Properties of High Entropy Alloy

MT291: Exploratory Project

Group 11

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Contents

1 | Introduction

High-entropy alloys (HEAs) are formed by mixing equal or relatively large proportions of (usually) five or more elements; unlike traditional alloys, which typically consist of one or two more primary elements, HEAs are designed to have a high degree of composition complexity, which results in unique physical and mechanical properties. These are named HEA because the entropy increase of mixing is substantially higher when there is a larger number of elements in the mix, and their proportions are nearly equal. The high entropy of HEAs means that they have a large number of possible combinations of elements, which can result in a range of different properties such as high strength, good corrosion resistance, high-temperature stability, and excellent wear resistance. The unique properties of HEAs make them attractive for use in a range of industrial applications where high-performance materials are needed.

2 | Properties of HEA

- **High Strength**: HEAs can exhibit high strength due to their unique crystal structure, which helps to prevent dislocation movement and increase strength.
- **Good Ductility**: Despite their high strength, HEAs exhibit good ductility, allowing them to deform without fracturing under stress.
- **High Hardness**: HEAs can also exhibit high hardness, making them suitable for cutting tools and wear-resistant coatings.
- **Excellent Corrosion Resistance**: Some HEAs have excellent corrosion resistance due to the formation of passive surface layers that protect against corrosion.
- **High-Temperature Stability**: HEAs can maintain their mechanical properties at high temperatures, making them suitable for use in high-temperature applications.
- **Low Density**: Some HEAs have a low density, making them attractive for lightweight structural materials.
- **Good Thermal Stability**: HEAs can maintain their mechanical properties at high temperatures for prolonged periods, making them suitable for use in high-temperature applications.

3 | Phase Rule

The phase rule is a fundamental principle in thermodynamics that relates the number of phases, components, and degrees of freedom in a system at equilibrium. For a high entropy alloy (HEA), the phase rule can be applied to predict the possible number of coexisting phases in the alloy.

The phase rule states that for a system in equilibrium, the number of degrees of freedom (F) is given by:

$$F = C - P + 2$$

where C is the number of components and P is the number of phases.

In a HEA, the number of components is usually five or more, and the number of phases can vary depending on the composition and processing conditions. In practice, HEAs are often designed to have a single-phase structure, such as a face-centered cubic (FCC) or body-centered cubic (BCC) structure, which simplifies processing and improves mechanical properties.

The phase rule can be used to predict the possible number of phases in a HEA and to design processing conditions that ensure a single-phase structure, which can improve the alloy's mechanical properties and overall performance.

4 | Thermodynamics

For multi-principal elements, the stability of the system is governed by the configurational entropy given by the equation $\Delta G = \Delta H - T\Delta S$. Since HEA has high enthalpy, ΔG becomes highly negative.

5 | Basic Definitions

- **Alloy**: An alloy is a homogeneous mixture of two or more metals or a metal and nonmetal in definite proportion. Example: Brass is an alloy of Copper and Zinc.
- **Composites**: It is formed by combining two or more materials that have different properties. There are two parts to it, i.e., matrix and reinforcement. The reinforcement is dispersed in the matrix to give unique properties. Examples: Reinforced Plastics, Concrete.
- **Intermetallic Compounds**: Class of substances composed of definite proportions of two or more elemental metals rather than continuous variable proportions.Example: Roman Yellow Brass.
- **Solid Solution**: Homogenous mixture of two or more elements or compounds in a solid state. Solid solutions can be formed when the atoms or ions of the components are of similar size and have similar chemical properties, allowing them to substitute for each other within the crystal lattice.
- **Substitutional Solid Solutions**: In a substitutional solid solution, one element's atoms substitute for another element's atoms in the crystal lattice. This type of solid solution is common in alloys, where different metals are mixed to improve their properties.
- **Interstitial Solid Solutions**: In an interstitial solid solution, small atoms or molecules occupy interstitial sites within the crystal lattice of a host material. This type of solid solution is common in ceramics and metal hydrides. Example: Titanium nitride is an interstitial solid solution of titanium and nitrogen, where the nitrogen atoms occupy interstitial sites within the crystal lattice of titanium.

6 | Phase Diagram

The phase diagram provides us with a brief overview via which we can determine the phases of different compositions. In our case, since we are dealing with High entropy alloys, the compositions in it can also be determined using this phase diagram.

