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The Passivation Behavior of Sputter-deposited W-Zr Alloys in NaCl and NaOH Solutions

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Abstract

The passivation behavior of the sputter-deposited amorphous or/and nanocrystalline W-Zr alloys is studied in 0.5 M NaCl and 1 M NaOH solutions at 25^oC, open to air using corrosion tests and electrochemical measurements. Zirconium metal acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Zr alloys so as to show lower corrosion rates than those of alloy-constituting elements (that is, tungsten and zirconium) in 0.5 M NaCl solution. In particular, corrosion rates of the binary W-Zr alloys containing 23-76 at % zirconium are more than one order of magnitude lower than that of tungsten (that is, about 0.8-1.1 × 10^{-3} mm.y^{-1}) and even lower than that of the sputter-deposited zirconium. On the other hand, the corrosion rates of the W-Zr alloys containing 54-76 at% zirconium are nearly two orders of magnitude lower than that of tungsten and even about one order of magnitude lower corrosion rate than that of sputter-deposited zirconium metal in alkaline 1 M NaOH solution. These results clearly revealed that the simultaneous additions of both tungsten and zirconium metals to the sputter-deposited amorphous or nanocrystalline W-Zr alloys are effective in enhancing the corrosion resistance of the alloys in both 0.5 M NaCl and alkaline 1 M NaOH solutions at 25^oC, open to air. The corrosion-resistant of all the examined binary W-Zr alloys in 0.5 M NaCl solution is higher than in 1 M NaOH solution at 25^oC. In general, the open circuit potentials of all the examined W-Zr alloys are shifted to more noble direction with increasing the alloy zirconium content in both 0.5 M NaCl and 1 M NaOH solutions.

Keywords: *Sputter-deposited W-Zr alloys, amorphous, corrosion test, electrochemical measurement, NaCl and NaOH solutions.*

Introduction

The development of new corrosion-resistant engineering materials is provoked by different reasons and one of them is the improved corrosion resistance properties of the materials. The research activities on amorphous or/and nanocrystalline alloys produced by sputter deposition technique are recently being of a widespread interest in the field of

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corrosion science which is motivated by practical importance of such novel materials. The sputter deposition technique is generally used as one of the potential techniques for the preparation of varieties of corrosion-resistant amorphous or/and nanocrystalline alloys.[1] In recent years, this technique is known to form amorphous or nanocrystalline structures over the widest composition range among the various methods. Therefore, the use of sputter deposition technique is quite suitable for tailoring of the corrosion–resistant metastable alloys. Furthermore, even if amorphous alloys are not formed by this technique, the alloys thus prepared are always composed of nanocrystals with very fine grains (that is, less than 20 nm)[2] and sometimes behaves similar to the single-phase amorphous alloys.[3] In particular, sputter deposition technique does not require melting of the alloying elements for alloy formation, and hence enables alloys to be produced even when there is significant difference in the melting points of both alloy constituents in binary alloys. By using this advantage of the sputtering method, Bhattarai et al.[4,5] had been successfully prepared amorphous or/and nanocrystalline W-Zr alloys in a wide composition ranges, even though there is a large difference between the melting points of tungsten and zirconium, i.e., 1565°C.

It has been reported that the sputter-deposited amorphous or/and nanocrystalline alloys are chemically more homogeneous structure than conventionally processed crystalline alloys,[2,6] and hence such sputter-deposited alloys are interesting for high corrosion resistance properties. Since homogeneous single-phase amorphous or nanocrystalline alloys possess many superior corrosion resistance properties, a variety of extremely high corrosion resistance single-phase amorphous or/and nanocrystalline chromium[7-11]- molybdenum[12-16]- tungsten[4,5,17-29]- and manganese[30,31]-transition metal alloys have been developed using sputter-deposition method. In particular, the sputter-deposited amorphous W-Zr alloys containing 23-76 at% zirconium were spontaneously passivated and showed significantly high corrosion resistance in 12 M HCl so as to show lower corrosion rates than those of the alloy-constituting elements. The pitting resistance of zirconium was greatly improved by alloying with tungsten. The formation of the homogeneous double oxyhydroxide of tungsten and zirconium ions acts synergistically in improving the corrosion resistance of W-Zr alloys in 12 HCl solutions open to air at 30°C.

