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The Corrosion Behavior of Sputter–deposited W–xTa Alloys in 0.5 M NaCl Solution

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Abstract

The corrosion behavior of the sputter–deposited amorphous and nanocrystalline W–xTa (x = 8–77) alloys was studied in 0.5 M NaCl solution open to air at 25°C using corrosion tests and electrochemical measurements. Tungsten and tantalum metals act synergistically in enhancing the corrosion resistance of the sputter–deposited W–xTa alloys and hence additions of 23 at. % of tantalum or more to the sputter–deposited W–xTa alloys were found to be effective to achieve significantly high corrosion resistance properties of the alloys than those of alloy–constituting elements. In particular, the corrosion rate of the W–60Ta alloy showed the lowest corrosion rate (that is, 2.0×10^{-3}). The open circuit potential of the alloys shifted noble (positive) direction with immersion time. Addition of tantalum metal in W–xTa alloys is effective for ennoblement of the open circuit corrosion potential of the tungsten metal in 0.5 M NaCl solution open to air at 25°C.

Key words: Sputter deposition, corrosion test, electrochemical measurement

Introduction

A novel corrosion resistance properties of the rapidly–quenched alloys even in aggressive environments generated tremendous interest for corrosion scientists for the last four decades. Since the extremely high corrosion resistance amorphous iron–base alloys were reported in 1970's (Hashimoto & Masumoto 1976, Hashimoto *et al.* 1976, 1979, Naka *et al.* 1974, 1976), varieties of corrosion–resistant rapidly quenched and sputter–deposited alloys were developed during the last four decades. Since 1990's, it has been reported that the sputter–deposited binary tungsten–titanium (Bhattarai 1998, 2009 a, b, Bhattarai *et al.* 1995), tungsten–zirconium (Bhattarai 1998, Bhattarai *et al.* 1997, Shrestha & Bhattarai 2010), tungsten–chromium (Basnet & Bhattarai 2010, Bhattarai 1998, Bhattarai *et al.* 1998 a), tungsten–niobium (Bhattarai 1998, 2011 a; Bhattarai *et al.* 1998 b, Jha & Bhattarai 2008), tungsten–tantalum (Bhattarai 1998, 2011 b, 2012 a, Bhattarai *et al.* 1998 c), tungsten–molybdenum (Bhattarai 1995, 2006, 2012 b, Khadka & Bhattarai 2010) and tungsten–nickel (Bhattarai 1995, Bhattarai *et al.* 2007, Sah & Bhattarai 2008/2009), and ternary tungsten–based (Aryal & Bhattarai 2010, 2011, Bhattarai 2010 a, b, 2011 c, d, Kumal & Bhattarai 2010) alloys showed higher corrosion resistance than those of alloy–constituting elements in different corrosive environments.

The passivating elements such as tungsten and tantalum can improve corrosion resistance as well as the localized corrosion of alloys. Several surface studies have been carried out for an understanding of the role of the tungsten in the passivation mechanisms of stainless steels in aggressive chloride media (Naka *et al.* 1978, Bui *et al.* 1983, Wang & Merz 1984, Habazaki *et al.* 1991). On the other hand, tantalum is widely known for its superior corrosion resistance in aggressive acidic media. Amorphous nickel–base alloys containing certain amounts of tantalum exhibit very high corrosion resistant in boiling acids (Kawashima *et al.* 1985). It has been reported that a beneficial effect of tantalum to improve the corrosion resistance of nickel–base alloys in 12 M HCl (Lee *et al.* 1997). A series of the sputter–deposited binary tantalum–containing alloys showed higher corrosion resistance than those of alloying elements due to spontaneous passivation in aggressive media (Kim *et al.* 1994, Park *et al.* 1996, Hashimoto *et al.* 1996, El–Moneim *et al.* 1997, Bhattarai *et al.* 1998c).

