Machine Learning-Based Classification, Interpretation, and Prediction of High-Entropy-Alloy Intermetallic Phases

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Abstract
The design of high-entropy alloys (HEA) with desired properties is challenging due to their large compositional space. While various machine learning (ML) models can predict specific HEA solid-solution phases (SS), predicting high-entropy intermetallic phases (IM) is underdeveloped due to limited datasets and inadequate ML features. This paper introduces feature engineering-assisted ML models that achieve detailed phase classification and high accuracy. By combining phase-diagram-based and physics-based features, it is found that the ML models trained on the Random Forest (RF) and Support Vector Machine (SVM) regressors, are able to classify individual SS and common IM (Sigma, Laves, Heusler, and refractory B2 phases) with accuracies ranging from 80 to 94%. The machine-learned features also enable the interpretation of IM formation. Furthermore, the efficacies of the RF, SVM, and neural network (NN) models are critically evaluated. The phase classification accuracies are found to decrease upon utilizing the NN model to train the datasets. Accuracy of the model prediction is validated by synthesizing 86 new alloys. This approach provides a practical and robust framework for guiding HEA phase design, particularly for technologically significant IM phases.

Keywords High entropy alloy · Phase prediction · Machine learning · Intermetallics · Phase formation controlling factor interpretation · Feature engineering

Introduction

The high-entropy alloy (HEA) design concept founded on the vast chemical degrees of freedom and nearly inexhaustible compositions has brought about a new paradigm in alloy discovery. The design space of HEAs is inevitably enormous. For example, a pool of 30 elements can constitute 142,506 different five-component HEA systems. Further inclusion of atomic percentages can easily lead to millions and even trillions of possible compositions. Thus, the new alloy design paradigm poses the fundamental challenge of selecting alloy phases and compositions endowed with desirable structural and functional properties. Predictions of alloy phases have been actively under development since the birth of HEA, including those involving ab-initio simulation, density functional theory (DFT), Calculation of Phase Diagrams (CALPHAD), empirical parameters, Machine Learning (ML), and artificial intelligence (AI) [1–3]. Compared to first-principles calculations and CALPHAD, ML is computationally much less intensive and yet the method has shown high accuracies, typically 70–90%, in classifying HEA phases [3–23]. Thus, it is not surprising that ML remains a primary method for identifying HEA phases on demand. Beyond phase classification, microstructures and properties are often optimized with the help of CALPHAD and DFT.

Machine learning models normally categorize the phases of HEA as face-centered cubic (FCC), body-centered cubic (BCC), FCC + BCC, hexagonal closed packed structure (HCP), solid solution phases (SS), amorphous phase (AM), non-specific intermetallic phase (IM), and single/multi-phase. However, two issues exist in the current ML phase classification models, namely, a low number of phase categories, and in some cases, a low level of detail within a classified category; that is, the categories are general instead...
of specific. As discussed in more detail below, many models only classify HEA phases into no more than three categories, because as additional categories are included, there is an increase in the complexity, and the challenge of attaining high accuracy increases. Only FCC, BCC, FCC + BCC, and HCP categories in these models represent specific phases. More general categories, such as SS, AM, IM, and single/multi-phase, correspond to unspecified structural phase groups. The low level of categorization detail gives limited guidance for HEA design, i.e., when a HEA is categorized as IM, it can be either B2 (ordered BCC), Laves, Sigma, or Mu phase. This report is dedicated to solving the two challenges mentioned above by addressing the questions: (1) Can we achieve a more specific/detailed IM classification? (2) Can we predict more phase categories simultaneously and accurately to guide HEA design?

Detailed IM classification and prediction are certainly important in advancing the ML design of HEA beyond the common phases. Current knowledge indicates that Laves, Sigma, B2, and Heusler (L21) phases are four of the most common IM in HEA [24]. Heusler [25] and B2 phases can improve the HEA structural and functional properties [26–30]. Heusler phases are known for their wide range of multifunctional properties, including magneto-optical, magnetocaloric, and spintronic properties [25]. In addition, the Heusler phase is reported to have a superior creep resistance [31, 32], and its presence in a HEA SS host can improve the mechanical properties [28, 33, 34]. A B2 phase generally consists of two types in HEAs: AlNi type [29] and Al-X–Y type (X and Y are specific groups of refractory elements) [35]. The AlNi type is widely used as a strengthening precipitate in HEAs [29], while the Al-X–Y type can improve high-temperature mechanical properties, lower physical density and cost, and enhance oxidation-resistance over the traditional disordered BCC refractory HEAs [35]. On the other hand, some IM, such as Sigma and Laves phases, are well-known for their embrittling effects [36, 37]. The need to achieve the predictive formation of beneficial IM while avoiding unfavorable IM has led us to develop a more accurate and interpretable phase prediction method.

Phase predictions can be made efficient using appropriate features in training ML models, especially in the case of a smaller dataset. Previously, we introduced a set of ML features derived from binary phase diagrams, called phenomenological features that were able to classify -850 HEAs into six categories [3, 21]. Recently, feature engineering (FE), which has been underused in data science-driven materials research, has been successfully adapted to formulating superconducting critical temperature equations [38] and designing HEA [7]. Corresponding algorithms such as the Genetic Programming and SISSO [39] can effectively improve the prediction accuracy, especially for the regression ML problems. HEA phase prediction is a complex problem that may not be efficiently executed by using individual features alone. Rather, features should interact with each other to expand the feature pool and transform the feature space through which the classification error is reduced. Apart from FE, certain ML algorithms (such as neural networks) inherently allow interaction among the features. This inherent capability may mitigate the need for employing engineered or transformed features as inputs to the ML model. However, the inherent use of transformed features at the expense of individual features often decreases the accuracy since now the model cannot isolate the dependencies on individual features. Conversely, the FE methodology adopted in the present study engineers the individual features before the application of ML algorithms. This process permits the utilization of both individual and transformed features in ML classification tasks. Furthermore, FE allows more flexible mathematical operations amongst individual features (as detailed in “Method” section), creating a broader set of engineered features. This method thus enables the model to better capture complex patterns and relationships in the data, potentially improving its predictive power and interpretability.