Quantitative surface analysis by X-ray photoelectron spectroscopy (XPS) has clarified that the spontaneously passivated films formed on the sputter-deposited amorphous or /and nanocrystalline W-Zr alloys are composed of homogeneous new passive double oxyhydroxide films consisting of both tungsten and zirconium ions {for example, $(0.37)W^{4.94+}(0.63)Zr^{4+}(1.73)O^{2-}(0.89)OH^{-}$ on the surface of amorphous W-50Zr alloy} in 12 M HCl solution at $30^{o}C$[32] having pH values less than one in which regions tungsten is passive and zirconium is active[33]. It is noteworthy to mention here that tungsten metal generally corrodes in solution having pH 4 or higher whereas zirconium metal does not corrode in neutral and slightly alkaline oxidizing solutions[33]. Therefore, it is very interesting to study the passivation behavior of the sputter-deposited W-Zr alloys in neutral 0.5 M NaCl and alkaline 1 M NaOH solutions.

Present research work is aimed at studying the passivation behavior of the sputter-deposited amorphous or/and nanocrystalline W-Zr alloys in 0.5 M NaCl and 1 M NaOH solutions at $25^{o}C$, open to air by using corrosion tests and electrochemical measurements.

Experimental Methods

The sputter-deposited binary W-Zr alloys containing 7-88 at% zirconium were characterized as single-phase solid solutions of amorphous or/and nanocrystalline structures having apparent grain size ranges from 2 to 21 nm as shown in Table 1 [4,5]. The compositions of the sputter-deposited W-Zr alloys hereafter are all denoted in atomic percentage (at %).

Table 1*: Structure and apparent grain size of the sputter-deposited W-Zr alloys*[4,5].

Name of Alloy	**Structure**	**Apparent Grain Size (nm)**
W-7Zr	nanocrystalline	21
W-23Zr	amorphous	2
W-76Zr	amorphous	2
W-88Zr	amorphous + nanocrystalline	4
Tungsten	nanocrystalline	20
Zirconium	nanocrystalline	24

Prior to the corrosion tests and electrochemical measurements, the W-Zr 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 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air using the formula as described elsewhere[5,22,34]. The time dependence of the corrosion rate of the W-Zr alloys was also estimated at various time intervals ranging from 2 to 240 hours.

The open circuit potentials of the binary W-Zr alloys were measured after immersion for 72 hours in 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air. 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 W-Zr alloys after immersion for 240 hours in both 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air as a function of alloy zirconium content. The corrosion rates of the sputter-deposited tungsten and zirconium metals are also shown for comparison. Corrosion rates of the W-Zr alloys containing 23-76 at % zirconium (that is, about $0.8\text{-}1.1 \times 10^{-3}$ mm.y^{-1}) are more than one order of magnitude lower than that of tungsten and even lower than that of the sputter-deposited zirconium in 0.5 M NaCl solution. In 1 M NaOH solution, the corrosion rates of the sputter-deposited W-Zr alloys decreased sharply with increasing zirconium content and the W-Zr alloys containing 54-76 at % zirconium showed the lowest corrosion rates (that is, $1.96\text{-}2.25 \times 10^{-3}$ mm.y^{-1}) among all the examined sputter-deposited W-Zr alloys. The corrosion rates of the W-Zr alloys containing 54-76 at % zirconium are nearly two orders of magnitude lower than that of tungsten and about one order of magnitude lower corrosion rate than that of the sputter-deposited zirconium metal in 1 M NaOH solution.

In particular, all the examined sputter-deposited W-Zr alloys, which are composed of either amorphous or/and nanocrystalline single phase solid solutions, showed lower corrosion rates than those of alloy-constituting elements (that is, tungsten and zirconium) even for prolonged immersion in aggressive 0.5 M NaCl and 1 M NaOH solutions at 25°C. These results clearly revealed that the simultaneous additions of tungsten and zirconium metals to the sputter-deposited amorphous or/and nanocrystalline W-Zr alloys are effective in enhancing the corrosion resistance of the alloys in both 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air.

