Pitting Corrosion of Amorphous Ni–Zr Alloys in Chloride Ion Containing Sulfuric Acid Solutions


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The pitting corrosion behavior of the melt-spun amorphous Ni-Zr alloys with 30–75 at% zirconium, the crystalline arc-melted counterparts and the sputter-deposited Ni-Zr alloys with 20–84 at% zirconium was examined by electrochemical measurements in deaerated 0.5 kmol/m³ H₂SO₄ with and without 0.1 kmol/m³ NaCl at 303 K. In the sulfuric acid solution without Cl⁻, these alloys were spontaneously passive and their potentiodynamic behavior was similar to each other. In the Cl⁻-containing solution, all the melt-spun amorphous alloys suffered pitting during anodic polarization and the pitting potential decreased with an increase in zirconium content. On the other hand, the crystalline arc-melted low zirconium alloys suffered pitting but no pitting observed for the crystalline alloys containing 70 at% zirconium or more. In addition, the pitting potential increased with the zirconium content of crystalline alloys. All the sputter-deposited alloys did not suffer pitting regardless of the amorphous and crystalline structures. Therefore, the melt-spun amorphous alloys were the most susceptible to pitting corrosion. A marked difference was observed in the pitting behavior between the shiny side (top side) and the dull side (wheel side) surfaces of the melt-spun ribbon. The pits initiated from the dull side surface. Thus, the dull side surface could be responsible for such an unusual pitting behavior of the melt spun ribbon.

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I. Introduction

Some amorphous alloys have been known to have remarkably high corrosion resistance particularly against pitting corrosion attack even in hot concentrated chloride solutions (10)-(12). The chemically homogeneous single phase nature of amorphous alloys without compositional fluctuations is primarily responsible for the high resistance to localized corrosion (10).

However, pitting corrosion has been found in Fe-Ni-B-Si alloys with less than 12% Si during anodic polarization in a chloride-containing borate buffer solution of pH 8.4 (13). This is attributed to the fact that Si atoms are insufficient in the surface to form a protective Si-rich passive film. Amorphous Ni-P alloys with and without the addition of molybdenum or tungsten suffered pitting corrosion by immersion in a FeCl₃ solution and by anodic polarization in the 1 kmol/m³ HCl solution along with the formation of a porous thick corrosion product film (14). In a NaCl solution, the amorphous Ni-12.5Cr-4Fe-8Si-12.5B alloy showed pitting susceptibility. The pitting potential decreased as chloride concentration and acidity of the solution increased (10). The metal-metal amorphous alloys also suffered pitting corrosion. The melt-spun amorphous Ni-40Ti, Ni-40Zr and Ni-30Ta-5Pd alloys suffered pitting during anodic polarization in 0.5 kmol/m³ NaCl (10) and some sputter-deposited amorphous Al-valve metal alloys showed a similar behavior in 1 kmol/m³ HCl (11,12).

Shimamura et al. (13) have reported that the melt-spun amorphous Ni-Zr alloys suffered pitting during anodic polarization in 1 kmol/m³ HCl while the sputter-deposited Ni-Zr alloys of similar composition did not suffer any pitting under the same condition. Asami et al. (14), in observing the pit development on melt-spun Ni-Zr alloys in situ by an optical microscope during anodic polarization, reported that the pits developed were accompanied by the evolution of hydrogen and by cracking as a result of hydrogen embrittlement and that most of them had a very characteristic shape with a radial dendritic pattern of cracks. Recently, Janik-Czachor (15) investigated the anodic behavior of melt spun amorphous Ni-Zr alloys with 25 to 70 at% Zr in a borate buffer with various addition of NaCl. It was found that pitting potential decreased with zirconium content in the alloys and decreased linearly with the logarithm of chloride concentration, suggesting a chemical breakdown of passivity. They could not, however, go into the details of such an unusual pitting behavior and the cause of the behavior.

The present work aims to investigate the pitting corrosion behavior of amorphous Ni-Zr alloys in an acidic chloride solution.

II. Experimental Procedure

Alloy ingots were prepared by argon-arc melting of 99.97 mass% nickel and 99.6 mass% zirconium. The
rotating wheel method under an argon atmosphere was used for the preparation of amorphous Ni–Zr alloy ribbons of about 1 mm width and 20–30 μm thickness from the argon arc-melted ingots. Prior to electrochemical measurements, both sides of the ribbons were polished mechanically about 1 μm in depth with silicon carbide paper up to No. 1000 in cyclohexane.

