Effects of Alloying Additions on the Glass Forming Ability and Corrosion Resistance of Bulk Zr-Based Amorphous Alloys

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Abstract—By using the real-place Recursion method, the effects of alloying additions (Nb, Ta, Y, La) on glass forming ability (GFA) and corrosion resistance of bulk Zr-based amorphous alloys are studied. An atomic group model in the Zr2Ni primary crystalline phase centered to Ni atom are constructed by computer programming. We have calculated the total bond order integral (∑BOI) between Ni atom and its neighbor elements (Nb, Ta, Y, La), also calculated the Fermi energy level of alloying elements. The calculation results show that the ∑BOI and the glass forming ability are greatly enhanced after Y substitution. Nb, Ta, La decrease the GFA and La has little influence on the GFA of the alloys. Nb, Y, La enable Zr-based amorphous easy to passive and increase corrosion resistance. Therefore, Y and La are most effective on glass forming ability and corrosion resistance of Zr-based amorphous alloys. By addition of minor Y and La can produce the new bulk amorphous alloys with good corrosion resistance.

1. INTRODUCTION
Bulk amorphous alloys with unique characteristics has been one of the most important topic in the materials science. Amorphous alloys has strong passivating, whose elements can be prepared on a widens, (3) suitable negative heats of mixing among their main elements. Now, Based on these three component parameters, new muti-component amorphous alloys were found in Pd-based, Zr-based, Fe-based, Ti-based and Co-based systems. The centimeter-sized in the Pd-based and Zr-based amorphous alloys are greater (Pd40Cu30Ni10P20 amorphous alloys, with diameter reaching 72 mm by water quenching method [3], Zr55Al10Ni5Cu30 amorphous alloys, with diameter reaching 30 mm under copper mold casting method [4]) than Other-based amorphous alloys. It is very important to research and explore the integrity theory on the formation of amorphous alloys.

Zr-based amorphous alloys currently have good glass forming ability, for instance, Zr55Al10Ni5Cu30 is a typical alloy former, which has excellent mechanical properties and possesses high tensile strength of 1.8Gpa and a higher corrosion resistance [5]. For the decade, the research of amorphous alloys have been much more progress. The golf poles in the application have been commercialized. In order to expand the application of amorphous alloys and study amorphous materials in the various environment corrosion behaviors and accumulate corrosion data are great significant in the application of actual working environment. S J Pang have studied the influence of alloying addition...
Nb on the GFA and corrosion behaviors of bulk Zr-Al-Ni-Cu glassy system. The alloy has higher GFA by the addition of 20at% Nb (the super-cooled liquid region). But the GFA of the amorphous alloys decreased with the increasing of Nb. The present investigations reveal that new bulk amorphous Zr-Al-Cu-Ni-Nb alloys containing small amounts of Nb exhibit increased corrosion resistance especially in chloride solutions. ZU F Q[6] have investigated the corrosion resistance behavior of Zr-Al-Ni-Cu bulk amorphous alloys in HNO3 solution; NaCl solution and NaOH solution has the function of passivating, and found that Zr-Al-Ni-Cu bulk amorphous has excellent corrosion resistance in acid, alkali and salt solutions, but serious corrosion in 5mol/L solutions, which shows that Zr based amorphous materials are not corrosion-resistant in any environment. It is affected by corrosion medium and alloy elements. The results indicate that the corrosion resistance ability of bulk Zr-based amorphous alloys is affected by many conditions such as the kind of corrosive medium and the compositions of amorphous alloys. Adding appropriate Nb element is an effective method to enhance corrosion resistance of Zr-based amorphous alloys. Jun Luo[7] have found that the GFA of the Zr55Al10Ni5Cu30 amorphous alloy is enhanced by addition of (0.5-3)at% Y. Cylindrical glassy Zr0.55Al0.10Ni0.05Cu0.30)100-x(x=0.5,1,2) rods can be easily obtained by copper mold casting. On the other hand, it has been found that by adding minor amount of rare-earth elements can enhance the GFA of the amorphous alloys, because the rare-earth elements Y, La with large atomic sizes may act on oxygen scavenger or stabilize the super cooled liquid alloy. Analogous to small atoms, additions of large atoms such as Y greatly help the GFA [8].

