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Roles of Alloying Elements on the Corrosion Behavior of Amorphous W–Zr–(15–33)Cr Alloys in 1 M NaOH Solution

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Abstract

Roles of alloy-constituting elements on the corrosion behavior of the sputter-deposited amorphous W-Zr-(15-33)Cr alloys was studied in 1 M NaOH solution open to air at 25^{o}C using corrosion tests and open circuit potential measurements. Zirconium and chromium metals act synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited amorphous W-Zr-Cr alloys containing 15-33 at % chromium content so as to show higher corrosion resistance than those of alloy-constituting elements in 1 M NaOH solution. The corrosion rates of the amorphous W-Zr-(15-33)Cr alloys containing 9-33 at % tungsten are in the ranges of 2.0-5.0×10^{-3} mm.y^{-1} after immersion for 240 h in 1 M NaOH solution which is about two orders of magnitude lower corrosion rates lower than that of tungsten and even slightly lower than that of the zirconium metal. The simultaneous additions of zirconium and chromium metals in W-Zr-(15-33)Cr alloys are effective for ennoblement of the open circuit potential of the tungsten metal.

Keywords*: W-Zr-Cr alloys, corrosion resistance, immersion test, open circuit potential, 1 M NaOH.*

Introduction

Corrosion problems are such that they are faced in all areas. There is a challenge to corrosionists as well as design engineers to investigate adequate corrosion control techniques and mechanisms through which a better understanding of corrosion process can be made. In fact, the damages caused by the corrosion phenomena are not totally prevented. However, it can be minimized or controlled. It is believed that the cost of corrosion is about 3-4 % of the gross national products (GNP) of the most industrialized countries[1]. Moreover, it is assumed that about 40 % of this GNP loss can be avoided by improving corrosion properties of the engineering materials.

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Last three decades, the use of the sputter deposition technique is becoming a quite suitable method for tailoring of varieties of amorphous or/and nanocrystalline corrosion–resistant metastable alloys. Even if amorphous alloys are 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 alloy. In addition, the sputter deposition method has emerged as one of the best techniques to prepare chemically homogeneous amorphous or nanocrystalline alloys because, the chemically homogeneous single-phase nature of amorphous or nanocrystalline alloys are generally responsible for their high corrosion resistance, owing to the formation of uniform protective passive films that are able to separate the bulk of the alloy from aggressive environments[2]. One of the present authors had reported that the sputter-deposited amorphous or/and nanocrystalline tungsten-based binary W–Ti[3–7], W–Zr[4,8,9], W–Ni[10,11], W–Cr[4,9,12–15], W–Nb[4,9,16–18], W–Ta[4,9,19], W–Mo[10,20] and ternary W-Cr-Ni[21,22] as well as Cr-Zr-W[23] alloys were spontaneously passivated showing significantly higher corrosion resistance than those of alloy–constituting elements in concentrated hydrochloric acid solutions. The significant improvement of the corrosion–resistant is attributed to the formation of double oxyhydroxide passive films containing both tungsten and alloy–constituting metal cations which are more resistance and stable for both the general and localized corrosion in comparison with the oxyhydroxides of tungsten and alloy–constituting elements.

Tungsten, zirconium and chromium are regarded as very effective alloying elements for enhancing the corrosion resistance of binary and ternary alloys in aggressive environments. It has been reported that the corrosion resistance of the sputter–deposited amorphous or/and nanocrystalline W–Zr alloys were passivated spontaneously and observed significantly high corrosion resistance in aggressive environments[4,8,9]. 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. On the other hand, 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[24], chromium[25] and molybdenum[26] greatly improved the corrosion resistance of the alloys in acidic solutions.

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 steels[27,28]. A series of the sputter–deposited chromium–metalloid alloys exhibited superior corrosion resistance compared to chromium metal in 12 M HCl[29]. On the other hand, 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 tungsten[12–15]. 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^{o}C[23].

Accordingly, it might be expected that effects of zirconium and chromium additions enhance in the corrosion resistance of the sputter–deposited amorphous W–Zr–(15–33)Cr alloys in NaOH solution.

