INTRODUCTION

The chemically homogeneous single-phase nature of amorphous or/and nanocrystalline alloys is generally responsible for their high corrosion resistance owing to the formation of uniform protective passive films those are able to separate bulk of alloys from aggressive environments. Last two decades, the use of the sputter deposition technique using direct current magnetron sputtering machine is becoming a quite suitable method for tailoring of varieties of amorphous or/and nanocrystalline corrosion-resistant alloys. Even if amorphous alloy is not formed by the sputter deposition technique, the sputter-deposited alloys are always composed of nanocrystals with very fine grains and sometimes behaves similar to the single-phase amorphous or/and nanocrystalline corrosion-resistant alloys. Accordingly, the sputter-deposited alloys consisting of either amorphous and nanocrystalline single-phase solid solutions are chemically homogeneous and hence are interesting in the view of corrosion resistance properties.

It has been reported that the sputter-deposited amorphous or/and nanocrystalline tungsten-based binary W–Ti, W–Zr, W–Ni, W–Cr, W–Nb, W–Ta, W–Mo, Al–W and ternary W–Cr–Ni, Al–W–Cr–Ni alloys were spontaneously passivated showing significantly higher corrosion resistance than those of alloy-constituting elements in concentrated hydrochloric acid solutions. It has been reported that only small amount of tungsten addition (that is, about 9 at %) was enough to cause spontaneous passivation of the sputter-deposited nanocrystalline W–91Cr alloy in 12 M HCl and these alloys showed about five orders of magnitude lower than that of sputter-deposited tungsten and even about one order of magnitude lower than those of the sputter-deposited zirconium in 1 M NaOH solution.

EFFECTS OF TUNGSTEN, CHROMIUM AND ZIRCONIUM ON THE CORROSION BEHAVIOR OF TERNARY AMORPHOUS W–Cr–Zr ALLOYS IN 1 M NaOH SOLUTION

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Abstract: Simultaneous additions of tungsten, chromium and zirconium in the chromium- and zirconium-enriched sputter-deposited binary W–xCr and W–yZr alloys are effective to improve the corrosion resistance property of the ternary amorphous W–xCr–yZr alloys after immersion for 240 h in 1 M NaOH solution open to air at 25°C. The corrosion rates of all the examined sputter-deposited (10–57)W–(18–42)Cr–(25–73)Zr alloys is higher than those of alloy-constituting elements (that is, tungsten, chromium and zirconium) in aggressive 1 M NaOH solution open to air at 25°C. The corrosion rates of all the examined sputter-deposited W–xCr–yZr alloys containing 10–57 at% tungsten, 18–42 at% chromium and 25–73 at% zirconium were in the range of 1.5–2.5 × 10⁻³ mm/y or lower which are more than two orders of magnitude lower than that of sputter-deposited tungsten and even about one order of magnitude lower than those of the sputter-deposited zirconium in 1 M NaOH solution.

Keywords: Ternary W–Cr–Zr alloys; Amorphous; Corrosion rate; Open circuit potential; 1 M NaOH.
high passivating ability for conventional steels and stainless steels. Only a small amount of chromium (8 at %) addition was enough to cause spontaneous passivation of steels in 1 M HCl and they showed significantly higher pitting corrosion resistance than stainless steels26,27. A series of the sputter–deposited chromium–metalloid alloys exhibited superior corrosion resistance compared to chromium metal in 12 M HCl28. In recent years, the sputter–deposited nanocrystalline W–Cr alloys containing 25–75 at% chromium showed nearly one to two orders of magnitude lower than that of tungsten and chromium in 0.5 M NaCl and 1 M NaOH solutions35. Zirconium is one of the corrosion–resistant elements in acidic environments, although it suffers pitting corrosion by anodic polarization in chloride containing solutions. The alloying of zirconium with aluminum29, chromium30 and molybdenum31 greatly improved the corrosion resistance of the alloys in acidic solutions. It has been reported that the corrosion resistance of the sputter–deposited amorphous or nanocrystalline W–Zr alloys were passivated spontaneously and observed significantly high corrosion resistance in aggressive environments24,36. The corrosion–resistant of the sputter–deposited W–Zr alloys is higher than those of tungsten and zirconium, and hence tungsten addition greatly enhanced the pitting corrosion resistance of zirconium in 12 M HCl.

