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The Corrosion Behavior of Sputter-deposited W-Ti Alloys in 0.5 M NaCl Solution

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Abstract

The corrosion behavior of the sputter-deposited amorphous or nanocrystalline W-Ti alloys was studied in neutral 0.5 M NaCl solution at 25°C, open to air by immersion tests, electrochemical measurements and confocal scanning laser microscopic(CSLM) techniques. Titanium metal acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Ti alloys so as to show higher corrosion resistance than those of alloy-constituting elements (that is, tungsten and titanium) in neutral 0.5 M NaCl solution. In particular, the amorphous W-Ti alloys containing 30-53 at% titanium showed lowest corrosion rates (that is, about 1×10^{-3} mm.y^{-1}). Open circuit potentials of all the examined W-Ti alloys were shifted to more noble direction than those of the open circuit potentials of alloy-constituting elements in 0.5 M NaCl solution.

Key words: Sputter deposition, W-Ti alloys, corrosion-resistant, CSLM, NaCl solution.

Introduction

Chemically homogeneous single-phase nature of amorphous or/and nanocrystalline alloys are 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 or/and nanocrystalline single-phase are chemically homogeneous, and hence are interesting in the view of corrosion resistance. In recent years, the sputter deposition technique has been used as quite suitable for tailoring of varieties of amorphous corrosion–resistant amorphous or/and nanocrystalline chromium (Kim *et al.* 1994, 1995, Li *et al.* 1997)- molybdenum (Park *et al.* 1995, 1996)- tungsten (Bhattarai 1998; Bhattarai *et al.* 1995, 1997, 1998)- and manganese (El-Moneim *et al.* 1997)- transition metal alloys.

The present author has been reported that the sputter-deposited amorphous or/and nanocrystalline tungsten-based binary alloys were spontaneously passivated, and hence showed significantly higher corrosion resistance than those of alloy-constituting elements in concentrated hydrochloric acid solutions (Bhattarai 1998, 2000, 2002, 2006). The significant improvement of the corrosion-resistance is attributed to the formation of double oxyhydroxide passive films containing both tungsten and alloy-constituting metal cations, which are more corrosion resistant, in comparison with the oxyhydroxides of tungsten and alloy-constituting elements.

The present author had successfully prepared novel sputter-deposited amorphous or/and nanocrystalline binary W-Ti alloys in a wide composition range, and reported high corrosion resistance in 12 M HCl (Bhattarai *et al.* 1995, Bhattarai 1998) and 1 M NaOH (Sharmah *et al.* 2007) solutions. In particular, only less than 15 at% of tungsten addition was enough to cause spontaneous passivation of the sputter-deposited amorphous or nanocrystalline W-Ti alloys and the alloys showed about three orders of magnitude lower corrosion rate than that of titanium metal in concentrated hydrochloric acid solutions at 30°C (Bhattarai *et al.* 1995, 2000, Bhattarai 1998, 2000, 2001). Quantitative surface analysis by X-ray photoelectron spectroscopy (XPS) has clarified that the spontaneously passivated films formed on the sputter-deposited amorphous or nanocrystalline W-

Ti alloys were composed of new passive double oxyhydroxide films consisting of both tungsten and titanium ions {that is, $(0.67)W^{4.91+}(0.33)Ti^{4+}(2.08)O^{2-}(0.45)OH^{-}$} in concentrated hydrochloric acid solutions at 30°C having pH values less than one in which regions tungsten is passive and titanium is active (Bhattarai 1998; Bhattarai *et al.*, 2000). It is noteworthy to mention here that tungsten metal generally corrodes in solution having pH 4 or higher whereas titanium metal does not corrode in neutral or slightly alkaline solutions (Pourbaix 1974). Therefore, it is very interesting to study the corrosion behavior of the sputter-deposited W-Ti alloys in neutral 0.5 M NaCl solution.

Present research work is aimed at studying the corrosion behavior of the sputter-deposited amorphous or nanocrystalline W-Ti alloys in 0.5 M NaCl solution at 25°C, open to air by using corrosion tests, electrochemical measurements and confocal scanning laser microscopic (CSLM) techniques.