The main objective of this research work is to clarify the roles of tungsten, zirconium and chromium additions on the corrosion behavior of the sputter-deposited amorphous W–Zr–Cr alloys in 1 M NaOH solution open to air at 25^{o}C using corrosion tests and electrochemical measurements.

Experimental Methods

The sputter-deposited ternary W–Zr–(15–33)Cr alloys containing 9-33 at % tungsten and 35-64 at % zirconium were characterized as single-phase solid solution of amorphous structure having apparent grain size ranges from 0.92 to 1.22 nm[23]. The compositions of the sputter-deposited ternary W–Zr–Cr alloys hereafter are all denoted in atomic percentage (at %).

Prior to the corrosion tests and electrochemical measurements, the sputter-deposited W–Zr–(15–33)Cr 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^{o}C. The weight loss for each alloy specimen was estimated two times or more and the average corrosion rate was calculated as described elsewhere[4,30]. The time dependence of the corrosion rate of the W–Zr–(15–33)Cr alloys was also estimated at various time intervals.

The open circuit potential of the sputter-deposited amorphous W–Zr–(15–33)Cr alloys was measured after immersion for 72 hours in 1 M NaOH solution open to air at 25^{o}C. 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 corrosion rates of the sputter-deposited amorphous W–Zr–(15–33)Cr alloys after immersion for 240 hours in 1 M NaOH solution open to air at 25^{o}C. Corrosion rates of the sputter-deposited binary W-(12,32)Cr[31] and W-Zr[32] alloys including sputter-deposited tungsten, chromium and zirconium metals are also shown for comparison. All the examined sputter-deposited W-(35-64)Zr-(15-33)Cr alloys containing 9-33 at % tungsten show higher corrosion resistance than those of alloy-constituting elements (that is, tungsten, chromium and zirconium) even for 240 h in an aggressive 1 M NaOH solution open to air at 25^{o}C. The corrosion rates of the sputter-deposited W-Zr-(15-33)Cr alloys containing 35-64 at % zirconium are about two orders of magnitude lower than that of sputter-deposited tungsten and even slightly lower than that of the sputter-deposited zirconium metal in 1 M NaOH solution.

In particular, the corrosion rates of the amorphous W-58Zr-33Cr and W-50Zr-20Cr alloys containing comparatively low amount of tungsten are lowest among all the examined alloys in this work. On the other hand, the corrosion rates of the W-Zr-Cr alloys containing 30-33 at % chromium are generally decreased with increasing the zirconium content and these corrosion rates are almost same as that of the sputter-deposited binary W-xZr alloys in 1 M NaOH solution. However, the corrosion rates of the W-Zr-Cr alloys containing 15 at % chromium are slightly higher corrosion rates than those of the W-Zr-Cr alloys containing 30-33 at % chromium. These results clearly revealed that about 32 at % chromium addition to ternary W-Zr-Cr alloys is more effective to enhance the corrosion resistance properties of the alloys than only 15 at % chromium addition. This is mainly due to high corrosion resistance of chromium metal than that of tungsten in 1 M NaOH.

