Synthesis, properties and XPS analysis of Cu-, Ni-, Ti-based metallic glasses

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**Abstract:** Metallic glasses (MG) represent an interesting group of materials as they possess outstanding physical, chemical and mechanical properties compared to their crystalline counterparts. This paper reviews the synergistic influence of Ni and Nb elements on thermal stability of supercooled liquid and corrosion resistance of as-cast Cu-Zr(Hf)-Ti-Ni-Nb bulk metallic glasses (BMGs). Additionally, in-situ second phase reinforced Cu-based BMG composites with high corrosion resistance and excellent mechanical properties are investigated. On the other hand, this paper reports the development of ultra-high corrosion resistant Ni-based metallic glasses at high temperatures for their potential applications. Corrosion resistance and XPS analysis of the Ni-free Ti-based BMG are also introduced.

**Key words:** metallic glasses; supercooled liquid region; corrosion resistance; mechanical properties; XPS analysis

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A glass is a disordered (or amorphous) solid which does not possess the long range periodicity as present in a typical crystal. The best known natural glass is obsidian, formed by solidification after volcanic activity [1]. The production of a metallic glass by rapid cooling of the molten Au75Si25 (compositions given in at.% throughout this paper) eutectic alloy in 1960 is generally considered to be the beginning of the era of metallic glasses [2]. Since then, a number of metallic glasses have been developed in Ni-, Fe-, Pd-, Al-, Zr-, Cu- and Ti-based alloy systems [1, 3-6]. More importantly, metallic glasses exhibit unique properties that are superior to the conventional crystalline metals and alloys, such as high strength, high elastic strain limit, high hardness, good soft magnetic properties, and good corrosion resistance [1, 3-6]. Additionally, the metallic glasses with different compositions can be fabricated in the form of powders, thin ribbons, fine wires, plates and bulk form with large dimensional size, for advanced structural and functional materials. Figure 1 shows regular, wide ribbon samples and bulk glassy alloys prepared by melt spinning, arc melting and copper mold casting.

The purpose of this paper is to present an overview of the Cu-, Ni- and Ti-based metallic glasses with useful properties. This paper includes three sections. The first section outlines the glass forming ability (GFA), mechanical properties and corrosion behavior of the as-cast Cu-Zr(Hf)-Ti-based bulk metallic glasses (BMGs) and their composites. In-situ Ta/ Nb-reinforced Cu-Zr(Hf)-Ti BMG composites with increased plasticity and enhanced corrosion resistance are also reviewed. The second section reviews the development of ultra-high corrosion resistant Ni-based metallic glasses at high temperature. The third section introduces the Ni-free Ti-based BMG with good corrosion resistance and its XPS analysis.
1 As-cast Cu-based BMGs/composites with good properties

1.1 Preparation and corrosion behavior of Cu-Zr(Hf)-Ti-Ni-Nb bulk glassy alloys

Cu-based BMGs are particularly interesting and show commercial potential as structural materials in some fields due to the combination of high strength of exceeding 2 GPa, high glass forming ability (GFA) and good wear resistance. This includes the discoveries of unusual glass-forming ability (GFA) and high strength in ternary Cu-Zr(Hf)-Ti(Al)\textsuperscript{[7-9]} and quaternary Cu-Zr-(Ti, Al)-Ag\textsuperscript{[10,11]} alloys. These bulk metallic glasses (BMGs) as an engineering material are now attracting attention for potential applications as advanced engineering materials in many areas such as surgical instruments and bipolar plates in fuel cells. However, the Cu-based BMGs exhibit low corrosion resistance in corrosive environments, especially, when the solutions contain chloride-ions\textsuperscript{[12-15]}.

In order to develop BMGs with a larger supercooled liquid region and good viscous flow workability as well as higher corrosion resistance, BMGs with critical diameters of 2.0–4.0 mm were synthesized in the (Cu\textsubscript{0.6}Zr\textsubscript{0.3}Ti\textsubscript{0.1})\textsubscript{100-x-y}Ni\textsubscript{y}Nb\textsubscript{x} (x = 0–6at.\% and y = 0–7at.\%) and (Cu\textsubscript{0.6}Hf\textsubscript{0.25}Ti\textsubscript{0.15})\textsubscript{100-x-y}Ni\textsubscript{y}Nb\textsubscript{x} (x = 0–6at.\% and y = 0–5at.\%) alloy systems by the copper mold casting method\textsuperscript{[16-17]}. Figure 2 shows DSC curves of the Cu-Zr(Hf)-Ti-Ni-Nb glassy rods with a diameter of 1.5 mm\textsuperscript{[16,17]}, where \(T_g\) and \(T_x\) correspond to glass transition temperature and onset temperature of crystallization, respectively. The addition of Ni element causes an extension of a supercooled liquid region (\(\Delta T_x = T_x - T_g\)) from 40 K for Cu\textsubscript{60}Zr\textsubscript{30}Ti\textsubscript{10} to 60 K for (Cu\textsubscript{0.6}Zr\textsubscript{0.3}Ti\textsubscript{0.1})\textsubscript{95}Ni\textsubscript{5} and from 60 K for Cu\textsubscript{60}Hf\textsubscript{25}Ti\textsubscript{15} to 70 K for (Cu\textsubscript{0.6}Hf\textsubscript{0.25}Ti\textsubscript{0.15})\textsubscript{95}Ni\textsubscript{5}, accompanying the change in the crystallization mode from two stages to a single stage. It is concluded that the addition of 5at.\% Ni is effective for the increase in thermal stability of the supercooled liquid before crystallization. The large \(\Delta T_x\) values of exceeding 40 K and the high reduced glass transition temperature (\(T_g/T_l\), where \(T_l\) is the liquidus temperature examined by differential thermal analysis) values of above 0.60 have enabled the formation of bulk glassy alloys with a critical diameter for glass formation (\(d_c\)) in the range from 2.0 mm to 4.0 mm in the Cu-Zr(Hf)-Ti-Ni-Nb alloy systems over a wide composition range by copper mold casting. The thermal properties \(T_g\), \(T_x\), \(\Delta T_x\), and critical diameter \(d_c\) for glass formation are summarized in Table 1.