In this article, we will describe a feature engineering strategy that synergistically blends phase diagram-based (PD) features, thermodynamic (Thermo) features, and Hume-Rothery rule (HR) features to interpret and predict the formation of different HEA phases. The unblended features are described in a recent review [3]. The feature engineering-based method enhances the accuracy of the ML models to near 90% for nine HEA phases categories: FCC, BCC, HCP, FCC + BCC, AlNi type B2 + , Sigma + , Laves + , Heusler + , and Al-X–Y type B2 + . The symbol “+” denotes possible coexisting phases. As such, the present method predicts more phase categories with a higher level of specificity and accuracy than other reported methods to date. In addition, we provide a feature importance analysis on the Thermo and HR factors to interpret the driving forces for specific phase formation. The ML-trained features have given deeper insights into the stability of IM in the complex landscape of phase competition. To validate the model’s predictive capability, alloy synthesis and characterization were conducted on 86 new compositions. The accurate and interpretable ML models presented herein can be integrated with other HEA property prediction models, based on which HEA compositions with targeted phases and properties can be designed with high reliability.

**Overview of Methodology and Model Accuracy**

The HEA phase classification methodology utilizes a two-layer method, as illustrated in Fig. 1. The first layer corresponds with the multi-phase prediction model for SS
(FCC, BCC, HCP, FCC + BCC) and common IM (AlNi type B2 +, Laves +, and Sigma +). Categories FCC, BCC, and HCP are indicative of single phase HEAs. FCC + BCC corresponds to coexistence of FCCs, BCCs, or FCCs and BCCs. The category AlNi type B2 + applies to HEAs that exclusively form B2 as the IM phase, potentially alongside other SS phases. Finally, category Laves + or Sigma + represents HEAs that form Laves or Sigma phase in combination with other phases. The model has an overall accuracy of 84% in classifying specific phases in 835 HEAs, a 4% improvement over that reported by the authors earlier [21]. In particular, the accuracy for AlNi type B2 + is high at 90%, while the accuracies for Laves + and Sigma + are lower by ~10%. Accordingly, the second layer consists of four models that are grouped into two pairs for IM prediction. If a HEA is predicted as one of the commonly occurring Laves + or Sigma + in the first layer, then the verification from two models in the second layer, as shown on the left in Fig. 1, will result in accuracies above 90% for both phases. On the other hand, if the multi-phase prediction model predicts no Laves + or Sigma + formation, two other models will evaluate whether the HEA can form IM Heusler or Al-X–Y type B2 phases, with accuracies of 92% and 80%, respectively. In other words, the two-layer method herein can predict single-phase HEAs as well as HEA composites comprising specific phases with high accuracy. Readers should be aware that Fig. 1 is a general alloy design path in our research where we eliminate the formation tendency of the typically undesired Laves and Sigma phases before more computation is conducted to predict the formation of functionally important phases such as Heusler and Al-X–Y type B2 phase. The sub-models in second layer are not mutually exclusive. If a user so chooses, these models can be adjusted to operate concurrently on the same HEAs.

**Method**

**Machine Learning (ML)**

In general, ML models are trained based on training datasets and then give predictions of new data points. ML is normally applied to regression and classification problems. The regression models predict continuous values, such as the hardness of HEAs. HEA phase prediction is a classification problem where HEAs are classified into different phase categories.

In this work, each HEA datum contains the phase category it belongs to and the features, which are the selected physical parameters for classifying and predicting the phase. ML classification algorithms, such as the Random Forest, Support Vector Machine (SVM), and Neural Network, serve to identify the relationship between features and phases in the feature space. Different classification algorithms are tested and compared, and the one with the highest accuracy is picked for each model. All computational processes related to this work, encompassing feature computation and ML, were carried out using the MATLAB programming language. Further specifics about ML training, and the comparison of different algorithms’ performance can be found in “Method” section of the supplementary material. In the ML HEA phase prediction problem, feature construction and selection are the most crucial parts. This process is described below.

**Raw Features**

Prior studies have utilized thermodynamic (Thermo), Hume-Rothery rule (HR), and phase diagram-based (PD) features [21] in HEA phase formation [3]. Thermo features represent the various thermodynamic driving
forces for forming SS and IM. HR features influence phase formation from the atomic size mismatch and electron configuration aspects. In this work, Thermo features $\Delta S_{\text{mix}}$ [40], $\Delta H_{\text{mix}}$ [41], $\Omega$ [42], $\Phi$ [43], $\eta$ [44], and $k_i^{\text{ef}}$ [45], and HR features $\delta$ [41], $E_i^{\text{dis}}$ [46], $\Delta \chi$ [47], and VEC [48–50] are used with their definitions given in Table 1. Following our previous study, alloy melting temperatures $T_m$ involved in the feature calculation are calculated by tracing the liquidus trends in the phase diagrams to capture the effect of alloying [21]. The PD features, introduced in the prior study [21], are extracted from binary phase diagrams. These PD features, PFPA1, PFPA2, PFPA3, PFPA4, PFPA5, PFPA6, PFPLaves, PFPSigma, and PSP, were defined as representing the probability of forming FCC_A1, BCC_A2, HCP_A3, AlNi type B2, Laves, and Sigma phases, as well as the phase separation [21]. In contrast to the Thermo and HR features, which typically overlook alloy preparation methods, PD features inherently incorporate thermal processing associated with alloy preparation. For example, for as-cast HEAs, PD features are computed at a ML optimized phase formation temperature, approximately 0.8 $T_m$; for the as-annealed HEAs, PD features are determined at the respective annealing temperatures [21]. A total of 17 Thermo, HR, and PD features are used as the raw features in this work.

