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Comparative study of the structure and corrosion behavior of Zr-20%Cr and Zr-20%Ti alloy films deposited by multi-arc ion plating technique

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ABSTRACT

The primary focus of the present work was to perform comparative study of the structure as well as corrosion behavior of two Zr-rich alloy films, i.e. Zr-20%Cr and Zr-20%Ti, as well as metallic Ti, Cr and Zr films, formed by multi-arc ion plating technique. The required alloy film composition was obtained by co-deposition with proper choice of current for the targets of the constituent metals. The deposited alloy film composition was determined by energy dispersion X-ray spectroscopy, X-ray fluorescence and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) techniques, which were in close agreement with each other. The film thickness lied in the range of 550-620 nm. The crystal structure was studied by X-ray diffraction, which revealed the formation of nanocrystalline and semi-amorphous structures. The corrosion rates of the films were determined through weight loss measurement in 1 M, 6 M and 12 M hydrochloric acid (HCl) by ICP-AES analysis of the solution after immersion for 200-350 h. Anodic (potentiodynamic) polarization was also performed. Zr-20%Cr alloy film exhibited the best corrosion resistance, and its dissolution rate was less than 0.5 μm/year in 6 M HCl and about 4 μm/year in 12 M HCl.

1. Introduction

Corrosion is inherently destructive and causes massive economic losses. Efforts have been made since its very first identification to comprehend the mechanism of its occurrence and to devise ways for enhancing the life of engineering metals and alloys. Among various strategies developed in this regard, perhaps the most effective one is to control the microstructure of a metal or alloy and make it amorphous or nanocrystalline [1–4]. This improvement in the material's performance is mainly the consequence of almost an ultimate homogeneous nature of the amorphous structures and smaller than a critical size of heterogeneity for nanocrystalline metals and alloys [1–3,5–11]; as well as, high diffusivity of passivating element in these structures for rapid passivating and repassivating ability [2]. Both kinds of these alloys can be deposited on an engineering substrate by several ways including chemical vapor deposition, electrodeposition, and physical vapor deposition (PVD) techniques.

Many corrosion-resistant alloy thin films have been deposited in the past using magnetron sputtering process [1,9–16]. Mehmood et al. have deposited Cr-Zr [1], Al-Cr [4], Cr-Nb [9] and Cr-Ti [11] alloy films by this technique and carried out investigations to understand the degradation mechanism and behavior of these films in concentrated hydrochloric acid (HCl) solutions before and after nanocrystallization. Other researchers from the same group had reported previously the preparation of corrosion-resistant coatings like W-Zr [10], W-Ti [16], Mo-Ti [17], and Mo-Zr [18] using the same technique and studied the corrosion behavior of these materials in aggressive conditions. Hard coatings comprising of nitrides and oxides of various elements have also been developed using both magnetron sputtering and multi-arc ion PVD coating techniques [19–23]. These hard coatings either single, binary or multi elemental nitrides, carbides and oxides have extensively been used in enhancing the life as well as performance of various cutting tools. Besides this, the aforementioned alloy and hard ceramic films have a variety of useful properties like low friction, corrosion and wear resistance, decoration requirements as well as for compatible biomedical implants [24–37].

Arc ion plating has inherent characteristic to form a dense film as compared with its other PVD variants because of intense ionization produced by its arc [38]. These ions can gain sufficient energy by substrate bias which is very useful for compact coatings [39–42]. The prior cleaning of the substrate and continued cleaning of the depositing layer by energetic ions of the inert gas and/or a part of the depositing species, also contribute to form adherent, compact and relatively more

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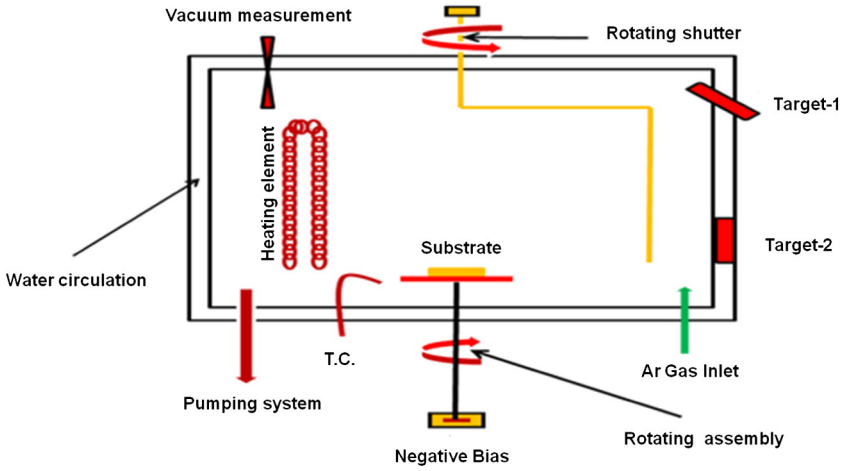

