



Corrosion resistance and XPS studies of Ni-rich Ni–Pd–P–B bulk glassy alloys

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ABSTRACT

New Ni-rich Ni–Pd–P–B bulk glassy alloys with high glass-forming ability were formed by water quenching. The Ni₆₀Pd₂₀P₁₇B₃ and Ni₆₅Pd₁₅P₁₇B₃ alloys possess high corrosion resistance in 1N H₂SO₄ and 3 mass% NaCl solutions. In both solutions, their corrosion resistance decreases with increasing Ni content in the alloys. The origin of high corrosion resistance for the Ni₆₀Pd₂₀P₁₇B₃ alloy in the corrosive solutions is explained by formation of the Pd-enriched sub-surface layer, which is able to protect the alloy against the corrosion.

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1. Introduction

Since the discovery of Mg- and Ln-based bulk glassy alloys [1,2], based on multicomponent alloys, in the late 1980s, bulk metallic glasses (BMGs) have been receiving much attention because they offer the extraordinary physical, chemical, and mechanical properties, and show great potentials for applications in many areas [3,4].

Despite their unique properties, the BMGs are currently only used in a few practical applications. The glass-forming ability (GFA) limitation, low ductility and high cost are the main challenges for inhibiting the use of bulk metallic glasses in engineering application. Recently, the critical diameter D_c for glass formation (i.e., the maximum diameter of a rod that can be cast fully glassy) has exceeded 1 cm for a wide variety of alloy systems such as those based on Fe [5], Ni [6], or Cu [7], resulting in significantly increased engineering importance for bulk metallic glasses. Among them, a new Ni-based glassy alloy with a composition of Ni₅₀Pd₃₀P₂₀ has been found to possess the unique features, i.e., the combination of high glass-forming ability and good mechanical properties. For instance, the B₂O₃ flux treated Ni₅₀Pd₃₀P₂₀ alloy can be formed into a fully glassy cylinder of 21 mm in diameter by water quenching the molten alloy in a quartz tube and shows a large plastic strain of 7.6% under a uniaxial compressive load. In order to further reduce the cost of the Ni–Pd–P bulk glassy alloys, a new series of Ni-rich Ni₆₀Pd₂₀P₁₇B₃, Ni₆₅Pd₁₅P₁₇B₃ and Ni₇₀Pd₁₀P₁₆B₄ bulk

glassy alloys containing a small amount of B element with high GFA have been developed [8,9]. However, there have been no data on their corrosion resistance in industrial environments, especially, in chloride-ion-containing solutions. As we know, the chemical properties must be taken into account for practical application of glassy materials. So in this work, we present the electrochemical properties of the Ni-rich Ni–Pd–P–B bulk glassy alloys in 1N H₂SO₄ and 3 mass% NaCl solutions by weight loss and electrochemical measurements. With the aim of clarifying the origin of the high corrosion resistance for the Ni₆₀Pd₂₀P₁₇B₃ glassy alloys, the surface properties of specimens before and after immersion in 1N H₂SO₄ solution with pH of 0 and 3 mass% NaCl neutral solution with pH of about 7 are quantitatively examined by X-ray photoelectron spectroscopy (XPS).

2. Experimental

Mother alloys of Ni–Pd–P–B were prepared by arc melting of a mixture of pure Pd and Ni metals, B crystal and pre-alloyed Pd–Ni–P ingot in an argon atmosphere. In order to improve the GFA, from a mother alloy ingot, cylindrical samples with a diameter of 10 mm were prepared by water quenching the molten alloy together with repeated B₂O₃ flux treatment in a vacuumed quartz tube. Subsequently, as-cast rod samples with a diameter of 2.5 mm were produced by an ejection copper mold casting method.

