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The Electrochemical and Surface Studies of the Corrosion Behavior of Sputter-deposited W-Ni Alloys in 0.5 M NaCl Solution

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Abstract

The corrosion behavior of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys is studied in neutral 0.5 M NaCl solution at 25^0C*, open to air using immersion tests, electrochemical measurements and confocal scanning laser microscopic (CSLM) techniques. In general, the corrosion rates of the W-Ni alloys containing less than 20 at% nickel content are slightly lower than that of tungsten metal whereas the corrosion rates of the alloys containing 20 at% nickel or more increased with the addition of nickel in the alloys. The pitting corrosion is observed in the nickel-rich W-69Ni alloy from CSLM studies. The open circuit corrosion potentials of all the examined W-Ni alloys are shifted to noble direction with the addition of nickel content in the alloys.*

Keywords: *W-Ni alloys, passivation, NaCl, electrochemical measurement, pitting.*

Introduction

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 the corrosion-resistant materials during last three decades. Since homogeneous single phase amorphous or nanocrystalline alloys possess many superior corrosion properties, a variety of corrosion resistance nickel-base alloys have been prepared.[1-6] 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.[7,8]

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The sputter deposition technique has been recently used as one of the appropriate methods for preparing highly corrosion-resistant single phase amorphous or nanocrystalline chromium[9-13] -, molybdenum[14-19] -, manganese[20,21] - and tungsten[22-43] - transition metal alloys. One of the present authors has been successfully prepared novel sputter-deposited amorphous or/and nanocrystalline W-Ni alloys in a wide composition range and reported high corrosion resistance in 12 M HCl at 30^{0}C.[22,26] 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 having the pH values less than one in which regions tungsten is passive and nickel is active.

On the other hand, tungsten metal generally corrodes in solution having pH of 4 or high whereas nickel metal does not corrode in neutral or slightly alkaline oxidizing solutions.[44] In this context, it is very interesting to study the corrosion behavior of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys in neutral 0.5 M NaCl solution.

This research work is aimed to study the corrosion behavior of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys in neutral 0.5 M NaCl solution at 25^{0}C, open to air, using immersion test, electrochemical measurements and scanning confocal 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.[22,23,26,30] An electron probe microanalysis was used to determine the compositions 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 as summarized in Table 1.[22,26]

Prior to the immersion tests, electrochemical measurements and surface morphological studies, the amorphous or/and nanocrystalline W-Ni 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 168 h in 0.5 M NaCl at 25^{0}C, open to air. The open circuit corrosion potentials of the alloys were measured after immersion for 2 hours in 0.5 M NaCl at 25^{0}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 0.5 M NaCl solution at 25^0C was observed using confocal scanning laser microscopy (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.[22,26] The apparent grain size of the sputter-deposited W-Ni alloys used in this research work was estimated by using Scherrer's equation[22,26,45] and the estimated apparent grain size of the W-Ni alloys is tabulated in Table 1.[22,26] The W-Ni alloys containing 23-69 at % nickel content were amorphous having the grain size less than 2.0 nm. The W-15Ni alloy showed the mixture of amorphous and nanocrystalline structures. The W-Ni alloys containing 7, 9 and 78 at % nickel content were crystalline structure having the grain size of 6 nm or less in size.

Table 1: Chemical composition, structure and apparent grain size of the sputter-deposited W-Ni alloys.[22,26]

Name of alloys	Tungsten content (at%)	Nickel content (at%)	Structure	Apparent grain size (nm)
W metal	100	0	Crystalline	20.0
W-7Ni	93	7	Crystalline	6.0
W-9Ni	91	9	Crystalline	5.0
W-15Ni	85	15	Cryst. + Amor.	2.5
W-23Ni	77	23	Amorphous	1.5
W-35Ni	65	35	Amorphous	1.5
W-45Ni	55	45	Amorphous	1.5
W-51Ni	49	51	Amorphous	1.5
W-69Ni	31	69	Amorphous	1.8
W-78Ni	22	78	Crystalline	6.0
Ni metal	0	100	Crystalline	40.0

Changes in corrosion rates of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys after immersion for 168 h in 0.5 M NaCl solution at 25^0C, open to air are shown in Fig.1. The corrosion rates of tungsten and nickel metal are also shown for comparison. The corrosion rates of tungsten and nickel metals are about 2.5×10^{-2} mm/y and 3.0×10^{-1} mm/y, respectively. The corrosion rates of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys containing 5-20 at% nickel are slightly lower than that of corrosion rate of tungsten metal. The corrosion rates of the W-Ni alloys containing 23 at% nickel or more increase gradually with increasing nickel content and nickel metal shows maximum corrosion rate. All these sputter-deposited W-Ni alloys, which are composed of either amorphous or/and nanocrystalline phases show lower corrosion rates than that of nickel metal. Consequently, the corrosion resistance of the sputter-deposited W-Ni alloys, which are composed of either amorphous or/and nanocrystalline, cannot remarkably exceed that of the tungsten metal.

