A study of the oxidation behavior of CrN and CrZrN ceramic thin films prepared in a magnetron sputtering system

S.Khamseh ^{1,*}, H.Araghi²

^{1*} Department of Nanomaterials and Nanocoatings, Institute for Color Science and Technology, Tehran, Iran

² Department of Materials Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

e-mail: khamseh-sa@icrc.ac.ir

Tel/fax: +98-2122969777 / +982122947537

Abstract

CrN and CrZrN ceramic thin films were produced by a planar type reactive sputtering system on glass and stainless steel substrates. We investigated oxidation resistance of CrN and CrZrN ceramic thin films with different Zr contents. The structure of the films at different thermal-annealing temperatures was investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The mechanical properties of the films at different thermal-annealing temperatures were measured by nano-indentation. The results of this study showed that the addition of few amount of Zr (0.4 at%), can improve thermal stability of CrZrN ceramic thin film and increase the oxidation temperature of the film from 600 °C to 800 °C. The relatively good oxidation resistance (800 °C) and high hardness of the film with the lowest Zr content, indicates that this film is a good candidate for high temperature applications.

Keywords: CrN; CrZrN; Ceramic thin films; Magnetron sputtering; Oxidation resistance

1. Introduction

CrN ceramic thin films have been widely used in many applications due to its good wear, corrosion and mechanical properties [1, 2]. Alloying of Zr element into CrN ceramic thin films has attracted much interest since ZrN film is a protective film due to its high hardness, and high corrosion and wear resistance [3, 4]. It has been shown that the incorporation of Zr could enhance the film hardness and wear resistance and decrease surface roughness [5-7]. Kim et al. showed that the structure and mechanical properties of CrZrN ceramic thin films depend strongly on the Zr content [5]. They showed that as the Zr content increases, more dense and compact microstructure develops and surface roughness is greatly decreased. Also, mechanical properties including hardness and wear property are largely improved in comparison with CrN ceramic thin film [5]. Chantharangsi et al. showed smoothing surface morphology and grain refinement as a result of increasing Zr content [7].

It is well-known that coated tools not only have to possess extreme mechanical properties, but also have to resist potentially aggressive operating environments such as lubricant, cooling solutions and high temperatures in dry machining. For instance in dry machining, the temperature at the cutting edge can reach 1000 °C [8, 9]. Consequently, the applied protective film must be able to withstand such extreme conditions. Kim et al. studied the high temperature characteristics of CrZrN ceramic thin films with various Zr contents after annealing at 500 °C in air [6]. They showed that surface roughness and friction coefficient of the films after annealing at 500 °C increases with increasing Zr content. It has been shown that, CrZrN films oxidize primarily by the inward transport of oxygen, along with outward diffusion of Cr and Zr to a small extent [10]. The rapid formation of ZrO_2 on the CrZrN film surface strongly limits high temperature resistance. However, there are a few reports about the high temperature characteristics of CrZrN ceramic thin films with different Zr contents. Accordingly, this paper

deals with the effects of Zr content on the oxidation resistance of CrZrN ceramic thin films prepared in a magnetron sputtering system.

2. Experimental

Films were prepared in a planar type magnetron sputtering apparatus, (Yarenikane saleh-DRS320) on mirror-polished 304 stainless steel wafers and microscopic glass slides of 20 mm². All the substrates were cleaned ultrasonically with acetone and ethanol, before sputtering deposition. Chromium target (2 inches diameter) (99.999 %) was sputtered in a mixture of argon and nitrogen ($N_2/Ar=1$), both of 99.999 % purity. To add Zr into the CrN film, rounded Zr coupons (diameter: 0.2 μ m) were placed homogeneously on the erosion track of the Cr target. Accordingly, zirconium content of the films could be controlled by varying the total number of coupons from 1 to 5. The system was evacuated to a vacuum down to 3×10^{-5} Torr prior to deposition. CrZrN layers prepared using DC-sputtering mode under DC current, ranged between 0.18- 0.2 A. Total working pressure was fixed at 2×10^{-2} Torr. The substrate temperature increased to 150 °C during deposition due to particle bombardment of the substrate even without bias application and substrate heating. The target-to-substrate distance was fixed at 110 mm.

Oxidation of the sample coupons was carried out using a temperature controlled standard box furnace operated in air, with no extra features to control humidity or air flow rate. Samples were placed horizontally on a ceramic holder with the coated surface upwards at the center of the furnace. The furnace temperature was controlled electronically and increased to the desired temperature at the rate of 10 °C/min. Annealing time was controlled to give a total oxidation period of five hours. After each increase in oxidation time, the furnace cooled to ambient temperature slowly.