D.C. Magnetron sputtering was used for preparation of sputter-deposited Ni–Zr alloys. The targets consisted of a 99.9 mass% zirconium disk of 100 mm diameter and 6 mm thickness, on the erosion region of which 99.7 mass% pure nickel plates of 15 mm × 15 mm × 1.5 mm were placed. The sputtering apparatus and conditions used were the same as those described elsewhere. The alloy composition was determined by electron probe microanalysis or inductively coupled plasma emission spectroscopy (ICP), and the structure was identified by X-ray diffraction with Cu Kα radiation at conventional and grazing incident angle modes.

Electrochemical measurements were carried out at 303 K in deaerated 0.5 kmol/m³ H₂SO₄ solutions with and without 0.1 kmol/m³ NaCl which were prepared from a reagent grade chemicals and deionized water. Polarization curves were measured by the potentiodynamic method with a potential sweep rate of 50 mV/min starting from the corrosion potential. Before the measurements, the specimens were cathodically polarized at a cathodic current density of 10 A/m² for 30 s. This particular cathodic pretreatment provided reproducible corrosion potential. Potentiostat potential was defined as a potential where the current density exceeded 2 × 10⁻⁷ A/m². All potentials reported are relative to the saturated calomel electrode (SCE).

III. Results

Figures 1 and 2 show X-ray diffraction patterns of melt-spun and sputter-deposited Ni–Zr alloy specimens. The melt-spun Ni–(30–75) at% Zr alloys and the sputter-deposited Ni–(20–74) at% Zr alloys exhibited halo patterns typical of amorphous structure. For the melt-spun Ni–20Zr alloy, an fcc nickel phase was observed. Thus, sputtering technique is more effective for the preparation of single amorphous phase with a wider composition range compared with the melt-spinning method. Because the atomic scattering factor of nickel is smaller than zirconium, the intensity of the first halo decreases with nickel content. The diffraction pattern of the sputter-deposited Ni–84Zr alloy, however, shows intense and week reflections close to 002 and 004 reflections of hcp Zr, although the lattice spacings of this alloy are slightly smaller than those of pure Zr. Thus this alloy can be regarded as that consisting of the hcp Zr phase supersaturated with nickel. This observation also suggests that this alloy film was deposited with a preferred orientation of 001, perpendicular to the substrate plane. Reflection based on the Cu Kα X-ray is also seen at 2θ of about 31.1 degrees for this alloy, because the X-ray source was not monochromatized. The phases in the arc-melted alloys, melt-spun alloy rib-
Table 1 Phases identified by X-ray diffraction.

<table>
<thead>
<tr>
<th>Ni-xZr (x; at%)</th>
<th>Arc-Melted Alloy</th>
<th>Melt-Spun Alloy Ribbon</th>
<th>Sputter-Deposited Alloy Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Ni$<em>2$Zr + Ni$</em>{1/2}$Zr$_5$</td>
<td>Amorphous</td>
<td>Amorphous</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>Ni$_{1/2}$Zr$_3$ + NiZr</td>
<td>Amorphous</td>
<td>Amorphous</td>
</tr>
<tr>
<td>55</td>
<td>NiZr + NiZr$_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>NiZr$_3$ + Zr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>NiZr$_3$ + Zr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>84</td>
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</tbody>
</table>

Fig. 3 Potentiodynamic polarization curves of melt-spin amorphous Ni-Zr alloys measured in deaerated 0.5 kmol/m$^3$ H$_2$SO$_4$ at 303 K.

Fig. 4 Potentiodynamic polarization curves of sputter-deposited Ni-Zr alloys measured in deaerated 0.5 kmol/m$^3$ H$_2$SO$_4$ at 303 K.

Fig. 5 Potentiodynamic polarization curves of argon arc-melted Ni-Zr alloys measured in deaerated 0.5 kmol/m$^3$ H$_2$SO$_4$ at 303 K.

Bonds and sputter-deposited alloy films observed by X-ray diffraction are summarized in Table 1. The arc-melted alloys, corresponding to the composition range where the ribbons and films become amorphous, are composed mainly of two phases. These phases are equilibrium phases, although the unknown phases presented in the alloys with less than 50 at%Zr.