With deep researching on the Zr-based amorphous alloys, it is urgent to study the effects of the components on the glass forming ability and corrosion performance, as well as their mutual relations. In order to guide the experiment to prepare the excellent corrosion resistance of the bulk Zr-based amorphous. Zhang G Y had successfully researched the electronic theory of the influence of alloying elements on the GFA. Transition element Ir, Pt, Rh, Pd, Au, Ag, Cu on the amorphous alloy forming ability weaken in the same order; electronic theory also have been studied on the corrosion mechanism of Mg alloys[9]. It is important to point out that the electronic theory has been calculated to study the effects of alloying additions elements Nb, Ta, Y and La on the GFA and corrosion resistance of bulk Zr-based amorphous alloys. The authors believe this research of some alloys for various benefits can lead to further studies in design of amorphous and can encourage the bulk structure material as a new type with high glass-forming ability and corrosion resistance.

2. METHODS AND MODELS

2.1. Atomic models

The Zr-based amorphous alloys (Zr66.7Ni33.5, Zr-Al-Ni-Cu) are characterized in that the primary crystalline phase is an fcc-Zr2Ni (a large lattice parameter of 1.12nm) with a unit volume of the big-cube phase consist of 96 atoms[10]. In Zr-based amorphous alloys, by adding a small amount of precious metals such as Ag or Pd, the primary crystalline phases were quasi-crystals items. With the prolongation of annealing time or the increase of heating temperature, the quasicrystals items occurred decomposition and then precipitated fcc-Zr2Ni phase, ultimately it turned into the stability crystal phase [11]. Theoretical studies indicate that, when icosahedral bernal tetrahedral aggregated minor deformation occurred. The phenomenon led the system to reduce the energy, which can produce icosahedral cluster structure. This shows that much more such structure in the super-cooled liquid region icosahedral clusters. That is precipitation of quasi-crystalline phase firstly and then turned into the meta-stable fcc-phase, or directly precipitated the meta-stable fcc-phase when Zr-based amorphous alloys crystallization. For instance, in the metal-metal type amorphous alloys, the high resolution TEM images reveal that the amorphous alloys structure is composed of icosahedral clusters. Fcc-Zr2Ni structure has two kinds of icosahedral clusters, whose center is Zr or Ni atom. Because the icosahedral cluster is a dense structure and low surface energy, the first quasi-crystalline phase based on the short program nucleation process grew up. The fcc-Zr2Ni phase is decomposition from the amorphous or quasicrystals. Because this fcc-Zr2Ni phase still retains the characteristics of amorphous clusters or
Icosahedral clusters in the quasi-crystals phase. According to the features of cluster structures existence gene structure. There is structural heredity in the mounting structure of amorphous clusters. Based on this structural feature, this paper constructs an atomic structure model of Zr based amorphous initial crystallization phase zr2ni, as shown in Figure 1(a), from which an icosahedral cluster is selected, and the part in the box in Figure 1(a) is used to simulate the icosahedral cluster in the amorphous. When the influence of alloy elements on the forming ability and corrosion resistance of amorphous is considered, Nb, Ta, Y and LA are used to replace 3# Zr atoms, as shown in Fig. 1(b). The icosahedron cluster centered on Ni is selected for total energy calculation (Figure 1(a),(b) inside the box, excluding the atoms on the box). The paper constructed an atomic group model of the Zr2Ni phase centered to Ni atom simulation icosahedral cluster was constructed to investigate. An atomic group structure model in the Zr2Ni primary crystalline phase of Zr-based amorphous alloy was set up by computer programming.

![Figure 1 Atomic structure models of the Zr2Ni crystalline primary phase before (a) and after (b) Nb, Ta, Y, La substitute for 3# Zr atom](image)

2.2. Theoretical method

The real space Recursion method [12] was discussed about glass formation and corrosion resistance behaviors of Zr-based amorphous alloys. This method had been applied successful on chemisorptions. The basic idea of the method is to set up Hamiltonian matrix based on the tight-binding approximation. The diagonal formula of the Hamiltonian matrix is the orbital free-energy of atoms, which is derived from the calculated results of Fischer (1972) by the Hartree-Fock approximation. The transition integral for our system can be well expressed from Hartree-Fock approximation. The non-diagonal formula of the Hamiltonian matrix—the transition integral between atoms were respectively taken to Slater-Koster integral. Universal parameters from solid table. The valence electron configurations of atoms are: Zr, 5s24d2; Ni, 4s23d8; Cu, 4s23d9; Nb, 4s23d3; Ta, 6s25d3; Y, 5s24d1; La, 6s26d1.

