences

Atomic radius mismatch is known to strongly influence solid solution formation. Following the approaches of Wang et al. and Yang et al. [23,24], we employed the atomic packing parameter γ and the polydispersity parameter δ to exclude compositions with large atomic size disparities.

$$\gamma = \left(1 - \sqrt{\frac{(r_s + \bar{r})^2 - \bar{r}^2}{(r_s + \bar{r})^2}} \right) / \left(1 - \sqrt{\frac{(r_L + \bar{r})^2 - \bar{r}^2}{(r_L + \bar{r})^2}} \right) \quad (1)$$

$$\delta = \sqrt{\sum_{i=1}^n x_i \left(1 - \frac{r_i}{\bar{r}} \right)^2} \quad (2)$$

Here, $\bar{r}$ is the average atomic radius, r_i the atomic radius of element i , x_i its molar fraction, and r_s and r_L the minimum and maximum atomic radii among the constituent elements, respectively. When all atomic radii are equal, $\gamma = 1$ and $\delta = 0$. In this study, compositions with $\gamma \geq 1.175$ and $\delta \geq 0.066$ were excluded.

2.2. Screening based on electronegativity differences

Electronegativity mismatch also affects solid solution stability. Following Dong et al. [25], we defined the electronegativity difference ΔX as:

$$\Delta X = \sqrt{\sum_{i=1}^n x_i (X_i - \bar{X})^2} \quad (3)$$

where X_i is the electronegativity of element i and $\bar{X}$ is the average electronegativity of the constituent elements. Compositions with $\Delta X > 0.15$ were excluded. Atomic radius and electronegativity values were taken from Miracle et al. [26]. The empirical parameters δ and ΔX were utilized to constrain the search space to compositions with a high probability of forming stable random solid solutions. It should be noted that these criteria are structure-independent; they do not bias the

stability toward FCC, BCC, or HCP. The structural preference is subsequently determined by DFT energy comparisons. Sensitivity checks confirmed that the core findings regarding VEC dependence remain robust regardless of minor variations in these initial screening thresholds.

2.3. Evaluation of mixing enthalpy using Miedema model

To further evaluate thermodynamic stability, we calculated the mixing enthalpy of atomic pairs using Miedema model [27–29], following the methodology of Takeuchi and Inoue [30]. In the present study, calculations based on the Miedema model were carried out using Fortran code that is publicly accessible on the web [28]. The validity of these computations was further corroborated by confirming that the obtained results are in full agreement with those originally produced in ALGOL code, as reported in the publication [29]. Gibbs free energy was then estimated by incorporating configurational entropy at the average melting temperature of the constituent elements.

2.4. Thermodynamic stability screening

According to Yang et al. [31], compositions with the following ratio of the two contributions to the Gibbs free energy exceeding 1.1 are favorable for solid solution formation:

$$\Omega = \frac{T_m \Delta S_{conf}}{|\Delta H|} \quad (4)$$

where T_m is the average melting temperature, ΔS_{conf} the configurational entropy, and ΔH the mixing enthalpy obtained from Miedema model. In this study, compositions with $\Omega > 1.1$ were retained.

2.5. Evaluation of phase separation

Finally, following King et al. [11], we excluded compositions where the Gibbs free energy of the RSS was higher than the sum of the Gibbs free energies of the possible phase-separated alloys.

Among the screening criteria, electronegativity difference proved the most restrictive, reducing candidate compositions to less than 7.9%. The polydispersity parameter and atomic packing parameter reduced candidates to 31.0% and 25.7%, respectively. Tightening the threshold for γ to 1.1 reduced candidates by 65%, while setting $\delta \geq 0.06$ reduced candidates by 6%. Adjusting the ΔX threshold to 0.1176 reduced candidates by 60%. The calculated values of mixing entropy, mixing enthalpy, and average melting point were consistent with those reported for equiatomic HEAs in previous studies [24].

