

*Full Length Research Paper*

# The corrosion behavior of sputter-deposited ternary W–Zr–(15–18)Cr alloys in 12 M HCl

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New series of amorphous or/and nanocrystalline W–Zr–(15–18)Cr alloys are successfully prepared by direct current (DC) magnetron sputtering. The role of alloy-constituting elements on the corrosion behavior of the W–Zr–(15–18)Cr alloys is studied by corrosion tests and electrochemical measurements in 12 M HCl solution open to air at 30°C. All the examined sputter-deposited W–Zr–(15–18)Cr alloys containing 12 to 73% zirconium are passivated spontaneously, and hence they showed more than one order of magnitude higher corrosion resistance than those of alloy-constituting elements. The corrosion rate of the alloys is in the range of  $1-2 \times 10^{-3}$  mm/y which is even lower than those of the sputter-deposited binary W–Zr and W–Cr alloys. The zirconium addition suppresses the anodic dissolution current, and hence the anodic current densities of the alloys decreased with increasing the zirconium content in the W–Zr–(15–18)Cr alloys. It is therefore considered that the simultaneous additions of zirconium and tungsten with 15 to 18% of chromium enhance synergistically the corrosion-resistant and pitting corrosion of the sputter-deposited W–Zr–(15–18)Cr alloys in 12 M HCl.

**Key words:** Amorphous/nanocrystals, sputter deposition, corrosion-resistant, W–Zr–Cr alloys, electrochemical measurement, pitting corrosion.

## INTRODUCTION

The sputter-deposited binary/ternary alloys consisting of either amorphous or/nanocrystalline single-phase are chemically homogeneous, and hence are interesting in the view of corrosion resistance properties of the alloys. The use of sputter deposition technique is becoming a quite suitable method for tailoring the corrosion-resistant alloys in the last two decades. Even if amorphous alloys are not formed by the sputter deposition, alloys thus prepared are always composed of nanocrystals with very fine grains and sometimes behaves similar to the single-phase amorphous alloys. It is believed that the single-phase nature of amorphous or nanocrystalline alloys is generally responsible for their high corrosion resistance, owing to the formation of uniform protective passive films, which are able to separate bulk of alloys from aggressive environments (Hashimoto, 1993). It has been reported that the sputter deposition of tungsten with

zirconium (Bhattarai et al., 1997, 2000; Bhattarai, 1998) and chromium (Bhattarai et al., 1998; Bhattarai and Hashimoto, 1998; Bhattarai, 1998, 2000) was effective in preparing binary amorphous or/and nanocrystalline tungsten-base alloys with a high corrosion resistance. Furthermore, Kim et al. (1993) had reported that the sputter-deposited amorphous binary Cr–Zr alloys showed high corrosion resistance than those of alloy-constituting elements in aggressive 6 M HCl solution at 30°C. The high corrosion resistance of these sputter-deposited binary W–Zr, W–Cr and Cr–Zr alloys was mainly based on the spontaneous passivation in aggressive environments.

Tungsten, zirconium and chromium are regarded as very effective alloying elements for enhancing the corrosion resistance of alloys in aggressive environments. It has been reported that only a small amount of tungsten

addition (that is, less than 10%) was enough to cause spontaneous passivation of the binary 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 (Bhattarai et al., 1998; Bhattarai and Hashimoto, 1998; Bhattarai, 1998, 2000, 2002). On the other hand, zirconium is also corrosion-resistant in acidic environments, although it suffers pitting corrosion by anodic polarization. It has been reported that the corrosion resistance of the sputter-deposited amorphous or/and nanocrystalline W–Zr alloys were passivated spontaneously and high corrosion resistance was observed significantly in aggressive environments (Bhattarai et al., 1997, 2000; Bhattarai, 1998). The corrosion-resistant of the sputter-deposited W–Zr alloys is higher than those of tungsten and zirconium, and hence addition of tungsten greatly enhanced the pitting corrosion resistance of zirconium in hydrochloric acid solutions (Bhattarai et al., 1997; Bhattarai, 1998). The alloying of zirconium with chromium (Kim et al., 1993) and molybdenum (Park et al., 1995) greatly improved the corrosion resistance of the Cr–Zr and Mo–Zr alloys, respectively, in aggressive environments. On the other hand, chromium and tungsten have different characteristics in corrosion behavior, especially in pitting corrosion.