For corrosion behavior measurements, the specimen dimensions were 2 mm long with a diameter of 10 mm for the Ni₆₀Pd₂₀P₁₇B₃ and Ni₆₅Pd₁₅P₁₇B₃ glassy alloys, and 2 cm long with a diameter of 2.5 mm for the Ni₇₀Pd₁₀P₁₆B₄ glassy alloy. Prior to immersion and electrochemical measurements, the surface finish on specimens was either a 1500 grit SiC or a 1 μm diamond finish. The corrosion rates were evaluated from the weight loss after immersion for 1 week in electrolyte solutions at room temperature (about 298 K). Three specimens for each alloy in the same solution were examined for the weight loss test. The average value was used for corrosion rate estimation. Electrochemical measurements were conducted

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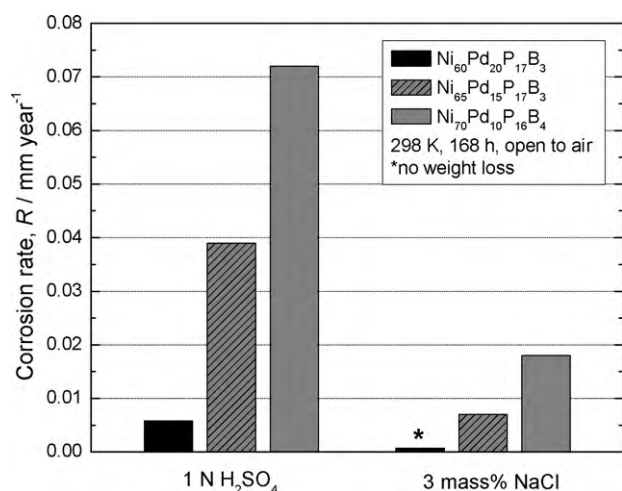


Fig. 1. Average corrosion rates of the Ni–Pd–P–B bulk glassy alloys in 1N H₂SO₄ and 3 mass% NaCl solutions at 298 K open to air.

in a three-electrode cell using a platinum counter electrode and an Ag/AgCl reference electrode. Potentiodynamic polarization curves were measured at a potential sweep rate of 50 mV min⁻¹ after open-circuit immersion for about 20 min when the open-circuit potential became almost steady. Scanning electron microscopy (SEM) was utilized to examine the surfaces of specimens after immersion in the corrosive solutions. For surface characterization, X-ray photoelectron spectroscopy (XPS) measurements were performed by means of a SSI SSX-100 photoelectron spectrometer with monochromatized Al K α excitation ($h\nu = 1486.6$ eV) for the specimens after immersion in solutions. The composition of the surface film and the composition of the underlying alloy surface were quantitatively determined with a previously proposed method using the integrated intensities of photoelectrons under the assumption of a three-layer model of an outmost contaminant hydrocarbon layer of uniform thickness, a surface film of uniform thickness and an underlying alloy surface of infinite thickness as regards X-ray-photoelectrons [10,11].

3. Results and discussion

The cylindrical bulk samples Ni₆₀Pd₂₀P₁₇B₃, Ni₆₅Pd₁₅P₁₇B₃ and Ni₇₀Pd₁₀P₁₆B₄ consisted of a single glassy phase which was evident from a main halo peak without crystalline peaks in their X-ray diffraction patterns. Fig. 1 shows the average corrosion rates of the Ni–Pd–P–B rod samples in 1N H₂SO₄ and 3 mass% NaCl solutions for 1 week open to air at 298 K. In 1N H₂SO₄ solution, the Ni₆₀Pd₂₀P₁₇B₃ alloys exhibit a low corrosion rate of ~ 0.0058 mmy⁻¹. As increasing Ni content in the alloys up to 65 or 70 at.%, the corrosion rates of the Ni₆₅Pd₁₅P₁₇B₃ and Ni₇₀Pd₁₀P₁₆B₄ alloys rise to the values of ~ 0.039 and 0.072 mmy⁻¹, respectively. On the other hand, after immersion in neutral 3 mass% NaCl which contains about 0.5N Cl⁻, no

weight loss is detected for Ni₆₀Pd₂₀P₁₇B₃ glassy alloy, which means the corrosion rate of the alloy is less than 1×10^{-3} mmy⁻¹ for the present measurements. Meanwhile, it also appears that the average corrosion rates of the Ni₆₅Pd₁₅P₁₇B₃ and Ni₇₀Pd₁₀P₁₆B₄ increase with increasing Ni content in the alloys. Thus, in both solutions, their corrosion resistance decreases with increasing Ni content in the alloys. Among the present glassy alloys, the Ni₆₀Pd₂₀P₁₇B₃ glassy alloy demonstrates highest corrosion resistance in the strong acidic and chloride-ions-containing solutions. Moreover, the surfaces of the specimens immersed in 3 mass% NaCl solution for 1 week were further examined by SEM. The SEM micrographs are shown in Fig. 2. The Ni₆₀Pd₂₀P₁₇B₃ alloy still keeps the previous metallic luster and almost no changes in its surface are seen before and after immersion (not shown here), indicating the high resistance to localized corrosion. This result obtained from SEM micrographs is in agreement with the corrosion rate of the Ni₆₀Pd₂₀P₁₇B₃ alloy. The Ni₆₅Pd₁₅P₁₇B₃ alloy after immersion suffers uneven chloride-induced localized corrosion, and its surface is covered with alveolate round-shaped corrosion products (Fig. 2(a)). In Fig. 2(b), when Ni content in the alloy rises to 70 at.%, several flaws are observed in the Ni₇₀Pd₁₀P₁₆B₄ alloy surface, which is evident that the alloy suffers crevice corrosion in chloride containing solution. More detailed investigation about the corrosion behavior dependence of their alloy compositions is being proceeded.