2.6. High-throughput first-principles sampling

We carried out the high-throughput spin-polarized first-principles simulations based on DFT [32] using the Vienna ab initio simulation package (VASP) [33,34] by inputting all screened HEA models. The PBEsol functional [35] was selected for the electronic structure calculations and geometry relaxation, with the lattice shape constrained and only the cell volume allowed to change. Projector-augmented wave (PAW) [36,37] potentials were used to consider the interactions between the ion cores and valence electrons. The Brillouin zone was integrated using the Monkhorst–Pack method [38] with a $1 \times 1 \times 1$ k-point mesh for 64 atoms. For the 64-atom supercells, a $1 \times 1 \times 1$ k-point mesh was primarily used to facilitate high-throughput screening. To validate this approach, we performed convergence checks using a $3 \times 3 \times 3$ mesh for several representative compositions. The results indicated that the energy ordering of the FCC, BCC, and HCP phases remained consistent between the two mesh densities, confirming that the Γ -point-only sampling is sufficient for capturing the broad phase-stability trends identified in this study. In addition, the convergence of relative energies

was confirmed for the cut-off energy, and the default values are large enough to achieve the 0.001 eV/atom accuracy with regard to the formation energy. For structural optimization, the convergence criteria for energy and force were set to be 10^{-4} eV and 10^{-3} eV/Å, respectively. As an initial condition, Fe, Co, and Ni were set as ferromagnetic, Cr and Mn were set as antiferromagnetic, whereas other elements were set as non-magnetic. For atoms of Cr and Mn, initial magnetic moments were set in an anti-parallel configuration to mimic an antiferromagnetic environment within the disordered supercell. The magnetic moments were allowed to relax during the self-consistent electronic iterations. This treatment is consistent with previous computational studies on 3d transition metal HEAs [21,22,39,40], where the local magnetic coupling of Cr and Mn plays a crucial role in structural stability, even in the absence of long-range magnetic order.

2.7. Formation energy and relative stabilities

To discuss crystal structure stability, the formation energy $E_f(\text{HEA})$ is defined as

$$E_f(\text{HEA}) = E(\text{HEA}) - \sum_i x_i E(X_i) \quad (5)$$

Here, $E(\text{HEA})$ denotes the total energy per atom of the HEA; x_i the molar fraction of element i ; and $E(X_i)$ the energy per atom of element i , in its ground state structure. Negative formation energies indicate stability relative to pure elements.

2.8. Average VEC and period

In this study, the VEC is defined as the average number of valence electrons per atom for a given alloy:

$$\text{VEC} = \sum_i x_i v_i \quad (6)$$

where v_i is the number of valence electrons of element i . Conventional valence counts were taken from Miracle et al. [26]. The average period of the constituent elements was defined as:

$$\text{Period} = x_i(\text{Period}_i) \quad (7)$$

where Period_i is the period of element i .

3. Results and discussion

In this study, a screening method based on metallurgical knowledge was applied to identify promising high-entropy alloy (HEA) compositions. Out of 40,920 equimolar quaternary alloys generated by selecting arbitrary combinations of four elements from a pool of 33 candidates, 1005 compositions were extracted as potential solid-solution formers. Performing first-principles calculations on all possible compositions would be computationally impractical and inefficient; therefore, the ability of the present method to efficiently select candidate materials with a high probability of solid-solution formation represents a major achievement of this work.

Fig. 1 illustrates the frequency of elemental occurrence in the screened compositions (middle panel) and in those compositions for which crystal structures (FCC, BCC, HCP) were identified by first-principles calculations (lower panel). The results reveal that elements such as Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Nb, Mo, Ru, Rh, Pd, Ag, Ta, Re, Os, Ir, and Pt appear with high frequency, whereas Mg, P, Sc, Y, Zr, In, Sn, Lu, Hf, and Au occur less frequently. This indicates that certain groups of elements are more likely to contribute to solid-solution formation, suggesting a systematic bias in elemental selection during HEA design. The observed elemental trends are consistent with previous reports highlighting the frequent occurrence of Fe, Ni, Cr, Co, Al, Cu, Ti,

