

Effects of Alloying Elements on the Corrosion Behavior of Sputter-deposited Zr-(12-21)Cr-W Alloys in 0.5 M NaCl Solution

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Abstract

The synergistic effect of the simultaneous additions of tungsten and zirconium in the sputter-deposited amorphous or nanocrystalline Zr-(12-21)Cr-W alloys is studied in 0.5 M NaCl solution open to air at 25°C using corrosion tests and open circuit potential measurements. Corrosion rates of the sputter-deposited Zr-(12-21)Cr-W alloys containing 10-80 at % tungsten (that is, $0.95-1.85 \times 10^{-2} \text{ mm.y}^{-1}$) are more than one order of magnitude lower than that of the sputter-deposited tungsten and even lower than those of zirconium as well as chromium in 0.5 M NaCl solution. The addition of 8-73 at % zirconium content in the sputter-deposited binary W-(12-21)Cr alloys seems to be more effective to improve the corrosion-resistant properties of the sputter-deposited ternary Zr-Cr-W alloys containing 12-21 at % chromium in 0.5 M NaCl solution. The sputter-deposited Zr-(17-21)Cr-W alloys containing an adequate amounts of zirconium metal showed the more stable passivity and showed higher corrosion resistance than those of alloy-constituting elements in 0.5 M NaCl solution open to air at 25°C.

Keywords: Zr-(12-21)Cr-W alloys, sputter deposition, corrosion test, open circuit potential, 0.5 M NaCl.

Introduction

The chemically homogeneous single-phase nature of amorphous alloys is generally responsible for their high corrosion resistance owing to the formation of uniform protective passive films those are able to separate bulk of alloys from aggressive environments. From the corrosion point of view, they can be considered as homogeneous alloys. Accordingly, the sputter-deposited alloys consisting of either amorphous and nanocrystalline single-phase solid solutions are chemically homogeneous, and hence are interesting in the view of corrosion resistance. Last two decades, the use of the sputter deposition technique is becoming a quite suitable method for tailoring of varieties of amorphous or/and nanocrystalline corrosion-resistant metastable alloys. Even if amorphous alloys are not

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formed by the sputter deposition technique, the alloys thus prepared are always composed of nanocrystals with very fine grains and sometimes behaves similar to the single-phase amorphous alloy.

One of the present authors (JB) had reported that the sputter-deposited amorphous or/and nanocrystalline tungsten-based binary W-Ti¹⁻⁵, W-Zr^{2,6,7}, W-Ni^{8,9}, W-Cr^{2,7,10-13}, W-Nb^{2,7,14-16}, W-Ta^{2,7,17}, W-Mo^{8,18} and ternary W-Cr-Ni^{19,20} as well as Cr-Zr-W²¹ alloys were spontaneously passivated showing significantly higher corrosion resistance than those of alloy-constituting elements in concentrated hydrochloric acid solutions. The significant improvement of the corrosion-resistant is attributed to the formation of double oxyhydroxide passive films containing both tungsten and alloy-constituting metal cations which are more resistance and stable for both the general and localized corrosion in comparison with the oxyhydroxides of tungsten and alloy-constituting elements.

Zirconium, chromium and tungsten are regarded as very effective alloying elements for enhancing the corrosion resistance of alloys in aggressive environments. Zirconium is one of the corrosion-resistant elements in acidic environments, although it suffers pitting corrosion by anodic polarization in chloride containing solutions. The alloying of zirconium with aluminum²², chromium²³ and molybdenum²⁴ greatly improved the corrosion resistance of the alloys in acidic solutions. Similarly, it has been reported that the corrosion resistance of the sputter-deposited amorphous or/and nanocrystalline W-Zr alloys were passivated spontaneously and observed significantly high corrosion resistance in aggressive environments.^{2,6,7} The corrosion-resistant of the sputter-deposited W-Zr alloys is higher than those of tungsten and zirconium, and hence tungsten addition greatly enhanced the pitting corrosion resistance of zirconium in 12 M HCl. On the other hand, chromium is one of the most effective alloying elements to provide a high passivating ability for conventional steels and stainless steels. Only a small amount of chromium (8 at %) addition was enough to cause spontaneous passivation of steels in 1 M HCl and they showed significantly higher pitting corrosion resistance than stainless steels.^{25,26} A series of the sputter-deposited chromium-metalloid alloys exhibited superior corrosion resistance compared to chromium metal in 12 M HCl.²⁷ On the other hand, it has been reported that only small amount of tungsten addition (that is, about 9 at %) was enough to cause spontaneous passivation of the sputter-deposited nanocrystalline W-Cr alloys even in 12 M HCl and these alloys showed about five orders of magnitude lower corrosion rate than the corrosion rate of chromium metal, and about one order of magnitude lower corrosion rate than that of tungsten.¹⁰⁻¹³

