Microstructure and Electrochemical Behavior of Pd–Cu–Ni–P Bulk Metallic Glass and Its Crystallized Alloys

F. X. Qin*, T. Wada, G. Q. Xie, S. L. Zhu and A. Inoue

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The microstructure and electrochemical behavior of the Pd42.5Cu30Ni7.5P20 as-quenched bulk metallic glass and its crystallized alloys after heat-treatment at 623 and 723 K were investigated. The results revealed that the Pd42.5Cu30Ni7.5P20 bulk metallic glass and its crystallized alloys were spontaneously passivated in 0.144 M NaCl and Hanks’ solution with a low passive current density and a wide passive region. The transpassive potential of the fully crystallized alloy heat-treated at a higher temperature was lower than those of the as-quenched bulk metallic glass and partially crystallized alloy. The difference in the microstructure of the as-quenched bulk metallic glass, the partially crystallized alloy and the fully crystallized alloy was responsible for their different transpassive potentials. The wider passive region of the alloys in Hanks’ solution is attributed to the presence of HCO3−, HPO42−, SO42− and H2PO4− ions in the solution, which act as corrosive inhibitors.

Keywords: microstructure, corrosion, palladium, bulk metallic glass

1. Introduction

The recent rapid developments in bulk metallic glasses reflect the high expectations for their applications as functional materials in many engineering fields. The highest glass-forming ability of bulk metallic glasses 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 thermal stability and mechanical properties4) of Pd–Cu–Ni–P bulk metallic glasses as well as their porosity counterparts5–7) have been extensively investigated. It was found8) that the nucleation behavior of the as-cast Pd-based bulk metallic glasses changed from an internal nucleation mode to a surface nucleation mode due to the optimization of the eutectic composition. This change is attributed to the elimination of heterogeneity, resulting in a longer incubation time. In addition, the porous Pd-based bulk metallic glasses with a lower Young’s modulus, a lower yield strength, a much higher absorption energy, was also investigated, and no difference in thermal stability was recognized between the porous alloys and the pore-free alloys. Porous bulk metallic glass rods can be prepared by water quenching the mixture consisting of Pd–Cu–Ni–P liquid plus NaCl solid, followed by leaching of the NaCl solid in water,6) as well as by the high hydrogen pressure melting-water quenching method.9) However, research on the electrochemical behavior of Pd-based BMG is relatively rare.10) It is known that Pd alloys have been utilized as dental materials. The Pd-based bulk metallic glasses are expected to have good corrosion resistance and biocompatibility due to their chemical and structural homogeneity. In this research, the microstructure and electrochemical behavior of Pd42.5Cu30Ni7.5P20 bulk metallic glass and its crystallized alloys were investigated in NaCl and Hanks’ solutions.

2. Experimental Procedures

The mother alloy with a nominal atomic composition of Pd42.5Cu30Ni7.5P20 was prepared by arc melting a mixture of Pd–P pre-alloy, pure Pd, Cu and Ni metals in an argon atmosphere. In order to eliminate the heterogeneous nuclei due to oxide contamination, a B2O3 flux treatment was carried out in a highly purified Ar atmosphere during alloy preparation. The Pd42.5Cu30Ni7.5P20 bulk metallic glasses with a diameter of 6 mm and a length of 50 mm were produced by a water quenching technique in a 0.1 MPa argon atmosphere. The as-quenched bulk metallic glass was heat-treated in a vacuum of about 10−3 Pa at each temperature of 623 K (between Tg, glass transition temperature and Tc, onset temperature of crystallization) and 723 K (50 K above the crystallization peak temperature) for 10 min. The structure was examined by X-ray diffraction (XRD) with Cu Kα radiation. The microstructure was investigated by conventional transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM, JEOL 2010). The samples for TEM observation were prepared by the ion milling method. Thermal stability was characterized by differential scanning calorimetry (DSC) under an argon atmosphere with a heating rate of 0.67 K/s. The corrosion behavior of the alloys was evaluated by electrochemical measurements in a three-electrode cell using a platinum counter electrode and a saturated calomel reference electrode (SCE). The electrolytes used were 0.144 M NaCl solution with pH 6.0 and 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, 0.2 MgSO4·7H2O, 0.06 KH2PO4 and 1.00 Glucose.11)

3. Results and Discussion

Figure 1 shows the XRD patterns of the Pd42.5Cu30Ni7.5P20 as-quenched bulk metallic glass and its crystallized alloys

*Corresponding author, E-mail: fxqin@imr.tohoku.ac.jp
after heat-treatment at 623 and 723 K. It is clear that only a halo peak appears in the XRD pattern of the Pd42.5Cu30Ni7.5P20 as-quenched bulk metallic glass, indicating that the as-quenched alloy is in a glassy state. Although some small peaks appear in the XRD pattern after heat-treatment at 623 K, the peaks do not indicate which phase they are from. However, some obvious diffraction peaks appearing in the XRD pattern of the alloy heat-treated at 723 K were identified as Pd6P, Pd7P3 and Ni2Pd2P phases. Figure 2 shows the DSC curves of the Pd42.5Cu30Ni7.5P20 as-quenched bulk metallic glass and its crystallized alloys heat-treated at 623 and 723 K for 10 min.

