INTRODUCTION

The use of the sputter deposition technique is becoming a quite suitable method for tailoring of corrosion–resistant amorphous alloys for last two decades. Even if amorphous alloy is not formed by the sputter deposition technique, the alloys thus prepared are always composed of nanocrystals with very fine grains and sometimes behaves similar to the single–phase amorphous or/and nanocrystalline alloys. 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. From the corrosion point of view, they can be considered as homogeneous 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.

Tungsten, chromium and zirconium are regarded as very effective alloying elements for enhancing the corrosion resistance of alloys in aggressive environments. It has been reported that the sputter–deposited amorphous or/and nanocrystalline tungsten–based binary W–Ti1,3, W–Zr2,6,7, W–Ni1,9, W–Cr5,7,10–13, W–Nb5,7,14–16, W–Ta2,7,17, W–Mo8,18 and ternary W–Cr–Ni19,20 as well as Cr–Zr–W21 alloys were spontaneously passivated showing significantly higher corrosion resistance than those of alloy–constituting elements in 12 M HCl solution. The significant improvement of the corrosion resistance properties of the amorphous or/and nanocrystalline alloys was attributed to the formation of double or triple oxyhydroxide passive films containing both tungsten and alloy–constituting cations which are more resistance and stable for both uniform and localized corrosion in comparison with the oxyhydroxides of tungsten and other alloy–constituting elements. 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 environments24,25. The corrosion–resistant of the sputter–deposited W–Zr alloys has been reported higher than those of tungsten and zirconium in 12 M HCl2,6,7, 0.5 M NaCl22 and 1 M NaOH22 solutions.

On the other hand, chromium is one of the most effective alloying elements to provide a 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 steels23,24. A series of the sputter–deposited chromium–metalloid alloys exhibited superior corrosion resistance compared to chromium metal in 12 M HCl25. 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–Cr alloys even in 12 M HCl and these alloys showed about five orders of magnitude lower corrosion rate than the corrosion rate of chromium metal, and about one order of magnitude lower corrosion rate than that of tungsten10–13. In recent years, the sputter–deposited nanocrystalline W–Cr alloys containing 25–75 at% chromium showed nearly two orders of magnitude lower corrosion rate than that of tungsten10–11.
of magnitude lower than that of tungsten and more than one order of magnitude lower corrosion rate than that of sputter-deposited chromium in 1 M NaOH solution\(^{26}\). Similarly, the sputter-deposited W–(25–91)Cr alloys showed about one order of magnitude lower corrosion rates than those of tungsten and chromium metals in 0.5 M NaCl solution at 25°C\(^{26}\).

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 aluminum\(^{27}\), chromium\(^{28}\) and molybdenum\(^{29}\) greatly improved the corrosion resistance of the alloys in acidic solutions. 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 metals\(^{30}\). 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 of the zirconium metal in 12 M HCl solution open to air at 30°C\(^{31}\). It is noteworthy for mentioning here that both zirconium\(^{31}\) and chromium\(^{2}\) metals are very corrodible in acidic or very alkaline (>13 pH) solutions. However, both zirconium and chromium metals do not corrode in neutral 0.5 M NaCl solution, mostly due to the formation of zirconium oxides\(^{31}\) and chromium hydroxide/oxides\(^{32}\), respectively. On the other hand, tungsten metal corrodes in solution having pH 4 or high\(^{33}\), for example, in 0.5 M NaCl solution. Accordingly, it might be expected that effects of tungsten, chromium and zirconium additions enhance in the corrosion resistance of the sputter-deposited amorphous or nanocrystalline W–Cr–Zr alloys in NaCl solution.

In this context, the main objective of the present work is aimed to clarify the effects of simultaneous additions of tungsten, chromium and zirconium metal on the corrosion behavior of the sputter-deposited ternary W–xCr–yZr alloys containing in 0.5 M NaCl 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 9–38 at% tungsten, 15–42 at% chromium and 39–73 at% zirconium were characterized as single-phase solid solution of amorphous structure having apparent grain size ranging 0.9 to 1.4 nm using X-ray diffraction (XRD) patterns (Table 1)\(^{1}\). The compositions of the sputter-deposited W–Cr–Zr alloys were determined using electron probe microanalysis (EPMA) and hereafter are all denoted in atomic percentage (at%).

**Table I:** Composition, structure and apparent grain size of the sputter-deposited ternary W–Cr–Zr alloys including sputter-deposited tungsten, chromium and zirconium \(^{21}\).