According to the method, the total energy of the system can be given by the sum of and can be calculated by formula (1) and (2). Here stands for the structural energy at some site, is energy, is the local density of state (LDOS) of orbital when energy equal to, the LDOS is the density of states of grid in the place of alloy elements, and is Fermi energy level.

\[
U_i = \sum \alpha \left( \int_{-\infty}^{E_f} \text{LDOS} \sqrt{E} \right) dE
\]

The structural energy at site is given as

\[
U_i = \sum \alpha \left( \int_{-\infty}^{E_f} \text{LDOS} \sqrt{E} \right) dE
\]

The Fermi energy level of the system can be determined by the following equation; Wherestands for the total number of valence electron situated in occupying state in the system.
\[ Z = \sum_{\alpha}^{E_{f}} \left[ \int_{-\infty}^{E} n_{\alpha}(E)dE \right] \]  

(3)

In order to discuss the interaction strength among atoms, the bond order integral\([21]\) (BOI) of the atoms is defined.

\[ Z = \sum_{\alpha}^{E_{f}} \left[ \int_{-\infty}^{E} n_{\alpha}(E)dE \right] \]  

(4)

\( \text{ImG} \) expresses the imaginary part of the early state Green function. The non-diagonal formula of the Green function express diagonal matrix of the linear combination. The diagonal formula of the Green function obtained by the Recursion method:

\[ G_{\alpha\alpha}(E) = \frac{1}{4} \left( G_{\alpha\alpha} + G_{\alpha\alpha} \right) \]  

(5)

In this paper, we have calculated the electronic structure for models of the Zr2Ni crystalline phase by the real-place Recursion method. According to the total energy, the density of states, the total bond integral and the Fermi energy level were calculated to discuss the effects of alloying addition elements Nb, Ta, Y, La on the GFA and corrosion resistance of bulk Zr-based amorphous alloys.

3. RESULTS AND DISCUSSION

3.1. Substitution

In order to compare conveniently, the local density of state of individual atoms before and after substitution were calculated. Fig.2 shows the LDOS curves of alloying additions Cu, Nb, Ta, Y or La substitutes for Ni (Zr) atom in the Zr2Ni primary crystalline phase and Ni (Zr) atom. It can be seen from Fig. 2 (a) that the LDOS shape of only Cu atom before and after element replacement is similar to that of Ni, and there is a double peak structure contributed by d electron in the low energy region, and the small peak near 0 electron volt is the contribution of s orbital electron. The LDOS shape of other Alloy Elements Nb, Ta, Y, La is quite different from that of Ni, so the substitution has a great influence on the surrounding environment, so the substitution is not easy to achieve. This shows that only Cu atom in the Zr2Ni crystalline phase and amorphous icosahedral clusters can substitute for Ni atom, which form the Cu-Zr phase that are similar to Ni-Zr icosahedral clusters of amorphous. Fig.2(b) shows the LDOS curves of element Nb, Ta, Y, La substitutes for Zr and Zr atom. Compared with curves in Fig.2(b), the LDOS curves of element Nb, Ta, Y, La and Zr atom are quite similar, thus it provides a reasonable explanation that alloying addition elements Nb, Ta, Y, La occupy the place of Zr in the Zr2Ni crystalline phase or Ni-Zr icosahedral clusters of amorphous. The following calculation all of the alloying elements substitute for the position of Zr atom.
Figure 2 LDOS of alloying additions substitute for alloying atom in the Zr2Ni crystalline phase; (a) Cu, Nb, Ta, Y or La substitutes for Ni atom; (b) Nb, Ta, Y or La substitutes for Zr atom