The iron-carbon phase diagram is a graphical representation of the phases and phase transformations that occur in the iron-carbon alloy system as a function of temperature and percentage of carbon. The iron-carbon phase diagram is important as it provides information of the composition and processing conditions of an iron-carbon alloy.

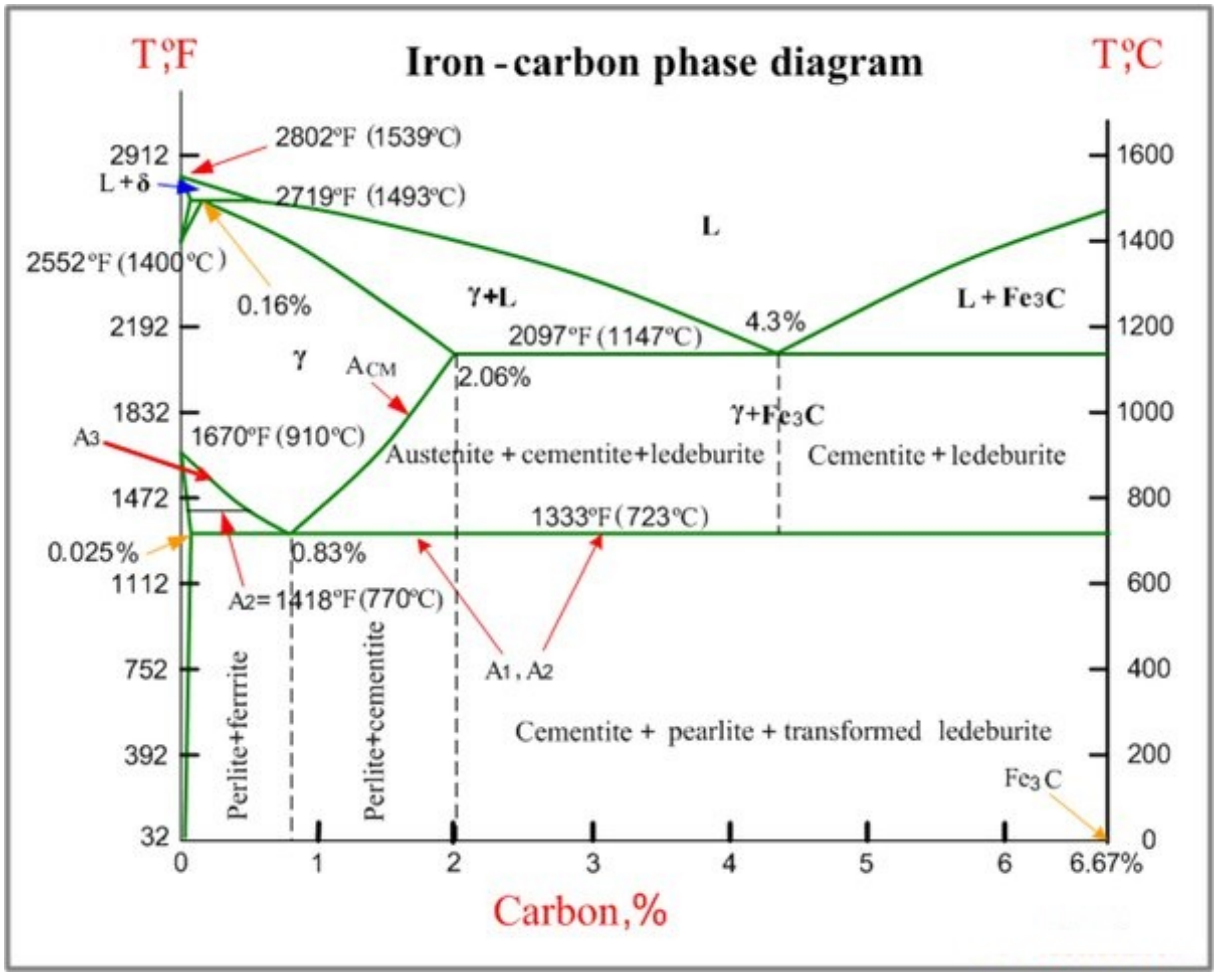
The iron-carbon phase diagram is typically divided into three regions based on the carbon content: the hypo eutectoid region (less than 0.8% carbon), the eutectoid region (0.8 - 2.1% carbon), and the hyper eutectoid region (greater than 2.1% carbon). Within each region, there are different phases and phase transformations that occur as the temperature is changed.