The potentiodynamic polarization curves of the Pd42.5Cu30Ni7.5P20 as-quenched bulk metallic glass and its crystallized counterparts are measured in 0.144 M NaCl and Hanks’ solutions at room temperature, as shown in Fig. 3. In 0.144 M NaCl solution (Fig. 3(a)), all alloys exhibit similar corrosion behavior. They are spontaneously passivated with a passive current density between $10^{-2}$ and $10^{-1}$ A/m² in anodic polarization curves. As the anodic potential increases, passivity breakdown occurs. At the same time, the transpassive potential of the fully crystallized alloy is about 100 mV lower than that of the as-quenched and the partially crystallized alloy in 0.144 M NaCl solution. The results in Hanks’ solution (Fig. 3(b)) are similar to that in 0.144 M NaCl solution. All the samples are passivated in the anodic polarization in Hanks’ solution, while the passive regions of the Pd42.5Cu30Ni7.5P20 as-quenched bulk metallic glass and its crystallized alloys in Hanks’ solution are about 150 mV wider than that in 0.144 M NaCl solution.

The TEM and HRTEM images and SAD patterns (Fig. 4) of the Pd42.5Cu30Ni7.5P20 as-quenched bulk metallic glass and its crystallized alloys reveal that the as-quenched alloy has a glassy structure, with only halo rings in the corresponding SAD pattern. After heat-treatment at 623 K, several ring patterns are superimposed on the diffuse halo rings in the
SAD pattern, indicating a mixture state of glassy matrix and nano crystallized particles. The nanoparticles are identified as a tetragonal Ni$_2$Pd$_2$P phase. By heat-treatment at 723 K, it is seen that the residual glassy matrix is completely crystallized, as presented in Fig. 4(c). The insert diffraction pattern are identified as a Pd$_6$P phase with crystal planes of (2/C2230), (310) and (140).

As mentioned above, a similar corrosion behavior was observed for the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ as-quenched bulk metallic glass and its crystallized alloys both in 0.144 M NaCl and Hanks’ solution. The as-quenched bulk metallic glass and the partially crystallized alloy have a wider passive region than the fully crystallized alloy, i.e., the fully crystallized alloy shows a lower transpassive potential in both solutions. This means that the partially crystallized alloy and the as-quenched bulk metallic glass have a higher chemical stability. In the HRTEM images shown in Figs. 4(a) and 4(b), the morphology can be seen more like atomic clusters in a very fine distribution in a glassy matrix than nanoparticles. The as-quenched bulk metallic glass shows a very similar atomic cluster slightly smaller in size than that of the alloy heat-treated at 623 K. It is not clear why the Pd-based as-quenched bulk metallic glass exhibits this type of morphology. Further investigation is necessary. It is believed that the volume fraction of the grain boundary is as much as 50% of the total crystal volume when the grain size is less than 100 nm.13) The existence of a large amount of grain boundary enhances the diffusion ability of the atoms, which is beneficial for the formation of a protective oxide film.14,15)

In the present research, the interface between the atomic clusters and the glassy matrix exists with a large volume fraction in the as-quenched and the partially crystallized samples. Therefore, a low passive current density and a wide passive region are obtained for the two alloys in both 0.144 M NaCl and Hanks’ solution. In Fig. 1 and Fig. 4(c), the random distribution of several kinds of crystal particles (Pd$_6$P, Pd$_3$P$_7$, and Ni$_3$Pd$_2$P) with sizes 20–200 nm in the fully crystallized alloy results in the heterogeneity of the matrix and an inhomogeneous passive film. As such, the fully crystallized alloy is susceptible to the formation of a micro- coupling cell which could trigger corrosion, and indicated by the preferential adsorption of Cl$^-$ at some weak sites. Consequently, the transpassive potential of the fully crystallized alloys is about 100 mV lower than that of two other alloys in both NaCl and Hanks’ solutions. Furthermore, the concentration 0.144 M of the NaCl solution used in this research is the same as the concentration of Cl$^-$ in Hanks’ solution. Therefore, the wider passive region of the alloys in Hanks’ solution is attributed to the presence of HCO$_3^-$, HPO$_4^{2-}$, SO$_4^{2-}$ and H$_2$PO$_4^-$ ions in the solution, which act as corrosive inhibitors.

4. Conclusions

The microstructure and corrosion behavior of the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ as-quenched bulk metallic glass and its crystallized alloys were investigated. All the alloys show a similar corrosion behavior both in the single Cl$^-$ containing solution and the more complex Hanks’ solution. The main difference is that the fully crystallized alloy exhibits a transpassive potential about 100 mV lower than those of the as-quenched and partially crystallized alloys. The results indicated that the difference in the transpassive potential among the as-quenched bulk metallic glass, the partially crystallized alloy, and the fully crystallized alloy originates from the differences in their microstructure. In addition, the presence of HCO$_3^-$, HPO$_4^{2-}$, SO$_4^{2-}$ and H$_2$PO$_4^-$ ions in Hanks’ solution can act as corrosive inhibitors which defer pitting corrosion.

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