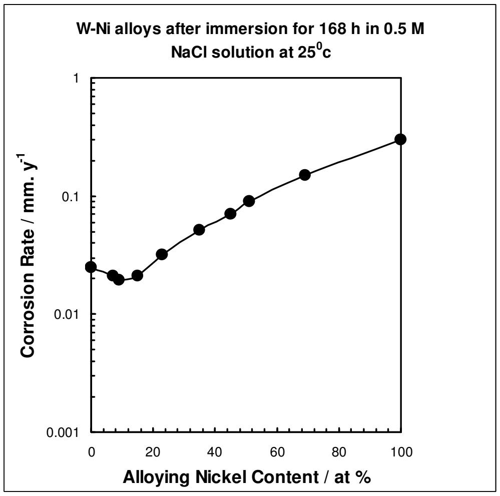

Figure 1: Changes in corrosion rates of the sputter-deposited W-Ni alloys including nickel and tungsten metals in 0.5 M NaCl solution at 25^0C, as a function of nickel content.

The change in surface morphology of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys gives important information about the dissolution process in nano-scales to study the corrosion behavior of the alloys. A series of CSLM images of the films formed on the W-23Ni and W-69Ni alloys before and after immersion for 24 hours in 0.5 M NaCl solution at 25^0C, open to air were observed. Figures 2(a) and (b) show SCLM images of W-23Ni and W-69Ni alloys specimens of as-prepared (that is, as- sputter-deposited), respectively. These CSLM images clearly revealed that the surfaces of the as-prepared W-Ni alloys are very smooth and highly reflective. Surfaces of the as-prepared W-Ni alloys were nearly 100% smooth. Figures 3 (a) and 3 (b) show images of W-23Ni and W-69Ni alloys, respectively, after immersion for 24 hours in 0.5 M NaCl solution at 25^0C. The surface morphologies of the passive films formed on W-23Ni and W-69Ni alloys after immersion for 24 hours in 0.5 M NaCl solution are different than those of the oxide films form on the surfaces of as-prepared W-23Ni and W-69Ni alloys specimens. The dissolution of both W-23Ni and W-69Ni alloys is obvious and surface is roughened considerably after immersion for 24 hours in

0.5 M NaCl. The W-69Ni alloy shows the pitting corrosion in 0.5 M NaCl solution whereas such behavior is not observed on the surface of the W-23Ni alloy.

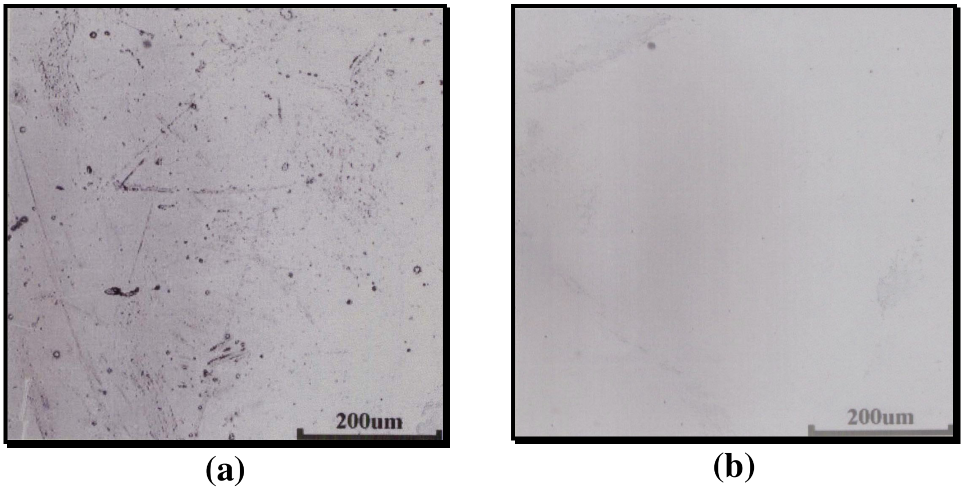

Figure 2: The confocal scanning laser microscopic images of as-prepared sputter-deposited (a) W-23Ni and (b) W-69Ni alloys.

