

The Corrosion Behavior of Sputter-deposited Nanocrystalline W-Cr Alloys in NaCl and NaOH Solutions

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Abstract

The corrosion behavior of the sputter-deposited nanocrystalline W-Cr alloys was studied in 0.5 M NaCl and alkaline 1 M NaOH solutions at 25°C, open to air using immersion tests and electrochemical measurements. Chromium metal acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Cr alloys so as to show higher corrosion resistance than those of alloy-constituting elements in both 0.5 M NaCl and 1 M NaOH solutions. In particular, the nanocrystalline W-Cr alloys containing 25-91 at% chromium showed about one order of magnitude lower corrosion rates (that is, about $1-2 \times 10^{-3} \text{ mm.y}^{-1}$) than those of tungsten and chromium metals even for prolonged immersion in 0.5 M NaCl solution at 25°C. On the other hand, the corrosion rate of the sputter-deposited W-Cr alloys containing 25-75 at % chromium was decreased significantly with increasing chromium content and showed lowest corrosion rates (that is, $1.5-2.0 \times 10^{-3} \text{ mm.y}^{-1}$) after immersed for prolonged immersion in 1 M NaOH solution. The corrosion rates of these nanocrystalline W-(25-75)Cr alloys are nearly two orders of magnitude lower than that of tungsten and more than one order of magnitude lower corrosion rate than that of sputter-deposited chromium metal in 1 M NaOH solution. The corrosion-resistant of all the examined sputter-deposited W-Cr alloys in 0.5 M NaCl solution is higher than in alkaline 1 M NaOH solution at 25°C. Open circuit potentials of all the examined W-Cr alloys are shifted to more noble direction with increasing the chromium content in the alloys after immersion for 72 h in both 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air.

Keywords: Sputter deposition, nanocrystalline W-Cr alloys, corrosion test, electrochemical measurement, NaCl and NaOH solutions.

Introduction

Last two decades, the research activities on amorphous or/and nanocrystalline alloys produced by sputter deposition technique have been widely used in the field of corrosion science which motivates by practical importance of the novel corrosion-resistant

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materials^{1,2}. The sputter deposition technique has been used as one of the best methods for preparing metastable single-phase alloys, including amorphous alloys. In particular, sputtering does not require melting of alloying elements for alloy formation, and hence sputtering enables us to prepare alloys even when the melting point of one of the alloy constituents is higher than the boiling points of the other alloy constituents. By using this advantage of the sputtering method, one of the present authors have succeeded in tailoring chemically homogeneous tungsten-transition metal alloys having high corrosion resistance in aggressive hydrochloric acid solutions³⁻¹⁷. In particular, an attempt has been made to prepare homogeneous sputter-deposited nanocrystalline W-Cr alloys^{5,7}, even though the melting point of tungsten is about 3420°C, more than 1100°C higher than the boiling point of chromium.