![Fig. 1: Ribbon samples prepared by melt spinning (a), bulk glassy alloys prepared by arc melting and copper mold casting (b), and wide ribbon samples fabricated by melt spinning (c).](image-url)

![Fig. 2: DSC curves of as-cast (Cu\textsubscript{0.6}Zr\textsubscript{0.3}Ti\textsubscript{0.1})\textsubscript{100-x-y}Ni\textsubscript{y}Nb\textsubscript{x} (a) and (Cu\textsubscript{0.6}Hf\textsubscript{0.25}Ti\textsubscript{0.15})\textsubscript{100-x-y}Ni\textsubscript{y}Nb\textsubscript{x} (b) glassy rods with a diameter of 1.5 mm at 0.67 K·s\textsuperscript{-1}.](image-url)
Figure 3 shows anodic polarization curves for the as-cast 1.5 mm (Cu_{0.6}Zr_{0.3}Ti_{0.1})_{100-x}Ni_{x}Nb_{y} and (Cu_{0.6}Hf_{0.25}Ti_{0.15})_{100-x}Ni_{x}Nb_{y} glassy alloys in 3 mass% NaCl solution at 298 K \[^{[16,17]}\]. It is clearly seen that the alloys with and without Ni exhibit different polarization behaviors. The alloys without Ni suffer general corrosion. However, the alloys containing Ni are spontaneously passivated with low passive current density, although they suffer pitting corrosion by anodic polarization. Moreover, their pitting corrosion potentials are nobler with an increase in Ni and Nb contents. In particular, the simultaneous addition of Ni and Nb to the alloys is beneficial for enhancing the pitting corrosion potential against localized corrosion in chloride-ion-containing solutions. Accordingly, the coexistence of Ni and Nb elements leads to the reduction of pitting susceptibility and the improvement of pitting corrosion resistance of the Cu-Zr(Hf)-Ti-Ni-Nb alloys. It is believed that (Cu_{0.6}Hf_{0.25}Ti_{0.15})_{100-x}Ni_{x}Nb_{y} alloy exhibits the highest pitting corrosion potential in comparison with the other Cu-based BMGs, such as Cu-Zr(Hf)-Ti-(Mo, Nb, Ta) and Cu-Zr-Ti-Ni-Nb alloys \[^{[12-14,16,17]}\]. XPS measurements revealed that the highly protective Zr-, Ti- and Nb-enriched surface film is formed by the rapid initial preferential dissolution of Cu and Ni, which is able to separate the bulk of the alloy from the corrosive solutions.

**Table 1.** Thermal properties and critical diameters \((d_c)\) of glassy alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(T_e) (K)</th>
<th>(T_i) (K)</th>
<th>(\Delta T_e) (K)</th>
<th>(T_i) (K)</th>
<th>(T_i/T_e)</th>
<th>(d_c) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_{0.6}Zr_{0.3}Ti_{0.1}</td>
<td>719</td>
<td>759</td>
<td>40</td>
<td>1170</td>
<td>0.61</td>
<td>4.0</td>
</tr>
<tr>
<td>(Cu_{0.6}Zr_{0.3}Ti_{0.1})<em>{0.5}Ni</em>{5}</td>
<td>727</td>
<td>787</td>
<td>60</td>
<td>1198</td>
<td>0.61</td>
<td>3.0</td>
</tr>
<tr>
<td>(Cu_{0.6}Zr_{0.3}Ti_{0.1})<em>{0.5}Ni</em>{1}</td>
<td>735</td>
<td>791</td>
<td>56</td>
<td>1225</td>
<td>0.60</td>
<td>2.5</td>
</tr>
<tr>
<td>(Cu_{0.6}Zr_{0.3}Ti_{0.1})<em>{0.5}Ni</em>{1}</td>
<td>728</td>
<td>778</td>
<td>50</td>
<td>1204</td>
<td>0.61</td>
<td>3.0</td>
</tr>
<tr>
<td>(Cu_{0.6}Zr_{0.3}Ti_{0.1})<em>{0.5}Ni</em>{1}</td>
<td>730</td>
<td>776</td>
<td>46</td>
<td>1209</td>
<td>0.60</td>
<td>3.0</td>
</tr>
<tr>
<td>(Cu_{0.6}Zr_{0.3}Ti_{0.1})<em>{0.5}Ni</em>{1}</td>
<td>735</td>
<td>775</td>
<td>40</td>
<td>1214</td>
<td>0.60</td>
<td>2.5</td>
</tr>
<tr>
<td>Cu_{0.6}Hf_{0.25}Ti_{0.15}</td>
<td>745</td>
<td>805</td>
<td>60</td>
<td>1182</td>
<td>0.63</td>
<td>4.0</td>
</tr>
<tr>
<td>(Cu_{0.6}Hf_{0.25}Ti_{0.15})<em>{0.5}Ni</em>{5}</td>
<td>752</td>
<td>822</td>
<td>70</td>
<td>1236</td>
<td>0.61</td>
<td>2.0</td>
</tr>
<tr>
<td>(Cu_{0.6}Hf_{0.25}Ti_{0.15})<em>{0.5}Ni</em>{5}</td>
<td>751</td>
<td>815</td>
<td>64</td>
<td>1220</td>
<td>0.62</td>
<td>3.0</td>
</tr>
<tr>
<td>(Cu_{0.6}Hf_{0.25}Ti_{0.15})<em>{0.5}Ni</em>{5}</td>
<td>753</td>
<td>800</td>
<td>47</td>
<td>1215</td>
<td>0.62</td>
<td>3.0</td>
</tr>
<tr>
<td>(Cu_{0.6}Hf_{0.25}Ti_{0.15})<em>{0.5}Ni</em>{5}</td>
<td>753</td>
<td>793</td>
<td>40</td>
<td>1228</td>
<td>0.61</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Fig. 3:** Anodic polarization curves of as-cast \((Cu_{0.6}Zr_{0.3}Ti_{0.1})_{100-x}Ni_{x}Nb_{y}\) (a) and \((Cu_{0.6}Hf_{0.25}Ti_{0.15})_{100-x}Ni_{x}Nb_{y}\) (b) glassy rods in 3 mass% NaCl solutions at 298 K.

