

Electrochemical and Surface Studies on the Passivation Behavior of Sputter-deposited W-Ni Alloys in NaOH Solutions

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Abstract

The passivation behavior of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys is studied in different concentrations of NaOH solutions at 25 °C, open to air using corrosion tests, electrochemical measurements and confocal scanning laser microscopic (CSLM) techniques. The corrosion rates of the W-Ni alloys containing about 60-80 at% nickel are nearly two orders of magnitude lower than that of tungsten and even lower than that of nickel metal in 1 M NaOH solution at 25 °C. The pitting corrosion is observed in the tungsten-rich W-9Ni alloy from CSLM studies. The open circuit potentials of all the examined W-Ni alloys are located between those of tungsten and nickel metals in 0.01, 0.1 and 1 M NaOH solutions. The stability of the passive films formed on the sputter-deposited W-Ni alloys increased with decreasing the concentrations of NaOH solutions.

Introduction

The research activities on amorphous or nanocrystalline alloys produced by sputter deposition technique are of a widespread interest in the field of corrosion science during the last three decades. It has been reported that the chemically homogenous single-phase nature of amorphous or nanocrystalline alloys is mainly responsible for their high corrosion resistance owing to the formation of uniform protective passive films that are able to separate bulk of alloys from aggressive environments.^{1,2} Since homogeneous single-phase amorphous or nanocrystalline alloys possess many superior corrosion properties, a variety of corrosion-resistant nickel-base alloys have been prepared.³⁻⁸

The sputter deposition technique has been recently used as one of the appropriate methods to prepare extremely high corrosion resistance single-phase amorphous or nanocrystalline chromium⁹⁻¹¹-, molybdenum¹²⁻¹⁵-, tungsten¹⁶⁻³¹- and manganese³²-transition metal alloys. Furthermore, one of the present authors had successfully prepared novel sputter-deposited amorphous or/and nanocrystalline binary W-Ni alloys in a wide composition range, and reported high corrosion resistance in 12 M HCl at 30 °C.^{16,19} In particular, the high corrosion resistance of the sputter-deposited W-Ni alloys is based on

spontaneous passivation. Quantitative surface analysis by X-ray photoelectron spectroscopy (XPS) has clarified that the spontaneously passivated films formed on the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys are composed of new passive double oxyhydroxide films consisting of both tungsten and nickel ions in 12 M HCl at 30°C¹⁹ having the pH values less than one in which regions tungsten is passive and nickel is active.

Tungsten metal generally corrodes in solution having pH of 4 or high whereas nickel metal also corrodes in strong alkaline oxidizing solutions.³³ In this context, it is very interesting to study the passivation behavior of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys in NaOH solutions.

This research work is aimed to study the passivation behavior of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys in NaOH solutions at 25°C, open to air using corrosion tests, electrochemical measurements and confocal scanning laser microscopic techniques.

Experimental Methods

The binary W-Ni alloys were prepared by direct current (D. C.) magnetron sputtering on glass substrate as described elsewhere.^{16,17,19,21} An electron probe microanalysis was used to determine the composition of the sputter-deposited alloys. The sputter-deposited binary W-Ni alloys were confirmed as amorphous or/and nanocrystalline single-phase solid solution by X-ray diffraction having the apparent grain size ranges from 1.5 to 6.0 nm.

Prior to the corrosion tests, electrochemical measurements and surface morphological studies, the W-Ni alloys 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 100 h in 1 M NaOH at 25°C, open to air. The time dependence of the corrosion rate of the W-Ni alloys was also estimated at various time intervals ranging from 2 to 168 hours. The weight loss measurement for each alloy specimens was done two times or more and the average corrosion rate of individual alloy was estimated.

The open circuit potentials of the alloys were measured after immersion for 2 hours in 0.01, 0.1 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).

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

Results and Discussion

It has been reported by one of the present authors that the sputter deposition technique is a quite effective method for preparing amorphous or/and nanocrystalline W-Ni alloys in a wide composition range.^{16,19} The W-Ni alloys containing 23-69 at % nickel were amorphous having the apparent grain size less than 2 nm. The alloys containing 7, 9 and 78 at % nickel were nanocrystalline structure having the grain size of 6 nm or less in size. The W-15Ni alloy was the mixture of amorphous and nanocrystalline structures from XRD pattern having the apparent grain size of 2.5 nm.

