Strength design of Zr\(_x\)Ti\(_x\)Hf\(_x\)Nb\(_x\)Mo\(_x\) alloys based on empirical electron theory of solids and molecules

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Abstract: In this paper, the valence electron structure parameters of Zr\(_x\)Ti\(_x\)Hf\(_x\)Nb\(_x\)Mo\(_x\) alloys were calculated based on the empirical electron theory of solids and molecules (EET), and their performance through these parameters were predicted. Subsequently, the alloys with special valence electron structure parameters were prepared by arc melting. The hardness and high-temperature mechanical properties were analyzed to verify the prediction. Research shows that the influence of shared electron number \(n_A\) on the strongest bond determines the strength of these alloys and the experiments are consistent with the theoretical prediction.

1. Introduction

In recent years, high entropy alloys (HEAs) were proposed as a new concept of material design [1-3]. The multi-principal elements provide more composition spaces to explore alloys with excellent performance, which gives rise to a wide range of researches around the world [4-7]. The alloys design is an important step in the process of new HEAs discovery, the traditional alloy design of the "cooking" method wastes plenty of manpower and material resources, which does not apply to HEAs research apparently today. In the recent research, the phase prediction from the viewpoint of thermodynamics has been developed. Zhang et al.[5, 6] predicted the single phase forming ability through \(\delta\) and \(\Omega\). Guo et al.[7, 8] further proposed the crystalline structure of single-phase rules through the valence electron concentration (VEC) in HEAs. Through these prediction rules, the brittle phase can be reduced, but the mechanical properties cannot reveal during the alloy design process. Therefore, it is necessary that the material design come into the level of the electronic structure, R H Yu et al. proposed an empirical electron theory of solids and molecules (EET) [9, 10] in the last century, which can solve the prediction of properties perfectly. Because the HEAs have simple structure similar to the traditional alloys, the EET has good applicability and the experiments results confirm it well.
2. Alloy design process

The bond length difference (BLD) is a new method of computing solid electronic structure, which bases on the experimental data of crystal structure to avoid solving the Schrodinger equation [9]. Before the analysis of BLD, the crystal structure type, the lattice constant and the atomic position need to be confirmed. Consequently, the crystalline constant prediction is the first step in the process of Zr(Ti, Hf, Nb, Mo) alloy design. Based on the elements constant of these refractory elements, the difference of size parameters (δ), solid solution ability (Ω) and the VEC are calculated, which is in the range of the single phase of body centered cubic.

The average cell was adopted due to the numerous kinds of atoms and complex combination. In this condition, the individual atoms and the position in the cell are roughly equivalent. The average lattice constant a:

\[ a = \sum c_i a_i (i = Zr, Ti, Hf, Nb, Mo) \]  

Where \(a_i\) is the lattice constant of the \(i\)th element and \(c_i\) is the concentration of the \(i\)th element in these HEAs. The distance between any two atoms can be calculated through the lattice geometry, which was named as the test distance of bond distance of covalent empirical equation:

\[ D(\alpha) = R(\alpha) + \beta \log n_{\alpha} \]  

Where \(\mu\) and \(\nu\) are the bonding atoms, \(R(\mu)\) and \(R(\nu)\) are the half single-bond length of \(\mu\) and \(\nu\), respectively. \(n_{\alpha}\) is the theoretical number of the covalent bond, and \(D(\alpha)\) is the theoretical bond length. \(\beta\) is equal to 0.06 nm in these Zr(Ti, Hf, Nb, Mo) alloys. The difference between theoretical bond length and test bond length is used to justify whether the atomic state matches the actual situation:

\[ |\Delta D(\alpha)| < 0.05 nm \]  

If inequation (3) is not satisfied, then the \(n_{\alpha}\) value needs to be recalculated and set as other mixed order of atoms. When the \(|\Delta D(\alpha)|\) is the minimum value, this state is regarded as the closest to the reality, the shared electron pair number of the strongest covalent bond is defined as \(n_{\alpha}\) in this condition. This paper computed the results of the calculation process through the MATLAB 2012(b) as they were complex, and displayed them on table 1.

