THE PASSIVATION BEHAVIOR OF SPUTTER-DEPOSITED W-XMO ALLOYS IN 0.5 M NaCl SOLUTION

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Abstract: The passivation behavior of the sputter-deposited W-xMo alloys was studied in 0.5 M NaCl solution open to air at 25°C using immersion tests and electrochemical measurements. Corrosion rates of the W-xMo alloys containing less than 50 at% molybdenum content are in the range of 1.7-2.0 x10^{-2} mm/y and are slightly lower than that of tungsten metal whereas the corrosion rates of the alloys containing more than 50 at% molybdenum increased with the addition of molybdenum in the alloys. The W-83Mo alloy showed active-passive transition and transpassive dissolution. The open circuit potential of all the examined W-xMo alloys is shifted to noble direction with the addition of molybdenum content in the alloys.

Keywords: Binary W-xMo alloys; Corrosion test; Open circuit potential; Polarization curve; Sputter deposition.

INTRODUCTION

Corrosion is defined as the undesirable deterioration of materials, usually metals or alloys by electrochemical or chemical reaction with its environment that adversely affects those properties of metals or alloys that are to be preserved[1]. It is generally accepted that measures of corrosion protection were discovered in the early of the 18th century when the miraculous observation was reported that iron corrodes heavily in dilute aqueous solutions of nitric acid, but remains inert or passive in concentrated nitric acid solutions[1,2]. Corrosion science received extra impetus with the beginning of the 20th century when stainless steels were widely used. Corrosion problems appeared with widespread uses of steels with high tensile strengths and of steel enforced concrete. Corrosion scientists and engineers, therefore, strive to develop newer materials with enhanced corrosion resistance properties. Engineers generally ignore the corrosion scenario during the initial stages of design hoping to check it later. However, in most cases it is wiser to take into account the corrosion properties at an early stage of materials development. The applicability of any novel materials for industrial purposes and developmental areas is ultimately determined by their long term corrosion resistance properties in its environment.

The sputter-deposited amorphous or nanocrystalline alloys are chemically more homogeneous than conventionally processed crystalline alloys and hence such sputter-deposited alloys are interesting to develop corrosion-resistant materials during last four decades. It has been reported that the chemically homogeneous single phase nature of the sputter-deposited amorphous and/or nanocrystalline alloys are responsible for their extremely high corrosion resistance owing to the formation of uniform protective passive films those are able to separate the bulk alloys from the aggressive environments[3,4].

The sputter deposition technique has been recently used as one of the appropriate methods for preparing highly corrosion-r esistant single phase amorphous or/and nanocrystalline chromium[5-9]-, molybdenum[10-12]-, tungsten[13-43] and manganese[44,45] -transition metal alloys. It has been successfully prepared novel sputter-deposited nanocrystalline W-xMo alloys in a wide composition range and reported high corrosion resistance in 12 M HCl 30°C having the pH values less than one in which regions tungsten is passive and molybdenum is active[26]. On the other hand, tungsten metal generally corrodes in solution having pH of 4 or high whereas molybdenum metal does not corrode in slightly neutral solutions[46]. In this context, it is very interesting to study the passivation behavior of the sputter-deposited W-xMo alloys in 0.5 M NaCl solution.

This research work is aimed to study the passivation behavior of the sputter-deposited nanocrystalline W-xMo alloys in 0.5 M NaCl solution open to air at 25°C using immersion tests and electrochemical measurements.

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Table 1: Chemical composition, structure and apparent grain size of the sputter-deposited W-*x*Mo alloys[13,26].

Name of Alloy	*Mo content (at%)*	*Apparent Grain size (nm)*	*Structure*
Tungsten metal	0.0	20.0	nanocrystal
W–9Mo	9.0	17.0	nanocrystal
W–24Mo	24.2	19.8	nanocrystal
W–34Mo	34.2	16.0	nanocrystal
W–52Mo	51.8	15.0	nanocrystal
W–69Mo	69.3	18.5	nanocrystal
W–83Mo	82.8	16.5	nanocrystal
Molybdenum metal	100.0	20.0	nanocrystal

EXPERIMENTAL METHOD

The sputter-deposited binary W-xMo alloys were prepared by direct current (D.C.) magnetron sputtering on glass substrate as described elsewhere[13,17,26]. An electron probe microanalysis was used to determine the compositions of the sputter-deposited alloys. The sputter-deposited binary W-xMo alloys were confirmed as nanocrystalline single phase solid solution by X-ray diffraction having the apparent grain size ranges from 15.0 to 19.8 nm as summarized in Table 1[13,26].