It has been recently reported that the simultaneous additions of 10 at % tungsten in presence of 15-17 at % chromium in the sputter-deposited amorphous or nanocrystalline Cr-Zr-W alloys enhanced significantly the pitting corrosion as well as uniform corrosion of the zirconium metal in 12 M HCl solution open to air at 30°C²¹. It is noteworthy for mentioning here that both zirconium²⁸ and chromium²⁹ metals are very corrodible in acidic or very alkaline (>13 pH) solutions. However, both zirconium and chromium metals do not corrode in neutral 0.5 M NaCl solution, mostly due to the formation of zirconium oxides²⁸ and chromium hydroxide/oxides²⁹, respectively. On the other hand, tungsten metal corrodes in solution having pH 4 or high³⁰, for example in 0.5 M NaCl solution. Accordingly, it might be expected that effects of zirconium, chromium and tungsten additions enhance in the

corrosion resistance of the sputter-deposited amorphous or nanocrystalline Zr-(12-21)Cr-W alloys in 0.5 M NaCl solution.

The present research work is aimed to clarify the effects of tungsten, zirconium and chromium additions on the corrosion behavior of the sputter-deposited Zr-(12-21)Cr-W alloys in 0.5 M NaCl solution open to air at 25°C using corrosion tests and open circuit potential measurements.

Experimental Methods

The sputter-deposited ternary Zr-(12-21)Cr-W alloys containing 10-80 at% tungsten were characterized as single-phase solid solutions of amorphous or nanocrystalline structures having apparent grain size ranges from 1 to 10 nm as shown in Table 1²¹. The compositions of the sputter-deposited Zr-(12-21)Cr-W alloys hereafter are all denoted in atomic percentage (at %).

Table 1: Structure and apparent grain size of the sputter-deposited Zr-(12-21)Cr-W alloys²¹.

Name of Alloy	Structure	Apparent Grain Size (nm)
Zirconium	nanocrystalline	24.0
Zr-17Cr-10W	amorphous	1.4
Zr-21Cr-38W	amorphous	1.0
Zr-18Cr-57W	amorphous	1.2
Zr-12Cr-80W	nanocrystalline	10.4
Zr-42Cr-19W	amorphous	0.9
Tungsten	nanocrystalline	20.0
Chromium	nanocrystalline	40.0

Prior to the corrosion tests and electrochemical measurements, the sputter-deposited Zr-(12-21)Cr-W 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 solution open to air at 25°C. The time dependence of the corrosion rate of the Zr-(12-21)Cr-W alloys was also estimated at various time intervals. The corrosion rate of the individual alloy was estimated by using equation (1) as given below^{2,8,31}:

$$\text{Corrosion Rate (mm.y}^{-1}\text{)} = \frac{\Delta w \times 8760 \times 10}{d \times A \times t} \quad (1)$$

where, Δw is weight loss of the alloy specimen in gram; d is density of the alloy specimen in gm/cm^3 ; A is area of the alloy specimen in cm^2 , and; t is time of immersion in hour.

The open circuit potential of the sputter-deposited Zr-(12-21)Cr-W alloys was measured after immersion for 72 hours in 0.5 M NaCl solution open to air at 25°C. 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

Figure 1 shows the changes in corrosion rates of the sputter-deposited Zr-(12-21)Cr-W alloys after immersion for 240 hours in 0.5 M NaCl solution open to air at 25°C. Corrosion rates of the sputter-deposited Zr-42Cr-19W, W-(12-42)Cr³² alloys including sputter-deposited tungsten, chromium and zirconium metals are also shown for comparison. The Corrosion rates of the Zr-Cr-W alloys containing 12-42 at % chromium are more than one order of magnitude lower than those of the sputter-deposited tungsten and even lower than that of zirconium. The corrosion rates of the Zr-(12-21)Cr-W alloys (that is, $0.95-1.85 \times 10^{-3} \text{ mm.y}^{-1}$) show lower corrosion rates than those of binary nanocrystalline W-(12-21)Cr³² alloys in 0.5 M NaCl solution. However, the corrosion rates of the ternary Zr-(12-21)Cr-W alloys show almost same corrosion rate that of the sputter-deposited binary W-42Cr³² alloy. It is meaningful for mentioning here that the corrosion rates of all the examined ternary Zr-(12-21)Cr-W alloys were almost same corrosion rates of the sputter-deposited binary W-Zr alloys in 0.5 M NaCl solution³³. These results revealed that the addition of 8-73 at % zirconium in the sputter-deposited binary W-(12-21)Cr alloys seems to be more effective to improve the corrosion-resistant properties of the Zr-Cr-W alloys than that of the sputter-deposited binary W-Cr alloys containing more than 21 at % chromium in neutral 0.5 M NaCl solution open to air at 25°C.