Chromium and tungsten are known to be effective elements in improving the pitting corrosion resistance of the alloys, whereas zirconium suffers pitting corrosion by anodic polarization in aggressive chloride-containing environments. The immunity to pitting corrosion is one of the most interesting characteristics of alloys. It has been reported that the synergistic improvement in the resistance to passivity breakdown in chloride-containing media was observed when chromium and zirconium were added simultaneously to the sputter-deposited Mn–Zr–Cr alloys instead of single addition of zirconium or chromium metals (El-Moneim et al., 1999). Furthermore, chromium is one of the most effective alloying elements to provide a high passivating ability for conventional steels and stainless steels, and hence Hashimoto (1993) has reported that the pitting potential of austenitic stainless steels shifted to higher anodic potentials with increasing chromium content of the surface film. In accordance with these facts, if zirconium and chromium with tungsten form a single-phase solid solution of ternary W–Zr–Cr alloys by sputter deposition, they might have high corrosion resistance in aggressive 12 M HCl solution. In this context, the main objectives of the present research work are to prepare corrosion-resistant ternary W–Zr–(15–18)Cr alloys containing 12 to 73% zirconium content by the sputter deposition method, and to clarify the effects of tungsten, zirconium and chromium additions on the corrosion behavior, as well as the passivity breakdown of the ternary W–Zr–(15–18)Cr

alloys, in 12 M HCl solution open to air at 30°C.

## MATERIALS AND METHODS

The DC magnetron sputtering was used for the preparation of the ternary amorphous or/and nanocrystalline W–Zr–Cr alloys. The target was composed of a 99.95% pure tungsten disk of 100 mm diameter and 6 mm thickness, on the erosion region of which 99.95% pure zirconium and chromium disks of 20 mm diameter each were symmetrically placed. The composition of the sputter deposits was changed by changing the numbers of zirconium and chromium disks on the tungsten disc. Glass plates were used as substrates which were rinsed by immersion in water containing a commercial detergent for cleaning at about 75°C. The sputtering apparatus and conditions used were the same as those described elsewhere (Bhattarai et al., 1997, 1998; Bhattarai, 1998).

An electron probe microanalysis (EPMA) was used to determine the composition of the sputter deposits. The structure of the sputter-deposited W–Zr–Cr alloys was confirmed by X-ray diffractometer (XRD) with  $\text{CuK}\alpha$  radiation at  $\theta$ – $2\theta$  mode. The apparent grain size of the alloys was estimated from the full width at half maximum (FWHM) of the most intense reflection according to Scherrer's formula (Cullity, 1977) as given in Equation (1):

$$t = 0.9\lambda/\beta\cos\theta$$

where,  $t$  is the apparent grain size in nm,  $\lambda$  is the X-ray wavelength ( $= 0.15148$  nm for  $\text{CuK}\alpha$ ),  $\beta$  is the FWHM in radian and  $\theta$  is the diffraction angle of the most intense peak.

Prior to corrosion tests and electrochemical measurements, the surface of the alloy specimens was polished mechanically with silicon carbide paper (grit No. 1500) in cyclohexane, rinsed with acetone and dried in air in order to obtain reproducible results by removal of the air-formed oxide film seen as sputtered alloys. Corrosion rates of the sputter-deposited amorphous or/and nanocrystalline Cr–Zr–W alloys including zirconium and tungsten metals were estimated from the weight loss after immersion for 216 h in 12 M HCl solution open to air at 30°C. For chromium metal, the corrosion rate was estimated after immersion for two hours in 12 M HCl.

Potentiodynamic cathodic and anodic polarization curves were measured in 12 M HCl open to air at 30°C after immersion for 24 h when the open circuit potential became almost steady. A platinum mesh and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All the potential given in this paper are relative to SCE.