The primary phase in the hypo eutectoid region is ferrite (alpha iron). As the carbon content increases, a small amount of cementite (Fe_3C) can form as a secondary phase. The eutectoid composition, where ferrite and cementite form simultaneously during cooling, occurs at 0.8% carbon.

In the eutectoid region, the primary phase is pearlite. The eutectoid reaction involves the transformation of austenite (gamma iron) to pearlite during cooling. The eutectoid reaction occurs at a specific temperature, called the eutectoid temperature, which is 727°C for the iron-carbon system.

In the hyper eutectoid region, the primary phase is cementite. As the temperature decreases, cementite can form in combination with either pearlite or ferrite, depending on the cooling rate and carbon content.

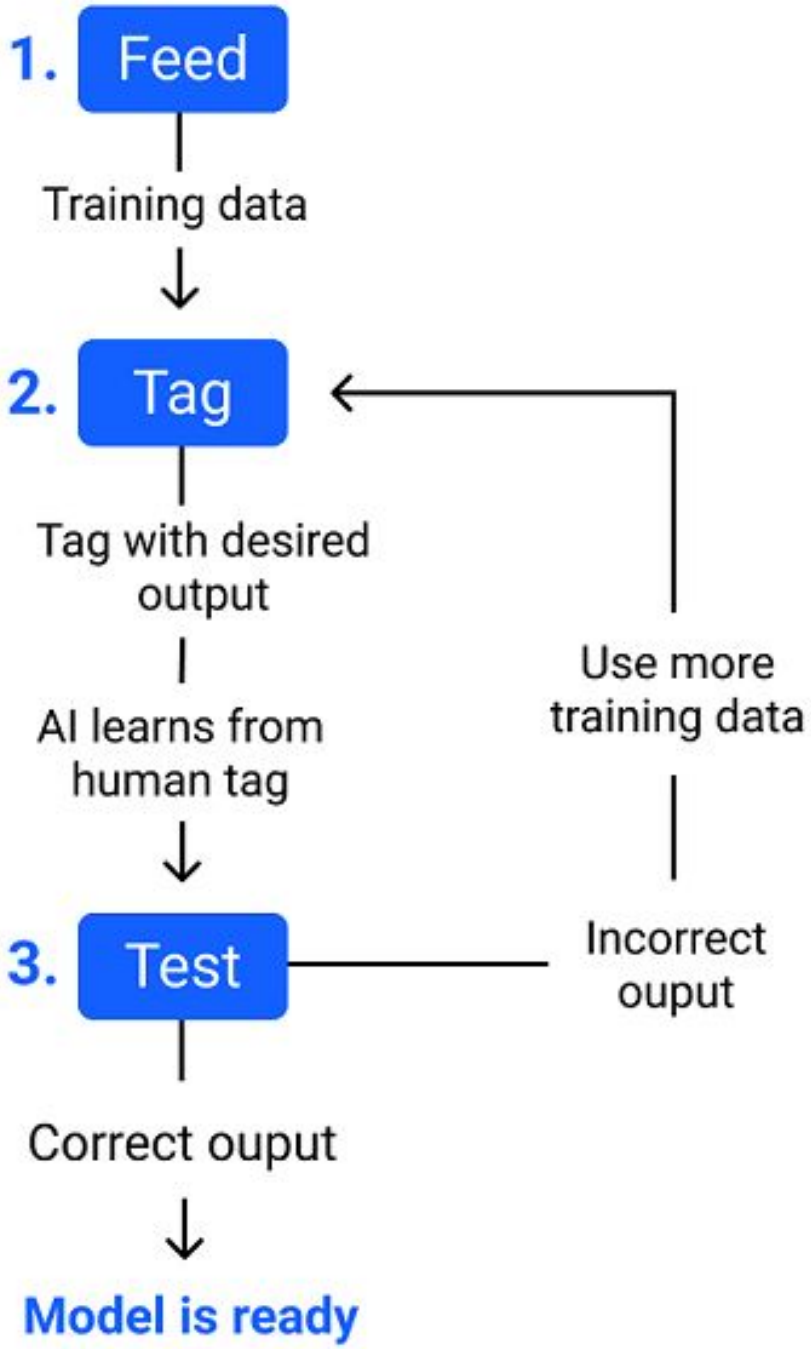
The iron-carbon phase diagram is important for understanding the microstructures and properties of steels and cast irons to meet specific performance requirements.