Both tungsten and chromium are effective elements in enhancing the corrosion resistance of alloys in aggressive environments. Several surface studies have been carried out to obtain better understanding of the role of tungsten in the corrosion protection mechanisms of stainless steels in aggressive chloride media¹⁸⁻²¹. The addition of tungsten remarkably improved the corrosion resistance of various amorphous alloys in aggressive chloride environments²²⁻²⁷. Similarly, chromium is one of the most effective alloying elements to provide high passivating ability for conventional steels and nickel-based alloys. Naka et al.²⁸ reported the remarkably high corrosion resistance of Fe-Cr metalloid metallic glasses. Addition of only a small amount of chromium (8 at %) was enough to cause spontaneous passivation in 1 M HCl and these alloys showed significantly higher pitting corrosion resistance than stainless steels. It has been reported that a thin oxide film containing a high concentration of chromium enhances the stability of the passive state for ferrite stainless steels in aggressive chloride solutions²⁹. On the other hand, the high corrosion resistance of spontaneously passivating amorphous Fe-Cr alloys has been attributed to the formation of a hydrated chromium oxyhydroxide film³⁰. A series of sputter-deposited binary chromium–metalloid alloys exhibited superior corrosion resistance compared with chromium metal in 12 M HCl solution³¹. It has also been reported that the alloying of chromium to sputter-deposited valve metals enhances the protective quality of the passive films in aggressive hydrochloric acid solutions³²⁻³⁷. In particular, the sputter-deposited nanocrystalline W-Cr alloys 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^{5,7}. Quantitative surface analysis by X-ray photoelectron spectroscopy (XPS) had clarified that the spontaneously passivated films formed on the sputter-deposited nanocrystalline W-Cr alloy was composed of homogeneous new passive double oxyhydroxide films consisting of both tungsten and chromium ions {for example, $(0.52)W^{4.83+}(0.48)Cr^{3+}(1.50)O^{2-}(0.95)OH^-$ passive film on the surface of the W-50Cr alloy}³⁸ in 12 M HCl solution open to air at 30°C having pH values less than one in which regions tungsten is passive³⁹ and chromium is active⁴⁰. It is noteworthy to mention here that tungsten metal generally corrodes in solution having pH 4 or higher whereas chromium metal does not corrode in neutral and slightly alkaline oxidizing solutions, mostly due to the formation of chromium hydroxide or oxides⁴⁰. Chromium is very corrodible in acidic or/and very alkaline solutions. Therefore, it is very interesting to study the passivation behavior of the sputter-deposited W-Cr alloys in neutral 0.5 M NaCl and alkaline 1 M NaOH solutions.

In this context, the present research work is aimed at studying the corrosion behavior of the sputter-deposited nanocrystalline W-Cr alloys in 0.5 M NaCl and alkaline 1 M NaOH solutions open to air at 25°C using corrosion tests and electrochemical measurements.

Experimental Methods

The sputter-deposited binary W-Cr alloys containing 9-91 at % chromium were characterized as single-phase solid solution of nanocrystalline structure having apparent grain size ranges from 9 to 18 nm as shown in Table 1^{4,5}. The compositions of the sputter-deposited W-Cr alloys hereafter are all denoted in atomic percentage (at %).

Table 1: Structure and apparent grain size of the sputter-deposited W-Cr alloys^{4,5}.

Name of Alloy	Structure	Apparent Grain Size (nm)
W-9Cr	nanocrystalline	18
W-25Cr	nanocrystalline	16
W-57Cr	nanocrystalline	17
W-76Cr	nanocrystalline	15
W-91Cr	nanocrystalline	8
Tungsten	nanocrystalline	20
Chromium	nanocrystalline	40

Prior to the corrosion tests and electrochemical measurements, the nanocrystalline W-Cr 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. The time dependence of the corrosion rate of the W-Zr alloys was also estimated at various time intervals.

The open circuit potential of the sputter-deposited W-Cr alloys was 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

The average corrosion rates of the sputter-deposited nanocrystalline W-Cr alloys were estimated using weight loss method after immersion for 240 hours in 0.5 M NaCl and alkaline 1 M NaOH solutions open to air at 25°C. The time dependence of the corrosion rate of the alloy specimens was also estimated at various immersion periods in both 0.5 M NaCl

and 1 M NaOH solutions. Figures 1 (a) and 1 (b) show changes in the corrosion rates of the sputter-deposited nanocrystalline W-Cr alloys including tungsten and chromium metals after immersion for 240 hours in 0.5 M NaCl and alkaline 1 M NaOH solutions, respectively, as a function of alloy chromium content. In 0.5 M NaCl solution, corrosion rates of the W-Cr alloys containing 25-75 at % chromium (that is, $1-1.6 \times 10^{-3} \text{ mm.y}^{-1}$) show about one order of magnitude lower corrosion rates than those of tungsten and chromium metals (Fig. 1. a). On the other hand, corrosion rates of the nanocrystalline W-Cr alloys containing 25-75 at % chromium (that is, $1.5-3.0 \times 10^{-3} \text{ mm.y}^{-1}$) are nearly two orders of magnitude lower than that of tungsten and more than one order of magnitude lower corrosion rate than that of sputter-deposited chromium in alkaline 1 M NaOH solution (Fig. 1. b). Accordingly, chromium metal acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Cr alloys so as to show the lower corrosion rates than the corrosion rates of the alloy-constituting elements in 0.5 M NaCl and alkaline 1 M NaOH solutions at 25°C. In general, the corrosion rates of all the examined sputter-deposited nanocrystalline W-Cr alloys were found slightly higher corrosion resistance in 0.5 M NaCl solution than in alkaline 1 M NaOH solution.