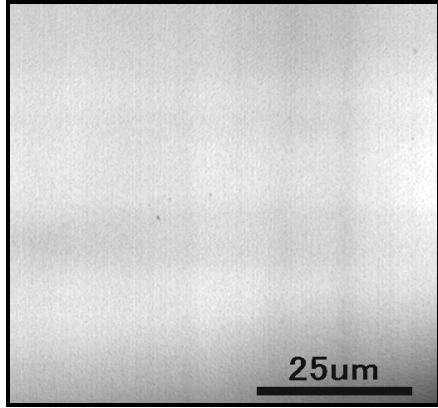
Figure 1 shows the changes in corrosion rates of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys after immersion for 100 h in 1 M NaOH solution at 25⁰C, open to air. The corrosion rates of the sputter-deposited tungsten and nickel are also shown for comparison. The corrosion rates of tungsten and nickel are about 3.5×10^{-1} mm/y and 4.9×10^{-3} mm/y, respectively. The corrosion rates of the W-7Ni and W-9Ni alloys are about 3.0×10^{-1} and 2.2×10^{-1} mm/y, respectively after immersion for 24 hours in 1 M NaOH solution. The corrosion rates of the W-Ni alloys containing more than 20 at% nickel, which are composed of either amorphous or nanocrystalline single phase, are about two orders of magnitude lower than tungsten and slightly lower than that of nickel metal in 1 M NaOH solution. Consequently, nickel metal acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Ni alloys in alkaline 1 M NaOH solution at 25⁰C.

The change in surface morphology of the W-Ni alloys gives important information about the dissolution process in nano-scales to study the passivation behavior of the alloys. Figures 2(a) and 2(b) show CSLM images of the W-Ni alloys (W-9Ni, W-23Ni and W-69Ni) before and after immersion for 24 hours in 1 M NaOH solution at 25⁰C, respectively. The surface of the passive films formed on the W-23Ni and W-69Ni alloys are very smooth and highly reflective similar to the surface oxide-films formed on the as-prepared sputter-deposited W-Ti alloys. Consequently, the dissolution of both W-23Ni and W-69Ni alloys is expected to be low as a result the corrosion rates of these alloys are significantly low as shown in Fig. 1. However, the W-9Ni alloy shows the pitting corrosion in 1 M NaOH solution as shown in Fig. 2(b). These results revealed that the significantly higher corrosion rate of the W-9Ni alloy than those of the W-Ni alloys containing 20 at % or more nickel is mostly due to the pitting corrosion on the surface of the W-9Ni alloy after immersion for 24 h in 1 M NaOH solution at 25⁰C.

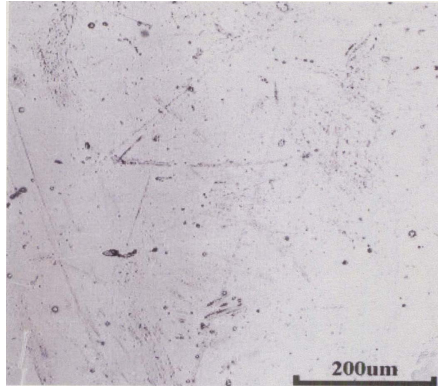
Figure 1: Changes in corrosion rates of W-Ni alloys including tungsten and nickel metals in 1 M NaOH solution at 25 °C, open to air.

In order to clarify the time dependence of corrosion rate of the W-Ni alloys, the corrosion rates of W-23Ni and W-78Ni alloys were measured after immersion in 1 M NaOH solution at various time intervals. Figure 3 shows the changes in the corrosion rates of the W-23Ni and W-78Ni alloys in 1 M NaOH solution, as a function immersion time. The corrosion rate of the W-23Ni alloy is higher than that of the W-78Ni alloy for all intervals of immersion periods. The corrosion rates of both the alloys become almost steady after immersion for about 36-168 h. Accordingly, initially faster dissolution of the W-Ni alloys results in faster passivation by forming a more protective passive film in alkaline 1 M NaOH solution.

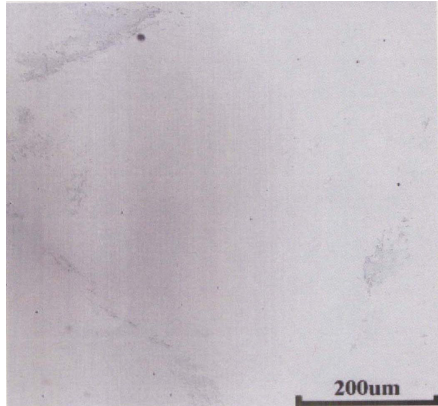
Electrochemical measurements were carried out for a better understanding of the corrosion behavior of the W-Ni alloys after immersion for 2 h in NaOH solutions at 25°C, open to air. Figure 4 shows the changes in open circuit potentials for the W-Ni alloys as well as tungsten and nickel metals with immersion time in 1 M NaOH solution. The open circuit potentials of the W-Ni alloys are shifted initially towards more negative direction after immersion for about 5 minutes and then shifted towards more positive direction with immersion time. The open circuit potentials of all the examined W-Ni alloys are located between those of tungsten and nickel metals. However, the open circuit potentials of the W-9Ni and W-23 Ni alloys are very close to that of tungsten, whereas, the open circuit potentials of the W-51 and W-78Ni alloys are in noble (more positive) than those of tungsten, W-9Ni and W-23Ni alloys. These facts coincide with the change in the corrosion rates of the W-Ni alloys with nickel content of the alloys in 1 M NaOH solution as shown in Fig. 1.