3.2. Glass forming ability

We further discussed the effects of alloying additional elements Nb, Ta, Y, La on the GFA of Zr-based amorphous alloys. After location of alloying elements substitute for 3# Zr atom. The total bond order integral (∑BOI) between Ni that in the Zr2Ni crystalline phase centered to Ni atomic clusters and neighbor element of 3# Zr atom (Nb, Ta, Y, La) were calculated by using formula (1), (2) and (4), as followed in Table 1. The ∑BOI of Y-Ni is higher than after Y substitutes for Zr. The results indicate that the interaction of the Ni-Y is stronger than the Ni-Zr. We have used the clusters of Zr2Ni crystalline phase centered to Ni atom to simulate icosahedral clusters model among amorphous. Zr-based amorphous precipitate quasicrystalline phase or crystallize, which need icosahedral clusters carrying on the long-rang diffusion. If these interaction of atoms among the clusters affects strongly, the atomic proliferation is difficult and vice verse. The indication of interaction of Y-Ni strengthens after it substitutes for Zr atom. Thus it is difficult to diffusion between Zr and Ni atoms. It’s hard to become Zr2Ni crystalline phases, which means that the GFA elevate. That is Y enhances the GFA of amorphous alloys after it substitutes for Zr atom. On the other hand, the results of ∑BOI values of Nb-Ni, Ta-Ni and La-Ni are less than Zr-Ni, but the values between Ni-La and Ni-Zr are almost the same. Which is evident that element Nb, Ta or La makes the GFA of amorphous cease, but La has little
influence on it. From all the above, we can significantly conclude that the alloying addition Y improves the GFA in Zr-based amorphous alloys.

Table 1. The total bond order integral ($\sum BOI$) between Ni atom in the clusters of Zr2Ni crystalline phase centered to Ni and neighbor element of 3# Zr atom (Nb, Ta, Y, La)

|     | Zr   | Nb   | Ta   | Y    | La   |
|-----|------|------|------|------|------|
| $\sum BOI$ | 0.2379 | 0.1943 | 0.2047 | 0.3189 | 0.2357 |

3.3. Corrosion resistance

In order to study effects of alloying additional elements Nb, Ta, Y, La on corrosion resistance of Zr-based amorphous alloys, we have calculated Fermi energy level in the Zr2Ni crystalline phases centered to the Ni atomic cluster, as shown in Table 2. The Fermi energy level expression electron packing level, the higher Fermi level is, the easier electron is to lose. Namely the material has big activeness and is oxidized easily. It is easy to passivation in the solution where contains the oxygen ions and to form the oxidation film. Zr is an easily passivated element, its surface can form a dense oxide film, so it has strong corrosion resistance. From Table 2, the Fermi energy level of Nb, Y or La is higher than Zr, which demonstrates Nb, Y or La can substitute for Zr atom that enable Zr-based amorphous easy to passive and increase corrosion resistance. Y or La greatly enhance corrosion resistance of Zr-based amorphous alloys. Fermi energy level of Ta is lower than Zr and decreases passivation ability of Zr-based amorphous alloys. From the results of 3.2, we can conclude that Y can enhance the corrosion resistance and greatly increase the GFA of Zr-based amorphous alloys. La has little influence on the GFA of Zr-based amorphous, but can well enhance corrosion resistance of Zr-based amorphous. In order to expand the application field of amorphous alloys, the bulk amorphous alloys with high corrosion resistance can be prepared by adding a small amount of Y element into Zr based amorphous alloys.

Table 2. Fermi energy level in the clusters of Zr2Ni crystalline phase centered to Ni (alloying additions substitute for 3# Zr atom)

|     | Zr   | Nb   | Ta   | Y    | La   |
|-----|------|------|------|------|------|
| $E_f/eV$ | -9.6612 | -9.6248 | -9.6911 | -9.6409 | -9.5308 |

4. CONCLUSION

The electronic structure for models of the Zr2Ni primary crystalline phase were calculated, and the effects of alloying additions Nb, Ta, Y, La on the GFA and corrosion resistance of the Zr-based bulk amorphous alloys by the real-place Recursion method were investigated. The conclusions are obtained as in the following:

(1) Alloying additions Nb, Ta, Y, La occupy the place of Zr in the icosahedral clusters of the amorphous.

(2) The $\sum BOI$ values after Y substitutes for Zr atom has elevated and increased the GFA of Zr-based amorphous alloys. Nb, Ta, La make the GFA of amorphous. La has had little influence on the GFA of bulk Zr-based amorphous alloys.

(3) Nb, Y, La enable Zr-based amorphous easy to passive and increase the corrosion resistance. But Ta decreases passivation ability of amorphous alloys.

According to our analysis of electronic theory in recent studies, we can conclude that by addition of minor alloying elements Y, La to the bulk Zr-based amorphous alloys are very effective in enhancing the GFA and increasing the corrosion resistance in Zr-based amorphous alloys.
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