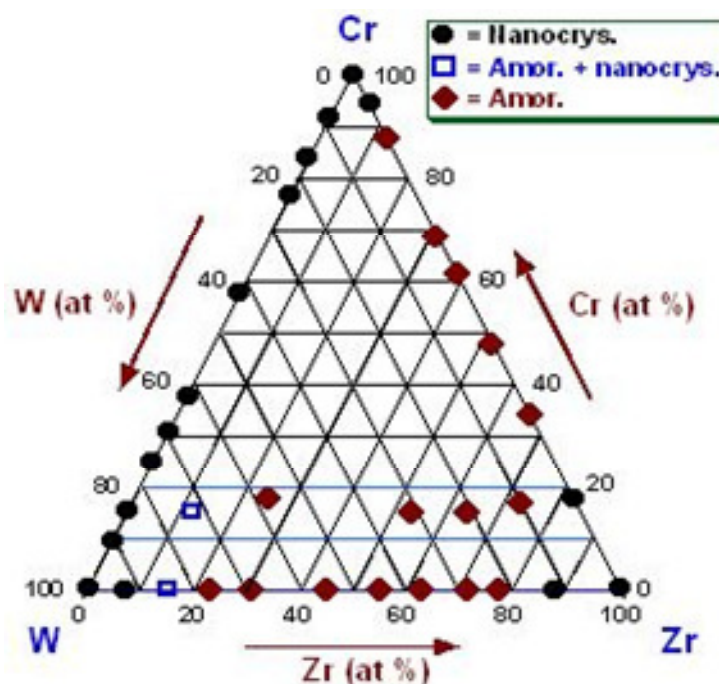
## RESULTS

The composition, structure and apparent grain size (AGS) of the sputter-deposited W–Zr–(15–18)Cr alloys were analyzed by an electron probe microanalysis (EPMA) and X-ray diffraction (XRD) patterns, respectively. Alloy compositions hereafter are all denoted in atomic percentage. The results of the characterization of the ternary W–Zr–(15–18)Cr alloys are tabulated in Table 1. The apparent grain size of the W–Zr–(15–18)Cr alloys containing 25 to 73% zirconium is of the order of about 1.1 to 1.4 nm, which is only a little larger than the size of the atom groups that are supposed to exist in liquid metals. Accordingly, the W–Zr–(15–18)Cr alloys

**Table 1.** Chemical composition, structure and apparent grain size (AGS) of sputter-deposited W–Zr–(15–18)Cr alloys including alloying elements.

Name of alloy/element	Tungsten (%)	Zirconium (%)	Chromium (%)	Structure from XRD*	AGS (nm)
W–73Zr–17Cr	10	73	17	amor.	1.37
W–64Zr–15Cr	21	64	15	amor.	1.22
W–54Zr–15Cr	31	54	15	amor.	1.10
W–25Zr–18Cr	57	25	18	amor.	1.19
W–12Zr–15Cr	73	12	15	amor.+ nanocryst.	10.5
Tungsten	100	–	–	nanocryst.	20.2
Zirconium	–	100	–	nanocryst.	23.0
Chromium	–	–	100	nanocryst.	17.5

\* amor. = Amorphous; amor.+nanocryst. = mixture of amorphous and nanocrystals.

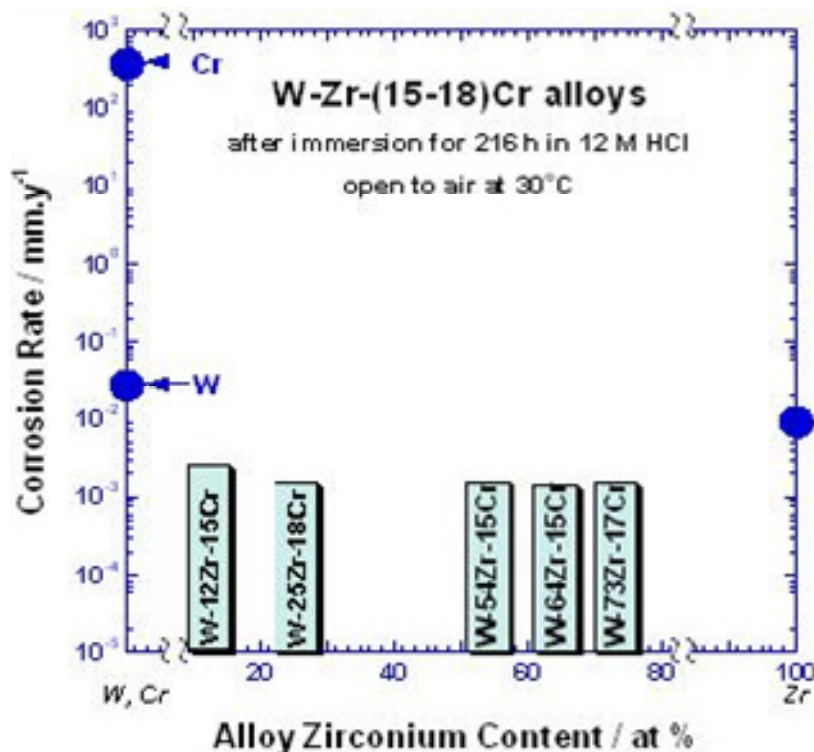
**Figure 1.** Composition structure diagram of the sputter-deposited W–Zr–(15–18)Cr alloys.