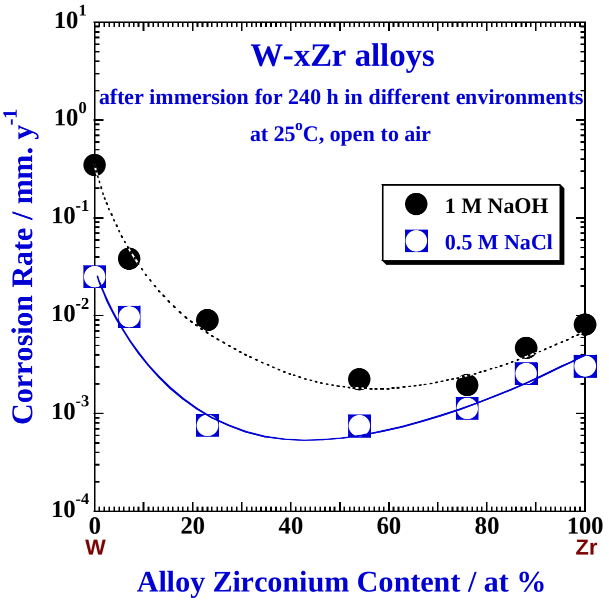

***Figure 1**: Changes in corrosion rates of the sputter-deposited W-Zr alloys including the sputter-deposited tungsten and zirconium metals in 0.5 M NaCl and alkaline 1 M NaOH solutions at 25°C, as a function of alloy zirconium content.*

Furthermore, a comparison of the corrosion rates of the sputter-deposited amorphous or/and nanocrystalline W-Zr alloys is discussed here in both 0.5 M NaCl and alkaline 1 M NaOH solutions. In particular, the corrosion rates of the tungsten-rich W-Zr alloys showed significantly higher corrosion rates in 1 M NaOH solution than in 0.5 M NaCl solution. However, the corrosion rates of the zirconium-rich W-Zr alloys contained 54 at % zirconium or more as well as the sputter-deposited zirconium metal showed almost same ranges of the corrosion rates and significantly high corrosion resistance in both the neutral and alkaline solutions. This is mostly due to the facts that the tungsten metal actively corrodes in alkaline solutions whereas the zirconium metal is passive in such alkaline media.

In order to clarify the time dependence of corrosion rate of the sputter-deposited W-Zr alloys, the corrosion rates of the sputter-deposited W-23Zr, W-76Zr and W-88Zr alloys including zirconium metal were measured after immersion in 0.5 M NaCl and alkaline 1 M

NaOH solutions at various time intervals. Figures 2 (a) and 7 (b) show the changes in the corrosion rates of W-23Zr, W-76Zr and W-88Zr alloys including the sputter-deposited zirconium metal in 0.5 M NaCl and 1 M NaOH solutions, respectively, as a function of immersion time. In general, the corrosion rates of all the examined W-Zr alloys are significantly high at initial periods of immersion (for example, about 2-8 h). The corrosion rate is decreased with immersion time till about 48-72 h for W-Zr alloys and zirconium metal. In particular, the corrosion rates of the W-Zr alloys become almost steady after immersion for about 72 hours while the corrosion rates of the W-Zr alloys become almost steady after immersion for about 48 hours in alkaline 1 M NaOH solution. Accordingly, initially fast dissolution of the sputter-deposited W-Zr alloys results in fast passivation by forming more protective passive films formed on the alloys, and hence the average corrosion rates of the sputter-deposited W-Zr alloys are lower than those of the alloy-constituting elements after immersion for 240 h in both 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air (Fig. 1).