### 1.2 Cu-based BMG composites with high corrosion resistance and excellent mechanical properties

Due to their high strength in excess of 2000 MPa and high glass forming ability, Cu-based BMGs are considered to have many potential applications as advanced engineering materials, such as surgical instruments and bipolar plates in fuel cells \[^{[7-11]}\]. Unfortunately, like conventional amorphous alloys, Cu-based BMGs fail due to the formation of highly localized shear band, which leads to catastrophic failure without much macroscopic plasticity. This inhomogeneous deformation behavior has seriously limited the application of BMGs as an engineering material so far. To solve this problem, there have been various attempts to produce reinforced BMGs \[^{[14-21]}\], by partial crystallization, particle reinforcements or in situ formation of ductile body-centered cubic (bcc)-phase precipitates. As a result, a new class of materials, i.e. BMG composites, combining ceramic-like strength with metal-like ductility has...
been produced.

Considering industrial and environmental applications, the (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{94}$Ta$_6$ [22] and (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{90}$Nb$_{10}$ BMG composite [23-24] with excellent combination of high corrosion resistance and superior mechanical properties was successfully synthesized. The XRD pattern [Fig. 4(a)] of the Ta/Nb-containing alloy exhibited a broad halo peak superimposed with the sharp diffraction peaks, indicating that Ta/Nb-rich solid solution precipitated in the glassy matrix. Figure 4(b) and (c) show the microstructure of the as-cast Φ2 mm (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{94}$Ta$_6$ and (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{90}$Nb$_{10}$ alloys. The Ta/Nb-rich solid solution phase with the dendritic structure disperses homogeneously in the glassy matrix. The volume fraction and mean size of the dendrite bcc phase are about 11% and 15 µm, respectively, for the (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{94}$Ta$_6$ alloy, and about 8% and 5–10 µm, respectively, for (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{90}$Nb$_{10}$ alloys.

Figure 4: XRD patterns of as-cast 2 mm diameter Cu-Hf-Ti-(Ta/Nb) glassy alloys (a) and SEM images of central region in transverse cross section of the as-cast (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{94}$Ta$_6$ (b) and (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{90}$Nb$_{10}$ (c) alloy rods

Figure 5(a) shows compressive stress-strain curves of the as-cast Φ2 mm (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{100-x}$Ta$_x$ (x = 0 and 6at.%) alloys and (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{90}$Nb$_{10}$ in a uniaxial compression at room temperature (298 K) [25]. Young’s modulus (E), compressive yield strength ($\sigma_{y}$), compressive fracture strength ($\sigma_{f}$) and compressive plastic strain ($\varepsilon_{p}$) are 124 GPa, 2010 MPa, 2160 MPa and 1.6%, respectively, for the Ta-free alloy [26], 104 GPa, 2125 MPa, 3325 MPa and 34%, respectively, for the Ta-reinforced alloy [22] and 106 GPa, 2248 MPa, 2625 MPa and 12.5%, respectively, for Nb-reinforced alloy [23,24]. Apparently, for the Ta- and Nb-reinforced alloys, the combination of strength and plasticity is superior to that for the Cu$_{60}$Hf$_{25}$Ti$_{15}$ glassy single phase alloy.

Figure 5(b) shows the outer shape and deformation structure on the outer surface of the as-cast Φ2 mm (Cu$_{0.6}$Hf$_{0.25}$Ti$_{0.15}$)$_{100-x}$Ta$_x$ composite alloy after compression test. It is seen that the final fracture occurs along the maximum shear stress plane which is declined by about 40° to the direction of applied load (as inset in Fig. 5b), and a large number of the shear bands distribute homogeneously throughout the surface of the specimen, reflecting the significantly improved plastic strain in the composite. The shear bands observed in the composite sample are characterized as being straight, wavy or twisting. In general, plastic deformation of glassy single phase alloys is highly localized into shear bands, followed by the rapid propagation of these shear bands and sudden fracture. For the Cu-Hf-Ti-(Ta/Nb) mixed structure composite with ductile dendrites, during the propagation of shear bands under loading,
the shear bands must interact with the micro-scale ductile dendrites and deflect their propagating direction, and result in the shear band branching. At the same time, the shear bands are also blocked or branched by other intersected shear bands. Thus, the increase in compressive strain-to-failure is due to the ductile dendrites restricting shear band propagation, promoting the generation of multiple shear bands.