<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>9W–33Cr–5Zr</td>
<td>amorphous</td>
<td>1.0</td>
</tr>
<tr>
<td>10W–17Cr–73Zr</td>
<td>amorphous</td>
<td>1.4</td>
</tr>
<tr>
<td>19W–42Cr–39Zr</td>
<td>amorphous</td>
<td>0.9</td>
</tr>
<tr>
<td>20W–30Cr–50Zr</td>
<td>amorphous</td>
<td>1.0</td>
</tr>
<tr>
<td>21W–15Cr–64Zr</td>
<td>amorphous</td>
<td>1.2</td>
</tr>
<tr>
<td>31W–15Cr–54Zr</td>
<td>amorphous</td>
<td>1.1</td>
</tr>
<tr>
<td>38W–21Cr–41Zr</td>
<td>amorphous</td>
<td>1.0</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–Cr–Zr alloys 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 0.5 M NaCl 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 Zr–(12–21)Cr–W alloys was also estimated at various time intervals. The corrosion rate of the individual alloy was estimated by using equation (1) as given below\(^{34,35}\):

\[
\text{Corrosion Rate (mm·year}^{-1}\text{)} = \frac{\Delta w \times 8760 \times 10^{-6}}{d \times A \times t}
\]  

(1)

where, \(\Delta w\) is weight loss of the alloy specimen in grams; \(d\) is density of the alloy specimen in g/cm\(^3\); \(A\) is area of the alloy specimen in cm\(^2\); and, \(t\) is time of immersion in hour.

The open circuit potential of the sputter-deposited ternary W–Cr–Zr alloys was measured after immersion for 72 hours in 0.5 M NaCl 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 corrosion rates of the sputter-deposited binary W–Cr and W–Zr alloys in 0.5 M NaCl solution. The corrosion rates of the nanocrystalline W–Cr alloys containing about 25–91 at% chromium showed about one order of magnitude lower corrosion rates than those of the sputter-deposited tungsten and chromium metals in 0.5 M NaCl solutions after immersion for 240 h at 25°C. Similarily, the sputter-deposited amorphous W–Zr alloys containing 23–76 at% zirconium showed lower corrosion rates than those of alloy-constituting elements (that is, tungsten and zirconium) in 0.5 M NaCl solution at 25°C. However, the corrosion rate of the W–88Zr alloy is almost same as that of the sputter-deposited zirconium metal. These results revealed that the synergistic effect of the chromium and zirconium additions to the W–Cr and WZr alloys, respectively, is clearly observed.
in 0.5 M NaCl solution open to air at 25°C. Furthermore, it is cleared form the results that both of the sputter–deposited W–Cr and W–Zr alloys showed almost same corrosion rates in 0.5 M NaCl solution. In this context, it is very interesting to study the simultaneous additions of tungsten, chromium and zirconium metals to enhance the corrosion resistance property of the ternary W–Cr–Zr alloys in 0.5 M NaCl solution.

In particular, the role of the simultaneous additions of tungsten, chromium and zirconium in the binary chromium– and zirconium–enriched W–Cr and W–Zr alloys, respectively, is focused in this study. Figure 2 shows the corrosion rates of two ternary W–xCr–yZr alloys, that is, 31W–15Cr–54Zr and 38W–21Cr–41Zr alloys in 0.5 M NaCl solution at 25°C. The corrosion rates of the binary 43W–57Cr and 46W–54Zr alloys are also shown for comparison. The corrosion rates of the ternary W–xCr–yZr alloys are almost same as those of the binary 43W–57Cr and 46W–54Zr alloys in 0.5 M NaCl at 25°C. These results revealed that the corrosion resistance property of these two ternary alloys is not significantly improved with the simultaneous additions of tungsten, chromium and zirconium in the binary W–Cr and W–Zr alloys containing 43–46 at% tungsten.

![Figure 1: Corrosion rates of the sputter–deposited nanocrystalline W–Cr and amorphous W–Zr alloys after immersion for 240 h in 0.5 M NaCl solution open to air at 25°C. Corrosion rates of the sputter–deposited tungsten, chromium and zirconium are also shown for comparison.](image1)

![Figure 2: Corrosion rates of amorphous ternary W–15Cr–54Zr and W–21Cr–41Zr alloys after immersion for 240 h in 0.5 M NaCl solution open to air at 25°C. Corrosion rates of the binary W–57Cr and W–54Zr alloys are also shown for comparison.](image2)

Similarly, the role of the simultaneous additions of tungsten, chromium and zirconium on the corrosion behavior of the sputter–deposited binary 22W–78Cr and 24W–76Zr alloys in 0.5 M NaCl was studied. Figure 3 shows the corrosion rates of three ternary W–Cr–Zr alloys, that is, 21W–15Cr–64Zr, 20W–30Cr–50Zr and 19W–42Cr–39Zr alloys after immersion for 240 h in 0.5 M NaCl solution open to air at 25°C. The corrosion rates of the binary 22W–78Cr and 24W–76Zr alloys are also shown for comparison. The corrosion rates of these three ternary W–xCr–yZr alloys containing different amounts of chromium and zirconium, in which the amount of tungsten is kept almost same (that is, about 20 at%), are almost same as those of the binary 22W–78Cr and 24W–76Zr alloys in 0.5 M NaCl at 25°C. These results revealed that the corrosion resistance property of these three ternary W–xCr–yZr alloys is not significantly improved with the simultaneous additions of tungsten, chromium and zirconium in the binary W–Cr and WZr alloys containing 43–46 at% tungsten. However, the corrosion rate of the ternary 21W–15Cr–64Zr alloy is slightly lower than those of other two 21W–15Cr–64Zr and 21W–15Cr–64Zr alloys. This is mostly due to the lower corrosion rate of the pure sputter–deposited zirconium than that of chromium metal as shown in Fig.1, because the 21W–15Cr–64Zr alloy contains higher amounts of zirconium than those of other two ternary alloys.