7 | Machine Learning

We are supposed to build a model that can predict different phases and microstructures of the vast dataset of the High Entropy Alloys based on the different features like density, different compositions of elements, melting temperature, enthalpy of formation, Gibbs free energy, entropy, and much more, It is basically a multiclass classification problem which could be easily resolved using Supervised Learning Algorithms like Logistic Regression, Random Forest Classifier, Decision Tree Classifier, etc. Let's take a look at the basic terminologies and algorithms used to build a predictive model.

- **Data Cleaning**: It is a crucial step in the machine learning (ML) pipeline, as it involves identifying and removing any missing, duplicate, or irrelevant data. The goal of data cleaning is to ensure that the data is accurate, consistent, and free of errors, as incorrect or inconsistent data can negatively impact the performance of the ML model.
- **Data Exploration**: It analyzes data to understand and summarize its main characteristics using statistical and visualization methods. At this stage, we basically follow a statistical protocol that consists of several steps like outlier detection, homogeneity in variance, accounting for null values, the interaction between variables with the help of a correlation chart, and independence in the dataset.
- **Preparing Data for Model Application**: At this stage, we generally divide the dataset into two parts: a training set and a test set. The training set includes 70% of the dataset from which the model sees and learns from this data to predict the outcome or to make the right decisions. Testing Set, generally containing the rest 30% of the dataset, is independent of the training set but has a somewhat similar type of probability distribution of classes and is used as a benchmark to evaluate the model, used only after training the model is complete.



- **Supervised Learning Algorithms**:
  - **Linear Regression**: Logistic regression for multi-class classification uses a one-vs-all approach to train N separate binary classification models, where N is the number of classes. Each model predicts the probability of the corresponding class versus the rest of the classes. The final prediction is made by selecting the class with the highest predicted probability. During training, logistic regression optimizes a loss function called cross-entropy loss to minimize the difference between predicted and actual probabilities. Logistic regression is simple and interpretable but assumes a linear decision boundary between classes.
  - **Decision Tree Classifier**: In a decision tree, the data is recursively split into subsets based on the value of a chosen feature. The splits are chosen based on the maximum information gain or minimum impurity criteria. During training, the decision tree algorithm learns a tree structure that can be used to classify new instances based on their features. In multi-class classification,

decision trees can be extended to predict multiple classes using a one-vs-all approach or a hierarchy of decision trees.

- **Random Forest Classifier**: It is an ensemble learning method used for multi-class classification tasks. It creates a collection of decision trees, where each tree is trained on a random subset of the features and data points. The class with the most votes from the individual trees is selected as the final prediction during prediction. Random Forest Classifier is robust to over-fitting and can handle non-linear relationships between features and the target variable.

- **Support Vector Machines(SVM) Classifier**: For multi-class classification, SVM can use either a one-vs-one (OVO) or a one-vs-all (OVA) approach. In the OVO approach, SVM trains a binary classifier for every pair of classes and combines the predictions from all classifiers to make the final prediction. In the OVA approach, SVM trains a binary classifier for each class against the rest of the classes. The class with the highest predicted probability is selected as the final prediction.