Prior to the immersion tests and electrochemical measurements, the nanocrystalline W-xMo alloys specimens were mechanically polished with a silicon carbide paper up to grit number 1500 in cyclohexane, rinsed by acetone and dried in air. The corrosion rate of the alloys was estimated from the weight loss after immersion for 98 h in 0.5 M NaCl solution open to air at 25°C. The measurement of corrosion rate was done two times or more so as to get average value. The open circuit corrosion potentials of the alloys were measured after immersion for 2 hours in 0.5 M NaCl 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

It has been reported by the present author that the sputter deposition technique is a quite effective method for preparing nanocrystalline W-xMo alloys in a wide composition range[13,26]. Changes in corrosion rates of the sputter-deposited nanocrystalline W-xMo alloys after immersion for 98 h in 0.5 M NaCl solution at 25°C, are shown in Fig. 1. The corrosion rates of tungsten and molybdenum metal are also shown for comparison. The corrosion rates of tungsten and molybdenum metals are about 2.5×10^{-2} mm/y and 6.0×10^{-2} mm/y, respectively. The corrosion rates of the sputter-deposited nanocrystalline W-Mo alloys containing 9-51 at% molybdenum are in the range of $1.7\text{-}2.0 \times 10^{-2}$ mm/y and are slightly lower than that of the corrosion rate of tungsten. The corrosion rates of the W-Mo alloys containing more than 51 at% molybdenum increase gradually with increasing

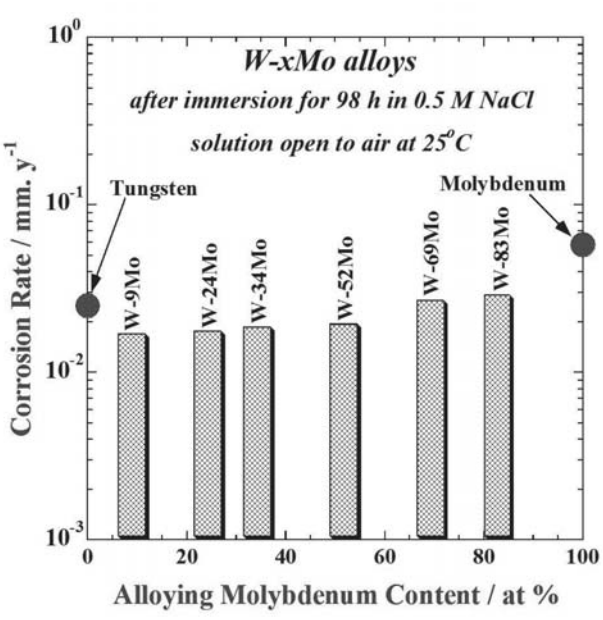

Fig. 1: Changes in corrosion rates of the sputter-deposited W-Mo alloys including tungsten and molybdenum in 0.5 M NaCl solution at 25°C, as a function of molybdenum content.

molybdenum content and molybdenum metal shows maximum corrosion rate. The entire examined sputter-deposited nanocrystalline W-Mo alloys show lower corrosion rates than that of molybdenum metal. Consequently, the corrosion resistance of the sputter-deposited nanocrystalline W-Mo alloys cannot remarkably exceed that of the sputter-deposited tungsten although the addition of tungsten greatly enhances the corrosion resistance of molybdenum in 0.5 M NaCl solution at 25°C.

Figure 2 shows the changes in open circuit corrosion potentials for the sputter-deposited W-Mo alloys including tungsten and molybdenum in 0.5 M NaCl solution at 25°C, as a function of immersion time. The open circuit corrosion potential of the tungsten metal reaches a stationary value of about –640 mV (SCE) within 20 minutes. The similar behavior of the stationary state of the open circuit corrosion potentials of the sputter-deposited nanocrystalline W-Mo alloys is observed in 0.5 M NaCl solution. The open circuit potentials of all the examined W-Mo alloys are in more noble direction than that of tungsten. These results revealed that more stable passive films are formed on the surface of the W-Mo alloys with increasing molybdenum content in the alloys.