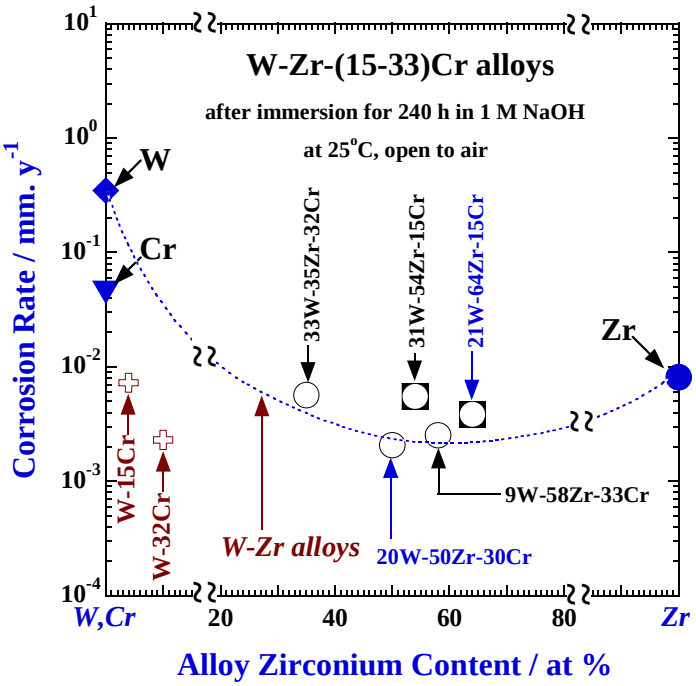

***Figure 1**: Changes in corrosion rates of the sputter-deposited amorphous W-Zr-(15-33)Cr alloys including sputter-deposited binary W-Cr[31] and W-Zr[32] alloys as well as tungsten, chromium and zirconium metals after immersion for 240 h in 1 M NaOH solution open to air at 25°C, as a function of alloy zirconium content.*

In general, it is important to identify the role of immersion time for rational understanding of the corrosion behavior of the alloys. Figure 2 shows the changes in the corrosion rates of the amorphous W-Zr-(15-33)Cr alloys including zirconium and chromium metals in 1 M NaOH solution, as a function of immersion time. In general, the corrosion rates of all the examined W-Zr-(15-33)Cr alloys as well as zirconium and chromium metals are generally high at initial periods of immersion (for example, about 2-8 h). The corrosion rate is decreased with immersion time till 48 h and after that the corrosion rates of the alloys become nearly steady. Accordingly, initially fast dissolution of the sputter-deposited

amorphous W-Zr-(15-33)Cr alloys results in fast passivation by forming more protective passive films formed on the ternary alloys in 1 M NaOH solution open to air at 25°C. Consequently, the average corrosion rates of all the examine sputter-deposited W-Zr-(15-33)Cr alloys are lower than those of the alloy-constituting elements as shown in Fig. 1.

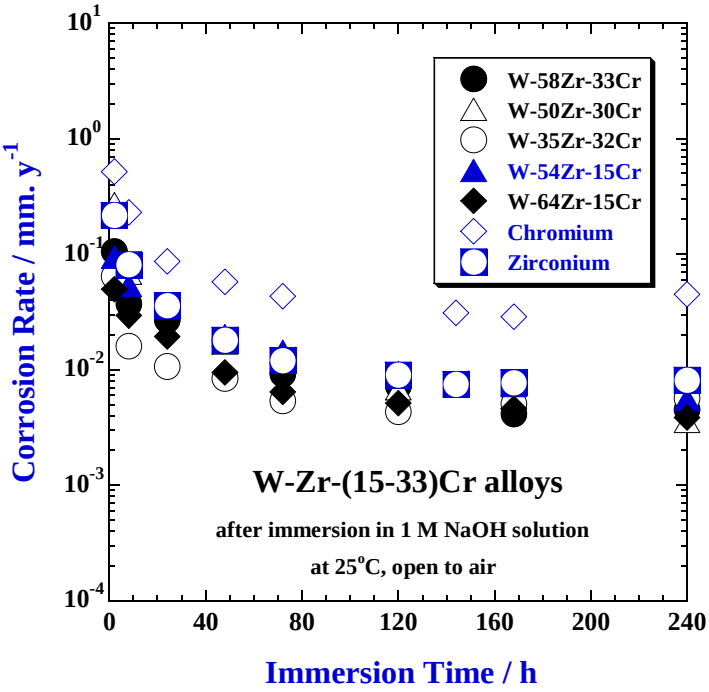

***Figure 2**: Changes in corrosion rates of the sputter-deposited W-Zr-(15-33)Cr alloys including chromium and zirconium in 1 M NaOH solution open to air at 25°C, as a function of immersion time.*