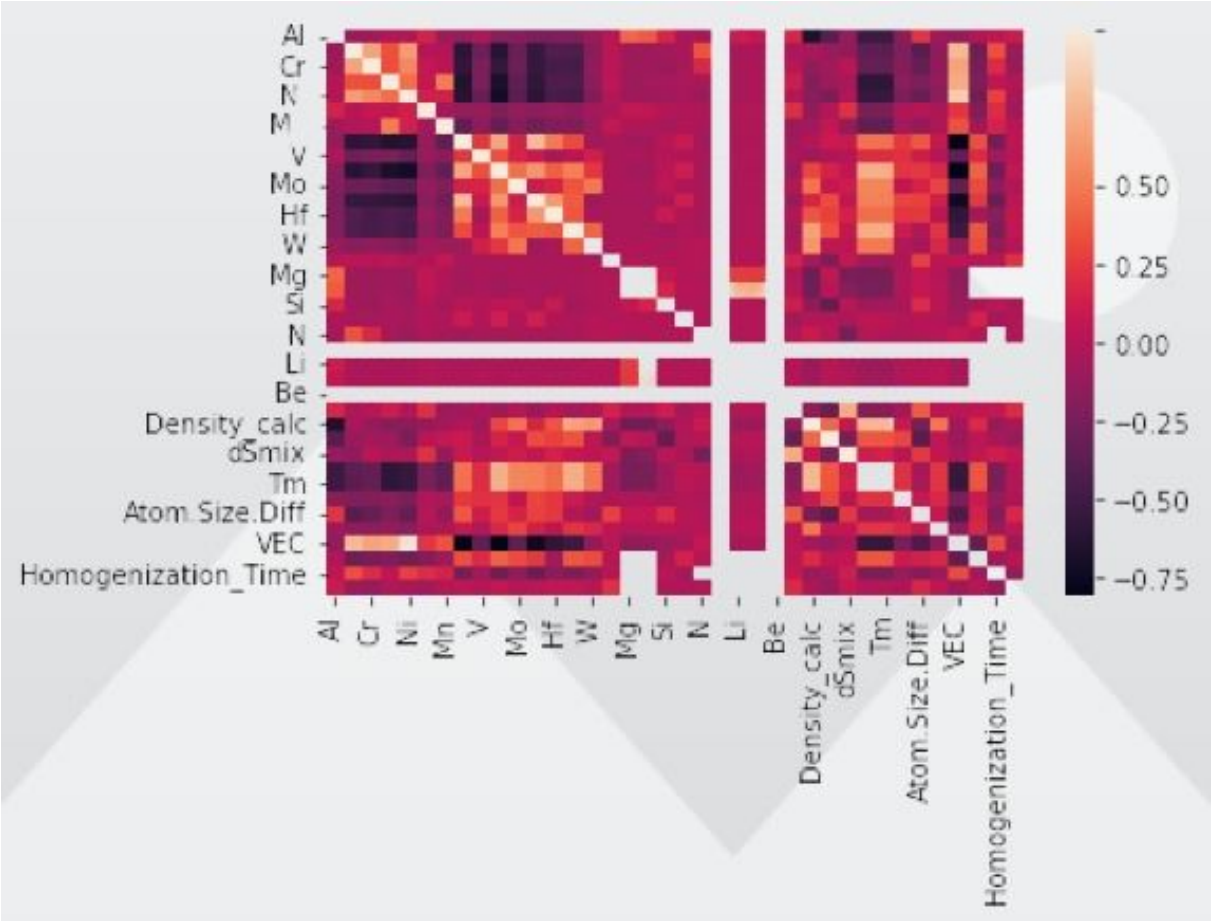
- **Feature Selection through RFE algorithm**: RFE(Recursive Feature Elimination) is an efficient approach for eliminating features from a training dataset for feature selection. Since, after even pre-processing the data, we are still remaining with 30+ features. Hence, we have to reduce it by selecting some of the most important features that have a comparatively higher impact on the microstructures and phases.

Table 7.1: Accuracy of Different Algorithms (Phase)

Algorithms	Before (RFE)	After (RFE)
Logistic Regression	75.29%	73.24%
Decision Tree Classifier	83.53%	82.36%
Random Forest Classifier	85.30%	84.41%
Support Vector Machines (SVM) Classifier	70.88%	71.18%

Table 7.2: Accuracy of Different Algorithms (Microstructure)

Algorithms	Before (RFE)	After (RFE)
Logistic Regression	75.00%	71.18%
Decision Tree Classifier	81.76%	81.76%
Random Forest Classifier	83.53%	82.64%
Support Vector Machines (SVM) Classifier	74.41%	70.59%



8 | Equipment Required

1. **Equipment required for Optical Microscopy**: Abrasive Belt Grinding Machine, Acrylic/polyester, Sandpaper of Grit size 1000, 1500, 2000, Cloth Polishing machine, Etchant: Aqua Regia, Optical Microscope.
2. **Equipment required for Vickers Hardness Test**: Vickers hardness testing machine.

9 | Procedure

This section explains the experimental procedure.

9.1 | Optical Microscopy

1. **Mounting**: First, apply the lubricant at the base of the ring, place the sample over it, and consecutively put casting liquid (acrylic/polyester) and power to mount the sample correctly.
2. **Grinding**: We grind the surface over the Rotating Belt grinder to make the sample uniformly even.
3. **Paper Polishing**: After making the surface uniform, we remove the further irregularities by polishing the surface over sandpaper with grits 1000, 1500, and 2000 respectively.
4. **Cloth Polishing**: Now, to create a shiny and lustrous surface, we do cloth polishing over the cloth wheel with alumina.
5. **Etching**: After doing the above steps, we etch the sample using Aqua Regia to clearly view the grain boundaries on the microscope.