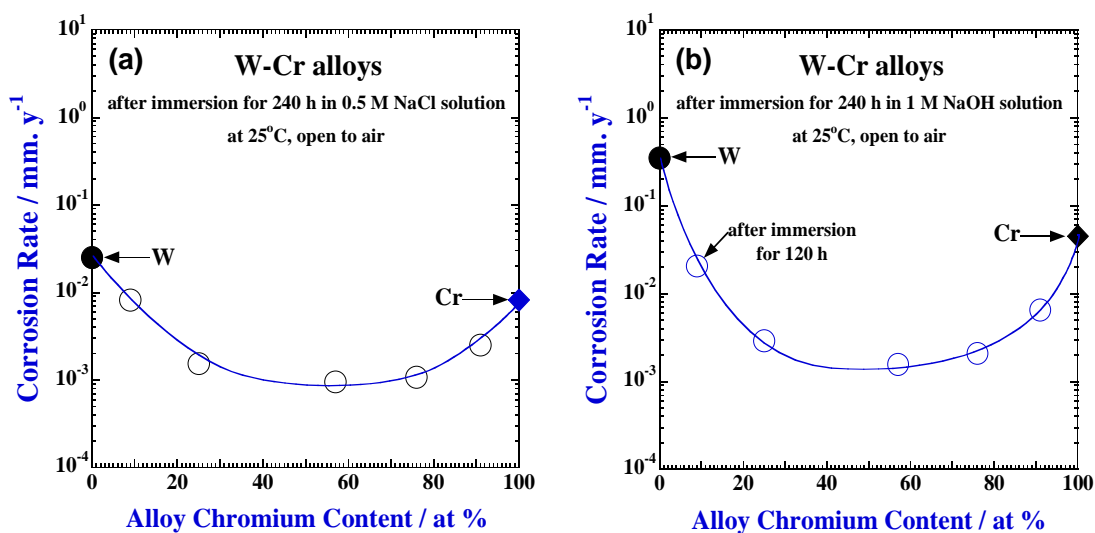


Figure 1: Changes in corrosion rates of the sputter-deposited W-Cr alloys including tungsten as well as chromium metals in (a) 0.5 M NaCl and (b) 1 M NaOH solutions open to air at 25°C, as a function of alloy chromium content.

In order to clarify the time dependence of corrosion rate of the sputter-deposited W-Cr alloys, the corrosion rates of the sputter-deposited W-Cr alloys were measured after immersion in 0.5 M NaCl and alkaline 1 M NaOH solutions at various time intervals. Figures 2 (a) and 2 (b) show the changes in the corrosion rates of W-25Cr and W-91Cr alloys including the sputter-deposited chromium 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-Cr 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 h for W-Cr alloys and chromium metal. In particular, the corrosion rates of the W-Cr alloys

become almost steady after immersion for 48-240 hours in both 0.5 M NaCl and alkaline 1 M NaOH solutions. Accordingly, initially fast dissolution of the sputter-deposited W-Cr 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-Cr 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 (Figs 1.a and 1.b).