**Feature Engineering and Feature Selection**

Feature engineering is a technique for developing and identifying the best math variations of raw features. The process includes feature construction, transformation, reduction, and selection.

The feature construction process collects the individual raw physical features that may influence phase formation. All relevant raw features are included regardless of the degree of importance they possess in determining the phase. Unimportant features are filtered out in the later steps.

The feature transformation process (Fig. 2A) transforms the raw features by first constructing mathematical variations $x^2, x^{-1}, \sqrt{x}, \ln(x)$, and $e^x$ for each feature $X$. The different expressions can mathematically change how features influence the phase prediction in ML algorithms. For example,

### Table 1 Definition of thermodynamic and Hume-Rothery rule features used in this work

| Formula                                                                 | Comments |
|------------------------------------------------------------------------|----------|
| Mixing entropy: $\Delta S_{\text{mix}} = -R \sum_{i=1}^{N} c_i \ln(c_i)$ | R: The gas constant. $c_i$: The atomic percentage of the $i$th element for a $N$-component system. (Definitions of $N$ and $c_i$ are the same elsewhere.) |
| Mixing enthalpy: $\Delta H_{\text{mix}} = \sum_{i,j}^N 4 \Delta H_{i,j}^{\text{max}} c_i c_j$ | $\Delta H_{i,j}^{\text{max}}$: The binary mixing enthalpy obtained from Miedema’s model of $i$-$j$ element pair |
| $\Omega = \frac{\tau_{i,j} \Delta S_{\text{mix}}}{\Delta H_{i,j}^{\text{max}}}$ | $T_m$: Alloy melting temperature |
| $\Phi = \frac{\Delta G_{\text{SS}}}{\Delta H_{i,j}^{\text{max}}}$ | $\Delta G_{\text{SS}}$: The Gibbs free energy change for forming a fully disordered SS phase |
| $\eta = \frac{\tau_{i,j} \Delta S_{\text{mix}}}{\Delta H_{i,j}^{\text{max}}}$ | $T_{\text{ann}}$: Annealing temperature. If $T_{\text{ann}}$ is not known, use $T_{\text{ann}} = 0.8 T_m$ |
| $k_i^{\text{ef}} = \frac{(1 - \frac{\sum_{i=1}^{N} c_i \Delta H_{i,j}^{\text{max}}}{\sum_{i=1}^{N} c_i \Delta H_{i,j}^{\text{max}}})^{\frac{1}{m}}}{\sum_{i=1}^{N} c_i \Delta H_{i,j}^{\text{max}}}$ | $T_m$: The larger absolute Gibbs free energy change of forming the strongest binary compound, or having phase segregation |
| $\delta = \sqrt{\sum_{i=1}^{N} c_i \left[ 1 + \frac{\sum_{j=1}^{N} c_j}{\sum_{j=1}^{N} c_j} \right]^{-1} - \sum_{i=1}^{N} c_i^2}$ | $T_m = \frac{\sum_{i,j} \tau_{i,j} \Delta S_{\text{mix}}}{\sum_{i,j} \tau_{i,j} \Delta H_{i,j}^{\text{max}}}$, where $\tau_{i,j}$ is the melting temperature of the $i$-$j$ elements for the relative ratio of the two elemental concentrations $c_i$ and $c_j$ of the HEA composition |
| $E_i^{\text{dis}} \propto (\Delta d)^2$ | $\Delta H_{i,j}^{\text{max}}$: The most negative binary mixing enthalpy for forming IM [44] |
| $= \sum_{i=1}^{N} c_i \left( \sum_{j=1}^{N} c_j \right)^{-1}$ | $\Delta H_{\text{IM}}$: Mixing enthalpy of forming IM. When $k_i^{\text{ef}} < 1$, IM tends to form. Otherwise, SS tends to form |
| $\frac{E_i}{E_6} \propto (\Delta d)^2$ | $r_i$: The atomic radius of the $i$th element. This definition is the same throughout the document |
| $= \sum_{i=1}^{N} c_i r_i$ | $\bar{r} = \sum_{i=1}^{N} c_i r_i$: Average atomic radius |
| $\Delta d$: The strain due to atomic radius difference | $\chi$: Electronegativity of $i$th element |
| $\Delta \chi = \sqrt{\sum_{i=1}^{N} c_i \left[ \bar{r} - \sum_{j=1}^{N} c_j \chi_j \right]^2}$ | $\text{VEC}_i$: Valence electrons count of the $i$th element |
| Mean valence electron concentration: $\text{VEC} = \sum_{i=1}^{N} c_i \text{VEC}_i$ | $\text{VEC} = \sum_{i=1}^{N} c_i \text{VEC}_i$: Valence electrons count of the $i$th element |
ln(x) or $e^x$ may reduce or inflate the effect of the outliers compared to using feature X. Then, the feature pool is further expanded by grouping any two math variations, A and B, using operations A + B, A − B, A/B, and AB. This step creates some synergetic effects from multiple features. For example, the comparison effects (A − B, A/B) or joint effects (A + B, AB) may bring new insights into phase prediction. At this point, the feature transformation constructs a huge feature pool, which potentially includes engineered features more qualified for phase prediction than the raw features. The current work expands 17 raw features to ~ 25,000 engineered features. Then to select the best features from the pool, a systematic method including feature reduction and selection is provided below. The feature reduction and selection methods contain filtering, intrinsic, and wrapper methods:

**Filtering Method**

The Pearson Correlation Coefficient (PCC) between two features indicates their linear correlation strength. As shown in Fig. 2B, PCC values approaching +1, −1, or 0 indicates a strong positive, strong negative, or no linear correlation. Strongly correlated features are considered to be inter-substitutable in ML. Therefore, only one feature is kept from any pair with |PCC| > 0.9 in this work.