Further examination was conducted using potentiodynamic polarization measurements. Figs. 3 and 4 show anodic polarization curves of the Ni–Pd–P–B glassy rods in 1N H₂SO₄ and 3 mass% NaCl solutions, respectively, open to air at 298 K. In 1N H₂SO₄ solution, the Ni₆₀Pd₂₀P₁₇B₃ and Ni₆₅Pd₁₅P₁₇B₃ glassy alloys is spontaneously passivated with a significantly low current density of the order of 10^{-3} to 10^{-2} A m⁻². The alloy with Ni content 60 at.% shows a lower passive current density in all the potential scheme. The Ni₇₀Pd₁₀P₁₆B₄ alloy also shows spontaneous passivation-like behavior though its current density is much higher than those of the Ni₆₀Pd₂₀P₁₇B₃ and Ni₆₅Pd₁₅P₁₇B₃ glassy alloys. In addition, the open-circuit potentials of the Ni₆₀Pd₂₀P₁₇B₃, Ni₆₅Pd₁₅P₁₇B₃ and Ni₇₀Pd₁₀P₁₆B₄ alloys are about 0.37, 0.33, and 0.077 mV (vs. Ag/AgCl), respectively. It is clearly seen that the open-circuit potentials of the alloys are nobler with an increase in Pd content. On the other hand, in 3 mass% NaCl solution, spontaneous passivation takes place for all the Ni–Pd–P–B glassy alloys. Increasing Ni content in the alloys results in an increase in the passive current densities of the present glassy alloys. As it will be shown later, the corrosion resistance of these glassy alloys decreases with increasing Ni content, because the Pd content decreases. Pd is the key element for the protection the alloys against corrosion.

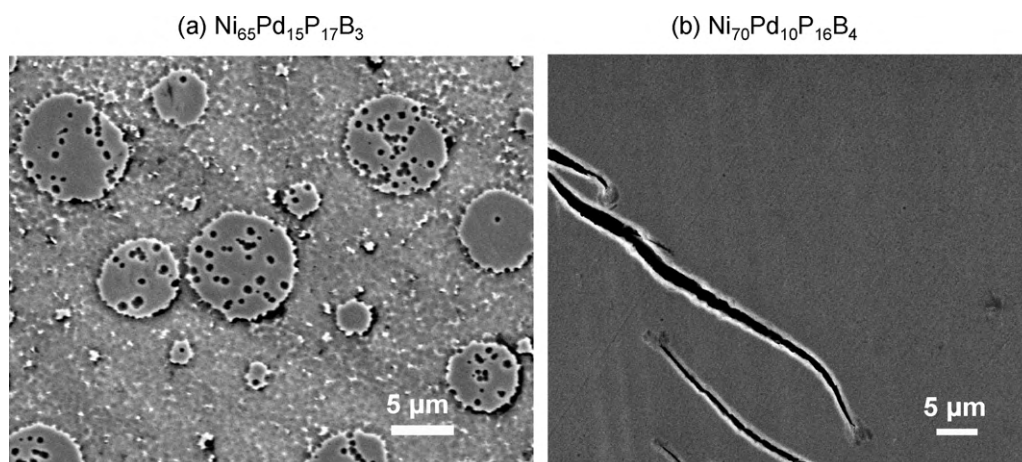


Fig. 2. SEM micrographs of the surfaces of the (a) Ni₆₅Pd₁₅P₁₇B₃ and (b) Ni₇₀Pd₁₀P₁₆B₄ glassy rods after immersion in 3 mass% NaCl solution for 1 week.