Hardness was measured by a Hysitron Inc. TriboScopes Nanomechanical Test Instrument with a Berkovich diamond indenter at room temperature. The load was selected to keep an impression depth of not more than 10 % of the film thickness, so that the influence of the substrate could be neglected. The crystal structure of the films was assigned using X-ray diffractometry (Cu K α radiation) (Phillips PW-1800). The surface morphologies was investigated by atomic force microscopy (AFM, DME Dual Scope C-26).

3. Results and discussions

1.3. Chemical composition and microstructures

The chemical composition of CrZrN ceramic thin films (measured using EDS) is shown in Table 1. As expected, Zr content increased from 0.5 to 9.1 at% with an increase in Zr coupons number, where Cr content shows an inverse trend, from 51.1 down to 21.5 at%. The nitrogen content of the ceramic thin films increased from 47.6 to 67.2 at% with an increase in Zr coupons number, indicating that nitrogen reacts more readily with Zr than it does with Cr. The oxygen content of the films was very low and ranged between 1.3 to 2.2 at%.

Fig. 1 shows the XRD investigations performed on CrN and CrZrN ceramic thin films with different Zr contents. As shown in Fig. 1, the as-deposited CrN ceramic thin film has face center cubic CrN phase. The three diffraction peaks shown in Fig. 1 corresponds to (111), (200) and (220) planes of such fcc structure, with a clear (111) preferential growth. It can be seen that, the CrN ceramic thin films became less crystalline with increasing Zr content. According to Adamik's structure zone model, Zr atoms added to the films stops grain growth and stimulate the renucleation of grains which results in smaller grain size and amorphous-like microstructure of CrZrN films [7, 11]. Furthermore, with increasing Zr content, the diffraction peaks also shifted to lower diffraction angles thus corresponding to higher lattice parameters

which could be a sign of the formation of a solid solution CrZrN whereby Cr atoms are substituted by Zr atoms [5, 7, 12, 13].

The surface morphologies and roughness of the CrN and CrZrN ceramic thin films were examined and the results summarized in Fig. 2. For CrZrN ceramic thin films, the root-mean-square roughness decreased in comparison with that achieved in CrN ceramic thin film [5, 6].

2.3. Oxidation resistance

Figure 3 shows the XRD investigations performed on CrN ceramic thin film annealed at 600 °C in ambient air for 5 hours. When the annealing temperature was 600 °C, the fcc-CrN diffractions were difficult to detect in the XRD pattern, while most of the XRD reflections were attributed to Cr₂O₃ (Fig. 3). The absence of the nitride phase shows the complete oxidation of the film.

In order to compare the oxidation resistance of CrZrN ceramic thin films with different Zr contents, three different samples were chosen and annealed at three different temperatures of 600, 800 and 900 °C in air for 5 hours. Fig.4 shows XRD investigations performed on CrZrN ceramic thin films annealed at 600 °C. It can be seen that fcc-CrN diffractions were well maintained in CrZr1N and CrZr3N ceramic thin films with lower Zr contents. Moreover, fcc-CrN diffractions grew in intensity and became sharper than that in the as-deposited state, indicating increased grain size at the evaluated temperature and film recovery process. The recovery process corresponds to the annealing of the deposition-induced lattice defects and residual stress due to increased diffusivity at elevated temperatures and the growth of the grains [14-16]. A phase transformation to Cr₂O₃ and ZrO₂ was observed in CrZr5N ceramic thin film with the highest Zr content. Absence of CrN diffractions demonstrates the complete oxidation of this film.

The XRD spectra of CrZrN ceramic thin films annealed at 800 °C in Fig. 5 showed the fcc-CrN diffractions retained in CrZr1N ceramic thin film. However, a phase transformation to Cr₂O₃ was observed in CrZr3N ceramic thin film. CrZr5N ceramic thin film, with the highest Zr content showed a mixed structure of Cr₂O₃ and ZrO₂ when oxide diffractions grew in intensity and became sharper than that in 600 °C. The absence of fcc-CrN diffractions demonstrates the complete oxidation of CrZr3N and CrZr5N ceramic thin films.