**Intrinsic Method**

Direct feature selection from the filtered-out features is computationally expensive and unnecessary as many features are irrelevant to phase formation. Therefore, a rapid ML method, logistic regression (LR) with L1 (or Lasso) regularization, is used to remove the irrelevant features (Fig. 2C). This algorithm will minimize the total prediction cost as follows:

$$J(\mathbf{W}) = \frac{1}{m} \sum_{j=1}^{m} \text{Cost}[h_{\mathbf{W}}(\vec{F}^{(j)}), y^{(j)}] + \gamma \sum_{i=1}^{n} |w_i|$$

Herein, $J(\mathbf{W})$ is the prediction cost with feature weight vector $\mathbf{W} = [w_1, w_2, \ldots, w_n]$. The first term is LR prediction cost $\text{Cost}[h_{\mathbf{W}}(\vec{F}^{(j)}), y^{(j)}]$ calculated by the log-loss function [51], which is directly related to the classification error, wherein the cost function of predicting the $j$th sample as $h_{\mathbf{W}}(\vec{F}^{(j)})$ while the correct category is $y^{(j)}$. $h_{\mathbf{W}}(\vec{F}^{(j)})$ is obtained based on feature weights $\mathbf{W}$ and feature values $\vec{F}^{(j)}$. $m$ is the total sample count in the dataset. The second term is the regularization cost. $n$ is the number of features. $\gamma$ is the regularization strength. $w_i$ is the $i$th feature’s weight in $\mathbf{W}$.

To reduce $J(\mathbf{W})$, the first term tends to use more features to reduce the prediction error, while the second term tends to invalidate more features by zeroing their weight $w_i$. The
trade-off between the two terms will activate the minimum number of essential features in ML. Tuning $\gamma$ changes the regularization strength and regulates the number of selected/activated features. After this step, about 100 features are retained.

**Wrapper Method**

Sequential learning (SL), shown in Fig. 2D, selects the best features iteratively from ~100 features. ML models built with different combinations of features are evaluated by the average error from thirty rounds of fivefold cross-validations with different random seeds. The error is calculated by $1 - f_1$ score (The same definition on error is used throughout this article). SL starts with an empty feature set in the first round, tests each feature in ML algorithm independently, and picks the feature producing the lowest error. In the subsequent rounds, each unselected feature is tested combinatorially with the previously picked ones. Finally, the best feature combination to minimize the classification error is constructed.

It is worth noting that all ML processes, including the LR algorithm in the intrinsic method section and the ML algorithms in the wrapper method, have been subjected to feature value normalization.

**Experimental Method**

Alloys for validation were synthesized using arc melting. Raw materials with a minimum purity of 99.97 wt.% were placed into a water-cooled copper crucible. Raw materials were melted five times under a high-purity argon atmosphere. Each melt was conducted for a minimum of a minute. The sample was flipped over between melts to ensure homogeneity. All HEAs were characterized in the as-cast state, consistent with most data used in training the presented ML models. The ML models are set in the high-temperature ranges most suitable for as-cast alloys or alloys annealed at high temperatures, e.g., ~0.8 of the melting temperatures [21]. Finally, alloys were polished using grinding papers with grit sizes 180, 320, 600, and 1200. X-Ray Diffraction (XRD) measurements were conducted on a PANalytical Empyrean diffractometer with Cu Kα radiation and a scanning rate of ~0.15 degree/s.

**Results and Discussion**

**Part 1: Multi-phase Prediction Model**

As described in the methodology section, the multi-phase prediction model in the first layer (Fig. 1) has seven categories: FCC, BCC, HCP, FCC + BCC, AlNi type B2+, Laves+, and Sigma+. Different classification algorithms are tested, and the Random Forest (RF) classification algorithm is used to perform sequential learning (SL). In comparison, the Neural Network (NN) has relatively low accuracy, likely as a result of the large amount of training data required. The performance comparison across different ML algorithms can be found in Fig. S1 of the supplementary material. Thirty rounds of SL were conducted. Figure 3A shows the overall classification errors and the error bars (standard deviation) plotted against the number of top-ranked raw features (labeled as “No FE”) and engineered features (labeled as “FE”), respectively. We only keep the first six engineered features to train the ML prediction model because adding more features only increases the risk of overfitting disproportionately to the diminishing gains in accuracy. A list of these features is presented in Table 2. The FE classification error with six features is 0.161, 10% smaller than the error without FE. Figure 3B shows the classification errors of the individual phase category plotted against the number of top-ranked engineered features. HCP, AlNi type B2+, FCC, and BCC predictions have lower errors, while FCC + BCC, Sigma+, and Laves+ predictions are relatively less accurate. Therefore, the IM formation needs to be verified by the models discussed in the next section. Figure 3C gives the database category size. The available HEA experimental data is continuously expanding. As shown in previous work [21], expanding the database may only improve marginally a well-trained model’s accuracy. Thus, we consider the up-to-date 835 data collected from literature are sufficient in training the ML.

We comprehensively evaluate the model performance based on the following criteria: ML accuracy, the level of detail on phase categories, the number of phase categories,
and the number of features. This model’s prediction error is among the lowest compared to other similar models [6–12, 17, 20, 22, 23, 52]. With the use of only six features, this model is able to classify up to seven phase categories with a high level of category detail, i.e., detailed phase content such as Heusler and Sigma can be identified instead of classifying them into a general category labeled as “IM”. In addition, we address the functionally important IM phase AlNi type B2 + , Laves + , and Sigma + , which have rarely been explored by ML methods. Overall, our FE-assisted ML model shows high capability in classifying HEA phases.