containing 25 to 73% zirconium are regarded as amorphous alloys. On the other hand, the apparent grain size of the W–12Zr–15Cr alloys is about 10.4 nm, and hence characterized as the mixture of amorphous and nanocrystalline structures.

Figure 1 shows the composition–structure diagram of the sputter-deposited ternary W–Zr–(15–18)Cr alloys. This figure reveals that both binary and ternary chromium–base alloys are apt to form amorphous structure over a wide composition range, except for the binary W–Cr alloys, which form nanocrystalline single-phase supersaturated solid solutions of tungsten and chromium metals (Bhattarai et al., 1998). Amorphization

of the sputter-deposited W–Cr alloys is not favored because both tungsten and chromium do not satisfy the prerequisites for easy formation of the amorphous structure, that is, negative mixing enthalpy (Niessen et al., 1983) and large atomic size difference (Egami and Waseda, 1984).

Figure 2 shows changes in the corrosion rates of the sputter-deposited W–Zr–(15–18)Cr alloys including tungsten, chromium and zirconium metals after immersion for 216 h in 12 M HCl solution open to air at 30°C, as a function of alloy zirconium content. Corrosion rates of all the examined ternary W–Zr–(15–18)Cr alloys, which are composed of either amorphous or/and



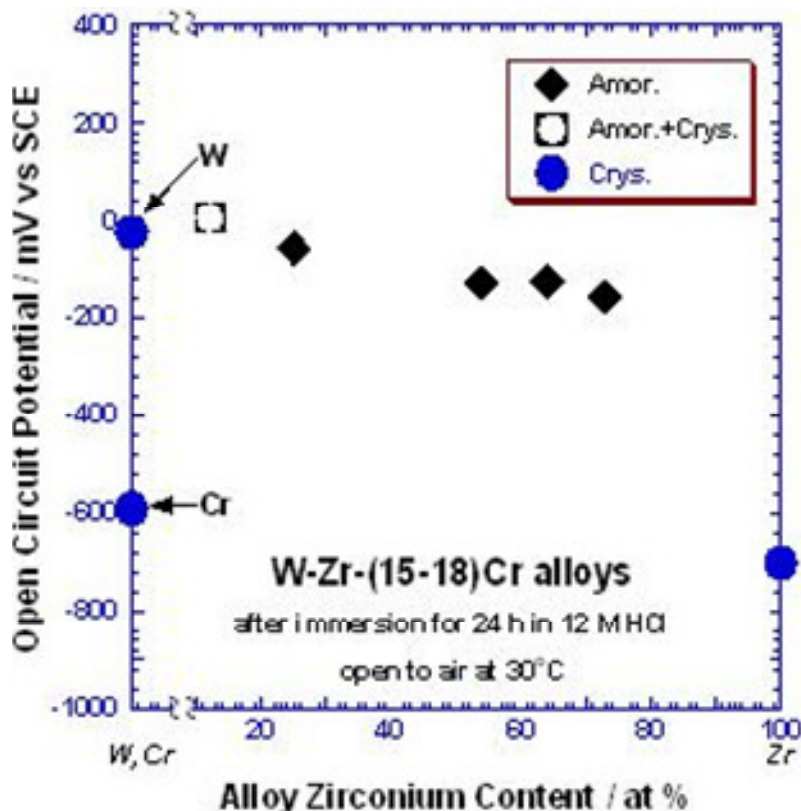
**Figure 2.** Changes in corrosion rates of the sputter-deposited W–Zr–(15–18)Cr alloys including those of tungsten, chromium and zirconium after immersion for 216 h in 12 M HCl open to air at 30°C, as a function of alloy zirconium content.