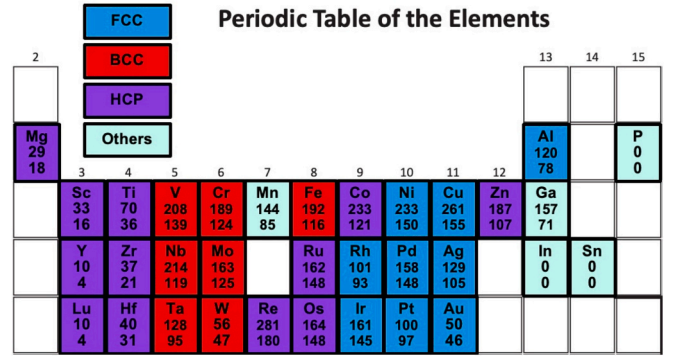


Fig. 1. Frequency of elemental occurrence in the screened HEA compositions (middle panel) and in the compositions for which FCC, BCC, and HCP crystal structures were identified by first-principles calculations (lower panel). The crystal structures of pure elements are classified as FCC, BCC, HCP, or other structures, and are represented in blue, red, purple, and light cyan, respectively. (The periodic table image is provided courtesy of [sciennotes.org](https://sciennotes.org/printable-periodic-table/) at <https://sciennotes.org/printable-periodic-table/>.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and Mn in HEAs [26]. In contrast, examples involving 4d and 5d transition metals remain limited, likely due to the historical focus on mechanical properties and the avoidance of expensive elements in conventional HEA studies.

The screening criteria used in this study are based on widely accepted empirical models for HEA formation. While these thresholds define the boundaries of the analyzed dataset, they do not alter the underlying physical correlation between VEC and phase stability. It should be noted that the screening process leads to a higher frequency of certain elements in the final 1005 compositions. This bias originates from the stringent requirements for solid-solution formation (low δ and $\Delta\chi$), effectively filtering out compositions that are prone to ordering or phase separation. Despite this elemental concentration, the identified correlations between VEC and crystal structure remain valid, as they are rooted in the fundamental electronic contributions of the elements. The consistency of these trends across a wide range of VEC values suggests that the findings are generalizable to other multicomponent systems that satisfy the conditions for RSS formation.

Subsequently, formation energies of FCC, BCC, and HCP structures were evaluated for the 1005 screened compositions using first-principles calculations. After excluding compositions with overlapping standard deviations, the most stable crystal structure for each composition was identified, and the dependence of formation energy on the VEC is presented in Fig. 2. For compositions near the structural crossover regions, we carefully evaluated whether the energy differences between FCC, BCC, and HCP phases exceeded the fluctuations associated with chemical disorder. In Fig. 2, only compositions where the energy separation between phases is larger than the standard deviation of the RSS configurations are presented. This ensures that the identified structural trends are not artifacts of specific atomic arrangements but reflect the true thermodynamic preference of the crystallographic structure. The majority of compositions exhibited negative formation energies, confirming the effectiveness of the screening approach. Moreover, a clear dependence of crystal structure distribution on VEC was observed. Specifically, HCP structures dominate near $\text{VEC} \approx 3$, BCC structures prevail in the range of $\text{VEC} \approx 3.5\text{--}7$, HCP structures reappear near $\text{VEC} \approx 7$, FCC structures become dominant above $\text{VEC} \approx 8.5$, and HCP structures reemerge at $\text{VEC} \geq 10$. These trends are consistent with the crystal structures of pure elements at corresponding VEC values, with the exception of Al ($\text{VEC} = 3$), which exhibits an FCC structure.

As shown in Fig. 2, the VEC regions for FCC, BCC, and HCP phases in quaternary HEAs generally follow the trends of pure 4d and 5d

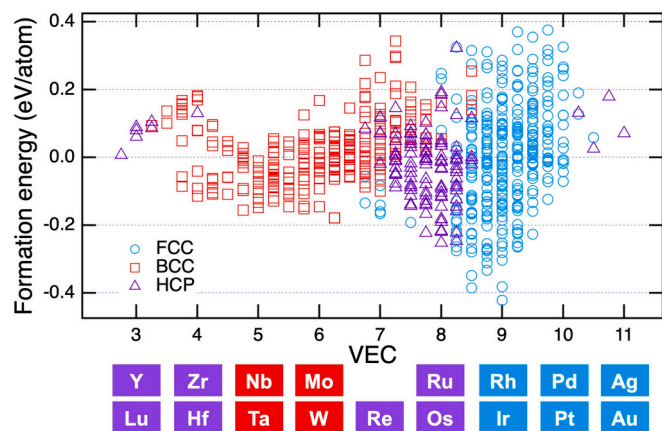


Fig. 2. Formation energies and VEC dependence of the most stable crystal structures obtained by first-principles calculations for the 1005 screened compositions. FCC, BCC, and HCP structures are shown in blue, red, and purple, respectively. At the bottom of this figure, the crystal structures of 4d and 5d transition metal elements are shown at their corresponding VEC positions. A total of 338 FCC, 241 BCC, and 114 HCP alloys were identified. The complete lists of compositions for each crystal structure are presented in the Supplementary Material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