For a better understanding of the anodic passivity of the W-xMo alloys, figure 3 shows the potentiostatic polarization curve for the sputter-deposited W-83Mo alloy after polarization for 1 hour in 0.5 M NaCl solution open to air at 25°C. The W-83Mo alloy shows active-passive transition in the potential range of -250 to -200 mV (SCE) and the passive region of this alloy is in very narrow potentials regions. The transpassivity is clearly seen at about 0 mV (SCE), mostly

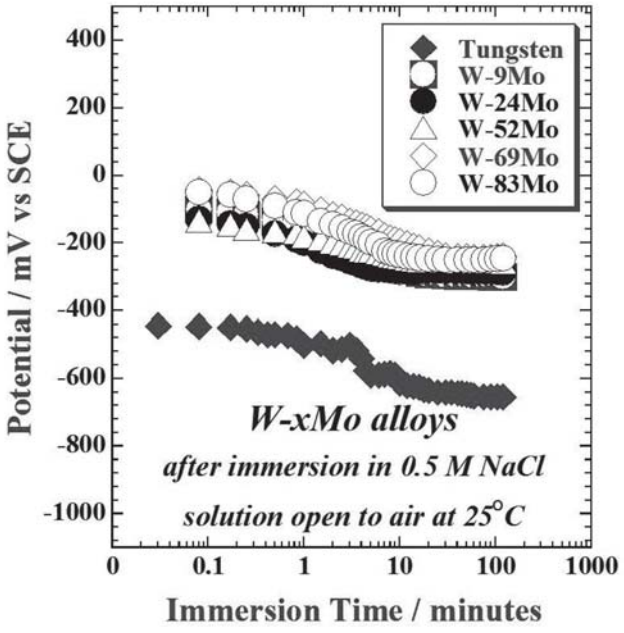

Fig. 2: Changes in open circuit corrosion potentials for the sputter-deposited W-Mo alloys including tungsten in 0.5 M NaCl solution at 25°C, as a function of immersion time.

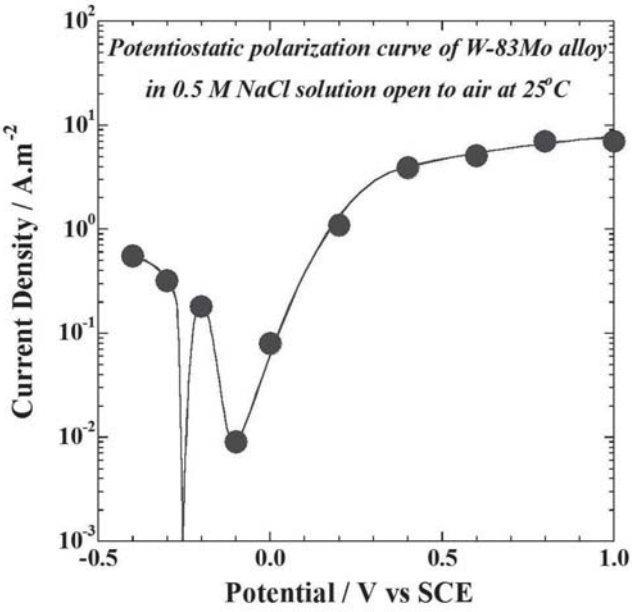

Fig. 3: The potentiostatic polarization curve of the W-83Mo alloy in 0.5 M NaCl solution at 25°C.

due to the formation of Mo^{6+} ion that is soluble in neutral NaCl solution.

CONCLUSION

The corrosion behavior of the sputter-deposited nanocrystalline W-**x**Mo alloys is studied in neutral 0.5 M NaCl solution open to air at 25°C by immersion tests and electrochemical measurements. The following conclusions are drawn:

1. Tungsten metal helps for enhancing the corrosion resistance properties of the sputter-deposited W-xMo alloys so as to show the lower corrosion rates with increasing tungsten.
2. Open circuit corrosion potentials of the entire examined sputter-deposited W-xMo alloys are shifted to more noble direction with addition of molybdenum content.
3. The molybdenum-rich W-83Mo alloy showed active-passive transition and transpassive dissolution.

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