Figure 6 shows the XRD investigations performed on CrZrN ceramic thin films annealed at 900 °C. XRD analysis showed a phase transformation to Cr₂O₃ and ZrO₂, which indicates complete oxidation of the ceramic thin films. Variation in oxygen content of CrN and CrZrN films on annealing temperature (measured using EDS) is shown in Fig.7. The oxygen content of CrN and CrZrN ceramic thin films increased with increasing annealing temperature. However, the Oxygen content of CrZr1N and CrZr3N ceramic thin films increased slowly on annealing temperature. When the Oxygen content of CrZr5N with the highest Zr content increased sharply with annealing temperature. These results indicate that the introduction of low Zr content can improve the oxidation resistance of CrZrN ceramic thin films when the presence of high Zr content markedly weakens the film oxidation resistance compared to that of CrN ceramic thin film.

Figure 8 shows the AFM image of the surface of the CrZr1N ceramic thin film after annealing in air at 600, 800 and 900 °C. For as-deposited ceramic thin film, a cone-like microstructure can be seen. The film annealed at 600 and 800 °C showed grain growth when a pebble-like coarse structure with large grains was formed at 900 °C. The AFM images of as-deposited CrZr5N ceramic thin film shows formation of a pebble like structure (Fig.9). Defect's density increased and grains were found to grow and coarsen on increasing the annealing temperature.

Figure 10 illustrates the variation in roughness (measured using AFM) of CrN and CrZrN ceramic thin films with annealing temperature. It can be seen that the root-mean-square roughness of CrN and CrZrN ceramic thin films exhibits an increase with annealing temperature. It seems that surface roughness of the ceramic thin films is dependent upon ZrO₂ phase formation via annealing. According to XRD patterns of the films, CrZr1N and CrZr3N ceramic thin films did not contain ZrO₂ phase up to 900 °C. It can be seen that surface roughness of these films increases slowly on increasing annealing temperature and then suddenly increases at 900 °C. In CrZr5N ceramic thin film, ZrO₂ phase was formed at all annealing temperatures. It can be seen that roughness values of this film increased abruptly on increasing annealing temperature. This can be attributed to oxidation mechanism of CrZrN ceramic thin films. In CrZr3N ceramic thin film with lower Zr content, Cr₂O₃ phase formed on the top surface of the films at annealing temperatures of 600 and 800 °C. Due to high thermal stability, slow-growth and high density, Cr₂O₃ is thought to be the ideal surface scales to protect the underlying materials from oxidation attack [17], whereas ZrO₂ seems to be non-protective and in addition, it is easily spalled from the surface [18]. Therefore, the introduction of high Zr into the CrN ceramic thin film encourages ZrO₂ phase formation and prohibits the continuous formation of Cr₂O₃ scales on the film surface during thermal exposure which will consequently weaken the oxidation properties [10]. It has been shown that as the Zr content in the films increased, more extensive oxidation occurred, which induced a further increase in surface roughness due to oxidation [6].

Figure 11 illustrates variations in plastic hardness of the films with annealing temperature. The plastic hardness of CrN and CrZrN ceramic thin films decreased gradually with increasing annealing temperature. However, the plastic hardness of CrZr1N and CrZr3N ceramic thin films decreased slowly on annealing temperature. The plastic hardness of CrZr5N with the highest Zr content decreased sharply with annealing temperature. It seems that variation in

plastic hardness of the films is dependent upon ZrO_2 phase formation via annealing. In CrZr1N and CrZr3N ceramic thin films, no ZrO_2 phase was formed up to 900°C and their plastic hardness decreased slowly with annealing temperature. This decrease in hardness with temperature can be attributed to the occurrence of several softening effects, such as reduction in lattice distortion, small grain growth, and surface oxidation (the last two effects occurred only in CrZr1N at 800°C and CrZr3N at 800 and 900°C) should induce a decrease in the hardness of annealed films. In contrast, CrZr5N ceramic thin film has ZrO_2 phase at different annealing temperatures and its plastic hardness decreases sharply with annealing. The evolution of hardness with increasing annealing temperature in these films follows the general observations in typical binary and ternary nitrides, that is, the hardness of the films decreases due to a decrease in the defect density and compressive stress and an increase in the grain size during the thermal annealing process [19].

