Electrochemical Properties of Porous Pd-Based Bulk Metallic Glasses

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The corrosion behavior of porous Pd₄₂.₅Cu₃₀Ni₇.₅P₂₀ bulk metallic glasses with various porosities in Hanks’ solution was investigated. The results revealed that all bulk metallic glasses exhibited similar corrosion behavior. The bulk metallic glasses with the porosity of 0 and 18% were spontaneously passivated with passive current densities between 10⁻²⁻ and 10⁻¹ A/m² in anodic polarization curves. The bulk metallic glasses with 40 and 55% porosity exhibited an anodic process with the current density increasing gradually. As the anodic potential increasing, no obvious passivity breakdown occurred in the anodic polarization process. The polarization resistance decreased with the increasing of the porosity from 0 to 55%. The breakdown potential of the passive film for the bulk metallic glass with 55% porosity was about 100 mV lower than that of the 0% porosity Pd₄₂.₅Cu₃₀Ni₇.₅P₂₀ bulk metallic glass.

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1. Introduction

Bulk metallic glasses (BMGs) have been rapidly developed in the past decades for application as functional materials in many fields. In particular, many researchers expect that bulk metallic glasses can be utilized as biomaterials. So far, the highest glass-forming ability (GFA) of BMGs was obtained in the Pd–Cu–Ni–P alloy system with a critical cooling rate of 0.067 K/s for glass formation and a maximum sample diameter of 75 mm, respectively.1–3) The investigations on Pd-based BMGs and their porosity counterparts have been extensively reported.4–7) The elimination of inhomogeneity in atomic configuration caused by optimization to the eutectic composition enhances the GFA and stability of the undercooled melt due to the decrease in the probability of nucleation event.1)

There is also interest in porous/foam BMGs because the porous/foam BMGs have a lower Young’s modulus, a lower yield strength, a much higher absorption energy and no difference in thermal stability was recognized between the porous BMGs and pore-free BMG.5–7) Porous BMG rods with a diameter of 10 mm and porosity of 55–65% were prepared by water quenching of the mixture consisting of Pd–Cu–Ni–P liquid plus NaCl solid, followed by leaching of the NaCl solid in water. The porous Pd–Cu–Ni–P bulk metallic glasses exhibited a yield strength of 75 MPa, an elastic modulus of 5.2 GPa and a large plastic elongation of about 80%.5) Porous Pd–Cu–Ni–P BMGs were also prepared by the high hydrogen pressure melting-water quenching method. The volume fraction of the pores and the size of the pores can be controlled by the temperature of the molten alloy before quenching.6) The authors found that the Young’s modulus and yield strength for the porous BMG rods were much lower comparing with those of the pore-free cast rod, while plastic strain and mechanical energy up to final rupture were larger, indicating that the porous BMG rods are characterized as much ductile and flexible materials. The significant difference in mechanical properties in comparison with those for the pore-free rod was interpreted on the basis of the nearly spherical shape of the pores.6) So far, although many research works have been published, the topics mainly focus on the fabrication, the thermal stability and the mechanical properties of the Pd-based BMGs. The researches on the electrochemical behavior of Pd-based BMGs or porous Pd-based BMGs are relatively rare.8,9)

Conventional Pd alloys have been widely utilized as dental materials. As-cast or porous Pd-based BMGs are also expected to have good corrosion resistance due to their chemical and structural homogeneity, which exhibit a potential in applying as biomaterials. In this research, the electrochemical behavior of various porous Pd₄₂.₅Cu₃₀Ni₇.₅P₂₀ BMGs prepared by high hydrogen pressure melting-water quenching method has been investigated in Hanks’ solution.

2. Experimental Details

Prior to preparing the master alloy, Pd–P binary pre-alloy was prepared using pure Pd (99.9 mass%) metal and pure phosphorous (98 mass%). The master alloy with a nominal atomic composition of Pd₄₂.₅Cu₃₀Ni₇.₅P₂₀ was prepared by arc melting a mixture of Pd–P pre-alloy, Pd, Cu and Ni metals in an argon atmosphere. The Pd–Cu–Ni–P alloy ingot placed in a quartz crucible was evacuated to less than 5 × 10⁻¹ Pa and then heated up to 853 K which was about 50 K above the melting temperature. Then, hydrogen gas of 1.5 MPa was induced into the crucible and the molten alloy was annealed for 600 s so that hydrogen was dissolved into it. After that, the crucible was evacuated and quenched immediately into water. As a result, the porous alloy rods with a diameter of 7 mm and a length of about 50 mm were obtained. The volume fraction and the size of the pore were changed by the temperature of the molten alloy before quenching. The pore-free Pd₄₂.₅Cu₃₀Ni₇.₅P₂₀ rod with a diameter of 7 mm and a length of 50 mm was also produced for comparison by the copper mold casting technique in 0.1 MPa argon atmosphere.