Figures 3, 4 and 5 show potentiodynamic polarization curves measured in deaerated 0.5 kmol/m$^3$ H$_2$SO$_4$ at 303 K for the melt-spun, sputter-deposited and arc-melted Ni–Zr alloys, respectively. Included in Fig. 3 for comparison are polarization curves of crystalline pure nickel and zirconium. As shown in Fig. 3, all amorphous alloy ribbons studied are spontaneously passive and the open circuit potentials are ennobled by increasing the nickel content. This is due to the lower hydrogen overpotential of nickel in comparison with that of zirconium. The passive current densities tend to decrease with increasing zirconium content although those of the alloys containing 50 at% zirconium or more are almost the same. It is interesting to note that these amorphous Ni–Zr alloy ribbons show lower passive current density than pure zirconium up to about 1.4 V (SCE). At this potential, an increase in nickel content raises the anodic current density due to the transpassive dissolution of nickel$^{17}$ and the oxygen evolution reaction on these alloys. The polarization behavior for the sputter-deposited and arc-melted alloys in 0.5 kmol/m$^3$ H$_2$SO$_4$ solution is similar to that of the melt-spin amorphous ribbons except for the behavior around the open circuit potential, where the sputter-deposited alloys exhibit much lower anodic and cathodic current densities than the melt-spin alloys.

The polarization behavior of the melt-spin, sputter-deposited and arc-melted Ni–Zr alloys measured in 0.5 kmol/m$^3$ H$_2$SO$_4$ + 0.1 kmol/m$^3$ NaCl solution at 303 K is shown as a function of alloy zirconium content in Figs. 6, 7 and 8, respectively. All the melt-spin alloy ribbons suffer pitting corrosion as shown in Fig. 6. There are no current spikes of pitting precursors which are often observed at ordinary pitting corrosion. It is worth noting that the pitting potential of the melt-spin amorphous Ni–Zr alloys decreases with increasing zirconium content. For example, the amorphous Ni–30Zr and Ni–75Zr alloys are pitted at about 280 and –50 mV (SCE), respec-
Fig. 6 Potentiodynamic polarization curves of melt-spun amorphous Ni-Zr alloys measured in deaerated 0.5 kmol/m$^3$ H$_2$SO$_4$+0.1 kmol/m$^3$ NaCl at 303 K.

Fig. 7 Potentiodynamic polarization curves of sputter-deposited Ni-Zr alloys measured in deaerated 0.5 kmol/m$^3$ H$_2$SO$_4$+0.1 kmol/m$^3$ NaCl at 303 K.

Fig. 8 Potentiodynamic polarization curves of argon arc-melted Ni-Zr alloys measured in deaerated 0.5 kmol/m$^3$ H$_2$SO$_4$+0.1 kmol/m$^3$ NaCl at 303 K.

Fig. 9 Change in pitting corrosion potential with zirconium content for various Ni-Zr alloys in deaerated 0.5 kmol/m$^3$ H$_2$SO$_4$+0.1 kmol/m$^3$ NaCl at 303 K.

tively. Another feature of interest is that for the crystalline Ni-Zr alloy ingots, shown in Fig. 8, the pitting potentials increase with an increase in zirconium content and, in addition, no pitting corrosion occurs by the addition of 70 at% zirconium or more to the Ni-Zr alloy. Pure bulk zirconium metal also does not suffer pitting. The third interesting feature is that all the sputter-deposited Ni-Zr alloys including the crystalline Ni–84Zr alloy and pure Zr do not suffer pitting corrosion. The anodic polarization behavior for the sputter-deposited alloys measured in 0.5 kmol/m$^3$ H$_2$SO$_4$ with and without 0.1 kmol/m$^3$ NaCl is similar to each other as shown in Figs. 4 and 7. It is clear that the stability of the passive film formed on the sputter-deposited alloys is higher than that on the melt-spun alloys although both alloys showed an amorphous structure. Therefore, the susceptibility to pitting corrosion is largely changed with the fabrication method of Ni–Zr alloys. Figure 9 summarizes the change in pitting potentials of the amorphous melt-spun and sputter-deposited Ni–Zr alloys and crystalline ingots as a function of zirconium content. From this figure, it is clear that the melt-spun amorphous Ni–Zr alloys are the most susceptible to pitting and the pitting potentials decrease with the zirconium content, whereas those of crystalline counterparts increase with the zirconium content and consequently the pitting resistance of the crystalline ones is greater than the amorphous ribbons, especially at high zirconium contents.

It is generally accepted that amorphous single phase alloys are uniform because they are free from defects associated with the crystalline state and those formed by solid-state diffusion during cooling. This nature of amor-
phous alloys is believed as one of the reasons for their extremely high corrosion resistance including pitting corrosion resistance. It is, therefore, difficult to explain such an unusual pitting behavior of amorphous melt-spun Ni–Zr ribbons by the amorphous nature. Several workers have found electrochemical differences between the wheel side (dull side) and top side (shiny side) of the same amorphous alloy ribbons prepared by melt spinning.