The average corrosion rates of the as-cast (Cu_{60}Hf_{25}Ti_{15})_{0-6}Ta_{x} (x = 0–6 at.%) and (Cu_{60}Hf_{25}Ti_{15})_{0-6}Nb_{x} alloys immersed in 1 N HCl, 3mass% NaCl and 1 N H_{2}SO_{4} + 0.01 N NaCl solutions, respectively, at 298 K open to air for one week are shown in Fig. 6. The corrosion rates of an industrial brass (60wt.% Cu + 40wt.% Zn) in those solutions are also displayed for comparison. The corrosion rate less than 1×10^{-3} mm·y^{-1} is out of detectable limits for the present measurements, and hence is taken as zero in the figure. It can be clearly seen that the addition of Ta or Nb to the Cu-Hf-Ti alloy results in a significant decrease in the corrosion rates in all the solutions examined, despite the fact that the BMG composites consist of micrometer-sized dendrite phase in glassy matrix. Moreover, the corrosion resistance of the Ta/Nb-containing Cu-based BMG composites is better than that of industrial brass. Therefore, the Cu-based BMG composite with its good ductility and high strength together with high corrosion resistance will be highly promising as new advanced engineering materials.

2 Development of ultra-high corrosion resistant Ni-based glassy alloys at high temperature

The Ni-Nb-based bulk glassy alloys with high strength of over 3000 MPa and large supercooled liquid region ΔT_g and excellent corrosion resistance in aggressive acids have been developed in 2002. In a supercooled liquid region, they can be fabricated into intricate shapes with a high level of dimensional accuracy. Hence, the high corrosion resistance together with easy forming ability in the viscous state lead to outstanding application potentials in place of traditional crystalline metals in some fields.

2.1 High corrosion resistant Ni-based glassy alloys as bipolar plate materials in fuel cell environments

High fabrication cost of conventional graphite bipolar plates of fuel cells is pushing the automobile industry to seek for alternatives. For this purpose, Ni_{60}Nb_{20-Ta_{x}Ti_{15}}Zr_{5} (x = 0, 5, 15 and 20at.%) and Ni_{60}Nb_{20-Ta_{x}Ti_{15}} (x = 0, 5, 15 and 25at.%) glassy alloys with high thermal stability and high corrosion resistance were developed successfully using the melt spinning technique. The DSC curves of the melt-spun Ni_{60}Nb_{20-Ta_{x}Ti_{15}}Zr_{5} and Ni_{60}Nb_{20-Ta_{x}Ti_{15}} alloys are shown in Fig. 7. In this figure, T_g and T_x correspond to glass transition temperature and onset temperature of crystallization, respectively. All the Ni-based glassy alloys show a distinct glass transition, followed by a large supercooled liquid region prior to crystallization. The glass transition temperature (T_g) and crystallization temperature (T_x) increase with an increase in the Ta content of the alloys. At the same time, the supercooled liquid region (ΔT = T_x–T_g) increases with an increase in tantalum content. Thus, the substitution of tantalum for niobium causes an extension of ΔT_g from 52 K for Ni_{60}Nb_{20-Ta_{5}Ti_{15}Zr_{5}} to 67 K for Ni_{60}Nb_{20-Ta_{15}Ti_{15}Zr_{5}} and from 47 K for Ni_{60}Nb_{20-Ta_{5}Ti_{15}} to 58 K for Ni_{60}Nb_{20-Ta_{15}Ti_{15}}, respectively. It can be concluded that the addition of tantalum to Ni-Nb-Ti-Zr and Ni-Nb-Ta alloys is effective for increasing the thermal stability of the supercooled liquid phase. A larger supercooled liquid region and a higher stability of the supercooled liquid phase are useful for the superplastic processing of these alloys in the supercooled liquid state to produce, for example, bipolar plates for fuel cells.

The fuel cell environment can be simulated by an H_{2}SO_{4} solution with pH of 2 and containing a small amount of chloride or fluoride of the order of 500 ppm at a high temperature of 353 K. All the Ni-based glassy alloys are spontaneously passivated in wide passive regions and at low passive current densities in H_{2}SO_{4} solution (pH = 2) at 353 K. Increasing Ta content of the alloys results in a decrease in the passive current density and thus an improvement in corrosion resistance. An example of the polarization curves of the Ni_{60}Nb_{20-Ta_{x}Ti_{15}Zr_{5}} alloys in H_{2}SO_{4} solution (pH = 2) at 353 K is shown in Fig. 8(a). In addition, the Ni-Nb-Ta-Ti-(Zr) alloys maintain their high corrosion resistance even after the addition of 500 ppm NaCl in the solution. No pitting corrosion due to the existence of chloride ions is observed during the anodic polarization up to 1.4 V vs. Ag/AgCl. On the contrary, the polarization curve of SUS316L stainless steel undergoes an active-passive transition with a narrow passive region until the transpassive dissolution of chromium occurs. Therefore, Ni-Nb-Ta-Ti-(Zr) glassy alloys with nobler open-circuit
potentials and a wider passive region exhibit much better corrosion resistance than SUS316L stainless steel in H$_2$SO$_4$ (pH = 2) and H$_2$SO$_4$+500 ppm NaCl (pH = 2) solutions at 353 K. On the other hand, in the H$_2$SO$_4$+500 ppm NaF solution (pH = 2) at 353 K, the alloys without Ta and with 5at.% Ta suffer general corrosion, while the passive current densities decrease by about two orders of magnitude with the addition of 15at.%-20at.% Ta to the Ni-based glassy alloys [Fig. 8(b)]. This indicates that the effect of the addition of tantalum (Ta) is more pronounced for improving the corrosion resistance in fluoride containing solutions than the other two types of solutions. Table 2 summarizes the average passive current densities of the Ni$_{60}$Nb$_{20-x}$Ta$_x$Ti$_{15}$Zr$_5$ and Ni$_{60}$Nb$_{25-x}$Ta$_x$Ti$_{15}$ glassy alloys obtained from their anodic polarization curves in pH 2 H$_2$SO$_4$, pH 2 H$_2$SO$_4$+500 ppm NaCl and pH 2 H$_2$SO$_4$+500 ppm NaF solutions at 353 K. The changes in the corrosion behavior with tantalum content and solutions examined are clearly visible in this table.

