

# Corrosion and Electrochemical Properties of Nanocrystalline W–Mo Alloys in NaOH Solutions

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## Abstract

The corrosion and electrochemical properties of sputter-deposited nanocrystalline binary W–Mo alloys were studied after immersion for 2429 h in different concentrations of NaOH solutions open to air at 25°C using corrosion tests and open circuit potential measurements. Molybdenum acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited binary W–Mo alloys so as to show higher corrosion resistance than those of alloy-constituting elements (i.e. tungsten and molybdenum) after immersion for 24 h in NaOH solutions. Open circuit potentials of all the examined sputter-deposited W–Mo alloys are shifted to the more positive (noble) direction with increasing molybdenum content in the alloys. The stability of the spontaneously passivated films formed on the binary W–Mo alloys is decreased with increasing concentrations of NaOH solutions. In spite of these facts, the corrosion rates of all the examined W–Mo alloys are almost independent of concentrations of NaOH solutions after immersion for 24 h at 25°C.

**Key words:** nanocrystalline W–Mo alloys, sputter deposition, corrosion resistance, open circuit potential, NaOH solutions

## Introduction

The development of new corrosion resistance engineering materials is provoked by different reasons and one of them is the improved corrosion resistance properties of the materials. The research activities on the sputter-deposited amorphous or/and nanocrystalline binary or ternary alloys are recently being of a widespread interest in the field of corrosion science and engineering. 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 (Zarzycki 1991). It has been reported that the sputter-deposited amorphous or/and nanocrystalline alloys are chemically more homogeneous structures than conventionally processed crystalline alloys (Heusler *et al.* 1988, Hashimoto 1993), and hence such sputterdeposited alloys are interesting for high corrosion resistance properties. A variety of extremely

high corrosion resistance sputter-deposited single-phase amorphous or/and nanocrystalline chromium (Kim *et al.* 1993, 1994; Li *et al.* 1997)– molybdenum (Park *et al.* 1994, 1995, 1996; Hashimoto 2007), tungsten (Bhattarai 1995, 1998, 2000, 2001, 2002, 2006, 2009; Bhattarai & Hashimoto 1998; Bhattarai *et al.* 1995, 1997, 1998 a, 1998 b, 1998 c, 2000)– and manganese (El-Moneim *et al.* 1997, 1999)– transition metal alloys have been developed for last two decades.

In 1990s Park *et al.* (1994, 1995, 1996), and Bhattarai (1995, 1998, 2009) and Bhattarai *et al.* (1995, 1997, 1998 a, 1998 b, 1998 c, 1999) had reported the synergistic effect of molybdenum addition on the sputter-deposited binary amorphous and/or nanocrystalline molybdenum– and tungsten–transition metals (nickel, chromium, zirconium, niobium, tantalum, molybdenum) alloys, respectively, for significantly high corrosion resistance properties in 12 M HCl solutions open to air at 30°C. It has also been found that the addition of

molybdenum improved the passivating ability of the sputter-deposited ternary Al–Cr–Mo alloys not by formation of molybdenum enriched passive film, but by the formation of chromium enriched passive film (Akiyama *et al.* 1996). In particular, the sputter-deposited nanocrystalline W–Mo alloys containing about 24–83 at % molybdenum were spontaneously passivated and showed high corrosion resistance than those of alloy-constituting elements in both 12 M HCl (Bhattarai 2006) and 0.5 M NaCl solutions (Bhattarai *et al.* 2010). It is meaningful for mentioning here that tungsten is passive in the acidic environments having  $\text{pH} < 4$ , whereas it corrodes in alkaline and neutral solutions from potential–pH diagram (Pourbaix 1974). On the other hand, molybdenum is passive only in a very narrow potential values at  $\text{pH} 4\text{--}8$  of the environments and corrodes in both acidic and alkaline solutions (Pourbaix 1974). Considering these facts, present work is focused to study the effect of molybdenum on the corrosion behavior of the binary nanocrystalline W–Mo alloys in different concentrations of NaOH solutions open to air at 25°C using corrosion tests and electrochemical measurements.

## Methodology

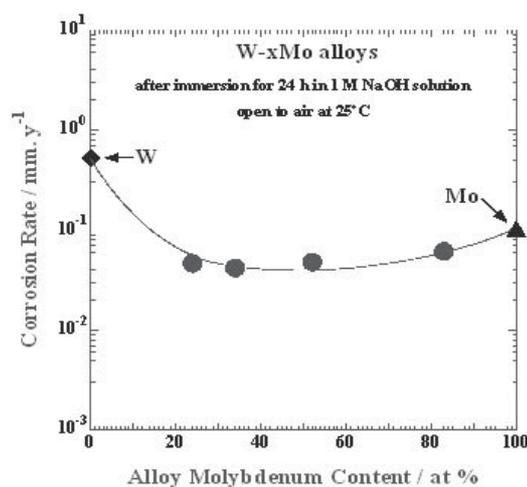
The binary W–Mo alloys were prepared by direct current (D. C.) magnetron sputtering on glass substrate as described elsewhere (Bhattarai 1995, 2006; Bhattarai *et al.* 2010). An electron probe microanalysis was used to determine the compositions of the sputter-deposited alloys. The sputter-deposited binary W–Mo alloys were confirmed as a nanocrystalline single phase solid solution by X-ray diffraction having the apparent grain size ranging from 15.0 to 19.8 nm (Bhattarai 1995, 2006; Bhattarai *et al.* 2010).