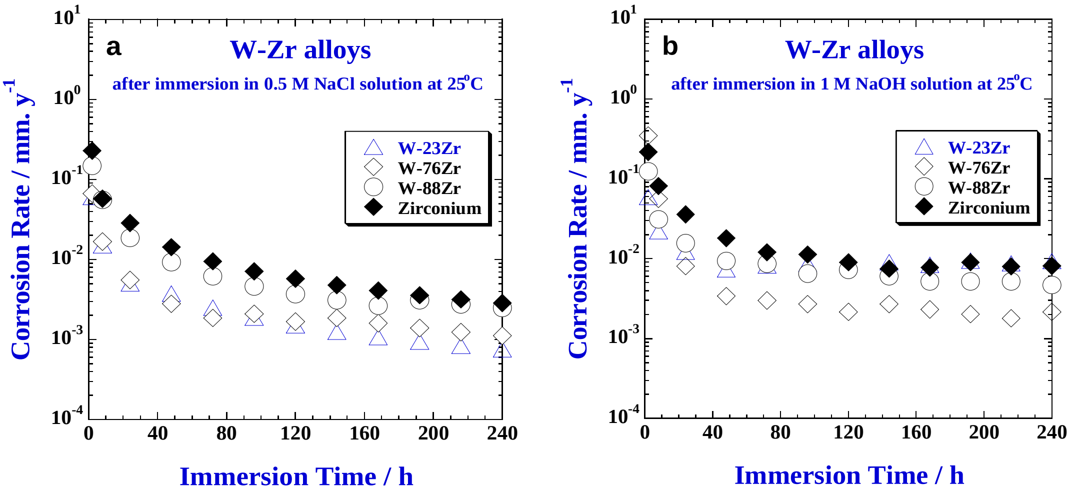

Figure 2: *Changes in the corrosion rates of the sputter-deposited W-Zr alloys including zirconium metal in (a) 0.5 M NaCl & (b) 1 M NaOH solutions at 25°C, as a function of immersion time.*

Electrochemical measurements were carried out for a better understanding of the passivation behavior of the sputter-deposited amorphous or/and nanocrystalline W-Zr alloys for 72 hours in neutral 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air. Figure 3 shows the changes in open circuit potentials of the sputter-deposited W-7Zr, W-23Zr, W-76Zr, W-88Zr alloys including tungsten and zirconium metals in both neutral 0.5 M NaCl and alkaline 1 M NaOH solutions at 25°C, as a function of immersion time. The open circuit potentials of all the examined sputter-deposited amorphous or/and nanocrystalline W-Zr alloys containing 7-88 at % zirconium are shifted towards more positive (noble) direction with immersion time in 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air. These results revealed that more stable passive films are formed on the surface of the sputter-deposited W-Zr alloys with increasing zirconium content in both aggressive environments. Furthermore, the open circuit potentials of all the examined W-Zr alloys are almost same than that of zirconium metal after immersion for 72 h in 0.5 M NaCl and 1 M NaOH solutions. These results revealed that the stability of the passive films formed on the W-Zr alloys is increased with increasing zirconium content in the W-Zr alloys and these passive films are more stable than those passive films formed on the sputter-deposited tungsten and zirconium metals in both solutions. These facts agree with the higher corrosion resistance of the sputter-deposited W-Zr alloys than those of tungsten and zirconium after immersion for 240 h in 0.5 M NaCl and 1 M NaOH solutions as shown in Figs 1 and 2.

Furthermore, it is clear from figure 3 that the open circuit potentials of all the examined W-Zr alloys in this study are in more positive (noble) direction after immersion for 72 h in neutral 0.5 M NaCl solution than in alkaline 1 M NaOH solution. However, the open circuit potentials of the zirconium-rich W-Zr alloys containing, for example, 76-88 at % zirconium and zirconium metal are reached almost same value after immersion for about 24-72 hours in both 0.5 M NaCl and 1 M NaOH solutions. These results supported the facts that the corrosion resistance of the sputter-deposited W-Zr in neutral 0.5 M NaCl solution is higher than that in 1 M NaOH solution at 25^{o}C, open to air.

Conclusions

The passivation behavior of the sputter-deposited amorphous or/and nanocrystalline W-Zr alloys is studied in 0.5 M NaCl and 1 M NaOH solutions at 25^{o}C by corrosion tests and electrochemical measurements. The following conclusions are drawn from the experimental results of the study:

1. Zirconium metal acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Zr alloys so as to show lower corrosion rates than the corrosion rates of the alloy-constituting elements in 0.5 M NaCl solution.
2. All the examined sputter-deposited W-Zr alloys, which are composed either amorphous or/and nanocrystalline single phase solid solutions, show lower corrosion rates than those of alloy-constituting elements in 1 M NaOH solution. The corrosion rates of the W-Zr alloys containing 54-76 at % zirconium are nearly two orders of magnitude lower than that of tungsten and about one order of magnitude lower corrosion rate than that of the sputter-deposited zirconium metal.
3. The corrosion rates of all the examined sputter-deposited W-Zr alloys showed lower corrosion resistance in 1 M NaOH solution than in 0.5 M NaCl solution.
4. The stability of the passive films formed on the sputter-deposited W-Zr alloys is increased with increasing the zirconium content after immersion for about 2-72 hours in both 0.5 M NaCl and 1 M NaOH solutions at 25^{o}C, open to air.

