Database of Refractory High Entropy Alloy: a First Principle Study

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Abstract: In this work, the database of refractory alloys was built by combining phase diagram calculation and density functional theory based molecular dynamic simulations. The possible alloy with binary, ternary, 4-, and 5-element compounds constructed according to the special quasi-random (SQS) structure were all contained in this database. A database which contains properties include ally configuration, phase, melting temperature (T_m), lattice constant (a), density (ρ), binding energy (E_b), Bulk module (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν), elastic constant (C_{11}, C_{12} and C_{44}) and Vickers hardness (H_v) were built. The calculation of phase diagram show that large numbers of refractory alloys are promising high temperature materials and have only single BCC phase at high temperature. The mechanical properties at 0 temperature based on DFT calculation show that refractory alloys, especially tungsten and rhenium alloys, have advanced mechanical properties.

Keywords: High entropy alloy, phase diagram, density functional theory, machine learning

1. Introduction

Based on the elements contained in HEA, it can be classified into 3D transition metal alloys (alloys contain 4 or more of the following elements: Al, Co, Cr, Cu, Fe, Mn, Ni, Ti, and V), refractory metal alloys (alloys contain 4 or more of the following elements: Cr, Hf, Mo, Nb, Ta, Ti, V, W, Re and Zr) and other alloys including light metal, lanthanide transition metal and so on. Plants of reports focused on 3D transition alloys. Refractory alloys were inspired by the objective to develop new high temperature metals because of the high melting temperature of certain refractory elements. Moreover, the wide rang in elemental properties also provide high flexibility of refractory multicomponent alloys. For example, as the first synthesized MoNbTaVW can resistant temperature as high as 1400 °C[1]. The yield stress of MoNbTaVW is 1246 MPa at room temperature and decreases to 842 MPa at 1000 °C[1], which demonstrated its much better high temperature performance by comparing the yield stress with those of the widely used Ni-based Inconel 718 [2] and Haynes 230 [3] alloys. On the other hand, coarse-grained MoNbTaVW showed a high Vickers micro-hardness of 5250 MPa [4], while nanocrystalline MoNbTaVW, with an average particle size of ~30 nm, had a high hardness of ~11.4 GPa at 1150°C [5].

Machine learning becomes an emerging field in materials design and property prediction due to the accumulation of data from both experimental and computational results. Machine learning based model can produce

accurate predictive performance for a new experiment setup to bridge the gap between the simulation and reality, but the model cannot be trained with sparse experimental data at extreme conditions. However, it is far from enough data for machine learning to explore refectory HEA with advanced properties due to the lack of experimental observations and the inconsistent method on prediction. In this work, we combined the calculation of phase diagram (CALPHAD) and the density functional theory (DFT) to search for RHAEs with stable single phase. More than 500 alloys with stable single phase at high temperature were found, and the mechanical properties of these alloys were studied. The database we built by DFT simulation make it possible to explore RHEAs with advanced properties using machine learning.

2. Computational method

Prediction of a stable crystal structure of complex compound with known composition is a challenging task. The special quasi-random structures (SQS) model[6] as the multicomponent alloy. The possible alloys with binary, ternary, 4-, and 5-element compounds constructed according to the SQS model were all contained in this database. The possible configurations of the alloys include A, AB, A_3B, ABC, A_2BC, ABCD, and ABCDE, in which A, B, C, D, E is one of the refractory elements: Cr, Hf, Mo, Nb, Re, Ta, Ti, V, W and Zr. The CALPHAD method, will be used to support developing the stable alloys by calculating the possible stable single-phase alloys. The CALPHAD based thermodynamic calculations were carried out by employing the Thermo-Calc-2019 software to predict the phase of refractory alloys. The Thermo-Calc's High Entropy alloy database (TCHEA1)[7] in this software was claimed to have good agreement with the experimental observations on the phase of refractory high entropy alloys[8-12]. At last, DFT based simulation would optimize alloys and mimic properties. Following this strategy, a reliable thermodynamic database for related alloys will be developed.

The first principle calculation of the structural and mechanical properties was carried out using the DFT [13, 14] based Vienna Ab-Initio Simulation Package (VASP 5.4) [15] installed in MedeA software [16]. The electron-ion interactions were described by the projector augmented wave (PAW) [17], while electron exchange-correlation interactions were described by the generalized gradient approximation (GGA) [18] in the scheme of Perdew- Burke-Ernzerhof (PBE) [19]. The structural relaxation was performed using the Congregate-Gradient algorithm [20] implemented in VASP. An energy cutoff was set to be 500 eV for the plane wave basis in all calculations, and the criteria for the convergences of energy and force in relaxation processes were set to be 10^{-4} eV and 10^{-4} eV/Å, respectively. A 3×3×3 K-point mesh via the Monkhorst-Pack method was generated for performing Brillion Zone calculations, and a smearing parameter of ~ 0.2 eV was used for the Methfessel-Paxton [21] technique.