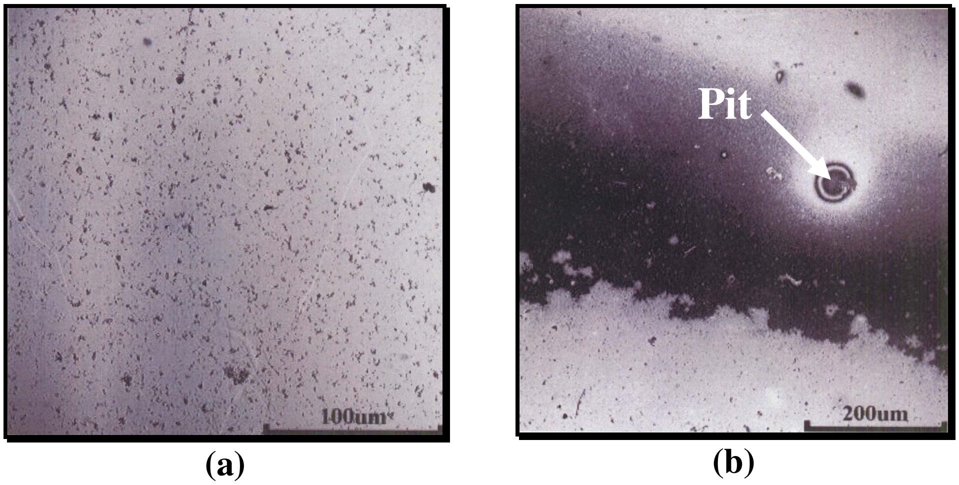

Figure 3: The confocal scanning laser microscopic images of sputter-deposited (a) W-23Ni and (b) W-69Ni alloys after immersion for 24 h in 0.5 M NaCl solution at 25^{0}C.

Figure 4 shows the changes in open circuit corrosion potentials for the W-Ni alloys including tungsten and nickel metals in 0.5 M NaCl solution at 25^{0}C, as a function of immersion time. The open circuit corrosion potential of the nickel is about – 440 mV (SCE) after immersion for 2 seconds and gradually increases with immersion time up to – 60 mV (SCE) after immersion for 2 h. The open circuit corrosion potential of the tungsten metal reaches a stationary value of about – 640 mV (SCE) within 25 minutes. The similar behavior of the stationary state of the open circuit corrosion potentials of the sputter-deposited W-Ni alloys is observed. The open circuit potentials of all the examined W-Ni alloys are located between those of nickel and tungsten, but are mostly close to that of tungsten. These results revealed that more stable passive films are formed on the surface of the W-Ni alloys with increasing nickel content in the alloys in neutral 0.5 M NaCl. However, due to the pitting corrosion observed on the surface of the nickel-rich W-Ni alloys, the corrosion rates of the W-Ni alloys increased with nickel content as shown in Fig.1.

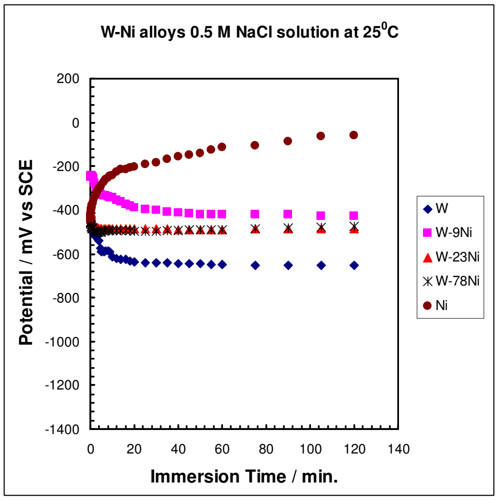

Figure 4: Changes in open circuit corrosion potentials for W-Ni alloys including tungsten and nickel in 0.5 M NaCl solution at 25^{0}C, as function of immersion time.

Conclusions

The corrosion behavior of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys is studied in neutral 0.5 M NaCl solution at 25^{0}C, open to air, by immersion tests, electrochemical measurements and confocal scanning laser microscopic techniques. The following conclusions are drawn:

1. The corrosion rates of the sputter-deposited amorphous or/and nanocrystalline W-Ni alloys containing 20 at% nickel or more increased linearly with nickel content in 0.5 M NaCl solution. The corrosion rates of the W-Ni alloys containing less than 20 at% nickel are slightly lower than that of tungsten metal.

2. Open circuit corrosion potentials of all the examined sputter-deposited W-Ni alloys shifted to more noble direction with addition of nickel content and are located between tungsten and nickel metals in 0.5 M NaCl solution.
3. The surface morphological studies by confocal scanning laser microscopy techniques seem to be effective to study the corrosion behavior of the sputter-deposited W-Ni alloys. The W-69Ni alloy shows the pitting corrosion from SCLM studies.

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