| Parameters | ZrTiHf\(_2\)NbMo | Zr\(_{2.8}\)TiHfNbMo\(_{2.0}\) | ZrTiHfNb\(_{0.9}\)Mo\(_{0.5}\) | ZrTiHfNb\(_{2.8}\)Mo\(_{2.0}\) |
|------------|------------------|--------------------------|--------------------------|--------------------------|
| Ω          | 1.5819           | 1.7447                   | 1.619                    | 2.1289                   |
| δ%         | 5.32%            | 5.90%                    | 5.10%                    | 5.33%                    |
| VEC        | 4.5              | 4.71                     | 4.38                     | 4.86                     |
| a/Å         | 0.3404           | 0.3371                   | 0.341                    | 0.333                    |
| \(n_{\alpha}\) | 0.3189          | 0.3231                   | 0.309                    | 0.3842                   |
3. Experimental
The Zr\(_{x}\)Ti\(_{x}\)Hf\(_{x}\)Nb\(_{x}\)Mo\(_{x}\) alloys were prepared through the arc melting under the protective atmosphere, and the cooling system employed the water-cooled copper crucible. In order to ensure the homogeneity of composition, the low-melt bulk materials were placed lower in turn and the ingots were flipped and remelted at least six times. The purity of row materials is greater than 99.9%.

The microhardness of the HEAs was measured by 450SVD\(^{TM}\) Vickers’s hardness tester under 300 g loaded applied for 15s, the ultimate hardness value was averaged by five different positions measurements at the specimen’s polished surface. The focused high temperature compressive performances were performed on a Gleeble-3500 thermal simulator. In this study, the thermocouple used Pt-Rh alloy, the specimens adopted cylinder of 6 mm×9 mm, the strain rate was 10\(^{-3}\) s\(^{-1}\), and the amount of compression was set as 40%. Each alloy was heated to 700\(^{\circ}\)C, 800\(^{\circ}\)C, 900\(^{\circ}\)C in turns, the heating rate was set as 300\(^{\circ}\)C and the holding time was 3 minutes.

4. Results and discussion
The relationship between the covalent electron pair number of the strongest covalent bond (\(n_A\)) and the strength of Zr\(_{x}\)Ti\(_{x}\)Hf\(_{x}\)Nb\(_{x}\)Mo\(_{x}\) alloys is shown in the figure 1. The value of \(n_A\) reflects the strength of bonding force among the atoms on the micro, and the \(n_A\) value increases with the bond strength enhance, which can be quantificated through the EET. On the macro, the hardness and high temperature fracture strength have close relationship with the bond strength. Through the EET, the relation between mechanical performance and valence electron parameter is established. The compressive stress at elevated temperature of these alloys is consistent with the hardness. The value of \(n_A(0.3842)\) of ZrTiHfNb\(_{2.0}\)Mo\(_{2.0}\) alloy is far more than others, the hardness (543.3HV) and high temperature fracture strength (1155MPa at 800\(^{\circ}\)C and 897MPa at 900\(^{\circ}\)C) are the highest among these alloys. The hardness and stress at high temperature are greater when the \(n_A\) value increase, which can predict the strength of the alloy with different content in the design process.

5. Conclusion
This paper researched the Zr\(_{x}\)Ti\(_{x}\)Hf\(_{x}\)Nb\(_{x}\)Mo\(_{x}\) high entropy alloys. The thermodynamic parameter (\(\Omega\) and \(\delta\)) and VECarein the range of the single phase of body centered cubic. Based on the crystal structure, the valence electron structure parameters were calculated to predict the mechanical properties

![Figure 1](image-url)
through empirical electron theory of solids and molecules (EET). The covalent electron pair number of the covalent bond \( n_A \) reflects the bond strength, and the hardness and compressive stress of these alloys increase with the \( n_A \) enhance, which can predict the strength of \( \text{Zr}_{(x)}\text{Ti}_{(x)}\text{Hf}_{(x)}\text{Nb}_{(x)}\text{Mo}_{(x)} \) through the EET.

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