Part 2: Laves + , Sigma + , Heusler + , and Al-X–Y Type B2 + Prediction Models

The four models in the second layer (Fig. 1) use Support Vector Machine as the classification algorithm, given its reduced prediction error compared to other algorithms, as demonstrated in Fig. S1 of the supplementary material. For the Sigma + and Laves + prediction models, the appreciable imbalanced data distributions require special handling. For example, the Sigma + prediction model database consists of 52 Sigma-containing HEAs (HEASigma) and 783 HEAs without the Sigma phase (HEANo-Sigma). The imbalance makes the ML model biased to the dominant category HEANo-Sigma and adversely affects the predictions for HEASigma. Conventional methods of handling imbalanced databases include under-sampling and over-sampling methods such as the Random Over-sampling, Adaptive Synthetic Sampling Approach for Imbalanced Learning (ADASYN) [53] and Synthetic Minority Over-sampling Technique (SMOTE) [54]. The under-sampling method is used here since it is more accurate and does not artificially generate virtual data to balance the two categories as some over-sampling methods do. More comparisons and technical details about the under/over-sampling methods can be found in Section 4 of Supplementary Materials. The under-sampling method will randomly pick 52 samples from the HEANo-Sigma to constitute a ML database with the 52 HEASigma. Thirty rounds of random samplings followed by sequential learning (SL) are conducted, and the average performance is presented.

Similarly, the Laves + prediction model database consists of 96 Laves-containing HEAs (HEALaves) and 739 HEAs without the Laves phase (HEANo-Laves). HEANo-Laves are under-sampled to 96 to constitute a ML database with the 96 HEALaves in each of the thirty random sampling rounds.

Figure 4A and B show how errors decrease with more features and compare the results with and without FE for Sigma + and Laves + predictions. In both models, only the first four engineered features will be kept for ML prediction, and we obtain low errors of 0.06 and 0.08 for Sigma + and Laves + predictions, respectively. FE suppresses the error by around 0.05 from No-FE results. The four features giving the lowest error among the thirty rounds are presented in Table 2.

Fig. 4 ML classification error decreases as the number of engineered features increases. The comparisons of the results between using and not using FE are presented for: A Sigma + ; B Laves + ; C Heusler + ; and D Al-X–Y B2 + prediction models. Error bars (standard deviation) are presented in all plots. Small error bars may be invisible in figure (D)
A Heusler phase has a general composition \(X_2YZ\), where \(X\), \(Y\), and \(Z\) symbolize specific groups of elements in the periodic table [55]. The database constitutes 77 HEAs containing the Heusler phase (HEA\(_{L21}\)), and 109 HEAs without the Heusler phase (HEA\(_{Non-L21}\)). HEA\(_{Non-L21}\) are selected based on the criteria: (1) they include appropriate \(X\), \(Y\), and \(Z\) elements for forming the Heusler phase; and (2) they are annealed to ascertain the non-emergence of the Heusler phase. Thirty rounds of SL are conducted. The average classification errors for using FE and not using FE are presented in Fig. 4C. As more features are included, FE error becomes saturated, and No-FE error increases due to over-fitting. The top-ranked four engineered features (listed in Table 2) are kept for ML prediction with a classification error of 0.08. FE suppresses the error by 0.05 over No FE. The HEAL21 database is included in the Section 1 of the Supplementary Materials.

The refractory Al-X–Y type B2 phase comprises at least three components: \(X\) is Ti, Zr, or Hf; and \(Y\) is Cr, Mo, Nb, or V [35]. The database consists of 52 HEAs with Al-X–Y type B2 phase (HEA\(_{AlXY-B2}\)) and 35 without Al-X–Y type B2 phase (HEA\(_{Non-AlXY-B2}\)) but having Al, X, and Y elements. From thirty rounds of SL, the average classification errors for using FE and not using FE are presented in Fig. 4D. As more features are included, the FE error continuously drops while the No-FE error increases rapidly due to over-fitting. The best three engineered features (listed in Table 2) are kept with a classification error of 0.2. The HEA\(_{AlXY-B2}\) database can be found in the Section 2 of the Supplementary Materials.

### Part 3: Interpreting the Important Phase Determination Features

Although ML is a powerful classification tool, it is a black box and does not show the input and output relationships. Therefore, appropriate techniques are needed to evaluate the features’ importance in determining phase formation [56]. The single accuracy method, which uses only one feature for ML at a time and takes the classification accuracy as individual features.

From Fig. 5A, the Heusler phase formation is mainly controlled by VEC, \(\Phi\), and \(E_0\). HEA\(_{L21}\) generally have lower VEC values than HEA\(_{Non-L21}\) (Fig. 6H1). The low VEC implies that a BCC-prone environment [48–50] is favored for the Heusler phase formation, potentially due to the structural similarity between the Heusler and BCC lattices. \(\Phi\) is a Thermo feature controlling IM/SS formation tendency. IM formation is favored when \(\Phi\) is small [43]. Figure 6H2 shows that HEA\(_{L21}\) are generally low in \(\Phi\) and energetically favored to form IM. Finally, HEA\(_{L21}\) have higher \(E_0\) values (Fig. 6H3), which represent larger atomic size difference [46]. This makes specific elements, such as Al, whose atomic size is different from the transition-metal elements, confined to certain sites on a crystal lattice, forming the ordered Heusler phase.