The passivation of the alloys generally occurs through the active dissolution of alloys at the initial periods of immersion in a corrosive environment. The high chemical reactivity of the alloys leads to the rapid accumulation of a beneficial species in the passive films formed on the alloys. This accounts for the high corrosion resistance of the alloys. Therefore, it is important to identify the role of immersion time for rational understanding of the corrosion behavior of the alloys. Figure 2 shows the changes in the corrosion rates of the Zr-(12-21)Cr-W alloys including zirconium and chromium metals in 0.5 M NaCl solution, as a function of immersion time. In general, the corrosion rates of all the examined Zr-(12-21)Cr-W alloys are significantly high at initial periods of immersion (that is, about 2-8 h). The corrosion rates of the sputter-deposited Zr-Cr-W alloys as well as zirconium and chromium metals are decreased with immersion time till 72 h and the corrosion rate becomes steady after immersion for 72-240 h in 0.5 M NaCl solution. Accordingly, initially fast dissolution of the Zr-(12-21)Cr-W alloys results in fast passivation by forming more protective passive films on the surface of the ternary Zr-Cr-W alloys in 0.5 M NaCl solution. Consequently, the average corrosion rates of all the examine sputter-deposited Zr-(12-21)Cr-W alloys are lower than those of the alloy-constituting elements as shown in Fig. 1 also.

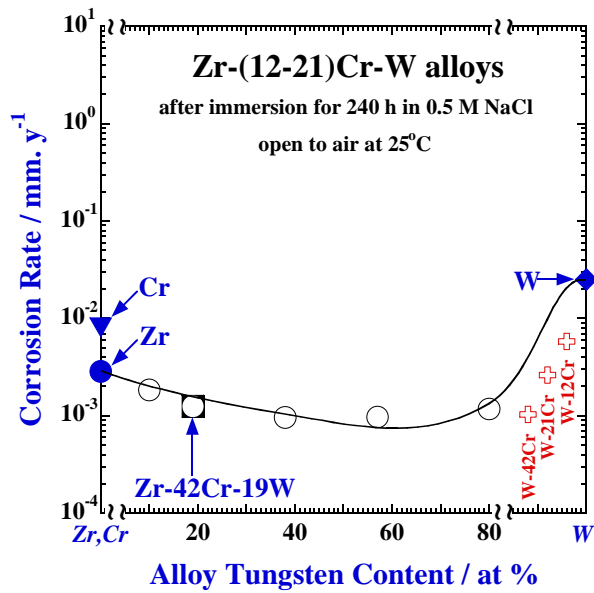


Figure 1: Changes in corrosion rates of the sputter-deposited ternary Zr-(12-21)Cr-W alloys including zirconium, chromium and tungsten metals after immersion for 240 h in 0.5 M NaCl solution open to air at 25°C, as a function of alloy tungsten content. The corrosion rates of the binary W-(12-42)Cr alloys are also shown for comparison³².

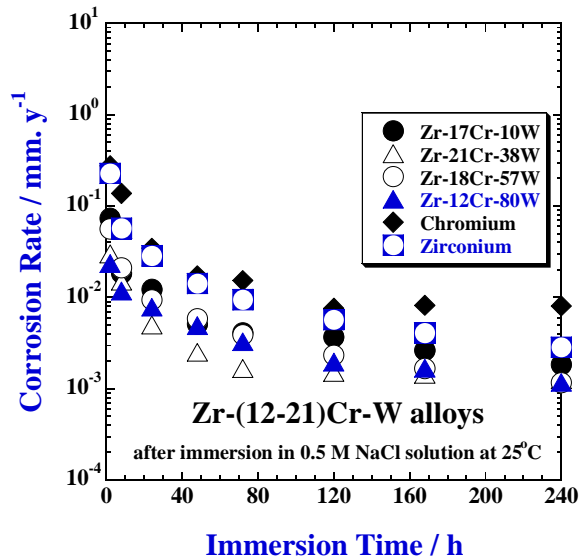


Figure 2: Changes in corrosion rates of the sputter-deposited Zr-(12-21)Cr-W alloys including zirconium and chromium in 0.5 M NaCl solution open to air at 25°C, as a function of immersion time.