Figures 3 shows the changes in open circuit potentials of the *W-Zr-(15-33)Cr alloys* including zirconium and chromium metals in 1 M NaOH solution open to air at 25°C, as a function of immersion time. The open circuit potentials of the zirconium and chromium are about –970 and –760 mV (SCE), respectively, after immersion for 2 seconds and gradually increased with immersion time up to about –75 and –150 mV (SCE) for zirconium and chromium, respectively, after immersion for 2 h in 1 M NaOH solution. However, the open circuit potential of the sputter-deposited tungsten showed a steady state open circuit potential of about –900 mV (SCE) after immersion for 10-120 minutes in 1 M NaOH. On the other hand, the open circuit potentials of the sputter-deposited amorphous W-Zr-(15-32)Cr alloys are shifted towards more noble (or positive) direction with immersion time and attained a stationary open circuit potential value in the ranges of about –50 to –150 mV (SCE) after immersion for about 24-72 hours in 1 M NaOH solution. The ennoblement of the open circuit potentials of the W-Zr-(15-32)Cr alloys are clearly observed as compared to that of tungsten metal. Therefore, the open circuit potentials of all the examined sputter-deposited amorphous W-Zr-(15-32)Cr alloy 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 1-72 hours. These results revealed that the sputter-deposited W-Zr-(15-32)Cr alloys show more stable passivity and higher corrosion resistance with simultaneous additions of alloy-constituting elements (that is, tungsten, zirconium and chromium) in alkaline 1 M NaOH solution. These facts also coincide with the average corrosion rates of the W-Zr-(15-32)Cr alloys as shown in Figs 1 and 2.

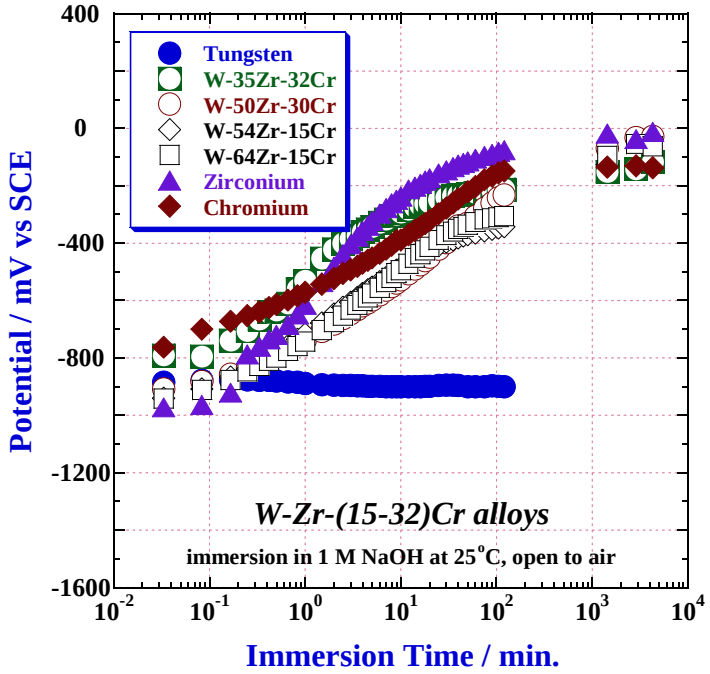

***Figure 3**: Changes in open circuit potential for amorphous W-Zr-(15-32)Cr alloys including chromium, zirconium and tungsten metals in 1 M NaOH solution open to air at 25°C, as a function of immersion time.*

Conclusions

The roles of tungsten, zirconium and chromium metals for enhancing the corrosion resistance of the sputter-deposited amorphous W-Zr-(15-32)Cr alloys was studied in 1 M NaOH solution open to air at 25°C using corrosion tests and open circuit potential measurements. The following conclusions are drawn from the present research work:

1. The simultaneous additions of tungsten, zirconium and chromium metals are effective in enhancing the corrosion resistance of the ternary amorphous W-Zr-Cr alloys so as to show higher corrosion resistance than those of the alloy-constituting elements in 1 M NaOH solution. The corrosion rates of all the examined sputter-deposited W-Zr-(15-33)Cr alloys are more than that of tungsten and even about one order of magnitude lower than those of zirconium as well as chromium metals after immersion for 240 h in alkaline 1 M NaOH solution at 25°C.

2. The simultaneous addition of zirconium and chromium metals in the ternary W-Zr-(15-33)Cr alloys are effective for ennoblement of the open circuit potential of the tungsten metal in 1 M NaOH solution so as to shift the open circuit potentials of the ternary alloys towards the more positive (noble) direction with increasing total amounts of zirconium and chromium in the alloys.

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