Prior to immersion tests and open circuit potential measurements, the nanocrystalline W–Mo alloy specimens were 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 about 24 h in 1 M NaOH solution open to air at 25°C. The average corrosion rate measurement was done two times or more so as to get precise results. The time dependence of the corrosion rate was also estimated after immersion for

2–29 h in 0.01 M, 0.1 M and 1 M NaOH solutions. The open circuit potential of all the examined W–Mo alloys was measured after immersion for 2 h in 1 M NaOH solution open to air at 25°C. Alloys and saturated calomel electrode were used as working and reference electrodes, respectively. All the potentials given in this paper are relative to saturated calomel electrode (SCE).

## Results and Discussion

Figure 1 shows changes in the average corrosion rates of the sputter-deposited nanocrystalline W–Mo alloys including tungsten and molybdenum after immersion for 24 h in 1 M NaOH solution open to air at 25°C, as a function of alloy molybdenum content. The corrosion rates of the sputter-deposited tungsten and molybdenum are about  $5.25 \times 10^{-1} \text{ mm.y}^{-1}$  and  $1.04 \times 10^{-1} \text{ mm.y}^{-1}$ , respectively. The corrosion rates of the sputter-deposited binary W–Mo alloys containing 24–83 at % molybdenum show about one order of magnitude lower corrosion rates than that of tungsten and even lower corrosion rates than that of the sputter-deposited molybdenum metal in 1 M NaOH solution at 25°C. In particular, the sputter-deposited W–Mo alloys containing 24–52 at % molybdenum show lowest corrosion rates (i.e., about  $4.5 \times 10^{-2} \text{ mm.y}^{-1}$ ) among all the examined W–Mo alloys than those of alloy-constituting elements (i.e. tungsten and molybdenum) after immersion for 24 h in an aggressive 1 M NaOH solution at 25°C. These results revealed that the synergistic effects of the simultaneous



**Fig. 1.** Changes in corrosion rates of the sputter-deposited nanocrystalline W–xMo alloys including tungsten and molybdenum metals in 1 M NaOH solution open to air at 25°C, as a function of alloy molybdenum content

additions of tungsten and molybdenum metals to the sputter-deposited nanocrystalline W–Mo alloys is clearly observed in 1 M NaOH solution. It is meaningful for mentioning here that the corrosion resistance of these alloys in 12 M HCl ( $1-2 \times 10^{-3} \text{ mm.y}^{-1}$  corrosion rates) (Bhattarai 1995, 2006) and 0.5 M NaCl ( $1.7-2.0 \times 10^{-2} \text{ mm.y}^{-1}$  corrosion rates) (Bhattarai *et al.*

2010) solutions were reported lower than in 1 M NaOH solution presented in this work. These results revealed that the general corrosion rates of the sputter-deposited W–Mo alloys showed lowest corrosion resistance in alkaline environment than those in neutral and acidic environments.