transition metals. However, a noticeable shift in the phase boundaries is observed. These deviations suggest that while the average VEC remains the primary descriptor, multicomponent effects—such as local lattice strain and the chemical environment of the constituent atoms—modulate the relative stability of the crystal structures. It should be noted that the phase stability in this study was evaluated based on the formation energies at 0 K. Due to the high-throughput nature of the screening, vibrational entropy and dynamical stability via phonon calculations were not performed. For some compositions where the energy difference between phases is very small, vibrational entropy could potentially influence the phase boundaries at elevated temperatures. However, for the majority of the screened alloys, the energy separation between the most stable and metastable structures is large enough that the 0 K results provide a reliable baseline for structural trends. Future studies focusing on specific candidate compositions would benefit from incorporating temperature-dependent vibrational effects.

Although several empirical parameters influence the formation of HEAs, the competition between FCC, BCC, and HCP phases is primarily driven by electronic contributions. Our results show that while δ and $\Delta\chi$ ensure the integrity of the random solid solution, the specific structural preference is highly sensitive to the VEC. The high-throughput data reveals that HCP structures are not randomly distributed but are concentrated in specific VEC windows (e.g., $\text{VEC} \approx 3, 7.25\text{--}8.25, >10$), suggesting that VEC is a robust and sufficient descriptor for large-scale structural screening in these systems.

While research on FCC and BCC HEAs has been extensive, studies on HCP-type HEAs remain relatively limited. Early experimental works demonstrated the feasibility of forming stable HCP phases in lanthanide systems [41–49], early transition metal-based system [50–54], and specific transition metal combinations [55–62]. Furthermore, the importance of the HCP phase in enhancing mechanical performance through phase transformation has been highlighted [62]. Despite these individual reports, a comprehensive theoretical framework that predicts HCP stability across a wide compositional space has been missing.

Reports of HCP-type HEAs remain limited [16,41–62]. Despite the restricted scope of lanthanide elements considered in this study (only Lu), the prediction of an HCP structure for FeCoRuRe agrees with experimental observations [55], supporting the validity of the computational results. Similarly, the predicted BCC structure for TiVNbTa, which is expected to exhibit superconductivity [63,64], are consistent

with experimental findings. For CrFeCoNi, where semi-ordered phases have been suggested experimentally [21,22,39], the random solid-solution (RSS) phase was predicted to favor HCP stability. This aligns with previous first-principles results showing lower formation energies for HCP compared to FCC in CrCoNi and CrMnFeCoNi systems when restricted to RSS phases [40,65]. The predictive capability of our model is further validated by its agreement with known experimental cases such as TiZrNbHf [66,67]. Although Ti, Zr, and Hf are HCP in their elemental states, TiZrNbHf is experimentally known to form a BCC structure. Our DFT results consistently show that the BCC phase is energetically more favorable than the HCP phase for this specific combination, even at a low VEC of 4. This stability shift can be attributed to the high-temperature BCC stability of Group 4 elements and the electronic effects of mixing, which are well-captured in our 64-atom supercell simulations.

Fig. 3 shows the occurrence probabilities of FCC, BCC, and HCP structures across different VEC ranges. Although the probabilities do not sum to 100% within each range due to the exclusion of overlapping compositions, the distribution provides quantitative insight into structural tendencies. Of particular interest is the emergence of HCP structures in the $\text{VEC} \approx 7\text{--}8$ region, traditionally considered a transition zone between BCC and FCC structures [15]. This finding suggests that HCP structures may occupy a competitive regime previously overlooked in conventional VEC-based classifications, offering new insights into their stability.

Recent work by Guo et al. reported that CoNiM ($M = \text{Ti, V, Cr, Mn, Fe, Cu}$) alloys exhibit BCC structures below $\text{VEC} = 8.0$ and FCC structures above $\text{VEC} = 8.3$, with HCP structures possible in the intermediate region [68]. This agrees with conventional VEC-dependent trends [15] and aligns well with the present results. Similarly, Takeuchi et al. [16] reported HCP structures in the $\text{VEC} = 3\text{--}4$ and $\text{VEC} = 7\text{--}8$ ranges, and Liang et al. [50] demonstrated that TiZrHf ($\text{VEC} = 3$) exhibits an HCP structure, further corroborating the predictions of this study.