Al-X–Y type B2 formation is predominantly controlled by \(\eta\), \(\Delta S_{mix}\), and \(\Omega\) (Fig. 5B). HEA\(_{AlXY-B2}\) generally have more negative \(\eta\) values (Fig. 6B1), which indicates the IM formation tendency, consistent with DFT results [44]. HEA\(_{AlXY-B2}\) also have a wide \(\Delta S_{mix}\) distribution spectrum (Fig. 6B2) while HEA\(_{Non-AlXY-B2}\) are clustered at the high \(\Delta S_{mix}\) value region. Higher \(\Delta S_{mix}\) prompts the disordering and suppresses the ordered HEA\(_{AlXY-B2}\) formation. \(\Omega\) is another Thermo feature showing the SS and IM formation tendencies [42]. HEA\(_{AlXY-B2}\) generally have low \(\Omega\) values (Fig. 6B3), which favors the ordered IM phase such as the B2 formation. More importantly, all three dominant features are thermodynamic, and HR features show limited influence.
Electron environment-related HR features, VEC and $\Delta \chi$, are found to be correlated to FCC, BCC [57], and topological close-packed Sigma and Laves [50, 58] but not B2 formation. Lattice distortion-related HR features, $E_2/E_0$ and $\delta$, are relatively more important for predicting the IM with non-cubic structures (e.g., Laves) which can accommodate the severe atomic size mismatch. The B2 phase retains the BCC structure, where small lattice distortion should be expected for both disordered BCC and B2 phases. Despite the low effectiveness of the HR features, the key to ML predicting Al-X–Y type B2 is to distinguish it from the disordered BCC, where enthalpy and thermodynamic consideration are proven to be crucial in determining BCC/B2 ordering by a Monte Carlo and DFT combined study [59]. Our ML model draws a similar conclusion. In future, first-principles methods such as ab-initio simulations and DFT are promising to give an accurate, in-depth analysis of the order–disorder transition of such alloy systems.

For the Laves phase formation, $E_2/E_0$, $\eta$, $\delta$, and $\Delta H_{\text{mix}}$ are the four most important features (Fig. 5C). $E_2/E_0$ and $\delta$ both indicate the atomic size difference and the internal strain. As shown in Fig. 6L1 and L3, HEA$_{\text{Laves}}$ have higher atomic size mismatches than the HEA$_{\text{Non-Laves}}$. The severe lattice distortion favors the ordered IM formation. From the thermodynamic aspect, the inset box plot in Fig. 6L2 shows that HEA$_{\text{Laves}}$ all cluster at a region with low $\eta$ absolute values while HEA$_{\text{Non-Laves}}$ has wide $\eta$ distribution. Besides, HEA$_{\text{Laves}}$ also show more negative $\Delta H_{\text{mix}}$ values than HEA$_{\text{Non-Laves}}$. The $\eta$ and $\Delta H_{\text{mix}}$ distribution trends of HEA$_{\text{Laves}}$ favors the IM formation.

Figure 5D shows that multiple features have weak impacts on Sigma formation. However, when these features are combined using FE, a low classification error of 0.05 is attained, illustrating the efficacy of the FE methodology used herein. The important roles of these features can be seen primarily in $\eta$, VEC, $\Delta \chi$, and $\Delta H_{\text{mix}}$ as examples. The inset of Fig. 6S1 shows that HEA$_{\text{Sigma}}$ cluster at a region with low $\eta$ absolute values, indicating a higher IM formation tendency. Similarly, HEA$_{\text{Sigma}}$ shows more negative $\Delta H_{\text{mix}}$ values that favors IM formation. The influence of VEC, and $\Delta \chi$, both electron-related features, is shown in Fig. 6S2 and S3. It is previously reported that the formation of the topological close-packed Sigma phase formation is favored when $\Delta \chi > 0.133$ [58] and $6.88 < \text{VEC} < 7.84$ [50]. The current work obtains similar results based on a larger database. The first, second (i.e., median), and third quartiles of VEC
distribution are 7.36, 7.61, and 7.86 (7.36 < VEC < 7.86 is the region for the middle 50% of the distribution). This new Sigma-prone VEC region overlaps the FCC-prone VEC region [57]. A further review of the database also shows that ~80% of HEA\textsubscript{Sigma} contain FCC phase. Finally, the larger $\Delta \chi$ values of HEA\textsubscript{Sigma} provide clear separation from the HEA\textsubscript{Non-Sigma}. Therefore, one should consider decreasing the electronegativity discrepancy of the constituent elements to avoid Sigma formation during HEA design. The current work identifies the electron configuration as the most important HR factor in controlling Sigma formation.

Part 4: Experimental Validation

Experimental validation is important to provide an unbiased evaluation of a ML model trained on available databases. As such, the palette of elements for the validation alloys should be an unbiased representation of the compositional space where the model is trained. Accordingly, of the 86 validation alloys, the multi-phase prediction model will have 60 alloys (Table 3A) with randomly chosen compositions based on the common element in the training database, located both inside and outside the feature space covered by the current database. The distributions of validation HEAs in each predicted phase category are proportional to the database phase distribution. 50 alloys are predicted correctly, giving a validation accuracy of 83%. Since the Laves +, Sigma +, and multi-phase prediction models are trained on the same database, the same 60 HEAs also validate the Laves + and Sigma + models, with validation accuracies of 92% and 95%, respectively (Table 3A). To validate the Al-X–Y B2 + prediction model, another 14 new HEAs containing the Al-X–Y type B2 phase essential elements are randomly chosen that involves two or more refractory elements (Table 3B). For Al-X–Y type B2 formation, 12 out of the 14 HEAs are predicted correctly with an accuracy of 86%. For a similar consideration, another 12 HEAs (Table 3C) containing the Heusler phase essential elements were synthesized to
### Table 3: Validation HEAs compositions, phase prediction results, and experimental phase characterization results obtained from XRD are listed