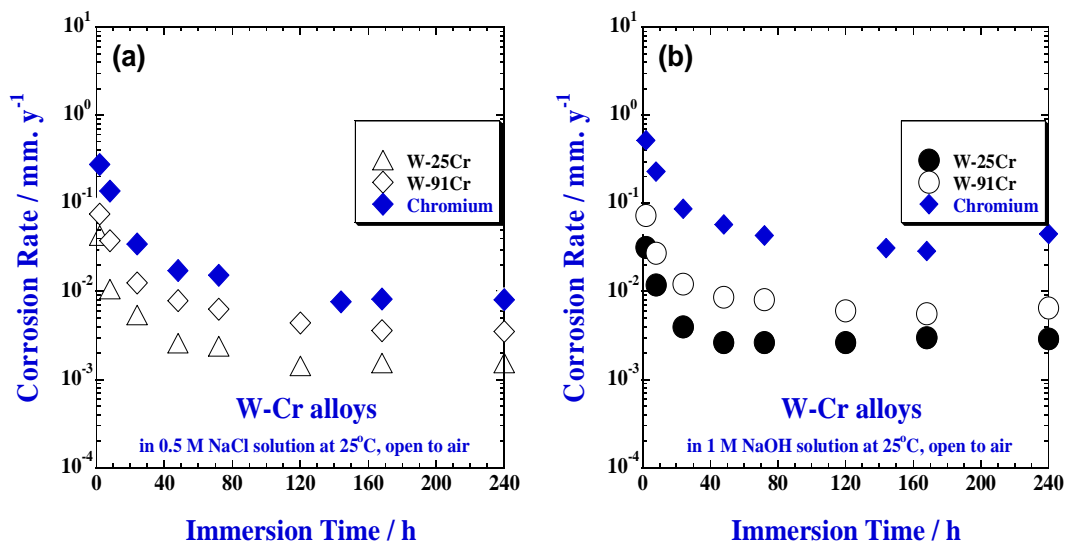


Figure 2: Changes in corrosion rates of the sputter-deposited W-Cr alloys and chromium metal in (a) 0.5 M NaCl and (b) alkaline 1 M NaOH solutions open to air at 25°C, as a function of immersion time.

Open circuit potential measurement was carried out for a better understanding of the corrosion behavior of the sputter-deposited nanocrystalline W-Cr alloys for about 72 hours in 0.5 M NaCl and alkaline 1 M NaOH solutions open to air at 25°C. Figures 3 (a) and 3 (b) show the changes in open circuit potentials for the sputter-deposited W-Cr alloys as well as the tungsten and chromium metals in both 0.5 M NaCl and 1 M NaOH solutions at 25°C, as a function of immersion time. The open circuit potentials of the sputter-deposited nanocrystalline W-Cr alloys containing 25-91 at % chromium are shifted towards more noble (positive) direction with immersion time and more ennoblement of the open circuit potentials of the W-25Cr and W-91Cr alloys are observed as compared to that of the W-9Cr alloy in both environments used in this study. Furthermore, the open circuit potentials of the W-25Cr and W-91Cr alloys are almost same as that of chromium metal after immersion for 24-72 hours in 0.5 M NaCl solution (Fig. 3.a).

On the other hand, the open circuit potentials of the W-(25-91)Cr alloys are shifted to more positive direction with increasing the chromium content in the alloys and the open circuit potential of the W-91Cr alloy is reached almost the same value of that of the sputter-deposited chromium after immersion for 24-72 hours in alkaline 1 M NaOH solution (Fig. 3.b) because, chromium is passive in 1 M NaOH solution⁴⁰ in contrast to the tungsten metal which is actively dissolves in alkaline solutions³⁹. These results revealed that more stable

and noble passive films are formed on the surface of the sputter-deposited W-Cr alloys with increasing chromium content in 0.5 M NaCl and alkaline 1 M NaOH solutions at 25°C. In particular, the W-Cr alloys containing 25-91 at% chromium showed the highest stability among the examined alloys in both 0.5 M NaCl and 1 M NaOH solutions. These facts agree with the higher corrosion resistance of the sputter-deposited W-Cr alloys than those of tungsten and chromium as shown in Figs 1 (a) and 1 (b).