The structure of the porous BMGs was examined by X-ray diffraction (XRD) with Cu Kα radiation and scanning electron microscopy (SEM). The corrosion behavior of the porous BMGs was evaluated by polarization curves and electrochemical impedance spectroscopy (EIS) in a three-
electrode cell using a platinum counter electrode and a saturated calomel reference electrode (SCE). The specimens were covered by resin, and the cross section area was testing area. Prior to corrosion testing, the samples were mechanically polished with silicon carbide papers up to frit 1500, degreased in acetone, washed in distilled water, dried in air and further exposed in air for 24h. The testing for each condition was performed at least three times for reproducibility. The electrolytes used were Hanks’ solution with pH 7.4 at room temperature open to air, which was prepared from reagent grade chemicals and deionized water. The composition of Hanks’ solutions (g/L) is 8.00 NaCl, 0.40 KCl, 0.35 NaHCO₃, 0.19 CaCl₂·2H₂O, 0.09 Na₂HPO₄·7H₂O, 0.20 MgSO₄·7H₂O, 0.06 KH₂PO₄ and 1.00 Glucose. Potentiodynamic polarization curves were measured via an electrochemical interface (Solartron SI1287) with a potential sweep rate of \( 0.83 \times 10^{-3} \text{V s}^{-1} \) after immersing the specimens for 600 s, when the open-circuit potentials became almost steady. EIS measurements were made using a frequency response analyzer (Solartron 1255 B) at open-circuit potential in Hanks’ solution, with a frequency range from \( 10^2 \) to \( 10^{12} \) Hz, and an amplitude perturbation of 10 mV. All the current densities were produced by the apparent surface area.

3. Results and Discussion

Figure 1 shows the XRD patterns of the Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} BMGs with different porosities. It is clear that only a halo peak located at between 38 and 42° appears in the XRD pattern for all of the porous Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} and as-quenched pore-free (0% porosity) BMG, indicating that the porous glasses are in a totally glassy state same as that of the as-quenched 0% porosity BMG. The details of the preparation of porous Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} BMGs were explained in previous works.⁶

Figure 2 shows the SEM morphologies of various porous Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} BMGs. As shown in the figure, the pore size and the volume fraction are different for the BMGs with different porosity. The nearly spherical shape pores with the average sizes of about 6, 16 and 30 µm are observed homogenously distributing in Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} BMG matrix with the increasing of the porosity from 18 to 55%.

The potentiodynamic polarization curves of the 0% porosity Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} BMG and its porous counterparts were measured in Hanks’ solution at room temperature, as shown in Fig. 3. All BMGs exhibit similar corrosion behavior. There is almost no difference in the open-circuit potentials, which depend on the balance of the kinetics between the anodic corrosion reaction of the testing sample and the cathodic supporting reactions. The 0 and 18% porosity BMGs are spontaneously passivated with passive current density between \( 10^{-2} \) and \( 10^{-1} \text{A/m}^2 \) in anodic polarization curves. The BMGs with 40 and 55% porosity exhibit an anodic process with the current density increasing gradually. The passive current density increases one order of magnitude with the increasing of porosity from 0 to 55%, which may partially origin from the larger area affect because the current densities were calculated from the apparent surface area. It should be mentioned that some small current

![Fig. 1 XRD patterns of the various porous Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} BMGs.](image1)