Furthermore, chromium and tungsten are known to be effective elements in improving the pitting corrosion resistance of the alloys, whereas zirconium suffers pitting corrosion by anodic polarization in aggressive chloride–containing environments. The immunity to pitting corrosion is one of the most interesting characteristics of alloys. It has been reported that the synergistic improvement in the resistance to passivity breakdown in chloride–containing media was observed when chromium and zirconium were added simultaneously to the sputter–deposited Mn–Zr–Cr alloys instead of single addition of zirconium or chromium metals32. It has been recently reported that the simultaneous additions of 10 at% tungsten in presence of 15–17 at% chromium in the sputter–deposited amorphous or nanocrystalline Cr–Zr–W alloys enhanced significantly the pitting corrosion as well as uniform corrosion breakdown in chlorine–containing solutions. It is noteworthy for mentioning here that chromium34 and zirconium35 metals do not corrode in 0.5 M NaCl solution, mostly due to the formation of zirconium oxides and chromium hydroxide/oxides, respectively. However, both chromium and zirconium are very corrodeable in acidic or very alkaline (>13 pH) solutions. On the other hand, tungsten corrosion in solution having pH 4 or high16, for example, in both 0.5 M NaCl and 1 M NaOH solutions. Accordingly, it is very interesting to study the effects of the simultaneous additions of tungsten, chromium and zirconium in the sputter–deposited amorphous or nanocrystalline W–xCr–yZr alloys in 1 M NaOH solution.

In this context, the present research work is aimed to identify the effects of simultaneous additions of tungsten, chromium and zirconium on the corrosion behavior of the sputter–deposited ternary W–xCr–yZr alloys in alkaline 1 M NaOH solution open to air at 25°C using corrosion tests and open circuit potential measurements.

**MATERIALS AND METHODS**

The sputter–deposited ternary W–xCr–yZr alloys containing 10–80 at% tungsten, 12–42 at% chromium and 8–73 at% zirconium were characterized as single–phase solid solution of amorphous or nanocrystalline structure having apparent grain size ranging 0.9 to 10.4 nm as summarized in Table 1. The compositions of the sputter–deposited W–xCr–yZr alloys were determined using electron probe microanalysis (EPMA) and hereafter are all denoted in atomic percentage (at%).

**Table 1:** Composition, structure and apparent grain size of the sputter–deposited ternary W–xCr–yZr alloys including sputter–deposited tungsten, chromium and zirconium.

<table>
<thead>
<tr>
<th>Name of Alloy</th>
<th>Structure</th>
<th>Apparent Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtered Tungsten</td>
<td>nanocrystalline</td>
<td>20.0</td>
</tr>
<tr>
<td>10W–17Cr–73Zr</td>
<td>amorphous</td>
<td>1.4</td>
</tr>
<tr>
<td>21W–15Cr–64Zr</td>
<td>amorphous</td>
<td>1.2</td>
</tr>
<tr>
<td>19W–42Cr–39Zr</td>
<td>amorphous</td>
<td>0.9</td>
</tr>
<tr>
<td>33W–32Cr–35Zr</td>
<td>amorphous</td>
<td>0.9</td>
</tr>
<tr>
<td>57W–18Cr–25Zr</td>
<td>amorphous</td>
<td>1.2</td>
</tr>
<tr>
<td>80W–12Cr–8Zr</td>
<td>nanocrystalline</td>
<td>10.4</td>
</tr>
<tr>
<td>Sputtered Chromium</td>
<td>nanocrystalline</td>
<td>40.0</td>
</tr>
<tr>
<td>Sputtered Zirconium</td>
<td>nanocrystalline</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Prior to the corrosion tests and electrochemical measurements, the sputter–deposited W–xCr–yZr alloy specimens were mechanically polished with a silicon carbide paper up to grit number 1500 in cyclohexane, degreased by acetone and dried in air. The average corrosion rate of the alloys was estimated from the weight loss after immersion for 240 h in 1 M NaOH solution open to air at 25°C. The corrosion rate measurement by weight loss method was carried out 2–3 times so as to get the average corrosion rate of the alloys. The time dependence of the corrosion rate of the W–xCr–yZr alloys was also estimated at various time intervals. The corrosion rate of the individual alloy was estimated by using equation (1) as given below24,36,37:

\[
\text{Corrosion Rate (mm.y}^{-1}\text{)} = \frac{\Delta w \times 8760 \times 10}{d \times A \times t} \quad (1)
\]

where, \(\Delta w\) is weight loss of the alloy specimen in grams; \(d\) is density of the alloy specimen in g/cm³; \(A\) is area of the alloy specimen in cm²; and; \(t\) is time of immersion in hour.