Methodology

The binary W-Ti alloys were prepared by direct current (D. C.) magnetron sputtering machine on glass substrate as described elsewhere (Bhattarai 1998). An electron probe microanalysis was used to determine the composition of the sputter-deposited W-Ti alloys (Bhattarai 1998, Bhattarai *et al.* 1995). The sputter-deposited binary W-Ti alloys were confirmed as amorphous or nanocrystalline single-phase solid solution by X-ray diffraction (Bhattarai 1998).

Prior to the corrosion tests, electrochemical measurements and surface morphological studies, the sputter-deposited amorphous or nanocrystalline W-Ti 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 corrosion rate was estimated from the weight loss after immersion for 180 h in 0.5 M NaCl solution at 25°C, open to air. The weight loss measurement for each alloy specimen was done two or more times and the average corrosion rates of individual alloys were estimated. The time dependence of the corrosion rate of the W-Ti alloys including titanium metal was also estimated at various time intervals ranging from 2 to 180 h.

The open circuit potentials were measured after immersion for 2 h. in 0.5 M NaCl solution at 25°C, open to air. A platinum mesh and saturated calomel electrode were used as counter and reference electrodes, respectively. The alloy specimen was used as a working electrode. All the potentials given in this paper are relative to saturated calomel electrode (SCE).

The change in surface morphology of the sputter-deposited amorphous or nanocrystalline W-Ti alloys before and after immersion for 24 hours in 0.5 M NaCl solution at 25°C was observed using confocal scanning laser microscope (CSLM). The laser source used was He-Ne having wavelength of 633 nm. The scan rates for the samples were ranged from 1 to 16 per second.

Results and Discussion

Figure 1 shows the change in the corrosion rate of the sputter-deposited W-Ti alloys after immersion for 180 h in 0.5 M NaCl solution at 25°C, as a function of alloy titanium content. The change in the open circuit potential of the alloys measured after open circuit immersion for 2 h in 0.5 M NaCl is also shown. The corrosion rate and the open circuit potential of the sputter-deposited tungsten and titanium metals are also shown for comparison. Corrosion rates of the W-Ti alloys containing 30 at% or more titanium are about one order of magnitude lower than that of the sputter-deposited tungsten and even lower than that of titanium. In particular, the amorphous W-Ti alloys containing 30-53 at% titanium show lowest corrosion rate in the range of $1 x 10^{-3}$ mm/y. Accordingly, all the examined W-Ti alloys, which are composed of either amorphous or nanocrystalline single-phase supersaturated solid solutions, show higher corrosion resistance than those of alloy-constituting elements even for prolonged immersion in an aggressive chloride containing neutral 0.5 M NaCl solution at 25°C. The open circuit potential of all the examined alloys is shifted to more positive direction than those of the alloy-constituting elements (that is, tungsten and titanium metal), and hence the corrosion rate of the W-Ti alloys is lower than those of alloy-constituting elements as described above. The addition of 30 at% or more titanium significantly shifts the open circuit potential into the passive region of titanium. The decrease in the corrosion rate of the W-Ti alloys corresponds to the ennoblement of the open circuit potential to the passive region of titanium (Pourbaix 1974). Consequently, titanium metal acts synergistically with tungsten in enhancing the corrosion resistance so as to show the lower corrosion rates than the alloy-constituting elements in 0.5 M NaCl solution at 25°C.

In order to clarify the time dependence corrosion rate of the alloys, the corrosion rates of the amorphous or nanocrystalline W-Ti including titanium metal were estimated after immersion for various time intervals. Figure 2 shows the changes in corrosion rates of the sputter-deposited W-Ti alloys including titanium metal in 0.5 M NaCl solution at 25°C, as a function of immersion time. In general, the corrosion rates of the W-Ti alloys are significantly high at initial periods of immersion (for example, 2 h). The corrosion rate is decreased with immersion time till 36 h for W-30Ti and W-53Ti alloys, and 60 h for the W-90Ti alloy and titanium metal, respectively. Accordingly, initially fast dissolution of W-30Ti and W-53Ti alloys results in fast passivation by forming a more protective passive films in comparison with the W-90Ti alloy and titanium metal in 0.5 M NaCl solution at 25Ë%C. As a result, the average corrosion rates of W-30Ti and W-53Ti alloys are lower than those of the W-90 Ti alloy and titanium metal after immersion for 180 h as shown in Fig. 1.