2.2 High corrosion resistant Ni-based glassy alloys in boiling nitric acid solutions for nuclear fuel reprocessing applications

Reprocessing of spent nuclear fuel involves use of nitric acid of high concentrations and high temperatures. The boiling nitric acid also contains small amounts of other ions such as Cr$^{6+}$, Ag$^{2+}$, Ce$^{4+}$, Cr$_2$O$_7^{2-}$, etc. Therefore, the materials for fabrication of reprocessing plant equipment should possess excellent corrosion resistance. Conventional materials such as AISI 304L stainless steel and even nitric acid grade stainless steel Uranus 65 do not have enough corrosion resistance [30]. This work presented high corrosion resistant Ni-based glassy alloys in severe environments, i.e. boiling 6 N (or 9 N) HNO$_3$ solutions with and without 5 g·L$^{-1}$ Cr$^{6+}$, for nuclear fuel reprocessing applications. Table 3 lists the average corrosion rates of the glassy alloys immersed in boiling 9 N HNO$_3$ and boiling (9 N HNO$_3$,
characteristics in boiling 6 N HNO₃ on the Ni element show the best corrosion resistance. Then, we focused on the environments. In addition, Ni-valve metal alloys containing Ta is effective in improving corrosion resistance in such severe metal alloy systems, it is found that the addition of 5 at.% Ta for 147 h. On the other hand, the Ni-based glassy alloys exhibit much better corrosion resistance as compared to the Ni-Cr-metalloid and Ni-valve alloys are about 0.0048 and 0.0034 mm·y⁻¹, respectively, which are about one order of magnitude lower than that of NAR-310Nb stainless steel, 0.022 mm·y⁻¹. In boiling Cr⁶⁺ containing solution, the corrosion rate for the Ni₆₀Nb₂₀Zr₁₅Ta₅ alloy is 0.031 mm·y⁻¹ and decreases to about 0.012 mm·y⁻¹ for the Ni₆₀Nb₁₀Zr₁₅Ta₄ alloy. On the other hand, NAR-310Nb stainless steel dissolves completely within 44 h, which corresponds to a very high corrosion rate of 23.74 mm·y⁻¹. These facts clearly indicate the superiority of the present Ni-based glassy alloys. Therefore, it can be concluded that Ni-based glassy alloys have much higher corrosion resistance than NAR-310Nb stainless steel in nitric acid of high concentration at high temperature. In particular, the Ni₆₀Nb₂₀Zr₁₅Ta₄ alloy with easy formability in the supercooled liquid region shows great potential as a new engineering material for nuclear fuel reprocessing applications.

It is important to clarify the surface compositions together with the chemical states for elucidation of the origin of the high corrosion resistance for these Ni-based glassy alloys. XPS analysis was applied to the Ni₆₀Nb₂₀Zr₁₅Ta₄ specimens as-polished mechanically in cyclohexane or immersed in boiling 6 N HNO₃, and boiling (9 N HNO₃+5 g·L⁻¹ Cr⁶⁺) solutions at 397 K open to air.

Table 2: Average passive current densities of Ni-based glassy alloys determined from their anodic polarization curves in different solutions at 353 K

<table>
<thead>
<tr>
<th>Alloys</th>
<th>pH 2 H₂SO₄</th>
<th>pH 2 H₂SO₄+500 ppm NaCl</th>
<th>pH 2 H₂SO₄+500 ppm NaF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₆₀Nb₂₀Zr₁₅Ta₅</td>
<td>0.046</td>
<td>0.061</td>
<td>7.582*</td>
</tr>
<tr>
<td>Ni₆₀Nb₂₀Ta₁₀Zr₁₅</td>
<td>0.036</td>
<td>0.049</td>
<td>2.531*</td>
</tr>
<tr>
<td>Ni₆₀Nb₁₀Zr₁₅Ta₄</td>
<td>0.022</td>
<td>0.027</td>
<td>0.115</td>
</tr>
<tr>
<td>Ni₆₀Zr₁₅Ta₁₀</td>
<td>0.017</td>
<td>0.023</td>
<td>0.075</td>
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<tr>
<td>Ni₆₀Nd₂₀Zr₁₅</td>
<td>0.038</td>
<td>0.042</td>
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<tr>
<td>Ni₆₀Nb₂₀Ta₁₀</td>
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<td>0.033</td>
<td>0.460*</td>
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<tr>
<td>Ni₆₀Nb₁₀Ta₁₀Ta₂₀</td>
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<td>0.022</td>
<td>0.048</td>
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<tr>
<td>Ni₆₀Ta₂₀Ta₁₀</td>
<td>0.015</td>
<td>0.016</td>
<td>0.014</td>
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</table>

*Current density

Table 3: Average corrosion rates (mm·y⁻¹) of glassy alloys in boiling 9 N HNO₃, and boiling (9 N HNO₃+5 g·L⁻¹ Cr⁶⁺) solutions at 397 K open to air

<table>
<thead>
<tr>
<th>Samples</th>
<th>Boiling 9 N HNO₃</th>
<th>Boiling (9 N HNO₃+5 g·L⁻¹ Cr⁶⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₆₀Cr₁₂P₅M₆B₄</td>
<td>1.40</td>
<td>0.46</td>
</tr>
<tr>
<td>Ni₆₀Cr₆P₅B₁₀Ta₅</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>Ni₆₀Nb₁₀Zr₁₅</td>
<td>0.23</td>
<td>0.27</td>
</tr>
<tr>
<td>Ni₆₀Nb₂₀Zr₃₀</td>
<td>0.01</td>
<td>0.033</td>
</tr>
<tr>
<td>Ni₆₀Nb₁₀Zr₁₅Ta₅</td>
<td>0.01</td>
<td>0.024</td>
</tr>
<tr>
<td>Fe₅₀Cr₁₅Mo₅C₁₀B₄</td>
<td>87.94</td>
<td>1.18</td>
</tr>
<tr>
<td>Fe₅₀Cr₁₅Mo₅C₆B₆Ta₅</td>
<td>74.89</td>
<td>1.03</td>
</tr>
</tbody>
</table>