It has been reported that the corrosion resistance of the sputter–deposited amorphous or nanocrystalline W–Ta alloys were passivated spontaneously and observed significantly high corrosion resistance in 12 M HCl solution having the pH value of less than 4 (Bhattarai 1998, Bhattarai *et al*. 1998c). It is meaningful for mentioning here that tungsten is hardly corroded by most of acid solutions, except some complex acids like HF acid which attacks it. However, tungsten metal is corroded in neutral and alkaline solutions (Pourbaix 1974a). On the other hand, tantalum metal is highly corrosion resistance in all pH values (Pourbaix 1974b), mostly due to the formation of stable and diffusion–barrier tantalum oxides. In this context, it is interesting to study the corrosion behavior of the sputter–deposited W–xTa alloys in neutral 0.5 M NaCl solution.

The main objectives of this study are to estimate the corrosion rate and study the electrochemical behavior of the sputter–deposited amorphous or nanocrystalline W–xTa alloys in 0.5 M NaCl solution open to air at 25°C.

Methodology

The sputter–deposited binary W–xTa (x = 23, 60 and 77 at. %) alloys were characterized as the single–phase solid solutions of amorphous or/and nanocrystalline structures having apparent grain size ranges from 1.6–22 nm as shown in Table 1(Bhattarai 1998, Bhattarai *et al.* 1998 c). The compositions of the sputter–deposited W–xTa alloys hereafter are all denoted in atomic percentage (at. %).

Table 1. Chemical composition, apparent grain size and structure of the sputter–deposited W–xTa alloys (Bhattarai 1998, Bhattarai *et al.* 1998c)

Alloys	Tungsten Content (at. %)	Tantalum Content (at. %)	Apparent Grain Size (nm)	Structure
Tungsten	100.0	–	20	Nanocrystal
W–8Ta	91.6	8.4	22	Nanocrystal
W–23Ta	76.4	23.2	18	Nanocrystal
W–60Ta	40.0	60.0	11	Nanocrystal
W–77Ta	22.6	77.4	1.6	Amorphous
Tantalum	–	100.0	10	Nanocrystal

Prior to corrosion tests and electrochemical measurements, the surface of the alloy specimen was mechanically polished with a silicon carbide paper up to grit number 1500 in cyclohexane, rinsed 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 using the formula as described elsewhere (Bhattarai 1998, 2010c). The time dependence of the corrosion rate of the W–xTa alloys was also estimated at various time intervals ranging from 2 to 240 hours.

The open circuit potentials of the W–xTa alloys were also measured after immersion for 72 hours in 0.5 M NaCl solution open to air at 25°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

Fig. 1 shows the changes in corrosion rates of the sputter–deposited W–xTa alloys after immersion for 240 hours in 0.5 M NaCl solution open to air at 25°C. The corrosion rates of the sputter–deposited tungsten and tantalum metal are also shown for comparison. The corrosion rates of tungsten and tantalum metals are about 2.5×10^{-2} mm.y^{-1} and 3.32×10^{-3} mm.y^{-1}, respectively. Corrosion rates of all the examined binary W–xTa alloys containing 8–77 at. % tantalum are more than one order of magnitude lower than that of tungsten (that is, about $2.0–4.4 \times 10^{-3}$ mm.y^{-1}) and even lower than that of the sputter–deposited tantalum metal. However, the corrosion rate of the nanocrystalline W–8Ta alloy is slightly higher than that of tantalum metal. In particular, the sputter–deposited W–xTa alloys containing 60–77 at. % tantalum content, which are composed of either amorphous or nanocrystalline single phase solid solution, show lower corrosion rates than those of alloy-constituting elements (that is, tungsten and tantalum) even immersion for 240 hours in 0.5 M NaCl solution at 25°C. The corrosion rate of the W–60Ta alloy shows lowest among the examined alloys' corrosion rates. Consequently, the addition of tantalum to the sputter–deposited W–xTa alloys is effective in enhancing the corrosion resistance of the alloys in 0.5 M NaCl solution.

