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# Effects of Zr/(Zr+Ti) Molar Ratio on the Phase Structure and Hardness of $Ti_xZr_{1-x}N$ Films

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**Abstract:** Ti<sub>x</sub>Zr<sub>1-x</sub>N hard films with Zr/(Zr+Ti) molar ratios from 20% to 80% were prepared by multi-arc ion plating using any two of elemental Ti, elemental Zr, and TiZr alloy targets. The as-deposited Ti<sub>x</sub>Zr<sub>1-x</sub>N films displayed similar surface and fracture cross-section morphologies and thicknesses. The effects of Zr/(Zr+Ti) molar ratio on the phase composition, preferred growth orientation, and hardness of the films were discussed. The results showed that the as-deposited films had a face-centered cubic structure and exhibited the typical characteristics of substitutional solid solutions. The lattice constant of the films increased monotonically with increasing Zr/(Zr+Ti) molar ratio. Two preferred growth orientations, corresponding to the two hardness peak values, occurred symmetrically at Zr/Ti molar ratios of 40:60 and 60:40. An inflection point with a small reduction in hardness was observed at the Zr/Ti molar ratio of 50:50.

**Keywords:**  $Ti_x Zr_{1-x}N$  hard film; Zr/(Zr+Ti) molar ratio; phase structure; preferred growth orientation; hardness

# 1. Introduction

Hard reactive films of transition element nitrides have been investigated for a long time, and thus significant progress has been made. Several hard multi-component nitride films have been developed.  $Ti_xZr_{1-x}N$  hard films have attracted attention in recent years because of their high hardness, good red hardness, and simple preparation process. In general,  $Ti_x Zr_{1-x}N$  exhibits higher hardness than TiN and ZrN [1,2]. Zr and Ti atoms can replace each other in the TiN and ZrN lattices to form a TiZrN substitutional solid solution with a face-centered cubic (FCC) structure [3,4]. Ti<sub>x</sub> $Zr_{1-x}N$  films typically display preferred growth along specific crystal plane orientations [1,2,5]. Nevertheless, different preparation methods and deposition parameters lead to inconsistent results in the preferred growth orientations and the peak values of the hardness of  $Ti_x Zr_{1-x}N$  films. For example, the preferred growth of the (111) plane was found in each of the TiN, ZrN, and  $Ti_xZr_{1-x}N$  films by cathodic arc ion plating [1,6]. Similarly, the preferred growth of the (111) plane was obtained in the  $Ti_x Zr_{1-x} N$  films by reactive sputtering [7,8]. However, the preferred growth orientations in the  $Ti_xZr_{1-x}N$  films were found to change from the (111) plane (ZrN) to the (200) plane (TiN) as x increased from 0 to 1 when deposited by reactive sputtering [9]. In contrast, the  $Ti_x Zr_{1-x}N$  films deposited by the cathodic arc method were reported to have the opposite trend, where the preferred growth orientations transitioned from the (111) plane (TiN) to the (200) plane (ZrN) as x increased from 0 to 1 [10]. In addition, the effect of bias on preferred growth orientation in  $Ti_xZr_{1-x}N$  films was reported [11]. A bias that is too low or too high can affect the preferred growth orientation of the films. Similar to the trends for the preferred growth orientation of the  $Ti_x Zr_{1-x}N$  films, the film hardness was found to depend on the composition and the deposition process [1,8,10]. Accordingly, there is no consistent understanding of how the chemical content affects the preferred



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). growth orientation and hardness of  $Ti_xZr_{1-x}N$  films owing to the diversity and complexity of deposition processes.

The present work aims to understand the effects of the Zr/Ti molar ratio on the phase structure and hardness of  $Ti_xZr_{1-x}N$  films. In particular, the investigation focuses on maintaining constant deposition conditions, microstructure, and thickness of the  $Ti_xZr_{1-x}N$  films to achieve consistent results.

#### 2. Materials and Methods

 $Ti_xZr_{1-x}N$  films were prepared using a cathodic arc ion plating system (Shenyang Vacuum Technology Research Institute, Shenyang, China) via co-deposition of two cathode targets. Any two of the elemental Ti, elemental Zr, and TiZr (50:50 at.%) alloy targets were co-deposited to vary the Zr/Ti molar ratio in the films. The two cathode targets were set at an angle of 90° relative to the central axis of the coating chamber. The dimensions of the high-speed-steel (W18Cr4V, HRC63-64) substrates used in the deposition were 18 mm × 12 mm × 1.8 mm. After fine polishing, the samples were cleaned by ultrasonication, blow dried, then hung near the central rotating axis of the coating chamber. Each sample was placed symmetrically and equidistantly from the two target surfaces to ensure uniform composition in the films.

The deposition of  $Ti_xZr_{1-x}N$  films includes arc bombardment cleaning, alloy transition layer deposition, and  $Ti_xZr_{1-x}N$  deposition. Arc bombardment cleaning was carried out by maintaining the two cathode arc currents at 55 A, applying a bias voltage of 350 V, and using an Ar gas flow of 12 sccm for 8 min, when the vacuum reached  $8 \times 10^{-3}$  Pa and the coating chamber temperature reached 220 °C. The deposition of the alloy transition layer was carried out by keeping the two cathode arc currents at 55 A and applying a bias voltage of 180 V while maintaining the Ar gas flow at 12 sccm for 5 min. Finally,  $Ti_xZr_{1-x}N$ deposition was carried out by choosing two targets and varying the cathode arc currents, as shown in Table 1, while maintaining a bias voltage of 120 V and N<sub>2</sub> gas flow of 120 sccm for 45 min. The deposition parameters were determined such that a constant temperature of the chamber and a consistent nitrogen content could be maintained during deposition of the  $Ti_xZr_{1-x}N$  films.