The open circuit potential of the sputter–deposited ternary W–xCr–yZr alloys was measured after immersion for 72 hours in 1 M NaOH solution open to air at 25°C. All the electrochemical measurements were performed 2–3 times. A platinum mesh and saturated calomel electrode were used as counter and reference electrodes, respectively. All the potentials given in this paper are relative to saturated calomel electrode (SCE).
RESULTS AND DISCUSSION

Figure 1 shows the changes in the corrosion rates of the sputter–deposited W–xCr–yZr alloys after immersion for 240 h in 1 M NaOH solution open to air at 25°C, as a function of alloy zirconium content. The corrosion rates of the sputter–deposited tungsten, chromium and zirconium metals are also shown for comparison. The corrosion rates of tungsten, chromium and zirconium are about $3.5 \times 10^{-2}$ mm.y$^{-1}$ and $8.1 \times 10^{-3}$ mm.y$^{-1}$, respectively, in 1 M NaOH solution. The corrosion resistance of the ternary W–xCr–yZr alloys increase with increasing the zirconium content in the alloys and the corrosion rates of the 57W–18Cr25Zr, 19W–42Cr–39Zr and 10W–17Cr–73Zr alloys are more than two orders of magnitude lower (that is, about $1.5\text{–}2.5 \times 10^{-3}$ mm.y$^{-1}$) than that of sputter–deposited tungsten and even about one order of magnitude lower than those of the sputter–deposited zirconium in 1 M NaOH solution. These results clearly revealed that all the examined sputter–deposited W–(18–42)Cr–Zr alloys containing 10–57 at% tungsten and 25–73 at% zirconium showed higher corrosion resistance than those of alloy–constituting elements (that is, tungsten, chromium and zirconium) even for prolonged immersion (that is, 240 h) in an aggressive 1 M NaOH solution open to air at 25°C.

It is noteworthy to mention here that the corrosion rates of the sputter–deposited binary W–12Cr, W–21Cr and W–42Cr alloys were $1.2 \times 10^{-2}$, $4.2 \times 10^{-3}$ and $2.0 \times 10^{-3}$ mm.y$^{-1}$, respectively, in 1 M NaOH solution at 25°C. Furthermore, the corrosion rates of the ternary W–xCr–yZr alloys containing 10–57 at% tungsten showed almost same corrosion rates of the sputter–deposited binary W–(25–73)Zr alloys in 1 M NaOH solution. On the other hand, the corrosion rate of the ternary 80W–12Cr–8Zr alloy ($5.7 \times 10^{-2}$ mm.y$^{-1}$) is significantly (that is, about one order of magnitude) lower than that of the sputter–deposited binary W–20Zr alloy in 1 M NaOH solution. Consequently, the addition of 12–42 at% of chromium to the sputter–deposited binary W–xZr alloys (particularly for the tungsten–rich W–xZr alloys) is more effective in enhancing the corrosion resistance in alkaline NaOH solutions.

In order to clarify the time dependence of the corrosion resistance of the sputter–deposited ternary W–xCr–yZr alloys in 1 M NaOH solution, the corrosion rates of the (1057)W–(15–42)Cr–(25–73)Zr alloys as well as sputter–deposited chromium and zirconium metals were estimated after immersion for various time intervals. Figure 2 shows the changes of corrosion rates of the W–xCr–yZr alloys in 1 M NaOH solution at 25°C, as a function of immersion time. The corrosion rates of all the examined W–xCr–yZr alloys as well as chromium and zirconium are generally high at initial periods of immersion (for example, for about 2–24 h). The corrosion rate is decreased with immersion time till 48 h and after that the corrosion rates of the ternary alloys become nearly steady in 1 M NaOH solution open to air at 25°C. Accordingly, initially fast dissolution of the sputter–deposited amorphous (10–57)W–(15–42)Cr–(25–73)Zr alloys results in fast passivation by forming a more protective passive film in comparison with chromium and zirconium in 1 M NaOH solution. Consequently, the average corrosion rates of all the examined sputter–deposited amorphous (10–57)W–(15–42)Cr–(25–73)Zr alloys are lower than those of the alloy–constituting elements as shown in Fig. 1 also.