nanocrystalline phases, are nearly one order of magnitude lower than those of tungsten and zirconium. The corrosion rates of all the sputter-deposited W–Zr–(15–18)Cr alloys containing 12 to 73% zirconium content are almost the same (that is, about  $1\text{--}2 \times 10^{-3}$  mm/y). It is noteworthy that the corrosion rates of the W–Zr–(15–18)Cr alloys are lower than those of the corrosion rates of the sputter-deposited binary W–Zr (Bhattarai, 1998; Bhattarai et al., 1997) and W–Cr (Bhattarai, 1998; Bhattarai et al., 1998) alloys in 12 M HCl at 30°C. It can, therefore, be said that the simultaneous additions of zirconium and tungsten to chromium enhance synergistically the corrosion resistance of the sputter-deposited W–Zr–Cr alloys in comparison with the single addition of zirconium or chromium with tungsten in 12 M HCl.

Electrochemical measurements were carried out for a better understanding of the corrosion behavior and passivity of the sputter-deposited W–Zr–Cr alloys. Figure 3 shows the changes in open circuit potentials (OCPs) for the sputter-deposited W–Zr–(15–18)Cr alloys including the sputter-deposited tungsten, chromium and zirconium metals in 12 M HCl solution open to air at 30°C, as a function of alloy zirconium content. The OCPs of the ternary W–Zr–(15–18)Cr alloys are located between those of tungsten and zirconium, as well as

chromium, but are close to that of tungsten. In general, the OCPs of the W–Zr–(15–18)Cr alloys are shifted to a better (positive) direction with the increasing tungsten content. Consequently, tungsten addition seems to be effective for OCPs ennoblement of the ternary W–Zr–(15–18)Cr alloys in 12 M HCl solution open to air at 30°C. Although the open circuit potential of the alloys is shifted to a more positive direction with the increasing tungsten content in the alloys, the corrosion rates of the alloys are almost independent with zirconium content in the W–Zr–(15–18)Cr alloys as shown in Figure 2.

In order to examine the effects of tungsten, zirconium and chromium contents on the corrosion behavior and anodic passivity of the alloys, the potentiodynamic polarization curves of the amorphous W–Zr–(15–17)Cr alloys were measured. Figure 4 shows the cathodic and anodic polarization curves for the sputter-deposited W–(54–73)Zr–(15–17)Cr alloys including tungsten, zirconium and chromium metals. Spontaneous passivation occurs for all the examined sputter-deposited W–(54–73)Zr–(15–17)Cr alloys in a wide potential region until the onset of transpassive dissolution of chromium metal. The chromium shows the active-passive transition and transpassive dissolution in 12 M HCl. The sputter-deposited zirconium suffers pitting corrosion after potentiodynamic polarization at about 0.05 V (SCE). The