![Fig. 2 SEM morphologies of the various porous Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} BMGs with porosity of 18% (a), 40% (b) and 55% (c).](image2)
peaks appear during anodic polarization process for the BMG with 55% porosity due to larger surface area resulting in an unstable passive film. As the anodic potential increases, no obvious passivity breakdown occurs in the anodic polarization process. At the same time, the approximate onset potential of the localized corrosion for the alloy with 55% porosity is about 100 mV lower than that of the 0% porosity Pd_{42.5}Cu_{30}Ni_{17.5}P_{20} BMG. The surface morphologies of the BMGs with the porosities of 0 and 55% after polarization testing were examined by optical microscopy, as shown in Fig. 4. It is seen that the localized corrosion, i.e., pitting sites, exist at the random on the surface of the 0% porosity BMG. While for the porous BMG, the localized corrosion primarily occurs on the pore regions, in particular on the edge of the pores. On the other hand, the blank areas are immune to the corrosion. It is known that EIS technique is a useful and non-destructive method for explaining corrosion mechanism. Figure 5 shows the Bode plots of various porosities Pd_{42.5}Cu_{30}Ni_{17.5}P_{20} BMGs in Hanks’ solution at open-circuit potential. One single peak is observed in phase vs. frequency plot for the 0% porosity BMG, corresponding to one time constant for the corrosion process between solution and the surface. While two peaks associated with two time constants for the BMGs with various porosities appear, which are solution/surface interface and solution/pores interface. In addition, with the increasing of porosity, impedance absolute values, |Z|, slightly decreases due to the increasing of pore volume fraction.

In general, corrosion of porous metals differs from that of the bulk metals with the same composition. Moreover, the pore morphology, porosity, pore size and pore surface condition influence on the corrosion properties. In the process of corrosion, porous alloys are attacked not only on its surface but also from inside. In addition, the pores in porous materials prepared by hydrogen pressure melting-water quenching method are separated which different from interconnected open porous materials. As mentioned above, in this research, corrosion resistance of various porosities Pd_{42.5}Cu_{30}Ni_{17.5}P_{20} BMGs was studied in Hanks’ solution. A similar corrosion behavior was observed for the 0% porosity Pd_{42.5}Cu_{30}Ni_{17.5}P_{20} BMG and its porous counterparts in polarization curves. Comparing the results for the porous BMGs and pore-free (0% porosity) BMG, it was found a slightly higher susceptibility of porous BMGs than the 0% porosity BMG in Hanks’ solution due to the higher surface area under the attack of chloride ions. The anodic current densities and break down potentials are different for different porosity BMGs. The 0% porosity BMG exhibit the lowest passive current density and has a wider passive region than those of the porous BMGs. The 0% porosity BMG is
uniform in chemical composition and structure, providing more homogeneous, uniform and dense passive film. With the increasing of the porosity, the breakdown potential decreases, i.e., the passive film of the porous BMGs shows a lower chemical stability with lower onset potential of localized corrosion in Hanks’ solution. The porous structure will introduce many small crevices which are conductive to localized corrosion, especially in the internal surfaces of the pores or bottoms of the pores. These sites favor the lowering of pH, accelerating the nucleation and development of pits. Hence the porous structure is qualitatively more susceptible to pitting corrosion than dense structure, which is to a certain extent expected from the larger real surface area.

Furthermore, the polarization resistance is inversely proportional to the general corrosion rate. Figure 6 shows the polarization resistances of the produced porous Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} BMGs with different porosities, which are deduced from the linear sweep voltammetry from 10 mV cathodic to 10 mV anodic to the corrosion potentials. The polarization resistances are decreased with the increasing of the porosity, suggesting the increasing of the corrosion susceptibility. Correspondingly, in Fig. 5, with the decreasing of porosity, the impedance which reflects the restriction of ion diffusion also increases. In addition, the passive current density slowly increases during anodic polarization indicating the passivity breakdown does not occur suddenly, suggesting that the passive film is partially destroyed before obvious pitting corrosion occurs. The slightly increasing in current densities and the decreasing of break down potentials of the passive film with the increasing of porosity are due to the much larger real surface areas for the porous BMGs. The continuous but not sharp increase of the current density in the anodic part of the curve could suggest a corrosion mechanism typical of crevice. While the onset potentials of localized corrosion are over 400 mV higher than open-circuit potentials, suggesting a stable state in nature corrosion for all the BMG samples.

4. Conclusions

The corrosion resistance of porous Pd–Cu–Ni–P BMGs with different porosities in Hanks’ solution was investigated. All BMGs were passivated with passive current density between $10^{-2}$ and $10^{-0}$ A/m² in anodic polarization curves. As the anodic potential increasing, no obvious passivity breakdown occurred in the anodic polarization process for all the BMGs. In addition the polarization resistance and electrochemical impedance decreased with the increasing of porosity from 0 to 55% due to the real surface area increasing for higher porosity BMGs.

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