Fig. 1. Schematic diagram of multi-arc ion plating system

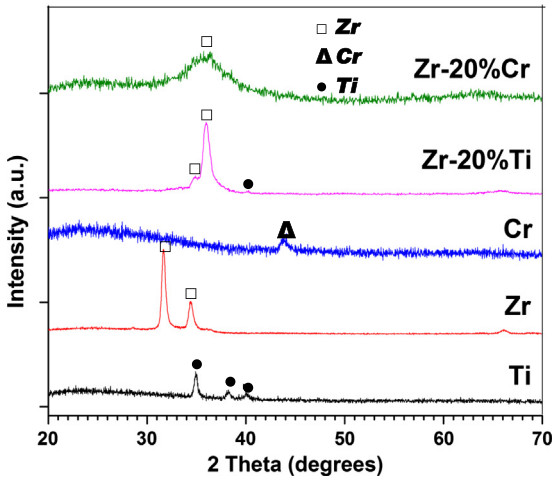

Fig. 2. XRD patterns of metal (Cr, Zr, Ti) and alloy (Zr-20%Cr, Zr-20%Ti) films.

pure coating [40]. Multi-arc ion plating provides added versatility to this technique in which more than one targets can be used simultaneously for producing alloy films of desired composition or alternatively for multi-layering [43–45].

The objective of the present work was to prepare zirconium-rich alloy films (Zr-20%Cr and Zr-20%Ti) by multi-arc ion plating technique, and investigate their corrosion behavior. The primary focus was to examine their passivation behavior and to assess whether they are comparable in corrosion resistance with their counterparts deposited by magnetron sputtering or not. The anti-corrosion characteristics of these two alloy films were also compared with their constituting elements.

2. Experimental details

Two different zirconium-rich binary alloy films, i.e. Zr-20%Cr and Zr-20%Ti, as well as metallic Cr, Zr and Ti films were prepared on aluminum and glass substrates using multi-arc ion PVD coating system. (% stands for atomic percent in this paper). The schematic diagram for film deposition system is shown in Fig. 1. Two targets were employed simultaneously. The targets were 99.997% pure metals with a diameter of 100 mm and 40 mm thickness. The alloy film composition was controlled by variation of respective target currents. Glass slides for substrates were ultrasonically cleaned using alcohol and distilled water. The metal substrates were prepared by abrasive grinding using SiC paper grit of 60 to 600, and then mechanical polishing by diamond paste up to 1 μm on a polishing cloth, followed by electropolishing. Before loading into the deposition chamber, the metal substrates were also subjected to ultrasonic cleaning in acetone and deionized water. After loading the substrates into the deposition chamber and pumping to a vacuum of about 1×10^{-4} Pa, the double-walled water-cooled chamber was preheated up to 200 °C using 3 U-shaped heating elements to ensure proper degassing. The chamber was then allowed to cool. In order to obtain a uniform alloy film stoichiometry, the substrate assembly was kept rotating during the coating process. The coating process was performed for a certain time period as per individual experiment requirements ranging from 30 min to 1 h. Both targets were pre-sputtered sufficiently before the start of each deposition run. Pure argon gas was used in the deposition process, and it entered the chamber after being cleaned by a drying unit and a dust filter.

Each individual alloy film composition was determined using three different techniques, i.e. scanning electron microscope –energy dispersion X-ray spectroscopy (SEM-EDX), X-ray fluorescence (XRF) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) respectively. Three techniques were used independently in order to get reliable information of film composition. The crystal structure of deposited films was determined by X-ray diffraction (XRD) equipment

Table 1
XRD data summary for different metallic and alloy films deposited by multi-arc ion plating process

Film description	Structure	Apparent crystallite size	Lattice parameters	Remarks (standard pattern)
Cr	Crystalline	9.97 nm	a = 2.9800 Å	03-065-3316
Ti	Crystalline	24.54 nm	a = 2.97 Å, c = 4.72 Å	00-071-4632
Zr	Crystalline	20.68 nm	a = 3.232 Å, c = 5.147 Å	00-005-0665
Zr-20%Cr	Semi-crystalline	1.88 nm	a = 3.231 Å, c = 5.1477 Å	00-065-3366
Zr-20%Ti	Crystalline	12.76 nm	a = 3.2623 Å, c = 5.14 Å	01-071-4633

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