![Figure 3: Corrosion rates of the sputter–deposited amorphous W–15Cr–64Zr, W–30Cr–50Zr and W–42Cr–39Zr alloys after immersion for 240 h in 0.5 M NaCl solution open to air at 25°C. Corrosion rates of the binary W–78Cr and W–76Zr alloys are also shown for comparison.](image3)

Figure 4 shows the effects of the simultaneous additions of tungsten, chromium and zirconium metals on the corrosion behavior of the sputter–deposited binary 9W–91Cr and 12W–88Zr alloys in 0.5 M NaCl solution after immersion for 240 h at 25°C. The corrosion rates of the binary 9W–91Cr and 12W–88Zr alloys are also shown for comparison. The corrosion rates of sputter–deposited ternary 9W–33Cr–58Zr and 10W–17Cr–73Zr alloys after immersion for 240 h in 0.5 M NaCl solution open to air at 25°C are clearly lower than those of the binary 9W–91Cr and 12W–88Zr alloys. These results revealed that the corrosion resistance property of the binary chromium– and zirconium–enriched W–91Cr and W–88Zr containing 9–12 at% tungsten is synergistically improved by simultaneous additions of tungsten, chromium and zirconium in 0.5 M NaCl. Consequently, it can be concluded that the simultaneous additions of tungsten, chromium and zirconium in the chromium– or/and zirconium–enriched binary W–91Cr and W–88Zr is effective to improve the corrosion resistance property of these ternary alloys.
The open circuit potentials of all examined binary and ternary alloys in NaCl solutions which is not the aims of the present study. After immersion for 72 h in 0.5 M NaCl, the almost same open circuit potential values of all examined alloys were observed. This result of showing the almost same open circuit potential values of all examined alloys in NaCl solutions which is not the aims of the present study. Open circuit potential measurement was carried out for a better understanding of the roles of the simultaneous additions of tungsten, chromium and zirconium in the sputter-deposited ternary W–xCr–yZr alloys for their corrosion behavior study in 0.5 M NaCl solution. Figure 5 shows the open circuit potential of the sputter-deposited binary W–xCr and W–yZr alloys including tungsten, chromium and zirconium metals after immersion for 72 h in 0.5 M NaCl solution open to air at 25°C. The open circuit potentials of all the examined nanocrystalline W–Cr and amorphous W–Zr alloys show almost same value between 0 to −60 mV (SCE) after immersion for 72 h in 0.5 M NaCl except the tungsten metal and W–9Cr alloy. The open circuit potentials of the sputter-deposited tungsten and W–9Cr alloy were found −654 and −446 mV (SCE), respectively. It is meaningful to mention here that why 72 h is selected to record the open circuit potentials of all the examined binary and ternary alloys in this study. Because it was found that the changes of corrosion rates of these binary and ternary alloys including tungsten, chromium and zirconium metals were observed a steady state corrosion values with immersion time after immersion for 48 to 240 h in 0.5 M NaCl solution (not presented the data here).

Similarly, Figs 6, 7 and 8 show the changes in the open circuit potentials of the sputter-deposited ternary W–xCr–yZr alloys after immersion for 72 h in 0.5 M NaCl solution open to air at 25°C. The open circuit potentials of the sputter-deposited chromium- and zirconium-enriched W–xCr and W–yZr alloys after immersion for 72 h in 0.5 M NaCl are also shown for comparison. The open circuit potentials of all examined sputter-deposited amorphous W–xCr–yZr alloys are almost same as those of the sputter-deposited chromium- and zirconium-enriched binary W–Cr and W–Zr alloys and are reached a steady state values between 0 to −60 mV (SCE) after immersion for 72 h in 0.5 M NaCl. This result of showing the almost same open circuit potential values of all examined alloys in NaCl solutions which is not the aims of the present study.
ternary W–xCr–yZr alloys in 0.5 M NaCl after immersion for 72 h is in agreement with showing the almost same corrosion rates of all these alloys in 0.5 M NaCl solutions as shown in Figs 1–4.

CONCLUSIONS

The simultaneous additions of tungsten, chromium and zirconium in the chromium– and zirconium–enriched binary W–Cr and W–Zr is effective to improve the corrosion resistance property of the sputter–deposited ternary W–xCr–yZr alloys after immersion for 240 h in 0.5 M NaCl solution open to air at 25°C. On the other hand, the simultaneous additions of tungsten, chromium and zirconium in the sputter–deposited W–xCr–yZr alloys is not effective to shift the open circuit potential of these alloys to more noble directions than those of the open circuit potential values of the chromium–or/and zirconium–enriched binary W–Cr and W–Zr alloys in 0.5 M NaCl solution.

REFERENCES