#### A. Multi-phase, Laves+, and Sigma+ prediction models validation HEAs

| Composition | Multi-phase prediction | Laves + prediction | Sigma + prediction | Experimental results |
|-------------|------------------------|--------------------|--------------------|----------------------|
| Ag_{20}Al_{20}Cr_{20}Mn_{20}Ni_{20} | AlNi B2+ | False | False | B2 + A1 |
| Ag_{20}Al_{20}Cr_{20}Mn_{20}Ni_{20} | AlNi B2+ | False | False | B2 + A1 |
| Al_{10}Co_{10}Cr_{10}Fe_{40}Ni_{10}Ti_{10} | **AlNi B2+** | **True** | False | A1 |
| Al_{10}Co_{20}Cu_{20}Fe_{20}Ni_{20}V_{10} | AlNi B2+ | False | False | B2 + A1 |
| Al_{10}Co_{22}Cr_{11}Cu_{11}Ni_{33}V_{12} | AlNi B2+ | True | False | B2 + A1 + A2 |
| Al_{13}Cr_{18}Mn_{10}Ni_{6} | AlNi B2+ | False | False | B2 + A1 + A2 |
| Al_{14}Cr_{18}Fe_{11}Mn_{11}Ni_{8} | AlNi B2+ | False | False | B2 |
| Al_{16}Co_{20}Fe_{20}Mn_{18}Ni_{20}V_{6} | AlNi B2+ | False | False | B2 |
| Al_{16}Co_{21}Cr_{21}Fe_{21}Ni_{21} | AlNi B2+ | False | False | B2 + A1 |
| Al_{16}Cr_{10}Fe_{10}Mn_{10}Ni_{10}V_{5} | AlNi B2+ | False | False | B2 |
| Al_{16}Cr_{19}Cu_{19}Fe_{19}Ni_{19}Si_{3} | AlNi B2+ | False | False | B2 + A1 + A2 |
| Al_{18}Co_{20}Cr_{20}Fe_{20}Mn_{20} | AlNi B2+ | False | False | B2 |
| Al_{18}Co_{21}Cr_{21}Cu_{21}Fe_{21}Mn_{21} | AlNi B2+ | False | False | B2 |
| Al_{18}Co_{25}Cr_{25}Fe_{25}Ni_{25} | AlNi B2+ | False | False | B2 |
| Al_{19}Co_{20}Fe_{20}Mn_{18}Ni_{20}V_{6} | AlNi B2+ | False | False | B2 |
| Co_{25}Ta_{15}Ti_{33}V_{3} | BCC | False | False | A1 |
| Cr_{8}Ti_{8}V_{12}Zr_{9} | BCC | False | False | A2 |
| Cr_{2}Mo_{2}Ta_{2}V_{23} | BCC | False | False | A2 |
| Cr_{13}Mo_{2}Nb_{2}V_{33} | BCC | False | False | A2 |
| Hf_{2}Nb_{2}Ta_{3}Zr_{25} | BCC | False | False | A2 |
| Hf_{3}Ni_{3}Ti_{3}V_{10} | BCC | False | False | A2 |
| Hf_{3}Ta_{3}O_{2}V_{10} | BCC | False | False | A2 |
| Mo_{2}Nb_{2}Ta_{2}O_{2}V_{29} | BCC | False | False | A2 |
| Nb_{2}Ta_{3}Ta_{2}V_{12}Zr_{12} | BCC | False | False | A2 |
| Nb_{2}Ta_{2}V_{2}V_{12}Zr_{12} | BCC | False | False | A2 |
| Co_{15}Cr_{15}Fe_{15}Mn_{15}Ni_{15}V_{8} | FCC | False | **True** | A1 |
| Co_{16}Cu_{16}Fe_{16}Mn_{16}Ni_{16}V_{10} | FCC | False | False | A1 + A1 |
| Co_{16}Cr_{20}Fe_{20}Ni_{16}Si_{4} | FCC | False | False | A1 |
| Co_{2}Cr_{1}Fe_{2}Ti_{15} | FCC | False | False | A1 |
| Co_{2}Cr_{2}Mn_{14}Ni_{44} | FCC | False | False | A1 |
| Co_{3}Cr_{3}Fe_{3}Ni_{45}Si_{4} | FCC | False | False | A1 |
| Co_{2}Fe_{2}Ni_{14}V_{5} | FCC | False | False | A1 |
| Co_{2}Cr_{1}Cu_{1}Fe_{2}Ni_{23}V_{12} | FCC | False | False | A1 |
| Cr_{10}Cu_{10}Fe_{2}Mn_{18}Ni_{18}Ti_{4} | FCC | False | **True** | A1 + A2 |
| Al_{10}Cr_{10}Cu_{10}Fe_{11}Mn_{21} | MIX A1-A2 | False | False | A1 + A2 |
| Al_{10}Cr_{10}Fe_{10}Mn_{22} | MIX A1-A2 | False | False | A2 |
| Al_{10}Co_{20}Cr_{10}Cu_{10}Mn_{20}Ni_{20} | MIX A1-A2 | False | False | A1 + A2 |
| Al_{10}Co_{20}Cr_{10}Fe_{2}Ti_{6} | MIX A1-A2 | False | False | B2 |
| Al_{10}Cr_{10}Cu_{10}Fe_{10}Mn_{16}Ni_{16}Ti_{6} | MIX A1-A2 | False | False | A1 + A1 |
| Co_{2}Cr_{2}Cu_{2}Fe_{2}Mn_{25} | MIX A1-A2 | False | False | A1 + A2 |
| Cr_{2}Cu_{2}Fe_{2}Mn_{25} | MIX A1-A2 | False | False | A1 + A2 |
| Cr_{10}Fe_{8}Mn_{10}Ni_{10} | MIX A1-A2 | False | False | A2 |
validate the Heusler + prediction model. For the Heusler phase formation, 11 out of the 12 HEAs are predicted correctly, with an accuracy of 92%. Overall, the validation accuracies essentially match the classification accuracies. All the XRD patterns can be found in the Section 5 of Supplementary Materials.