It is obvious from the above results that Zr content influenced the oxidation resistance of CrZrN ceramic thin film. Globally, the ceramic thin films studied in this work could be split into two main groups with similar oxidation resistance: the films with low (0.5 at%) and high (9 at%) Zr content. The introduction of low Zr content can improve the oxidation resistance of CrZrN ceramic thin film when the presence of high Zr content markedly weakens the film oxidation resistance compared to that of CrN ceramic thin film. In the high Zr films, the onset temperature of CrZrN ceramic thin film oxidation did not change. However, the onset temperature of CrZrN ceramic thin film oxidation can increase from 600°C to 800°C for films with low Zr additions. It has been suggested that CrZrN ceramic thin film oxidized via the outward diffusion of Cr, Zr and nitrogen and inward diffusion of oxygen and formation of mixed structure of Cr_2O_3 and ZrO_2 phases [10, 20]. Lee et al. suggested that Zr does not change the oxidation mechanism of the CrN ceramic thin films, and it would not, at least, increase the oxidation resistance of the CrN ceramic thin films [10]. However, Zr content of the films in

this study (0.5-9 at%) were different from that previously reported (9-16 at%) [10]. Lower Zr content of the films in the current study resulted in lower formation of ZrO_2 phase which is shown to be responsible for lower oxidation resistance of CrZrN ceramic thin films. Moreover, in the current study, oxidation resistance of CrZrN ceramic thin films with low Zr content was better than that of CrN ceramic thin film. The films with low Zr content encouraged Cr_2O_3 phase formation which is a quite protective oxide and can act as a diffusion barrier and prevents high inward oxygen diffusion, enabling the achievement of better oxidation resistance of the films. In contrast, CrZrN ceramic thin films with high Zr content showed lower oxidation resistance. Lee et al. demonstrated that ZrO_2 formation increases the oxidation rate of CrZrN ceramic thin films during oxidation [10]. Consequently, it can be concluded that the absence of ZrO_2 phase in the films with low Zr content increases its oxidation resistance. Moreover, the relatively good oxidation resistance (800 °C) and high hardness of the film with the lowest Zr content, indicates that this film is a good candidate for high temperature applications.

4. Conclusions

CrN and CrZrN ceramic thin films with different Zr content were produced by a planar type reactive sputtering system. The effects of Zr content on thermal stability of CrZrN ceramic thin film were investigated. The addition of few amount of Zr (0.4 at%), improved thermal stability of CrN ceramic thin film and increased the oxidation temperature of the film from 600 to 800 °C. The CrZrN ceramic thin film with the lowest Zr content retained a hardness of 24 GPa after annealing at 800 °C for 5 h. The relatively good oxidation resistance (800 °C) and high hardness of CrZrN ceramic thin film with the lowest Zr content up to 800 °C indicates that this film is a good candidate for high temperature applications. Finally, it can be concluded that the addition of few amount of Zr can reduce disruptions of the film's nanostructure and improve oxidation resistance of CrZrN films.

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Table 1 Chemical composition of CrZrN films.

Fig 1. X-ray diffraction patterns of as-deposited CrN and CrZrN films with different Zr contents measured by thin film mode.

Fig 2. AFM image and Rms of as-deposited CrN and CrZrN films.

Fig 3. X-ray diffraction patterns of CrN film as-deposited and after annealing at 600 °C measured by thin film mode.

Fig 4. X-ray diffraction patterns of CrZrN films with different Zr contents after annealing at 600 °C measured by thin film mode.

Fig 5. X-ray diffraction patterns of CrZrN films with different Zr contents after annealing at 800 °C measured by thin film mode.

Fig 6. X-ray diffraction patterns of CrZrN films with different Zr contents after annealing at 900 °C measured by thin film mode.

Fig 7. Variation of oxygen content of CrN and CrZrN films on annealing temperature.

Fig 8. AFM image of CrZr1N film with varying annealing temperature (a) as deposited (b) 600 °C (c) 800 °C (d) 900 °C.

Fig 9. AFM image of CrZr5N film with varying annealing temperature (a) as deposited (b) 600 °C (c) 800 °C (d) 900 °C.

Fig 10. Variation of roughness (measured using AFM) of CrN and CrZrN films on annealing temperature.

Fig 11. Influence of annealing temperature on the plastic hardness of the films.

Table 1 Chemical composition and sputtering conditions of CrZrN films.

Zr coupons number	Sample name	Chemical composition			
		(at%)			
		Cr	Zr	N	O
0	CrN	51.1	-	47.6	1.3
1	CrZr1N	39.2	0.5	58.2	2.1
2	CrZr2N	34.9	2.5	60.4	2.2
3	CrZr3N	29.3	4.5	64.1	2.1
4	CrZr4N	24.9	7.3	65.5	2.3
5	CrZr5N	21.5	9.1	67.2	2.2