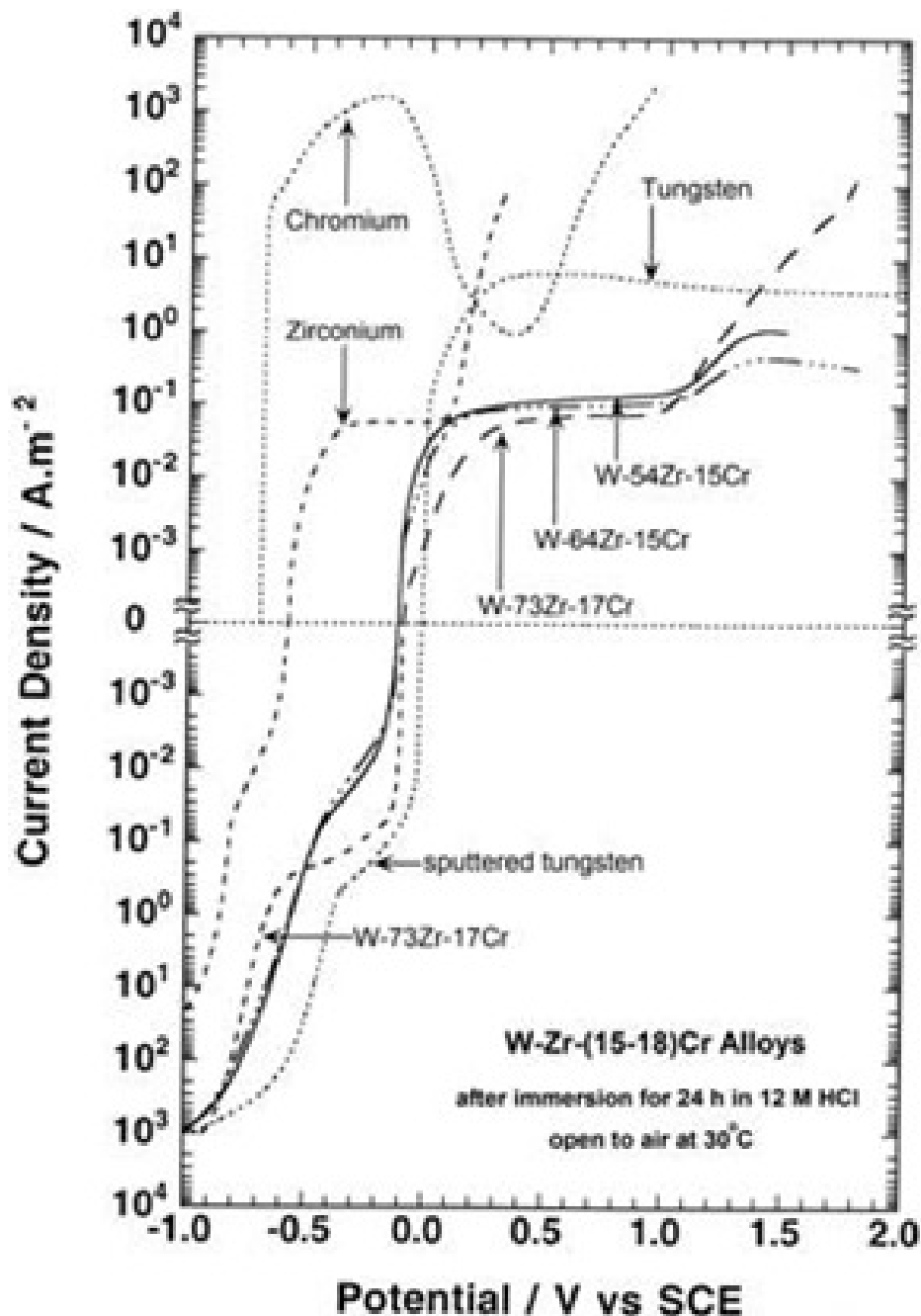
**Figure 3.** Changes in open circuit potential for the sputter-deposited W–Zr–(15–18)Cr alloys after immersion for 24 h in 12 M HCl open to air at 30°C, as a function of alloy zirconium content.

OCPs of the ternary W–(54–73)Zr–(15–17)Cr alloys are located between those of tungsten and zirconium, as well as chromium, but are mostly close to that of tungsten. Anodic passive current densities of the ternary W–(54–73)Zr–(15–17)Cr alloys containing 10 to 31% tungsten decreased with increasing the zirconium content in the alloys. Furthermore, all these three W–(54–73)Zr–(15–17)Cr ternary alloys containing 10 to 31% tungsten do not suffer pitting corrosion in the aggressive chloride containing 12 M HCl solution. The abrupt increase in the anodic current density of the W–(54–73)Zr–(15–17)Cr alloys, in the potential region that is higher with about 1.0 V (SCE), is attributable to transpassive dissolution of chromium. The sputter-deposited binary W–Zr alloys containing 24% tungsten or less and pure zirconium metal showed the pitting corrosion in 12 M HCl at 30°C (Bhattarai et al., 1997; Bhattarai, 1998). Additionally, it has been reported that the sputter-deposited amorphous Cr–Zr alloys containing more than 50% zirconium showed the pitting corrosion after potentiodynamic polarization even in 6 M HCl, while the rest of the alloys remained passive until the onset of transpassive dissolution of chromium (Kim et al., 1993). Similarly, Mehmood et al. (1998) reported that the sputter–