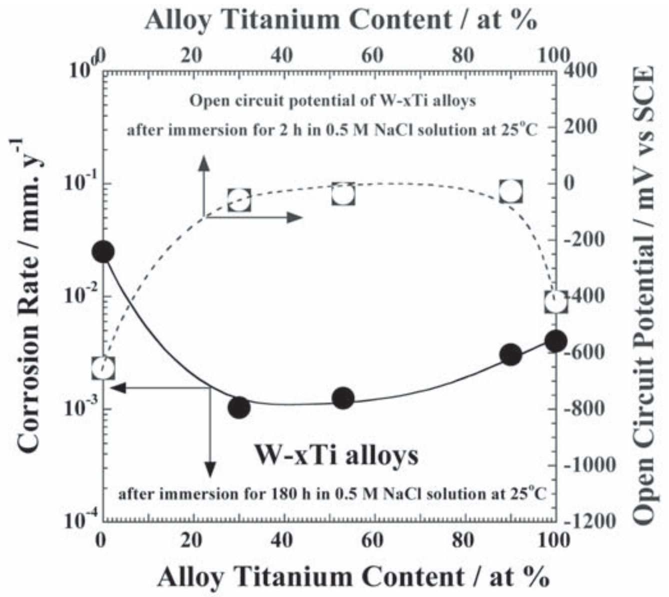

Fig. 1. The changes in corrosion rates of the sputter-deposited W-xTi alloys including tungsten and titanium metals in 0.5 M NaCl solution at 25Ë%C as a function of alloy titanium content. Open circuit potentials of the alloys & alloying elements after immersion for 2 h in 0.5 M NaCl are also shown

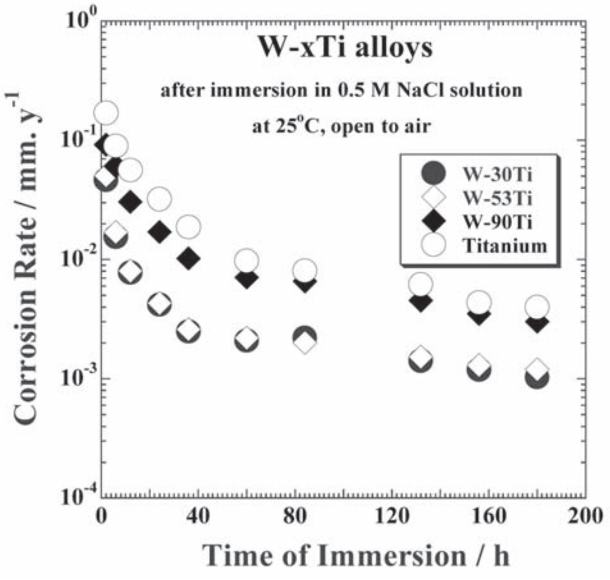

Fig. 2. The changes in corrosion rates of the sputter-deposited W-xTi alloys and titanium metal in 0.5 M NaCl at 25°C as a function of immersion time

The change in surface morphology of the W-Ti alloys gives important information about the dissolution process in nano-scales to study the corrosion behavior of the alloys. Figures 3(a) and (b) show CSLM images of the W-Ti alloys (W-30Ti, W-50Ti and W-90Ti) before and after immersion for 24 h in 1 0.5 M NaCl solution at 25°C, respectively. The surface morphologies of the passive films formed on all the examined W-Ti alloys in 0.5 M NaCl solution are clearly different than those of the oxide-films formed on the surface of the as-deposited alloy specimens as shown in the Fig. 3 (a) and (b). The dissolution is obvious and surface is roughened considerably for all the examined W-Ti alloys. The surface of the passive film formed on the W-90Ti alloy is more roughened than those on the surfaces of the passive films formed on the W-30Ti and W-53Ti alloys in 0.5 M NaCl solution. Accordingly, the corrosion rates of the W-30Ti and W-53Ti alloys are clearly lower than that of the corrosion rate of the W-90Ti alloy which is also clearly observed from Fig. 1 and 2.