+ 5 g·L⁻¹ Cr⁶⁺ solutions, open to air for 1 week. The Fe based glassy alloys dissolved rapidly within 2 h in boiling 9 N HNO₃ solution, while the Fe-based alloys dissolved completely after immersion in boiling 9 N HNO₃ + 5 g·L⁻¹ Cr⁶⁺ solution for 147 h. On the other hand, the Ni-based glassy alloys exhibit much better corrosion resistance as compared to the Fe-based glassy alloys. For the Ni-Cr-metalloid and Ni-valve metal alloy systems, it is found that the addition of 5 at.% Ta is effective in improving corrosion resistance in such severe environments. In addition, Ni-valve metal alloys containing Ta element show the best corrosion resistance. Then, we focused on the Ni₆₀Nb₁₀Zr₁₅Ta₄ and Ni₆₀Nb₁₀Zr₁₅Ti₁₅Ta₄ glassy alloys to further investigate their corrosion resistance and surface characteristics in boiling 6 N HNO₃ solutions.

Figure 9 shows the corrosion rates of the Ni₆₀Nb₁₀Zr₁₅Ta₅ and Ni₆₀Nb₁₀Zr₁₅Ti₁₅Ta₄ glassy alloys immersed in boiling 6 N HNO₃, and boiling (6 N HNO₃ + 5 g·L⁻¹ Cr⁶⁺) solutions, open to air for 2 weeks. For comparison, the stainless steel NAR-310Nb, which is known for high corrosion resistance in nitric acid, is also examined in the same solutions. The temperature in both solutions is as high as about 385 K. After immersion in boiling 6 N HNO₃ solution for 2 weeks, both of the Ni-based glassy alloys maintained their previous metallic luster, whereas some cracks resulting from grain boundary attack were observed in the corroded surface for NAR-310Nb stainless steel. The corrosion rates of the Ni₆₀Nb₁₀Zr₁₅Ta₄ and Ni₆₀Nb₁₀Zr₁₅Ti₁₅Ta₄ alloys are about 0.0048 and 0.0034 mm·y⁻¹, respectively, which are about one order of magnitude lower than that of NAR-310Nb stainless steel, 0.022 mm·y⁻¹. In boiling Cr⁶⁺ containing solution, the corrosion rate for the Ni₆₀Nb₁₀Zr₁₅Ta₄ alloy is 0.031 mm·y⁻¹ and decreases to about 0.012 mm·y⁻¹ for the Ni₆₀Nb₁₀Zr₁₅Ti₁₅Ta₄ alloy. On the other hand, NAR-310Nb stainless steel dissolves completely within 44 h, which corresponds to a very high corrosion rate of 23.74 mm·y⁻¹.
boiling 6 N HNO₃ and boiling (6 N HNO₃ + 5 g L⁻¹ Cr⁶⁺) solutions for 2 weeks. The XPS spectra of the specimens over a wide binding energy region exhibited peaks of Ni 2p, Nb 3d, Zr 3d, Ti 2p, Ta 4f, Cr 2p, O 1s, C 1s etc [31]. Figure 10 shows cationic concentration (%) of surface films formed on the Ni₈Nb₅Zr₅Ti₅Ta₅ alloy as-polished and immersed in boiling 6 N HNO₃ and boiling (6 N HNO₃ + 5 g L⁻¹ Cr⁶⁺) solutions for 2 weeks [33]. The surface film on the specimen as-polished was formed by air exposure after mechanical polishing. The Ti and Zr cations are enriched in the surface film, whereas Ni cations are largely deficient. On the other hand, the concentrations of Nb and Ta cations slightly change with respect to the alloy composition. This fact reveals that the preferential oxidation of Ti and Zr takes place during air exposure whereas Ni is scarcely oxidized. The major cation in the as-polished surface of Ti and Zr takes place during air exposure whereas Ni is exclusively of Nb and Ta cations. The XPS spectra of the specimens over 2 weeks after mechanical polishing revealed that the air-formed film was not stable in boiling 6 N HNO₃ or Cr⁶⁺ solutions open to air for 2 weeks. The XPS spectra of the specimens over 2 weeks exhibited peaks of Ni 2p, Nb 3d, Zr 4f, Ta 5d and Nb 3d + 2p + 5d. Furthermore, after immersion in 3 mass% NaCl, 1 N HCl solutions open to air at 298 K were measured. Those for SUS316L and SUS304 stainless steel of fabrication. During 1998 to 2004, several Ti-based BMGs have been developed, including Ti-Ni-Cu-Sn [32] and Ti-Zr-Cu-Ni-(Sn, Zr, Be) BMGs systems [32,34], etc. However, all the alloys contained Ni because only the addition of the Ni helped to improve their glass-forming ability. It has been noticed that pure Ni is a toxic element and causes Ni-hypersensitivity. So, it was a big challenge to develop a Ni-free Ti-based BMG for biomedical applications. In 2007, success was achieved in the development of a new Ni-free Ti-based BMG, i.e. Ti₈Zr₅Pd₁₀Cu₁₀Sn₁ [31]. The Ti₈Zr₅Pd₁₀Cu₁₀Sn₁ BMG possessed high strength of 1970 MPa and low Young’s modulus of 95 GPa, together with good corrosion resistance in simulated body fluids [4]. In addition, the Ti₈Zr₅Pd₁₀Cu₁₀Sn₁ BMG shows promise in applications in the industrial field as well as in biomaterials. For application in industrial use, the alloy must have a good corrosion resistance and electrochemical stability in industrial environments where the conditions are more severe in comparison to biomaterial environments. So, this work aimed to investigate the corrosion behavior of the alloy in various corrosive solutions in order to obtain basic knowledge for industrial application. X-ray photoelectron spectroscopy is used to clarify the origin of high corrosion resistance of the alloy. 3 Electrochemical properties and XPS analysis of a Ni-free Ti-based BMG Among BMG systems developed so far, Ti-based BMGs are particularly interesting and show commercial potential as structural and functional materials in some fields due to the combination of superior strength, low Young’s modulus, and excellent corrosion resistance as well as relatively low cost of fabrication. During 1998 to 2004, several Ti-based BMGs have been developed, including Ti-Ni-Cu-Sn [32] and Ti-Zr-Cu-Ni-(Sn, Zr, Be) BMGs systems [32,34], etc. However, all the alloys contained Ni because only the addition of the Ni helped to improve their glass-forming ability. It has been noticed that pure Ni is a toxic element and causes Ni-hypersensitivity. So, it was a big challenge to develop a Ni-free Ti-based BMG for biomedical applications. In 2007, success was achieved in the development of a new Ni-free Ti-based BMG, i.e. Ti₈Zr₅Pd₁₀Cu₁₀Sn₁ [31]. The Ti₈Zr₅Pd₁₀Cu₁₀Sn₁ BMG possessed high strength of 1970 MPa and low Young’s modulus of 95 GPa, together with good corrosion resistance in simulated body fluids [4]. In addition, the Ti₈Zr₅Pd₁₀Cu₁₀Sn₁ BMG shows promise in applications in the industrial field as well as in biomaterials. For application in industrial use, the alloy must have a good corrosion resistance and electrochemical stability in industrial environments where the conditions are more severe in comparison to biomaterial environments. So, this work aimed to investigate the corrosion behavior of the alloy in various corrosive solutions in order to obtain basic knowledge for industrial application. X-ray photoelectron spectroscopy is used to clarify the origin of high corrosion resistance of the alloy.