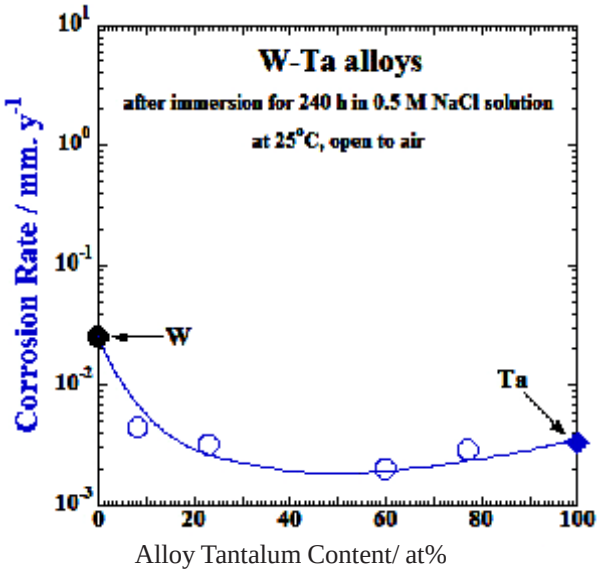

Fig. 1. Changes in corrosion rates of the sputter-deposited W-xTa alloys including the sputter-deposited tungsten and tantalum metals in 0.5 M NaCl solution open to air at 25°C, as a function of alloy tantalum content

In general, alloys show high corrosion resistance through the active dissolution of the alloys at the initial periods of immersion in the corrosive environments. High chemical reactivity of the alloys leads to the rapid accumulation of a beneficial species in the passive films. This accounts for the high corrosion resistance of the alloys. Therefore, it is important to identify the role of immersion time for better understanding of the corrosion nature of the alloys. In order to clarify the time dependence of the corrosion rate of the sputter–deposited W–xTa alloys, the corrosion rates of the sputter–deposited W–8Ta, W–23Ta, W–60Ta, W–77Ta alloys including tantalum metal were estimated after immersion in 0.5 M NaCl solution at various time intervals. Figure 2 shows the changes in the corrosion rates of all the examined W–xTa alloys including the sputter–deposited tantalum metal in 0.5 M NaCl solution open to air at 25°C, as a function of immersion time. In general, the corrosion rates of all the examined W–xTa alloys are significantly high at initial period of immersion (for example, for about 2 h). The corrosion rate is decreased with immersion time till about 2–72 h for all the examined W–xTa alloys including tantalum metal. In particular, the corrosion rates of the W–xTa alloys become almost steady after immersion for about 72–240 hours. Accordingly, initially fast dissolution of the W–xTa alloys results in fast passivation by forming a more protective passive films in 0.5 M NaCl solution at 25°C. As a result, the average corrosion rates of all the examined W–xTa alloys are lower than those of the sputter–deposited tungsten metal after immersion for 240 h as shown in Fig. 1 also.

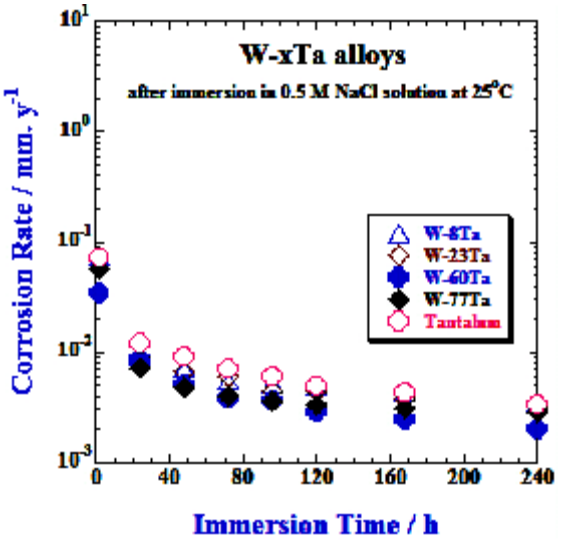

Fig. 2. Changes in corrosion rates of the sputter-deposited W-xTa alloys including the sputter-deposited tantalum metal in 0.5 M NaCl solution open to air at 25°C, as a function of immersion time