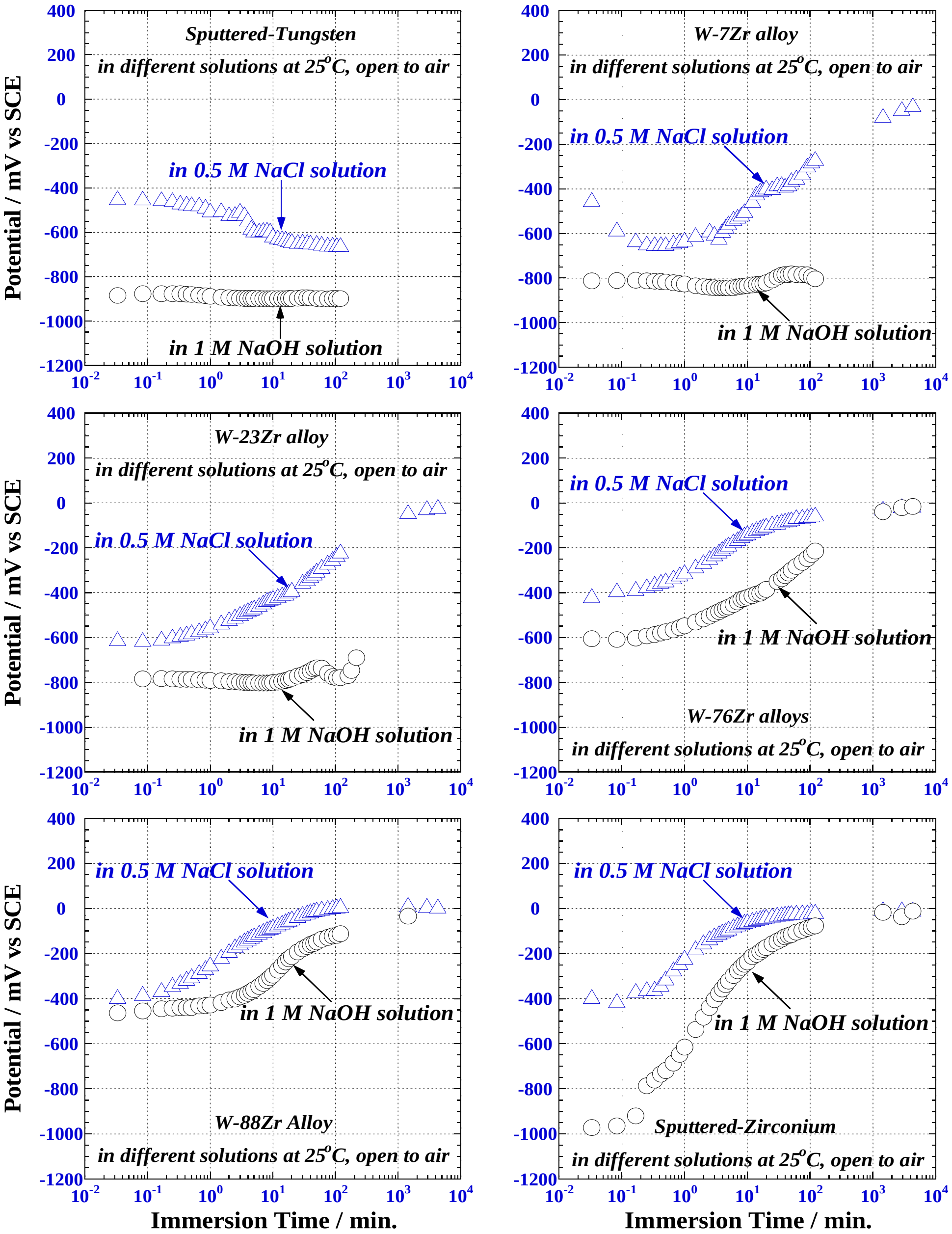

***Figure 3**: Changes in open circuit potentials for the sputter-deposited W-Zr alloys including tungsten and zirconium metals in 0.5 M NaCl and 1 M NaOH solutions at 25°C, as a function of immersion time.*

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