W-9Ni



W-23Ni



W-69Ni

(a)

(b)

Figure 2: The confocal scanning laser microscopic images of sputter-deposited W-Ni alloys (a) before and (b) after immersion for 24 hours in 1 M NaOH solution at 25 °C, open to air.

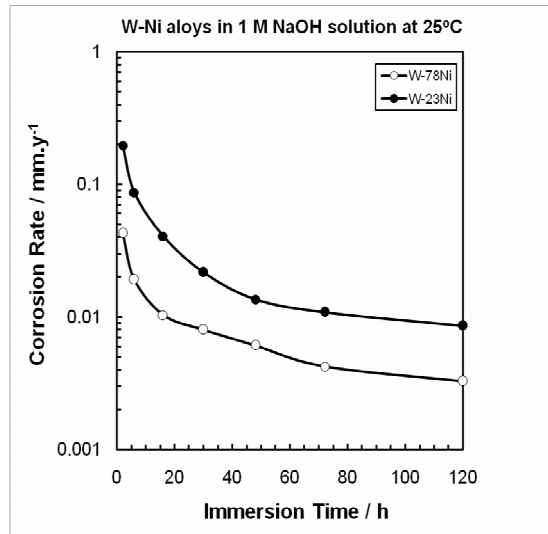


Figure 3: Changes in corrosion rates of the sputter-deposited W-23Ni and W-78Ni alloys in 1 M NaOH solution at 25 °C, open to air as a function of immersion time.

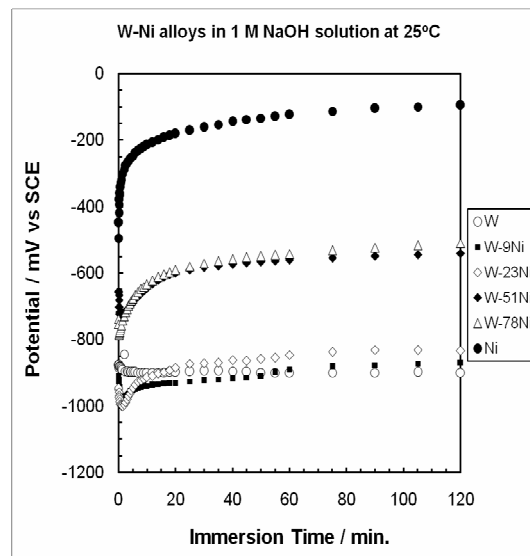


Figure 4: Changes in open circuit potentials of the W-Ni alloys including tungsten and nickel metals in 1 M NaOH solution at 25 °C, open to air as a function of immersion time.

Furthermore, Fig. 5 shows the changes in the open circuit potentials for the sputter-deposited W-Ti alloys including tungsten and nickel metals in different concentrations of NaOH solutions at 25°C, open to air as a function of immersion time. In general, the open circuit potentials of all the examined W-Ni alloys shifted towards noble direction with dilution of NaOH solution. This result revealed that the stability of the passive films formed on the W-Ni alloys increased with decreasing the concentration of NaOH solutions.

Figure 5: Changes of open circuit potentials of the sputter-deposited W-Ni alloys including tungsten and nickel metals in different concentrations of NaOH solutions at 25 °C, open to air as a function of immersion time.

Conclusions

The passivation behavior of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys is studied in alkaline NaOH solutions at 25°C, open to air by corrosion tests,

electrochemical measurements and confocal scanning laser microscopic techniques. The following conclusions are drawn:

1. Nickel metal acts synergistically with tungsten in enhancing the corrosion resistance of the W-Ni alloys so as to show about two orders of magnitude lower corrosion rate than the corrosion rate of tungsten and even slightly lower than that of nickel in 1 M NaOH solution.
2. Nanocrystalline W-9Ni alloy shows the pitting corrosion from CSLM studies in 1 M NaOH solution.
3. The open circuit potentials of all the examined W-Ni alloys are located between those of tungsten and nickel metals in NaOH solutions.
4. The open circuit potentials of the W-Ni alloys are shifted towards less noble direction with increasing concentration of NaOH solutions.

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