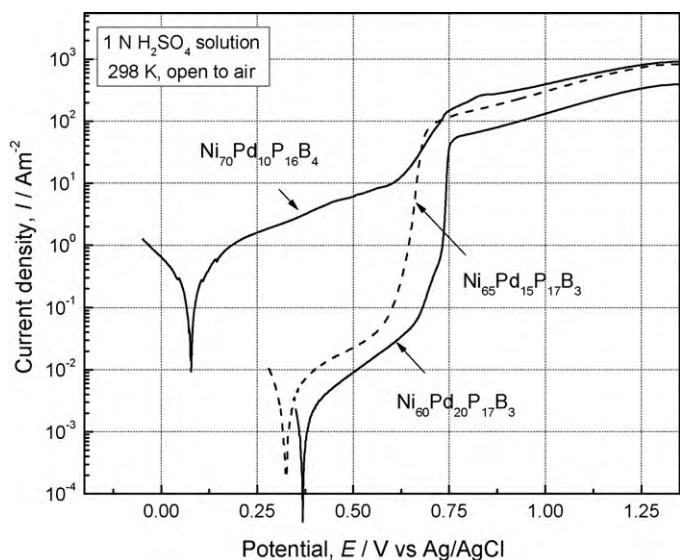


Fig. 3. Anodic polarization curves of the Ni–Pd–P–B bulk glassy alloys in 1N H₂SO₄ solution open to air at 298 K.

According to the corrosion rates and polarization curves of Ni–Pd–P–B glassy alloys, we can see that Ni₆₀Pd₂₀P₁₇B₃ glassy alloy demonstrates high corrosion resistance in the H₂SO₄ and NaCl solutions. Next, it is important to make clear its surface composition together with their chemical states to elucidate the origin of the high corrosion resistance. XPS analyses were performed for the Ni₆₀Pd₂₀P₁₇B₃ specimens as-polished mechanically or immersed in 1N H₂SO₄ solution for 1 week. The XPS spectra of the specimens over a wide binding energy region exhibited peaks of Ni 2p, Pd 3d, P 2p, P 2s, B 1s, O 1s, C 1s. The C 1s spectrum showing a peak at around 285.0 eV arose from a contaminant hydrocarbon layer covering the topmost surface of the specimen. The O 1s spectrum was composed of at least two overlapping peaks which are assigned to OM and OH oxygen. The OM oxygen corresponds to O²⁻ ions in oxyhydroxide and/or oxide, and the OH oxygen is oxygen linked to proton in the film, being composed of OH⁻ ions and bound water in the surface film [10,12]. The photoelectron spectra of Cl and S arising from the solution species were less

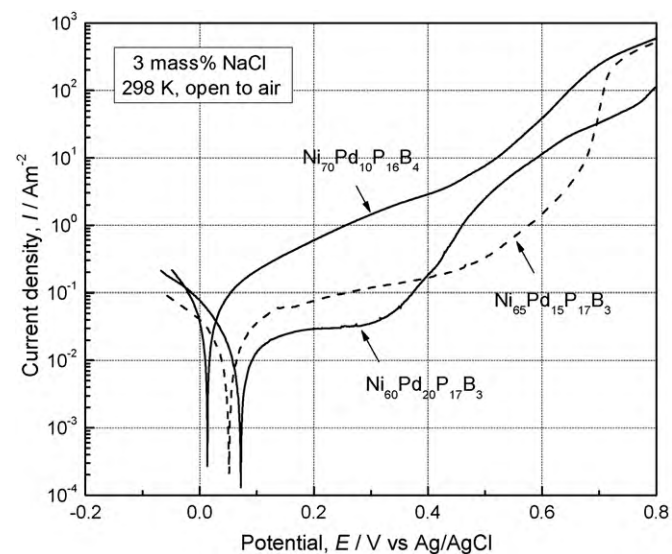


Fig. 4. Anodic polarization curves of the Ni–Pd–P–B glassy alloys in 3 mass% NaCl solution open to air at 298 K.

than the detectable level. The Ni 2p_{3/2} spectrum consisted of two peaks of oxidized state (Ni²⁺) and metallic state (Ni^m) whose binding energies were approximately 856.0–856.2 and 852.5–852.7 eV, respectively. By comparison with the standard spectra of pure Pd metal, the Pd 3d peaks were confirmed to exhibit a pair of peaks at about 335.2–335.8 and 340.5–341.1 eV, which was identified as Pd metal (Pd^m). A doublet of the P 2p peaks was assigned to be metallic phosphorus (P⁰) at 129.7–130.3 eV and pentavalent phosphorous (P⁵⁺) at 133.0–133.9 eV. Because B 1s and P 2s are overlapped each other, we cannot get B element content in the surface according to the B 1s peaks. In this work, we only consider Ni, Pd and P content in the surface. The 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 oxidized layer and underlying alloy surface just beneath the oxidized layer, respectively.