In order to further assess the pitting behavior of the amorphous ribbons, the anodic polarization tests were conducted by masking off either the dull or shiny surface by enamel paint. Figures 10 and 11 depict the potentiodynamic polarization curves for the shiny and dull sides of the amorphous alloy ribbon samples measured in 0.5 kmol/m³ H₂SO₄ at 303 K, respectively. As mentioned in the experimental procedure, both surfaces were mechanically polished with SiC abrasive paper No. 1000 in cyclohexane, removing the surface layer of about 1 μm depth.

It is clear that the anodic polarization behavior for both surfaces in 0.5 kmol/m³ H₂SO₄ is almost the same. However, in a chloride-containing solution, a marked difference in anodic polarization behavior between the two surfaces was evident. Figures 12 and 13 show the anodic polarization curves of the shiny and dull side surfaces of the amorphous melt-spun Ni–Zr alloy ribbons in the 0.5 kmol/m³ H₂SO₄ + 0.1 kmol/m³ NaCl solution at 303 K, respectively. In the case of the shiny side surface, pitting occurs during anodic polarization for the amorphous Ni–30Zr and 40Zr alloys but no pitting occurs by the addition of 55% zirconium or more. These curves (Fig. 12) show a similar trend to those of the crystalline arc-melted alloys (Fig. 8). However, for the dull side surface, all the samples studied suffer pitting. Figure 14 illustrates the changes in pitting potential of the two surfaces of amorphous alloy ribbons as a function of zirconium content. The pitting potentials of the shiny side surface of the amorphous alloy ribbons are much higher than
those of the crystalline arc-melted alloys at the same zirconium content. On the other hand, the pitting behavior of the dull side surface is almost consistent with that of melt-spun ribbons with both side surfaces illustrated in Fig. 9. It can, therefore, be said that the dull side surface could be responsible for the unusual pitting behavior observed when the both sides of the melt-spun ribbons were exposed to a chloride-containing solution. This suggests that some physical and chemical inhomogeneities may be present in the dull side surface even after mechanical polishing 1 μm in depth.

In order to confirm the inhomogeneities in the surface region of melt-spun ribbons, the grazing incident angle X-ray diffraction patterns for both surfaces of the ribbons were measured. Figure 15 shows the XRD patterns for both surfaces of the melt-spun Ni–Zr alloy ribbons measured at the incident angle of 2 degrees. The analyzing depth for the XRD calculated by the same method as described elsewhere[21] is of the order of 0.2–0.4 μm. As shown in this figure, all the alloys exhibit a halo pattern typical of amorphous structure and no difference in the XRD patterns between the dull and shiny sides is observed. This suggests that the inhomogeneities are undetectable by X-ray diffraction.

IV. Discussion

The excellent pitting corrosion resistance of some amorphous alloys has been known for two decades. However, Shimamura et al.[13], in their work on sputter-deposited Ni–Zr alloys in 1 kmol/m³ HCl, reported that the melt-spun amorphous Ni–Zr alloy was found to be susceptible to pitting during anodic polarization, while the sputtered amorphous film was resistant. In the present study, all the sputtered Ni–Zr alloys are not pitted by anodic polarization but pitting corrosion occurs for the melt-spun Ni–Zr alloys. One of the advantages of the sputtering technique in the fabrication of amorphous alloys is the substantially high quenching rate (over 10⁶ K/s)[23]. The sputtering method allows the formation of a more uniform structure than the melt-spinning method (about 10⁴ K/s)[23] along with the formation of some new

Fig. 14 Changes in pitting corrosion potential with zirconium content for the shiny and dull side surfaces of melt-spun amorphous Ni–Zr alloys in deaerated 0.5 kmol/m³ H₂SO₄ + 0.1 kmol/m³ NaCl at 303 K.