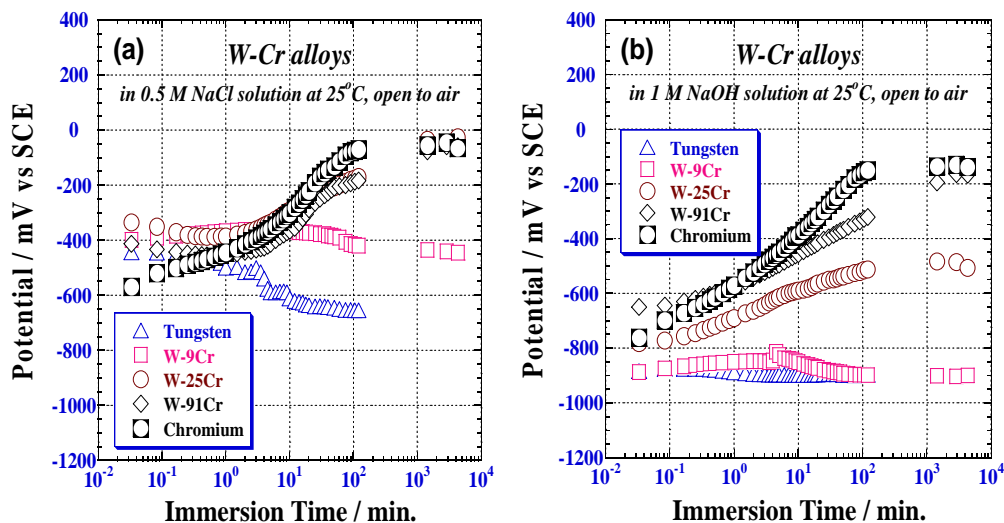


Figure 3: Changes in open circuit potential for the sputter-deposited W-Cr alloys including chromium metal in (a) 0.5 M NaCl and (b) alkaline 1 M NaOH solutions open to air at 25°C, as a function of immersion time.

It was found that the open circuit potentials of the tungsten-rich nanocrystalline W-Cr alloys as well as tungsten metal are in more positive (noble) direction in 0.5 M NaCl solution than in alkaline 1 M NaOH solution after immersion for 72 h. However, the open circuit potentials of the chromium-rich nanocrystalline W-Cr alloys (for example, W-91Cr alloy) and chromium metal are reached almost same open circuit potential values in both 0.5 M NaCl and 1 M NaOH solutions. It is noteworthy to mention here that tungsten is very reactive in alkaline solutions than in neutral solutions while chromium metal is passive in both neutral as well as in moderately alkaline environments like 1 M NaOH solution. These results supported the facts that the corrosion resistance of the sputter-deposited tungsten-rich W-Cr in neutral 0.5 M NaCl solution is higher than that in alkaline 1 M NaOH solution open to air at 25°C.

Conclusions

The corrosion behavior of the sputter-deposited nanocrystalline W-Cr alloys is studied in 0.5 M NaCl and alkaline 1 M NaOH solutions open to air at 25°C using immersion tests and electrochemical measurements. The following conclusions are drawn from above results and discussion:

1. Chromium metal acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited binary W-Cr alloys so as to show about one order of magnitude higher corrosion resistance than the corrosion resistance of the alloy-constituting elements (that is, tungsten and chromium) in 0.5 M NaCl solution.
2. The corrosion rates of the W-Cr alloys containing 25-75 at% chromium (that is, about $1.5-3.0 \times 10^{-3} \text{ mm.y}^{-1}$) are nearly two orders of magnitude lower than that of tungsten and more than one order of magnitude lower corrosion rate than that of sputter-deposited chromium metal in alkaline 1 M NaOH solution at 25°C.
3. The corrosion resistance of all the examined sputter-deposited W-Cr alloys is lower in 1 M NaOH solution than in 0.5 M NaCl solution.
4. More ennoblement of the open circuit potentials of the W-Cr alloys containing 25-91 at% chromium are observed as compared to those of W-9Cr and tungsten metal after immersion for 72 h in both 0.5 M NaCl and 1 M NaOH solutions. These results revealed that more stable passive films are formed on the surface of the sputter-deposited W-Cr alloys with increasing chromium content in 0.5 M NaCl and 1 M NaOH solutions at 25°C.

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