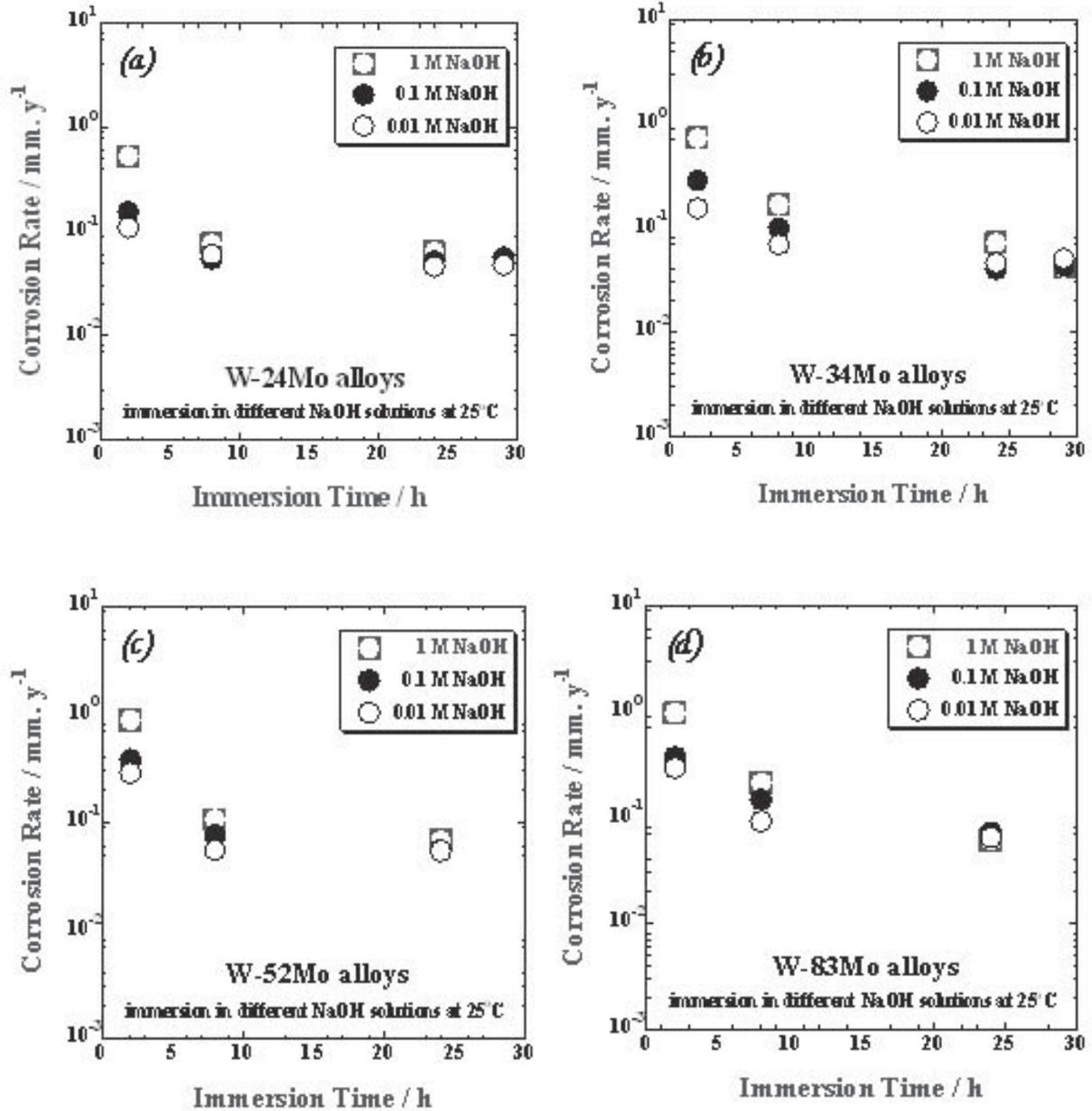


Fig. 2. The change in corrosion rate of the sputter-deposited nanocrystalline (a) W–24Mo, (b) W–34Mo, (c) W–52Mo and (d) W–83Mo alloys in 0.01 M, 0.1 M and 1 M NaOH solutions open to air at 25°C, as a function of immersion time

Furthermore, the average corrosion rates of all the examined W–Mo alloys in 0.01 M and 0.1 M NaOH solutions were found to be almost same as that in 1 M NaOH solution after immersion for about 24 h at 25°C. 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 corrosion rates of the sputter-deposited nanocrystalline W–xMo alloys, corrosion rates of W–24Mo, W–34Mo, W–52Mo and W–83Mo alloys were estimated after immersion in 0.01 M, 0.1 M and 1 M NaOH solutions at various time intervals. Figure 2 shows the changes in the corrosion rates of W–xMo alloys in 0.01 M, 0.1 M and 1 M NaOH solutions open to air at 25°C, as a function of immersion time. In general, the corrosion rates of all the examined W–xMo alloys were significantly high at initial period of immersion (i.e. for 2 h). The corrosion rate was decreased with immersion time till about 8 h for W–xMo alloys containing 24–83 atomic % molybdenum and the corrosion rates of all the examined sputter-deposited nanocrystalline W–Mo alloys became almost steady after immersion for about 24 h. In particular, the corrosion rates of the alloys were remarkably higher in 1 M NaOH solution than in 0.01M and 0.1 M NaOH solutions after immersion for about 8 h or short times. However, the corrosion rates of the W–xMo alloys were almost same in all three different concentrations of NaOH solutions after immersion for 8–29 h. Accordingly, initially fast dissolution of the W–Mo alloys resulted in fast passivation by forming more protective passive films formed on the alloys in 1 M NaOH solution open to air at 25°C. Consequently, the average corrosion resistance of the sputter-deposited binary W–Mo alloys containing 24–83 % molybdenum was higher than those of pure tungsten as well as molybdenum after immersion for about 24 h as shown in figure 1.