3.1 Corrosion rates in various solutions

The average corrosion rates of the as-cast 2.5 mm diameter Ti₈Zr₅Pd₁₀Cu₁₀Sn₁ BMG immersed in different solutions open to air at 298 K were measured. Those for SUS316L and SUS304 stainless steel samples were also examined for comparison. In 1 N HCl solution, a SUS304 stainless steel was dissolved actively, showing a very high corrosion rate of 4.5 mm·y⁻¹ on average for a week immersion. The corrosion rate of a SUS316 stainless steel was about 0.28 mm·y⁻¹. On the other hand, the corrosion rate of the Ti-based alloy was about 0.046 mm·y⁻¹, which was about one or two orders of magnitude lower than those of stainless steel samples. Accordingly, it is clear that the Ti-based BMG has much higher corrosion resistance than stainless steels in strong corrosive environment. Furthermore, after immersion in 3 mass% NaCl, 1 N H₂SO₄ or 1 N H₂SO₄ + 0.01 N NaCl solutions open to air at 298 K for 2 months, the weight loss of all the Ti-based BMG samples was undetectable, indicating that the Ti₈Zr₅Pd₁₀Cu₁₀Sn₁ BMG possesses excellent corrosion resistance in 3 mass% NaCl, 1 N H₂SO₄ and 1 N H₂SO₄ + 0.01 N NaCl solutions.

Fig. 10: Cationic concentration (%) of surface film formed on Ni₈Nb₅Zr₅Ti₅Ta₅ alloy exposed to air and samples immersed in boiling 6 N HNO₃ and boiling (6 N HNO₃ + 5 g L⁻¹ Cr⁶⁺) solutions open to air for 2 weeks after mechanical polishing.
3.2 Electrochemical properties in sulfuric acids

Figure 11 shows the anodic polarization curves of the as-cast Ti_{45}Zr_{10}Pd_{10}Cu_{31}Sn_{4} BMG rods with a diameter of 2.5 mm and a SUS316L stainless steel in 1 N H_2SO_4 and 1 N H_2SO_4 + 0.01 N NaCl solutions, respectively, open to air at 298 K \cite{36}. The polarization curves of the Cu-based BMGs are also shown for comparison in those solutions at the same conditions. The alloy is passivated with a significant low current density of the order of 10^{-2} A·m^{-2} and a wide passive potential region in sulfuric acids with and without Cl- ions. According to their polarization curves, it is interesting to note that the Ti-based BMG exhibits unique polarization characteristics in sulfuric acid solutions with and without 0.01 N NaCl as compared to the Cu-based alloys and a SUS316L. One feature of interest is that the Ti-based alloy demonstrates a very noble open circuit potential, which is related to an increase in the difficulty for anodic oxidation reaction of the alloy. The open circuit potentials of the alloy were about 136 mV, 452 mV and 248 mV (vs. Ag/AgCl) in NaCl, H_2SO_4 and H_2SO_4 + NaCl solutions, respectively. This is in accord with their high corrosion resistance during open circuit immersion of long duration. The presence of a noble element, Pd, in the alloy helps to enable the open circuit potential due to its high cathodic activity.

Another interesting feature is that the Ti-based alloy shows a highly stable passivation in high potential region, whereas the Cu-based alloys are slowly dissolved and a SUS316L displays a high transpassive dissolution current density at the same potential region. Therefore, the Ti_{45}Zr_{10}Pd_{10}Cu_{31}Sn_{4} BMG with its high corrosion resistance and unique electrochemical properties has significant potential not only for human body implant applications, but also for structural uses in industry.