Fig. 15 A grazing incident angle X-ray diffraction patterns for the shiny and dull side surfaces of melt-spun Ni–Zr alloys.
corrosion-resistant amorphous alloys such as Al-refractory metals\textsuperscript{(11)(12)}, Cu\textsuperscript{(16)}, Cr\textsuperscript{(24)-(27)} and Mo-valve metal\textsuperscript{(28)(29)} alloys, which cannot be produced by melt quenching techniques. This suggests that the higher quenching rate for the sputtered alloys may be responsible for the high corrosion resistance, particularly against localized attack. Amorphous chromium-bearing metal-metalloid alloys passivated spontaneously in various acids\textsuperscript{(14)(30)(31)}, forming a passive hydrated chromium oxyxohydroxide film. Amorphous Fe-Mo-metalloid alloys were also passivated spontaneously in 1 kmol/m\textsuperscript{3} HCl, forming a passive hydrated iron oxyxohydroxide film\textsuperscript{(30)}. No pitting corrosion was observed in the alloys prepared by the melt-spinning method. Similar results were obtained for the amorphous metal-metal alloys, such as copper\textsuperscript{(30)(33)} and nickel-based\textsuperscript{(34)} alloys containing tantalum or niobium. The high resistance against occluded cell corrosion is attributed to the high passivating ability and high homogeneity of the amorphous alloys. However, pitting corrosion has been found for some amorphous alloys\textsuperscript{(7)-(15)}. Melt-spun amorphous Ni-(30–70 at\% Zr) alloys suffered pitting during anodic polarization in the borate buffer with varying additions of NaCl\textsuperscript{(15)}. Janik-Czachor has reported that pitting potential decreases with Zr content in the alloys and the pitting nucleates predominantly at the shiny side of the ribbon, where the cooling rate is presumed to be the lowest. In the present paper, similar results are obtained except for the fact that pits do initiate predominantly at the dull side of the melt-spun ribbons. During melt-spinning, the dull side surface in contact with the wheel may be cooled with a faster rate than the shiny side surface. But at the same time, as mentioned previously, the melt-spinning produces the relatively deep gas entrainment furrows on the dull side, resulting in further complicating the distribution of cooling rate at the dull side. These, anyhow, suggest that the chemical and physical inhomogeneities exist in the amorphous ribbons. There have been some reports that chemical inhomogeneities of compositional gradients or fluctuations have been detected in the as-formed amorphous alloys fabricated by melt-spinning\textsuperscript{(35)} and by sputtering\textsuperscript{(36)}. Some workers\textsuperscript{(18)-(20)} indicated electrochemical differences between the dull and the shiny sides of the same ribbons. For example, Devine\textsuperscript{(39)} found a marked difference in the potentiodynamic anodic polarization curves between the dull and shiny sides of as-received Metglass 2826A (amorphous Ni–30Fe–15Cr–14P–6B) in 0.17 kmol/m\textsuperscript{3} NaCl. According to his AES studies, on the as-received alloys, the shiny side surface was greatly enriched in chromium and the dull side surface was enriched in iron, whereas the Auger spectra of both surfaces after ion milling for 5 min with argon (equivalent to removal of about 70 nm) are practically identical. It is to be noted that these electrochemical and compositional differences existed only in the as-received sample and a slight mechanical polishing removed the superficial effects\textsuperscript{(18)-(20)}. However, in our work, both surfaces of all the ribbon samples were mechanically polished to a depth of about 1 \textmu m before electrochemical measurements and yet the difference in pitting behavior is retained. In addition, as shown in Fig. 15, the grazing incident angle X-ray diffraction patterns for both sides are not changed. Therefore, these inhomogeneities may come from the compositional gradients, fluctuations and microcrystallites undetectable by X-ray diffraction. To confirm these inhomogeneities, XPS and TEM experiments along with electrochemical measurements have been performed and will be reported elsewhere\textsuperscript{(77)}.

V. Conclusions

A comparison of the pitting corrosion behavior of melt-spun, sputter-deposited and argon arc-melted crystalline Ni–Zr alloys in acidic chloride solution has been made. The following conclusions can be drawn:

(1) The melt-spun alloys containing 30–75 at\% zirconium and the sputter-deposited alloys containing 20–74 at\% zirconium became amorphous. The sputter-deposited Ni–84Zr alloy consists of the hcp Zr phase supersaturated with nickel.

(2) In the sulfuric acid solution without Cl\textsuperscript{−}, these alloys are spontaneously passive and the polarization behavior of these alloys is similar to each other.

(3) In Cl\textsuperscript{−} containing sulfuric acid solution, all the melt-spun amorphous alloys suffer pitting during anodic polarization and the pitting potential decreases with an increase in zirconium content. The arc-melted crystalline counterparts suffer pitting only for the alloys with low zirconium contents. The pitting potential increases with zirconium content and no pitting corrosion occurs with high zirconium contents. All the sputter-deposited alloys do not suffer pitting on anodic polarization. Therefore, the melt-spun amorphous alloys are the most susceptible to pitting.

(4) A marked difference in the pitting behavior exists between the shiny and dull side surfaces of the melt-spun ribbons. The pitting initiates predominantly from the dull side surface. The unusual pitting behavior of the melt-spun ribbons exposed to both surfaces could be attributed to the dull surface which contains much inhomogeneity in comparison with the shiny side.

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