Open circuit potential measurement of the alloys was carried out for a better understanding of the corrosion behavior of the sputter-deposited amorphous or nanocrystalline Zr-(12-21)Cr-W alloys for about 72 hours in 0.5 M NaCl solution. Figures 3 shows the changes in open circuit potentials of the Zr-(12-21)Cr-W alloys including zirconium and chromium metals in 0.5 M NaCl solution open to air at 25°C, as a function of immersion time. The open circuit potentials of all the examined sputter-deposited amorphous Zr-(17-21)Cr-W alloys are shifted towards more noble (or positive) direction with immersion time and attained a stationary value of about -30 mV (SCE) after immersion for about 24-72 hours. The open circuit potential of the nanocrystalline Zr-12Cr-80W alloy decreased slightly towards the more negative direction with immersion time up to 2 h and then slightly increased towards the noble (positive) direction and attained a stationary value of about -190 mV (SCE) after immersion for 24-72 h in 0.5 M NaCl solution. The ennoblement of the open circuit potentials of the amorphous Zr-17Cr-10W, Zr-21Cr-38W and Zr-18Cr-57W alloys are clearly observed as compared to those of the nanocrystalline Zr-12Cr-80W alloy and tungsten metal. However, the open circuit potentials of the all the examined ternary Zr-(12-21) Cr-W alloy are located between those of zirconium and tungsten metals, and are mostly located very close to that of zirconium as well as chromium metals after immersion for about 24-72 hours. These results revealed that the sputter-deposited Zr-(12-21)Cr-W alloys containing an adequate amounts of chromium and zirconium metals show the more stable passivity and show higher corrosion resistance than those of alloy-constituting elements (that is, tungsten, chromium and zirconium) in neutral 0.5 M NaCl solution open to air at 25°C. These facts coincide with the change in the corrosion rates of the Zr-(12-21)Cr-W alloys as shown in Figs 1 and 2 also.

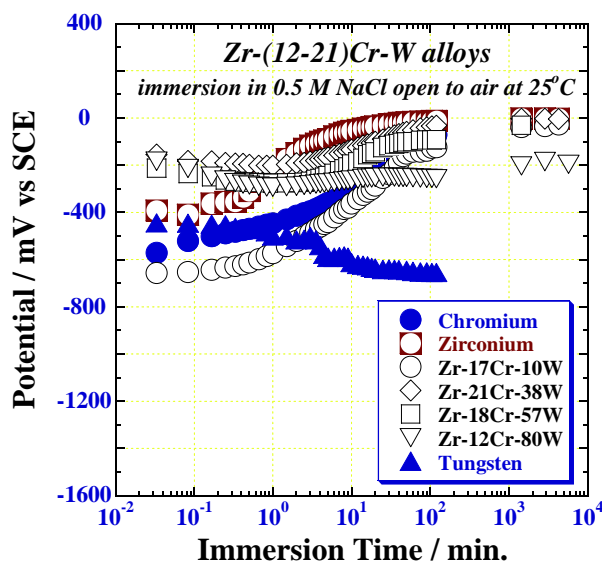


Figure 3: Changes in open circuit potential for the sputter-deposited Zr-(12-21)Cr-W alloys including zirconium, chromium and tungsten metals in 0.5 M NaCl solution open to air at 25°C, as a function of immersion time.

Conclusions

The roles of zirconium, chromium and tungsten metals for enhancing the corrosion resistance of the sputter-deposited ternary Zr-(12-21)Cr-W alloys containing 10-80 at% tungsten was studied in 0.5 M NaCl solution open to air at 25°C using corrosion tests and open circuit potential measurements. The following conclusions are drawn from the present research work:

1. Zirconium and chromium metals act synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited amorphous or nanocrystalline Zr-(12-21)Cr-W alloys so as to show higher corrosion resistance than the corrosion resistance of the alloy-constituting elements in 0.5 M NaCl solution.
2. The corrosion rates of all the examined ternary Zr-(12-21)Cr-W alloys are in the range of $0.95-1.85 \times 10^{-3} \text{ mm.y}^{-1}$ which is lower than those of the sputter-deposited binary nanocrystalline W-(12-21)Cr alloys in 0.5 M NaCl solution.
3. The sputter-deposited Zr-(17-21)Cr-W alloys containing an adequate amounts of zirconium metal showed the more stable passivity and showed higher corrosion resistance than those of alloy-constituting elements in 0.5 M NaCl solution at 25°C, open to air.