![Fig. 11: Anodic polarization curves of as-cast 2.5 mm diameter Ti_{45}Zr_{10}Pd_{10}Cu_{31}Sn_{4} alloy rods measured in 1 N H_2SO_4 (a) and 1 N H_2SO_4 + 0.01 N NaCl (b) solutions open to air at 298 K. Polarization curves of SUS316L stainless and Cu-based alloys are also shown for comparison.](image)

3.3 XPS analysis

In order to clarify the surface-related chemical characteristics of the alloy, XPS analysis was performed for the specimens as-polished mechanically in cyclohexane or immersed for 168 h in 1 N HCl, 3 mass% NaCl, 1 N H_2SO_4 and 1 N H_2SO_4 + 0.01 N NaCl solutions. The XPS spectra of the specimens over a wide binding energy region exhibited peaks of Ti 2p, Pd 3d, Zr 3d, Cu 2p, Sn 3d, O 1s, C 1s etc. The deconvolution spectrum peaks from alloy constituents were composed of peaks of oxidized states and metallic states. The oxidized states (ox) and metallic states (m) are assigned to signals from the surface film and underlying alloy surface just beneath the surface film, respectively. By XPS analysis, the major cation in the immersed surface film is Ti^{4+} and followed by Zr^{4+}, Cu^{2+}, Cu^{4+} and Sn^{4+}.

Figure 12 shows the cationic fraction of elements in the surface film and the atomic fraction of elements in the underlying alloy just below the surface film for the alloys after air exposure and immersion for 168 h in various solutions after mechanical polishing, respectively \cite{[190]. Immersion for 168 h in different solutions gives rise to the formation of a new film which is different from the air-formed film. When the alloy is immersed in various solutions, the fractions of Ti and Zr cations in the surface film increase as compared with air-formed surface composition, whereas the contents of Cu and Sn cations decrease. Therefore, the high corrosion resistance of the alloy is attributed to its chemically homogeneous single phase nature and the formation of Ti^{4+} and Zr^{4+}-enriched highly protective thin surface film in corrosive solutions. The new Ti-based BMG with excellent corrosion resistance and unique electrochemical properties is very promising as a new advanced engineering material.

4 Conclusions

This work reviews the development of the Cu-, Ni-, Ti-based metallic glasses/composites and their unique properties. The results obtained are summarized as follows:

(1) Bulk metallic glasses (BMGs) with critical diameters of 2.0–4.0 mm were synthesized in the (Cu_{x+y}Zr_{y}Ti_{x}Nb_{1-x})_{100-y}Ni_{y}Nb_{x} (x = 0–6 at.% and y = 0–7 at.%) and (Cu_{x+y}Hf_{x}Ti_{x}Nb_{1-x})_{100-y}Ni_{y}Nb_{x}
Cu-Ti-NaCl glasses demonstrate high corrosion resistance in boiling 6 N HCl from 60 K for Cu60-xTa50-x alloy systems by the copper mold casting method. The addition of Ni element causes an extension of a supercooled liquid region (ΔTg = Tm − Ts) from 40 K for Cu60-xTa50-xTi10 to 60 K for (Cu60-xTa50-xZr15)0.5Ni0.5 and from 60 K for Cu60-xTa50-xTi15 to 70 K for (Cu60-xTa50-xZr15)0.5Ni0.5. The simultaneous addition of Ni and Nb to the Cu-Zr(Hf)-Ti alloys is effective for synergistically improving the corrosion resistance of the alloys by remarkably decreasing the anodic current densities in chloride containing solutions and enhancing the pitting potential against the localized corrosion.

(2) In-situ Ta/Nb-reinforced (Cu0.8Hf0.125Ta0.125)0.6Ta0.4 and (Cu0.8Hf0.125Ti0.125)0.6Ti0.4 BMG composites with excellent combination of high corrosion resistance and superior mechanical properties was successfully synthesized. The micrometer-sized ductile Ta/Nb-rich dendrite phase disperses homogeneously in the glassy matrix. The addition of Ta/Nb to the Cu-Hf-Ti alloy results in a significant decrease in the corrosion rates in the solutions examined. The Ta-reinforced composite alloy exhibits high compressive true yield strength of 2,125 MPa, fracture strength of 3325 MPa together with large plastic strain of 34%.

(3) Ni0.6Nb0.4Ta0.1Ti1.5 (x = 0, 5, 15 and 20 at.%) and Ni0.6Nb0.4Ta0.2Zr0.5Ti1.5 (x = 0, 5, 15 and 25 at.%) glassy alloys with high thermal stability and ultra-high corrosion resistance in fuel cell environments at high temperature were developed successfully by the melt spinning technique. The substitution of tantalum for a portion of niobium in the alloys causes a significant increase in the supercooled liquid region. These alloys have great potential application as bipolar plate materials of fuel cells.

(4) The Ni0.6Nb0.4Zr0.5Ta0.5 and Ni0.6Nb0.4Zr0.5Ti0.5Ta0.5 metallic glasses demonstrate high corrosion resistance in boiling 6 N HNO3 solutions with and without Cr3+ ions, which may be of great potential for nuclear fuel reprocessing applications. X-ray photoelectron spectroscopy analysis reveals that the high corrosion resistance of the alloys is due to the formation of the passive film composed exclusively of Nb5+ and Ta5+ cations after immersion in the solution without Cr6+ ions, and Nb5+, Ta5+ and Cr3+ cations after immersion in the solution with Cr6+ ions.

(5) The Ni-free Ti40Zr19Pd10Cu31Sn4 BMG exhibits excellent corrosion resistance after immersion in 3mass% NaCl, 1 N H2SO4 and 1 N H2SO4 + 0.01 N NaCl solutions. X-ray photoelectron spectroscopy (XPS) measurements were used to analyze the changes of the elements on the alloy surface before and after immersion in various solutions. The formation of Ti- and Zr-enriched highly protective thin surface film is responsible for high corrosion resistance of the alloy in the corrosive solutions.

References


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