deposited binary Cr–67Zr alloy showed the pitting corrosion after potentiodynamic polarization at about -0.1 V (SCE) in 6 M HCl. On the other hand, the sputter-deposited Mo–Zr alloys containing 60% or more zirconium suffered pitting corrosion by anodic polarization exceeding 1.3 V versus SCE (Park et al., 1995). In these contexts, it can be said that the addition of only 10% tungsten with 15 to 17% chromium in the present study is significantly effective in improving the resistance against the pitting corrosion of the ternary amorphous or/and nanocrystalline W–Zr–Cr alloys in 12 M HCl solution at 30°C.

## DISCUSSION

By using the advantages of the sputtering method, an attempt was made in this work to prepare successfully amorphous or/and nanocrystalline W–Zr–Cr alloys in a wide composition range, even though the sputter-deposited binary W–Cr alloys were not formed by the amorphous structure. This revealed that the sputter deposition technique is quite an effective method for the preparation of amorphous or/and nanocrystalline ternary



**Figure 4.** Anodic and cathodic polarization curves for the sputter-deposited W–Zr–(15–18)Cr alloys in 12 M HCl solution open to air at 30°C. Polarization curves for sputter-deposited chromium, zirconium and tungsten are also shown for comparison.

W–Zr–(15–18)Cr alloys. The sputter-deposited ternary W–Zr–Cr alloys consist of single-phase amorphous or/and nanocrystalline solid solutions supersaturated with alloy-constituting elements, and hence these alloys are regarded to be homogeneous from a corrosion point of view to have a clear insight into the role of alloying tungsten, zirconium and chromium metals on the

passivity breakdown and general corrosion behavior of the alloys in 12 M HCl.

Spontaneous passivation is observed for all W–Zr–(15–18)Cr alloys, similarly to sputter-deposited tungsten, zirconium and chromium, although the sputter-deposited zirconium suffers pitting corrosion with anodic polarization in 12 M HCl solution as shown in Figure 4.



The anodic current densities of the ternary W–Zr–(15–18)Cr alloys are decreased by increasing the zirconium content in the alloys. The addition of only 10% tungsten with 15 to 17% chromium in the ternary amorphous or/and nanocrystalline W–Zr–Cr alloys is significantly effective in improving the anodic passivity. As a result, resistance against the pitting corrosion of these ternary alloys occurs in 12 M HCl solution at 30°C.

The simultaneous additions of tungsten, zirconium and chromium, and the spontaneously passivation of all the alloys examined in this study enhanced synergistically the corrosion resistance of the sputter-deposited ternary W–Zr–(15–18)Cr alloys. Consequently, these sputter-deposited ternary alloys showed higher corrosion resistance than those of alloying elements after immersion for 216 h in 12 M HCl solution open to air at 30°C as shown in Figure 2.

## Conclusion

The sputter-deposited amorphous or/and nanocrystalline single-phase W–Zr–(15–18)Cr alloys containing 12 to 73% of zirconium were successfully prepared using direct current magnetron sputtering, and their corrosion behavior was examined in comparison with those of the sputter-deposited binary W–Cr and W–Zr alloys in 12 M HCl solution open to air at 30°C. The W–Zr–(15–18)Cr alloys were passivated spontaneously until the onset of transpassive dissolution of chromium and more protective anodic passive films were formed on the W–Zr–(15–18)Cr alloys by increasing the zirconium content in the alloys. The simultaneous additions of zirconium and tungsten metals to 15 to 18% chromium enhanced synergistically the corrosion-resistance of the ternary W–Zr–(15–18)Cr alloys, and hence these alloys showed higher corrosion resistance than those of alloy-constituting elements. The addition of about 10 to 31% tungsten with 15 to 18% chromium was significantly effective in improving the resistance against the pitting corrosion of the sputter-deposited W–Zr–Cr alloys.

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