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References

1. J. Bhattarai, E. Akiyama, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1995, **37**, 2071.
2. J. Bhattarai, *Tailoring of Corrosion-Resistant Tungsten Alloys by Sputtering*, Doctoral Thesis, Department of Materials Science, Faculty of Engineering, Tohoku University, Japan. 1998, pp. 229.
3. K. Hashimoto, J. Bhattarai, X. Y. Li, P. Y. Park, J. H. Kim, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Shimamura, in *Proc. of the Special Symposium on Passivity and its Breakdown* (eds P. M. Natishan, H. S. Isaacs, M. Janik-Czachor, V. A. Macagno, P. Marcus and M. Seo). The Electrochemical Society Inc., Pennington, USA, 1998, pp. 369.
4. J. Bhattarai, *J. Nepal Chem. Soc.*, 2000, **19**, 32.
5. J. Bhattarai, *Nepal J. Sci. Technol.*, 2002, **4**, 37.
6. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1997, **39**, 353.

7. J. Bhattarai, A. Kawashima, K. Asami and K. Hashimoto, in *Proc. 3rd National Conference on Science and Technology*, Kathmandu, Nepal, 1999, vol. 1, pp. 389.
8. J. Bhattarai, *The Corrosion Behavior of Sputter-deposited Tungsten-base Alloys*. Research Reports, Institute for Materials Research (IMR), Tohoku University, Sendai, Japan, 1995, pp. 43+IV.
9. J. Bhattarai, *J. Nepal Chem. Soc.*, 2001, **20**, 24.
10. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1998, **40**, 155.
11. J. Bhattarai and K. Hashimoto, *Tribhuvan University J.*, 1998, **21(2)**, 1–16.
12. J. Bhattarai, *J. Nepal Chem. Soc.*, 2001, **19**, 1.
13. J. Bhattarai, *J. Insti. Sci. Technol.*, 2002, **12**, 125.
14. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1998, **40**, 19.
15. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1998, **40**, 1897.
16. H. Jha and J. Bhattarai, *J. Alloys & Compounds*, 2008, **456**, 474.
17. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1998, **40**, 757.
18. J. Bhattarai, *J. Nepal Chem. Soc.*, 2006, **21**, 19.
19. J. Bhattarai, *Scientific World*, 2009, **7(7)**, 24.
20. J. Bhattarai, *Trans. Mater. Res. Soc. Japan*, 2010, **35**, in press.
21. J. Bhattarai, in *Proc. 13th Middle East Corros. Conf.-2010*, Bahrain Soc. Eng., Bahrain, 14-17 February 2010. Paper No: **107-CR-01**, in press.
22. H. Yoshioka, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1992, **33**, 425.
23. J. H. Kim, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1993, **34**, 1817.
24. P. Y. Park, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1995, **37**, 307.
25. K. Hashimoto and K. Asami, *Corros. Sci.*, 1979, **19**, 251.
26. M. Naka, K. Hashimoto, A. Inoue and T. Masumoto, *J. Non-Cryst. Solids*, 1979, **31**, 347.
27. T. P. Moffat, R. M. Latanision and R. R. Ruf, *Electrochimic Acta*, 1995, **40**, 1723.
28. M. Pourbaix, in *Atlas of Electrochemical Equilibrium in Aqueous Solution*, National Association of Corrosion Engineers, Huston, TX, 1974, pp. 221.
29. M. Pourbaix, in *Atlas of Electrochemical Equilibrium in Aqueous Solution*, National Association of Corrosion Engineers, Huston, TX, 1974, pp. 256.
30. M. Pourbaix, in *Atlas of Electrochemical Equilibrium in Aqueous Solution*, National Association of Corrosion Engineers, Huston, TX, 1974, pp. 280.
31. B. R. Aryal, “*Corrosion Behavior of Sputter-deposited Zr-(12–21)Cr–W alloys in 0.5 M NaCl and 1 M NaOH Solutions*”, M. Sc. Dissertation, Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal. pp. 69 + VI (2010).
32. M. Basnet and J. Bhattarai, *J. Nepal Chem. Soc.*, 2010, **25**, 60.
33. P. Shrestha and J. Bhattarai, *J. Nepal Chem. Soc.*, 2010, **25**, 36.