| Composition | Multi-phase prediction | Laves + prediction | Sigma + prediction | Experimental results |
|-------------|------------------------|--------------------|-------------------|---------------------|
| Co23Fe20Mn20Ni20Ti10V10 | Laves + | True | False | Laves + A2 |
| Co23Fe20Mo20Ni20Ti20 | Laves + | True | False | Laves + A1 + A2 |
| Co23Cr21Cu21Mn16Ti21 | Laves + | True | False | Laves + A1 |
| Co23Cr23Fe23Nb13Ti12 | Laves + | True | False | Laves + A1 + A2 |
| Cr23Ni20Ni20Ti20Zr20 | Laves + | True | False | Laves + A2 |
| Cu16Fe17Mn17Ni17Ti12 | Laves + | True | False | Laves + A1 + A2 |
| Co13Cr13Cu13Fe13Ni5Ni38Ti8V8 | Sigma + | True | True | A1 |
| Co13Cr13Fe18Mo18Ni18V10 | Sigma + | False | True | Sigma + A1 |
| Co23Cr20Fe20Mo20V20 | Sigma + | False | True | Sigma + A2 |
| Co23Cr26Fe26Mo22 | Sigma + | False | True | Sigma + A2 |
| Cu20Fe20Mn20Ni20V20 | Sigma + | False | True | Sigma + A1 |

B. Al-X–Y type B2 + prediction model validation HEAs

| Composition | Al-X–Y B2 + prediction | Experimental results | Composition | Al-X–Y B2 + prediction | Experimental results |
|-------------|-------------------------|----------------------|-------------|-------------------------|----------------------|
| Al10Hf20Nb22Ti33V15 | True | B2 | Al20Nb20Ta15Ti20V10Zr5 | True | B2 |
| Al12Hf23Ti28 | True | B2 | Al20Nb20Ta15Ti20Zr5 | True | B2 + unknown |
| Al12Hf23Nb20Ti27 | True | B2 | Al20Nb20Ta15Ti20Zr5 | False | A2 |
| Al12Hf23Nb20Ti27 | True | B2 | Al20Nb20Ta15Ti20Zr5 | False | A2 |
| Al12Mo21Nb13Ti21V21 | True | A2 | Al20Nb20Ta15Ti20Zr5 | False | A2 |
| Al10Mo20Nb20Ti30 | True | B2 | Al20Nb20Ta15Ti20Zr5 | False | A2 |

C. Heusler + prediction model validation HEAs

| Composition | Heusler + prediction | Experimental results | Composition | Heusler + prediction | Experimental results |
|-------------|----------------------|----------------------|-------------|----------------------|----------------------|
| Al10Co25Fe25Mn25Ti15 | True | A2 + Unknown | Al10Co25Fe25Mn25Ti15 | True | L21 |
| Al10Cr5Fe45Mn12Ni20Ti8 | True | L21 + A1 | Al10Co25Fe25Mn25Ti15 | False | A1 + A2 |
| Al12Co23Fe9Ni5Ti12 | True | L21 + A1 | Al10Co25Fe25Mn25Ti15 | False | A1 |
| Al12Cr16Fe9Ni5Ti12 | True | L21 + A1 | Al10Co25Fe25Mn25Ti15 | False | A2 |
| Al12Cr16Fe9Ni5Ti12 | True | L21 + A1 | Al10Co25Fe25Mn25Ti15 | False | A2 |
| Al12Fe20Mo20Ni5Ni38Ti10 | True | L21 + A1 | Al10Co25Fe25Mn25Ti15 | False | A2 |

The number subscripts in compositions are elemental atomic percentages. Detailed phase contents are listed in the experimental results column. True or False in Laves +, Sigma +, Al-X–Y B2 +, and Heusler + prediction columns represent forming or not forming the corresponding IM phases, respectively. Abbreviations AlNi B2 +, A1, A2, Mix A1-A2, Al-X–Y B2 +, and L21 represent the AlNi type B2 forming with other solid solution phases, disordered FCC_A1 phase, BCC_A2 phase, mixed A1-A2 phase (coexistence of multiple A1 or A2, or mixture of A1 and A2), Al-X–Y type B2 + forming with other phases, and Heusler phase. The incorrect predictions are underlined and bolded.

### Summary

This work demonstrates a machine learning methodology assisted by feature engineering (FE) in predicting the common high entropy alloy (HEA) phases.

1. The multiphase prediction model, utilizing six engineered features in conjunction with the Random Forest algorithm, which is determined to exhibit the lowest prediction error amongst various algorithms, currently...
stands out as one of the top-performing methods and precisely predicts seven distinct phase categories.

(2) Mixed-phase compositions are further evaluated by four other models trained to predict the formation of four commonly occurring intermetallic phases that include Sigma, Laves, Heusler, and Al-X–Y type B2 phases with high accuracies. These models, with high degree of accuracies, incorporate the use of four engineered features and the Support Vector Machine algorithm which is the optimal performing algorithm for these scenarios.

(3) The models are experimentally validated with 86 new compositions. The experimental accuracy aligns with the model accuracy, further attesting to their reliability.

(4) We identify the most relevant thermodynamic (Thermo) and Hume-Rothery rule (HR) features that control the formation of the four intermetallic phases. Thermo feature $\Phi$, and the valence electron and atomic size discrepancies in HR features have an impact on the Heusler phase formation. Al-X–Y type B2 phase formation is mainly determined by the Thermo features, implying that the ordering transformation from BCC to B2 is a thermodynamic process with limited influence from HR features. Laves phase is determined by the Thermo feature $\eta$ and the atomic size discrepancy in HR features, while the Sigma phase is mainly influenced by Thermo feature $\eta$ and the electronic effect encoded in the HR features.

We have developed feature variants-based models that can enhance the phase classification and prediction accuracies while also providing insight into the physics behind these predictions. The creation of the machine learning toolset is the practical value of the present study. The scientific significance is the discovery of links between scientific parameters and phase formation inside the ML black box. Thus, the machine learning method in this work can be further developed to explore other material phases. Currently, the ML Heusler and Al-X–Y type B2 phase prediction models are trained to predict the HEAs with corresponding IM formation elements. Active learning can be employed to explore novel elemental combinations. Additionally, a comprehensive HEA design model can be constructed with the help of the properties prediction models to automatically search for compositions that fulfill specific phase and property requirements.

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**Declarations**

**Conflict of interest** The authors declare no competing interests.

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