Open circuit potential measurement was carried out for better
understanding effects of simultaneous additions of tungsten, chromium and zirconium in the sputter-deposited ternary W–xCr–yZr alloys for their corrosion behavior study in 1 M NaOH solution. Figure 3 shows the changes in open circuit potentials for the sputter-deposited W–xCr–yZr alloys as well as the sputter-deposited tungsten, chromium and zirconium metals in 1 M NaOH solution at 25°C, as a function of immersion time. The open circuit potentials of the chromium and zirconium are about −760 and −970 mV (SCE), respectively, after immersion for 2 seconds and gradually increases with immersion time up to about −150 and −75 mV (SCE) for chromium and zirconium, respectively, after immersion for 2 h in 1 M NaOH solution. However, the open circuit potential of the sputter-deposited tungsten shows a steady state open circuit potential of about −900 mV (SCE) after immersion for about 1–72 h in 1 M NaOH. On the other hand, the open circuit potentials of the sputter-deposited amorphous (10–57)W–(15–42)Cr–(25–73)Zr alloys including chromium and zirconium are shifted towards more noble (or positive) direction with immersion time and attained stationary value in the ranges of about 20 to −180 mV (SCE) after immersion for about 24–72 hours in 1 M NaOH solution. On the other hand, the open circuit potential of the nanocrystalline 80W–12Cr–8Zr alloy decreases very slightly towards the more negative direction with immersion time up to 1 minute and then slightly increased towards the positive direction and obtained a stationary value of about −700 mV (SCE) after immersion for 24–72 h in 1 M NaOH solution. The ennoblement of the open circuit potentials of the amorphous (10–57)W–(15–42)Cr–(25–73)Zr alloys are clearly observed as compared to those of the nanocrystalline 80W–12Cr–8Zr alloy and tungsten metal. In particular, the open circuit potentials of the sputter-deposited amorphous (10–57)W–(15–42)Cr–(25–73)Zr alloys are located between those of zirconium and tungsten metals and are mostly located very close to that of zirconium as well as chromium metals after immersion for about 24–72 hours. These results revealed that the sputter-deposited amorphous (10–57)W–(15–42)Cr–(25–73)Zr alloys containing an adequate amount of chromium and zirconium metals show the more stable passivity and show higher corrosion resistance than those of alloy–constituting elements (that is, tungsten, chromium and zirconium) in alkaline 1 M NaOH solution. Furthermore, the open circuit potential of the sputter-deposited nanocrystalline 80W–12Cr–8Zr alloy is located very close to that of sputter-deposited tungsten eventhough it is located between tungsten and zirconium. This is mostly due to the high amount of tungsten in the 80W–12Cr–8Zr alloy because tungsten metal is actively dissolved in alkaline solution36. This result reveals that high amounts of tungsten with low amounts of zirconium and chromium is not effective to form the more protective passive film formed on the surface of the ternary W–xCr–yZr alloys particularly in alkaline environments. Therefore, the corrosion rate of the nanocrystalline 80W–12Cr–8Zr alloy is significantly higher than those of the other sputter-deposited ternary amorphous (10–57)W–(15–42)Cr–(25–73)Zr alloys in 1 M NaOH solution open to air at 25°C shown in Figs 1 and 2.

Figure 3: Changes in open circuit potentials for the sputter-deposited W–xCr–yZr alloys including sputter-deposited tungsten, chromium and zirconium in 1 M NaOH solution at 25°C, as a function of immersion time.

Figure 4: Changes in the corrosion rates and open circuit potentials of the sputter-deposited ternary W–xCr–yZr alloys including tungsten, chromium and zirconium metals after immersion in 1 M NaOH open to air at 25°C, as a function of alloying zirconium content.

Figure 4 shows the changes in the corrosion rates and the open circuit potentials of the ternary amorphous or nanocrystalline W–xCr–yZr alloys in 1 M NaOH solution open to air at 25°C, as a function of alloy zirconium content. The open circuit potentials of the alloys are shifted to more positive direction with increasing the chromium content in the ternary W–xCr–yZr alloys and hence the ternary alloys containing 25–73 at% zirconium show the most noble open circuit potential than those of 80W–12Cr–8Zr alloy and sputter-deposited tungsten metal. This revealed that high corrosion resistance of the sputter-deposited amorphous W–xCr–yZr alloys is mostly due to the ennoblement of the open circuit potential of the alloys in 1 M NaOH solution open to air at 25°C.
CONCLUSIONS

The synergistic effect of tungsten, chromium and zirconium metals for enhancing the corrosion resistance of the sputter-deposited amorphous or nanocrystalline W–xCr–yZr alloys was studied in 1 M NaOH solution open to air at 25°C using immersion tests and electrochemical measurements. The following conclusions are drawn:

1. Chromium and zirconium metals act synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited amorphous or nanocrystalline W–xCr–yZr alloys so as to show higher corrosion resistance than the corrosion resistance of the alloy–constituting elements in 1 M NaOH solution.

2. The corrosion rates of all the examined sputter-deposited W–(12–42)Cr–(25–73)Zr alloys containing 10–57 at% tungsten are more than two orders of magnitude lower than that of tungsten metal and even about one order of magnitude lower than those of the sputter-deposited W–(12–42)Cr alloys as well as zirconium metal after immersion for 240 h in 1 M NaOH solution. In particular, the addition of 12–42 at% of chromium to the sputter-deposited tungsten–rich W–Zr alloys is very effective in enhancing the corrosion resistance of the ternary amorphous or nanocrystalline W–xCr–yZr alloys in NaOH solution.

REFERENCES