Overall, these results strongly support the validity of VEC-based predictions of HEA crystal structures. In particular, the identification of conditions favoring HCP structures provides important insights into their formation, thereby advancing the understanding of HEA design. VEC-guided structural prediction is expected to serve as a robust design principle for future HEA development, bridging experimental and theoretical approaches.

The findings reveal that the VEC-dependent phase stability in HEAs closely mirrors that of constituent elements. This consistency underscores that the electronic contribution of individual atoms remains a robust descriptor even in complex multicomponent systems. Notably, this correlation becomes clear only by incorporating the HCP phase into the predictive framework, which has been overlooked in many conventional FCC/BCC-centric studies.

In this work, all first-principles calculations were performed

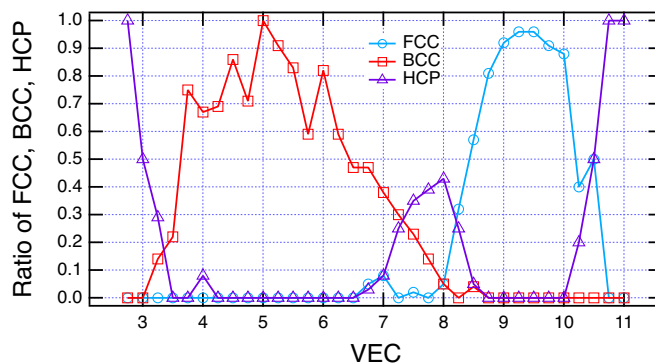


Fig. 3. VEC dependence of the occurrence probabilities of FCC, BCC, and HCP structures, calculated after excluding compositions with overlapping standard deviations.

assuming an RSS. It is important to note that many HEAs can exhibit chemical short-range order (SRO) or partial ordering, which may deviate from the ideal RSS model. For instance, SRO has been reported to influence phase stability and mechanical properties in 3d transition metal HEAs [21,22,39] and other complex concentrated alloys [40]. While SRO effects can further stabilize certain phases, the overall structural competition between FCC, BCC, and HCP as a function of VEC remains a dominant factor. Our RSS-based high-throughput approach provides a foundational stability map, though refined models considering SRO may be necessary for specific, narrowly-defined compositional optimizations.

4. Conclusion

In this study, we performed a systematic computational survey of the formation conditions of equimolar quaternary HEAs, with a particular focus on integrating the rarely reported HCP structure into the existing VEC-based framework. From a pool of 33 metallic elements, 40,920 compositions were screened. By applying metallurgical criteria including atomic radius and electronegativity mismatches, thermodynamic stability, and mixing enthalpy calculated via the Miedema model, we narrowed the candidates down to 1005 compositions. First-principles calculations were then employed to evaluate their structural stability assuming an RSS.

Analysis revealed that HCP stability follows a specific VEC dependence, mirroring the trends observed in elemental metals. These results suggest that even in complex equimolar quaternary systems, the intrinsic electronic characteristics of constituent elements remain a significant factor in phase determination. By focusing on HCP-type HEAs, this work provides a foundational dataset that complements previous studies dominated by FCC and BCC structures.

While this study is limited to equimolar quaternary alloys and based on RSS-level calculations, the findings offer a consistent theoretical map for exploring HCP stability. Rather than a definitive design rule, this work serves as a predictive reference to guide experimentalists toward promising compositional spaces, such as the low-VEC region around 3, the $VEC \approx 7.25$ – 8.25 and $VEC > 10.5$ regions. Future studies extending to non-equimolar compositions and incorporating experimental validation will be essential to further refine these observations and explore the full potential of HCP-containing complex concentrated alloys.

CRedit authorship contribution statement

Hiroshi Mizuseki: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Ryoji Sahara:** Writing – review & editing, Validation, Resources, Methodology, Funding acquisition, Formal analysis. **Kenta Hongo:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this manuscript, the authors used ChatGPT 5 in order to improve its language and readability. After using this tool, all the authors reviewed and edited the content as needed and takes full responsibility for the content of the publication.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.commatsci.2026.114584>.

Data availability

Data will be made available on request.

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