After integrated intensities of the peaks for individual species were obtained, the thickness and composition of the oxidized layer and the composition of the underlying alloy surface (metallic states) were determined quantitatively using a previously proposed method [10,11]. Fig. 5 shows the cationic fraction of elements ($[M^{ox}]/[Ni^{ox}] + [Pd^{ox}] + [P^{ox}]$) in the oxidized layer and the atomic fraction of elements ($[M^m]/[Ni^m] + [Pd^m] + [P^m]$) in the underlying alloy surface just below the oxidized layer for the Ni₆₀Pd₂₀P₁₇B₃ alloy exposed to air and a sample immersed in 1N H₂SO₄ solution open to air for 1 week after mechanical polishing. For air-exposed Ni₆₀Pd₂₀P₁₇B₃ sample after mechanical polishing, a large amount of Ni²⁺ and P⁵⁺ were detected in the outer oxidized surface. In addition, the chemical affinity of elemental Pd to oxygen is very low and Pd metal is extremely stable in air at room temperature. So, no elemental Pd is observed in the oxidized layer. On the contrary, the content of Pd element (Pd^m) in metallic state increases in the underlying alloy surface just beneath the oxidized layer, while those of metallic Ni (Ni^m) and P (P^m) elements decrease with respect to the alloy composition. The thickness of the outer oxidized surface is about 16 Å. Immersion in 1N H₂SO₄ solution for 1 week gives rise to the reconstruction of alloy surface which is different from the air-formed surface. When the alloy is immersed in the solution, illustrated in Fig. 5, Pd element in oxidic state (Pd^{ox}) could not be found in the outer layer. In contrast, Ni²⁺ and P⁵⁺ cations are detected in the outer layer. On the other hand, we can see the noble metal Pd in metallic state (Pd^m) is remarkably concentrated in the underlying alloy surface, whereas the metallic Ni and P elements are significantly deficient in this surface. The outer layer after immersion becomes much thinner and is less than 8 Å. The formation of these distinct regions should imply a diffusion mechanism which comes from the interaction between the constituent elements Ni, P and Pd, and corrosive solutions. The diffusion of Ni and P moves towards the outer surface, while Pd element diffuses with a short distance to form a dense and protective underlying surface layer (also called sub-surface layer).

It is worthy noting that, generally, the high corrosion resistance of the alloy is attributed to the highly protective oxidized surface films of the alloys. However, the mechanism of corrosion resistance of the present alloy is quite different. During the immersion of the alloy in H₂SO₄ solution, Ni and P elements preferentially dissolve into the acidic solution. Some of Ni²⁺ and P⁵⁺ cations from the acidic solution are also re-adsorbed in the alloy surface together with contaminant C and hydrates in different forms to form an outer surface layer. The composition of the outer surface layer after immersion is similar to that of the air-formed outer surface except for the thinning thickness. Several researches [13,14] reported that the amorphous Ni–P alloys exhibit low corrosion resistance in acidic solutions owing to forming thick porous surface films. The outer oxidized layer consisting of a large amount of Ni and P cations cannot protect the alloy against corrosion in the strong acidic solution.