Electrochemical measurements were carried out for a better understanding of the corrosion behavior of the sputter–deposited amorphous or/and nanocrystalline W–xTa alloys for 72 hours in 0.5 M NaCl solution. Figure 3 shows the changes in open circuit potentials of the sputter–deposited W–8Ta, W–23Ta, W–60Ta, W–77Ta alloys including tungsten and tantalum metals in neutral 0.5 M NaCl solution open to air at 25°C, as a function of immersion time. The open circuit potential of all the examined sputter–deposited amorphous or/and nanocrystalline W–xTa alloys containing 23–77 at % tantalum including pure tantalum metal is shifted towards more positive (noble) direction with immersion time in 0.5 M NaCl solution. These results revealed that more stable passive films are formed on the surface of the sputter–deposited W–xTa alloys with increasing tantalum content. Furthermore, the open circuit potentials of all the examined W–xTa alloys containing 23–77 at % tantalum are almost same as that of tantalum metal after immersion for 72 h in 0.5 M NaCl. These results revealed that the stability of the passive films 0f the

W–(23–77)Ta alloys is increased with increasing tantalum content in the W–xTa alloys and the passive films are more stable than those passive films formed on the sputter–deposited tungsten and tantalum metals. These facts agree with the higher corrosion resistance of the W–xTa alloys than those of tungsten and tantalum metals after immersion for 240 h in 0.5 M NaCl as shown above in Figs. 1 and 2.

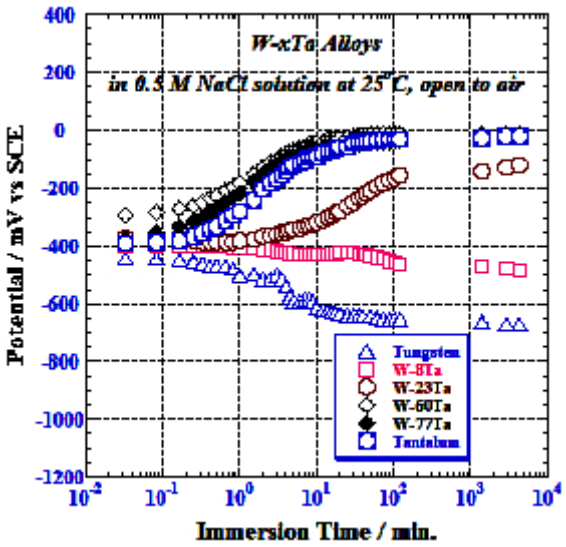

Fig. 3. Changes in open circuit potentials for the sputter–deposited W–xTa alloys including tungsten and tantalum metals in 0.5 M NaCl solution open to air at 25°C, as a function of immersion time

In conclusion, a beneficial effect of tungsten and tantalum in the corrosion behavior of the sputter–deposited binary W–xTa alloys was studied using corrosion tests and electrochemical measurements in this study. Tantalum metal acts synergistically with tungsten in enhancing the corrosion resistance properties of the sputter–deposited W–xTa alloys so as to show lower corrosion rates than the corrosion rates of the alloy–constituting elements (that is, tungsten and tantalum) in 0.5 M NaCl solution open to air at 25°C. More ennoblement of the open circuit potentials of the W–60Ta and W–77Ta alloys are observed as compared to those of W–8Ta and W–23Ta alloys after immersion for 72 h in 0.5 M NaCl and hence more stable passive films were formed on the surface of the sputter–deposited tantalum–rich W–xTa alloys. The stability of the passive films formed on the W–xTa alloys is generally increased with increasing the tantalum content.

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