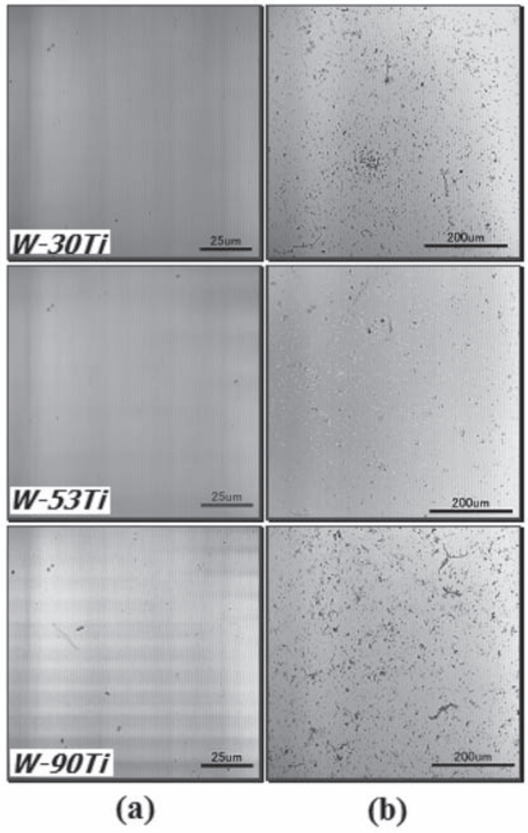

Fig. 3. The confocal scanning laser microscopic images of the sputter-deposited W-xTi alloys (a) as-prepared sputter-deposited and (b) after immersion for 24 hours in 0.5 M NaCl solution at 25°C

Electrochemical measurements were carried out for a better understanding of high corrosion resistance properties of the sputter-deposited amorphous or nano-crystalline W-Ti alloys. Figure 4 shows the changes in open circuit potentials for the sputter-deposited W-Ti alloys as well as tungsten and titanium metals after immersion in 0.5 M NaCl solution at 25°C, open to air, as a function of immersion time. Initially, the open circuit potentials of the alloys are sharply shifted to more positive direction with immersion time up to about 20 minutes and then become almost steady after immersion for about 1-2 hours. However, the open circuit potentials of the sputter-deposited tungsten and titanium metals are about -640 and -400 mV (SCE), respectively, within 25 min. The open circuit potentials of the alloys are located more positive direction than those of the OCPs of the alloy-constituting elements (that is, tungsten and titanium metals) after immersion for 2 h. These results revealed that more stable passive films are formed on the surface of the W-Ti alloys than those of pure tungsten and titanium metals in neutral 0.5 M NaCl solution. These facts agree with the higher corrosion resistance of the W-Ti alloys than those of tungsten and titanium in 0.5 M NaCl solution as shown in Fig. 1 and 2.

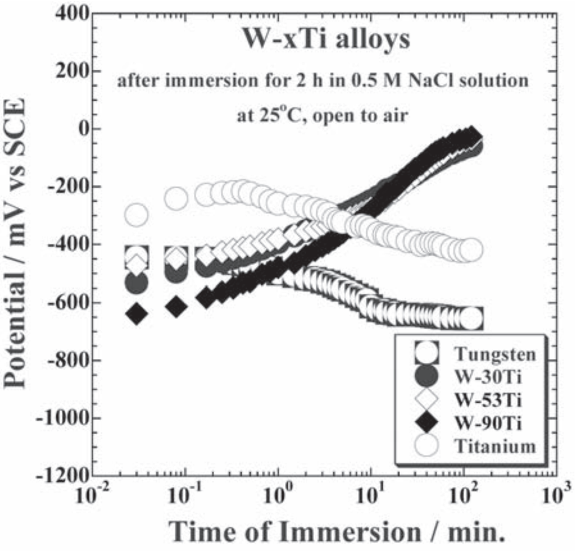

Fig. 4. The change in open circuit potential of the W-xTi alloys in 0.5 M NaCl at 25°C, as a function of immersion time

The following conclusions are drawn from the present study:

All the sputter-deposited amorphous or nanocrystalline W-Ti alloys showed lower corrosion rates than those of alloy-constituting elements in an aggressive chloride containing neutral 0.5 M NaCl solution. The surface of the passive film formed on the W-90Ti alloy was more rough than those on the surfaces of the passive films formed on the W-30Ti and W-53Ti alloys in 0.5 M NaCl solution. Accordingly, the corrosion rates of the W-30Ti and W-53Ti alloys are lower than that of the corrosion rate of the W-90Ti alloy. The surface morphological study by CSLM technique seems to be effective to study the corrosion behavior of the sputter-deposited W-Ti alloys. The addition of about 30 at% or more titanium significantly shifted the open circuit potential into the passive region of titanium.