Electrochemical measurements were carried out for a better understanding of the corrosion behavior of the sputter-deposited nanocrystalline W–Mo alloys for about 2 h in alkaline 0.01 M, 0.1 M and 1 M NaOH solutions open to air at 25°C. Figures 3 (a), 3 (b) and 3(c) showed the changes in open circuit potentials for the sputter-deposited nanocrystalline W–Mo alloys as well as the tungsten metal in 1 M, 0.1 M and 0.01 M NaOH solutions, respectively, as a function of immersion time. The open circuit potentials of the sputter-deposited nanocrystalline W–Mo alloys were

in more noble (positive) direction with increasing the molybdenum content particularly in 1 M NaOH solution as shown in Fig. 3 (a).

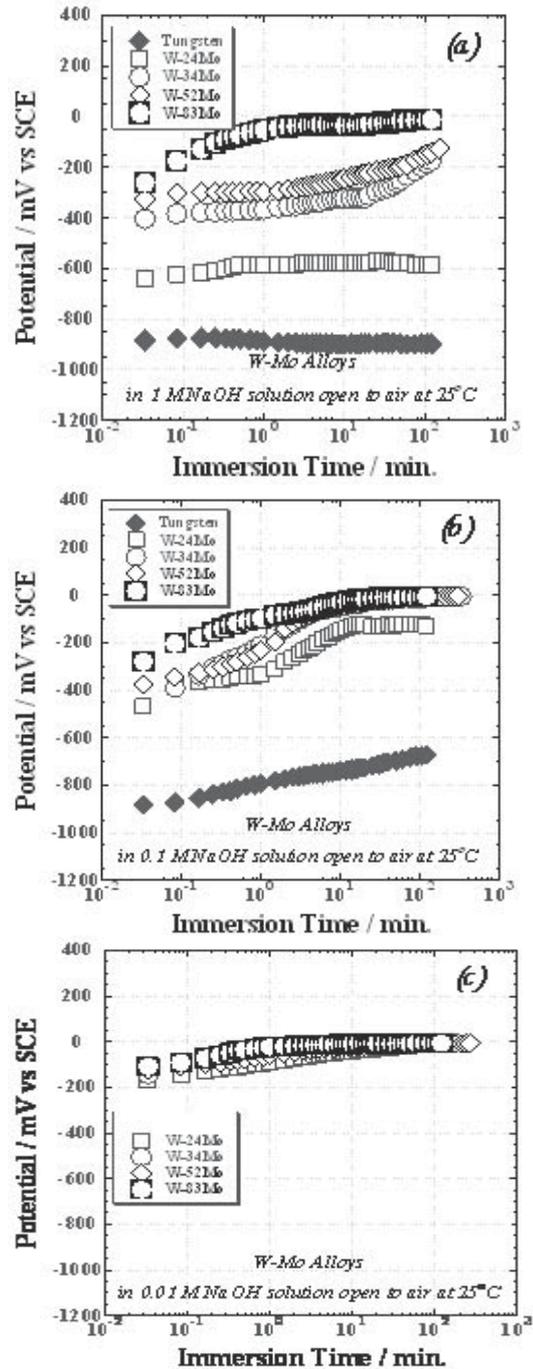


Fig. 3. Changes in open circuit potentials for the sputter-deposited nanocrystalline W-Mo alloys including tungsten metals in (a) 1 M, (b) 0.1 M and (c) 0.01 M NaOH solutions open to air at 25°C, as a function of immersion time

Furthermore, the open circuit potentials of all the examined W–Mo alloys were increased with immersion time and attained a steady state after immersion for about 10 min in different concentrations of NaOH solutions. In particular, the open circuit potentials of all the W–Mo alloys containing 24–83 at % molybdenum were almost same in 0.01 M NaOH solution. These facts coincide with the changes in the corrosion rates of the sputter–deposited nanocrystalline W–Mo alloys after immersion for 2 h in different concentrations of NaOH solutions as shown in Fig. 2.

From the above results and discussion we have drawn these conclusions from our present study. Corrosion rates of all the examined sputter–deposited nanocrystalline W–Mo alloys showed about one order of magnitude lower corrosion rates ( that is,  $4\text{--}5 \times 10^{-2} \text{ mm.y}^{-1}$ ) than that of sputter–deposited tungsten and even lower corrosion rate than that of the sputter–deposited molybdenum after immersion for 24 h in NaOH solutions. The corrosion rates of the W–Mo alloys were almost independent of NaOH concentrations at 25°C. Open circuit potentials of the W–Mo alloys are shifted to the noble (more positive) direction with increasing molybdenum content in NaOH solutions. The stability of the spontaneously passivated films formed on the binary tungsten–rich W–Mo alloys is increased with decreasing NaOH concentrations, although such effect is not observed for the molybdenum–rich W–Mo alloys after immersion for two hours in NaOH solutions.

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