3. Results and discussion

According to the CALPHAD method, totally 536 refractory alloys which have stable body centered cubic (BCC) single phase and could resist very high temperature were screened out. The transition temperature which represents the starting temperature of single BCC phase and melting temperature of 2,3,4,5-component alloys are listed in Fig. 1, in which ΔT represents the difference between transition and melting temperature. Refractory alloys have shown promising prospect as the high temperature material since the meting temperature of all calculated alloys are

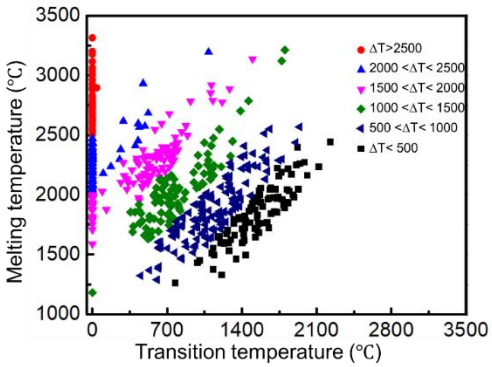

Fig. 1. Melting temperature and transition temperature of refractory alloys.

above 1000 °C, 76.7 % of the alloys have melting temperature above 2000 °C and 7.0 % even above 3000 °C. Moreover, 39 % of refractory alloys have zero transition temperature, which may be easier for experiment to synthesize. Among all alloys, ReMoTiVW is the 5-component alloy which contains only single BCC phase. Some 4-component alloy including MoNbTaW, MoReTaW and so on also have stable single BCC phase.

The SQS model for BCC crystal structures based on CALPHAD are shown in Fig. 2, *Ab initio* type DFT and thermal dynamics method were employed to simulate all SQS BCC structures. The dynamic stability of BCC structures was confirmed by the phono vibration model. The furthering studies on structural and mechanical properties of the multicomponent alloys were performed by the density functional theory based molecular dynamic simulations. Bulk module (B), shear modulus (G) and Pugh's ratio (B/G) [22] at 0 K were calculated by using the Voigt-Reuss-Hill averaging scheme[23] Young's modulus (E), Poisson's ratio (ν) are calculated by the following equations: $E=9BG/(3B+G)$ and $\nu=(3B-2G)/2(3B+G)$. The Vickers hardness (H_v) obtained by Tian's model[24]. In this case, a database which contains 16 properties including configuration, phase, transition temperature (T_c), melting temperature (T_m), lattice constant (a), density (ρ), binding energy (E_b), Bulk module (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν), elastic constant (C_{11}, C_{12} and C_{44}) and Vickers hardness (H_v) can be constructed.

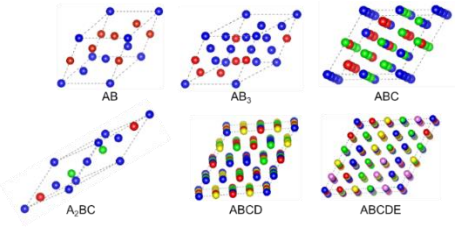

Fig. 2. Unit cell of BCC compounds with 2~5 elements based on SQS model

It is important to analysis features of the properties in the database before proceeding machine learning study since the performance of machine learning model is highly related by data features. The database should include features which contribute to the prediction value and are correlated to the desired output. However, the irrelevant features in the model may and make the model learn from irrelevant parameters, which decrease the accuracy of the model. The repeating features, on the other hand, have no contribution to the training and could slow down the machine learning process. In this case, the data cleansing which help to screen out highly correlated and irrelevant parameters goes first for an effective machine learning study. As seen in Fig. 3, three groups of parameters were classified by features: Thermal properties (T_c and T_m), structural properties (a, ρ, and E_b), and mechanical properties (B, G, E, ν, C_{11}, C_{12}, C_{44} and H_v). Correlation parameters of T_c to features which describe structural properties and mechanical properties are very small, representing irrelevant relation between T_c and other fractures. In this case, T_c should be dropped for the training for building machine learning model. On the other hand, the high correlation parameters were found between shear model and young's model (0.98), and between shear model and hardness (0.96), which indicate that the feature of shear model has almost no help to the training model. As the consequence, the database for the efficient and accurate training model was built with 14 features included.

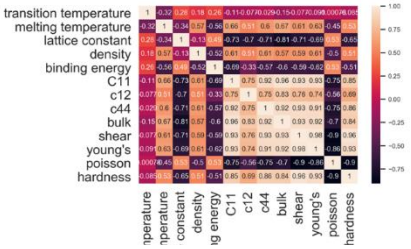

Fig. 3. Heat-map representation of correlation coefficient values between all data attributes for alloys

4. Conclusion

In this report, we built a database of refractory alloys by combining phase diagram calculation and DFT based optimization. The featured in the database include thermal properties (T_m), structural properties (a, ρ, and E_b), and mechanical properties (B, G/E, ν, C_{11}, C_{12}, C_{44} and Hv). The of correlation coefficient between each features shows

that the database we built have no repeated or irrelevant parameters. The database lay the foundation on machine learning to explore refractory high entropy alloys which have advanced properties.

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6. References

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