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References

Bhattarai, J. 1998. *Tailoring of Corrosion-Resistant Tungsten Alloys by Sputtering,* Doctoral Thesis, Department of Materials Science, Faculty of Engineering, Tohoku University, Japan. pp. 229.

Bhattarai, J. 2000. The effect of immersion time in the corrosion rate and surface composition of the sputter-deposited W-22Ti and W-58Ti alloys. *Journal of Nepal Chemical Society* **19**: 32-41.

Bhattarai, J. 2001. Electrochemical and XPS studies on the corrosion behavior of sputter-deposited amorphous W-Ni alloys in 12 M HCl. *Journal of Nepal Chemical Society* **20**: 24-40.

Bhattarai, J. 2002.The anodic passivity of sputter-deposited W-Ti alloys in hydrochloric solutions. *Nepal Journal of Science and Technology* **4**: 37-43.

Bhattarai, J. 2006. Structure and corrosion behavior of sputter-deposited W-Mo alloys. *Journal of Nepal Chemical Society* **21**: 19-25.

Bhattarai, J., E. Akiyama, A. Kawashima, K. Asami and K. Hashimoto. 1995. The corrosion behavior of sputter-deposited amorphous W-Ti alloys in 6 M HCl solution. *Corrosion Science* **37**: 2071-2086.

Bhattarai, J., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto. 1997. Electrochemical and XPS studies of the corrosion behavior of sputter-deposited amorphous W-Zr alloys in 6 and 12 M HCl solutions. *Corrosion Science* **39**: 355-375.

Bhattarai, J., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto 1998. Electrochemical and XPS studies of the corrosion behavior of sputter-deposited amorphous W-Nb alloys in concentrated hydrochloric acid solutions. *Corrosion Science* **40:** 19-42.

Bhattarai, J., A. Kawashima, K. Asami and K. Hashimoto. 2000. Role of alloying elements in the extremely high corrosion resistance of sputter-deposited binary tungsten alloys in concentrated hydrochloric acids. In : *Proc. 3rd National Conference on Science and Technology*, Nepal Academy of Science and Technology, Kathmandu, Neapl. **vol. 1**, pp. 389-407.

El-Moneim, A. A., B. P. Zhang, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto. 1997. The corrosion behavior of sputter-deposited amorphous Mn-Ti alloys in 0.5 M NaCl solutions. *Corrosion Science* **39**: 305-320.

Kim, J. H., E. Akiyama, H. Yoshioka, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto. 1993. The corrosion behavior of sputter-deposited amorphous Ti-Cr alloys in 1 M and 6 M HCl solutions. *Corrosion Science* **34**: 975-987.

Kim, J. H., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto. 1994. An XPS study of the corrosion behavior of sputter-deposited amorphous Cr-Nb and Cr-Ta alloys in 12 M HCl solution. *Corrosion Science* **36**: 511-523.

Li, X. Y., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto. 1997. Spontaneously passivated films on sputter-deposited Cr-Ti alloys in 6 M HCl solution. *Corrosion Science* **39**: 935-948.

Park, P. Y., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto. 1995. The corrosion behavior of sputter-deposited amorphous M0-Zr alloys in 12 M HCl. *Corrosion Science* **37**: 307-320.

Park, P. Y., E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto 1996. The corrosion behavior of sputter-deposited Mo-To alloys in concentrated hydrochloric acid. *Corrosion Science* **38:** 1649-1667.

Pourbaix, M. 1974. *Atlas of Electrochemical Equilibrium in Aqueous Solution*. National Association of Corrosion Engineers, Huston, TX, 1974. pp. 213-280.

Sharmah, A., H. Jha and J. Bhattarai. 2007. The passivation behavior of sputter-deposited W-Ti alloys in 1 M NaOH solution. *Journal of Nepal Chemical Society* **22**: 17-25.