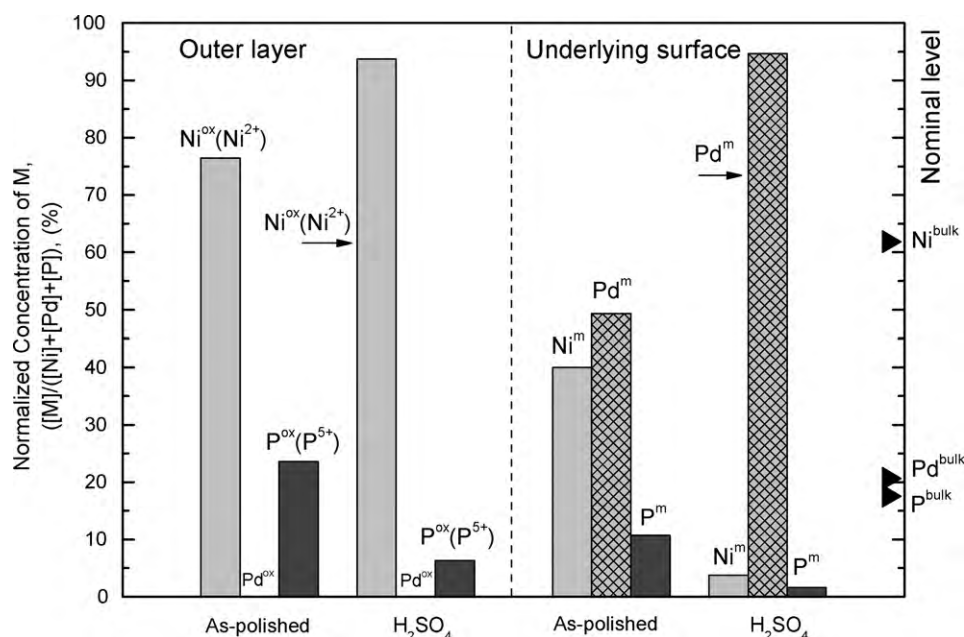


Fig. 5. The cationic fraction of elements ($[M^{ox}]/[Ni^{ox}] + [Pd^{ox}] + [P^{ox}]$) in the oxidized layer and the atomic fraction of elements ($[M^m]/[Ni^m] + [Pd^m] + [P^m]$) in the underlying alloy surface just below the oxidized layer for the $Ni_{60}Pd_{20}P_{17}B_3$ alloy exposed to air and that immersed in 1N H_2SO_4 solution open to air for 1 week after mechanical polishing.

In contrast, from XPS result in Fig. 5, we can see the noble metal Pd in metallic state is significantly enriched on the surface just beneath the outer layer. The immersion process results in rapid initial selective dissolution of less noble Ni and P elements into the solution and the formation of the metallic Pd-enriched sub-surface structure by the self-assembly of Pd atoms at alloy/electrolyte interfaces. The metallic Pd-rich sub-surface layer just beneath the outer oxidized surface plays a vital role in the high corrosion resistance of the $Ni_{60}Pd_{20}P_{17}B_3$ alloy. It is clear that Pd is the key element for the protection the alloy against corrosion. In addition, we also measured the surface properties of the $Ni_{70}Pd_{10}P_{16}B_4$ glassy alloy with a less Pd content, the dense and protective Pd-enriched sub-surface layer could not be formed for the alloy after immersion in the H_2SO_4 solution. The surface of the $Ni_{70}Pd_{10}P_{16}B_4$ alloy after immersion for 1 week is covered with the thick and porous black corrosive products.

Similar XPS results have been found for the $Ni_{60}Pd_{20}P_{17}B_3$ alloy immersed in 3 mass% NaCl solution. After immersion in NaCl solution, the Pd metal is also largely enriched in the underlying alloy surface just beneath the outer layer. As indicated by the results of the immersion tests, the present alloy exhibit high corrosion resistance in H_2SO_4 and NaCl solutions, which in turn verifies the Pd-enriched sub-surface layer is dense, compact, and stable. Therefore, it can be concluded that the high corrosion resistance is based on the formation of the Pd-enriched sub-surface layer with high protective quality and high uniformity.

4. Conclusions

The electrochemical properties and surface composition analysis of the Ni-rich Ni–Pd–P–B glassy alloys were investigated. The Ni–Pd–P–B glassy alloys are spontaneously passivated in 1N H_2SO_4 and 3 mass% NaCl solutions. In both solutions, their corrosion resistance decrease with an increase in the Ni content in the alloys. Among Ni–Pd–P–B glassy alloys, the $Ni_{60}Pd_{20}P_{17}B_3$ alloy possesses highest corrosion resistance in 1N H_2SO_4 and 3 mass% NaCl solutions. X-ray photoelectron spectroscopy analysis reveals that the high corrosion resistance of the alloy is attributed to the formation of the highly protective Pd-rich sub-surface layer after immersion in the corrosive solutions.

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