9.2 | Vickers Hardness Test

1. Prepare the sample metallographically to be tested. Ensure that the surface of the sample is flat and polished to remove any surface irregularities.
2. Apply the load on the test sample.
3. Place the sample on the stage of the testing machine and then position the indentor over the desired location of the sample.
4. Hold the load for a 30 seconds time interval.
5. Measure the diagonal lengths of the resulting diamond-shaped impression using a microscope and take the average of the values measured.
6. Now, Calculate the Vickers Hardness Number using the formula VHN = 1.854(F/D2), where F is the load applied, and D is the average diagonal length of indentation.

10 | Results

Final accuracy obtained for predicting the phases and microstructures by using optimal Supervised Learning Algorithms i.e, **Random Forest Classifier**:

(i) **Phase**: 85.30%
(ii) **Microstructure**: 83.53%

Using table (Table 10.1) we get VHN as 726.63±35.92 kgf/mm^2

Table 10.1: Values of VHN at different loads.

Load (gm)	VHN (kgf/mm^2)
100	728.22±42.69
300	718.97±24.70
500	732.70±40.36

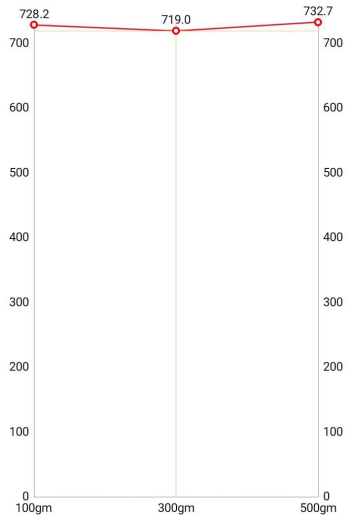


Figure 10.1: Variation of VHN with load

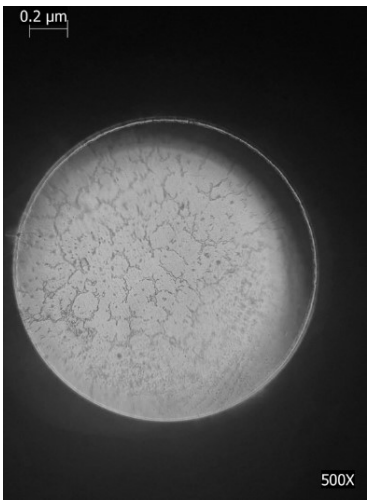


Figure 10.2: Microstructure of HEA

11 | Discussion

In the Machine Learning task of predicting the microstructure and phases of high entropy alloy, eventually, we got an accuracy close to 85%, which is not considered a good score, according to industry standards. This may be due to the limitations discussed in the later section. Therefore, this shows scope for improvement and exploration in the given dataset. Some anomalies like small datasets, and lack of use of more complex algorithms can be dealt with more computational power, but there are some characteristics like complex properties of HEA that are to be more researched upon and further used the more optimal properties in this task. Moreover, the value of Vickers Hardness Number appears to be almost constant with the varying load depicting that the experiment is well performed. Optical microscopy yields us the microstructure of the specimen of HEA through which we can strongly influence physical properties such as strength, toughness, ductility, hardness etc.

12 | Limitations

1. **Limited training data**: One of the main limitations is the availability of sufficient training data. Machine learning models require large amounts of high-quality data to learn patterns and make accurate predictions. However, in the case of predicting phases and microstructures, the amount of data available may be limited, especially for rare or complex materials.
2. **Complex physics**: The underlying physics of material behavior can be highly complex and difficult to model accurately. Machine learning models may struggle to capture all the relevant physics and predict outcomes with sufficient accuracy.
3. **Lack of interpretability**: Machine learning models can be highly accurate in predicting outcomes, but they are often considered ”black boxes” because they don’t provide an explanation for why a particular prediction was made. This lack of interpretability can be a significant limitation when understanding and optimizing material properties.
4. **High dimensionality**: The number of features or variables that can be used to describe a material’s microstructure can be very large. Machine learning models can struggle with high-dimensional data, leading to increased computational complexity and potentially reduced accuracy.
5. **Overfitting**: Machine learning models can overfit to the training data, meaning that they learn to predict outcomes based on noise or irrelevant features rather than the underlying physics. When applied to new data, this can lead to poor generalization and inaccurate predictions.

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