	Cathodic Arc Current (A)		
Sample No.	Ti Target	Zr Target	Ti-Zr Alloy Target
1	62	_	48
2	55	_	55
3	48	-	62
4	62	48	_
5	54	56	_
6	48	62	_
7	-	48	62
8	_	62	48

**Table 1.** Cathodic arc current combination during the deposition of  $Ti_x Zr_{1-x}N$  films (total current = 110 A).

The surface and cross-sectional morphology of the as-deposited  $Ti_xZr_{1-x}N$  films were observed using field emission scanning electron microscopy (FE-SEM, S-4800, Hi-tachi, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS). The surface and cross-sectional compositions were determined using EDS mapping and line scanning, respectively. Phase structure analysis of the as-deposited films was performed using a Rigaku D/max-rA X-ray diffractometer (Dandong Aolong Radiative Instrument Group Co.Ltd, Dandong, China) with CuK $\alpha$  radiation (40 kV and 40 mA). The scanning angle (20) ranged from 10 to 80° at 2°/min. The hardness of the as-deposited films was determined using the Vickers micro-indentation test at a load of 0.1 N for 20 s.

# 3. Results and Discussion

# 3.1. Surface Morphology and Surface Composition

SEM was adopted to observe the surface morphology of  $Ti_xZr_{1-x}N$  hard films. As shown in Figure 1, some "large particles" are randomly distributed on the film layer surface for each of the  $Ti_xZr_{1-x}N$  film samples. These particles are generally less than 6 µm in size, and are formed from the micro-droplets sprayed from the cathode target surface during the deposition of the  $Ti_xZr_{1-x}N$  films [6,12,13]. Some scattered micro-pits are also observed on the surface of the  $Ti_xZr_{1-x}N$  hard films, which are caused by the shedding of the "large particles", as shown in the figure. Similar surface morphologies were observed in all the films, suggesting that the choice of targets had no significant effect on the surface morphology of the films. This finding could be attributed to the constant deposition conditions.



**Figure 1.** Surface morphologies of the deposited  $Ti_xZr_{1-x}N$  films. The numbers (1)–(8) correspond to sample numbers 1–8, respectively.

The surface compositions of the as-deposited  $Ti_xZr_{1-x}N$  films under the deposition conditions in Table 1 were characterized using SEM and EDS, and the results are shown in Figure 2. The vertical axis presents the content of each component of the as-deposited film samples. The horizontal axis data is the ratio of metal components, which, from left to right, corresponds to samples 1–8. The nitrogen content in almost all the films was larger than 50 at.% and within 56 at.%–59 at.%, except for sample No. 1. The microstructure and hardness of metal nitride films are affected by the nitrogen to metal component molar ratio in the films [14–17]. In addition, both the phase structure and hardness are very sensitive to the nitrogen content in the films. To ensure the same nitrogen content (at.%) in the films, a relatively high N<sub>2</sub> flow of 120 sccm was selected to supply sufficient N atoms needed to form metal nitride films during the deposition process, despite different arc current combinations forming different targets. As a result, the nitrogen content in the  $Ti_xZr_{1-x}N$ hard films was high and basically constant. At the same time, a monotonous change in the Zr/Ti atom ratio was achieved by the control of different cathode target currents.



Figure 2. Chemical composition of the surface of the films.

#### 3.2. Cross-Sectional Morphology and Elemental Distribution

The cross-sectional SEM photographs of the as-deposited  $Ti_x Zr_{1-x}N$  films are shown in Figure 3. The thickness of the films was similar (1  $\pm$  0.1  $\mu$ m), and all the films exhibited a dense columnar crystal morphology. The consistent thickness and morphology of the films could be attributed to controlled deposition conditions, such as the co-deposition of cathode targets, the small difference between the two arc currents, the sum of the two arc currents kept constant at 110 A, and the constant deposition time of 45 min.

EDS line scanning was employed to observe the elemental distribution in the growth direction of the films, as shown in each inserted figure in Figure 3. The change of relative energy spectrum intensity of Zr and Ti reflects the change of Zr/Ti molar ratio of each film sample, as shown in Figure 3(1)–(8). A gradual increasing trend in the Zr/Ti molar ratio is displayed from sample 1 to sample 8. This is consistent with the surface composition analysis results, as shown in Figure 2. Due to using pure Ar to deposit the alloy transition layer at the initial deposition stage, the energy spectrum intensity of N is zero near the interface between film and substrate and monotonously increases along the film growth direction in each film. The remaining Ar in the coating chamber after the deposition of the transition layer may influence the inflow of N<sub>2</sub> gas. This approximate gradient distribution of nitrogen element could be advantageous in film adhesion [18,19].



**Figure 3.** Cross-sectional morphology and elemental distribution in the growth direction of the films. The numbers (1)–(8) correspond to sample numbers 1–8, respectively.

The above discussion shows that the surface morphology, cross-sectional morphology, film thickness, and nitrogen content of the  $Ti_xZr_{1-x}N$  hard film samples are consistent with each other, but the relative contents of metal elements (Zr/Ti molar ratio) are different. Therefore, it may be reasonably asserted that in the present study, the relative contents of metal elements (i.e., the Zr/Ti molar ratio) is the only, or the most important, factor influencing the change in the phase composition and mechanical properties of the  $Ti_xZr_{1-x}N$  hard films.

#### 3.3. Phase Structure and Preferred Growth Orientation

The XRD patterns of the films are shown in Figure 4. All the films were composed of a nitride phase with an FCC cubic structure and a few metal particles (phase). The 20 angles of the peaks attributed to the nitride phase are larger than those of the ZrN phase and smaller than those of TiN phase. No ZrN or TiN phase existed in the  $Ti_xZr_{1-x}N$  films. Moreover, the diffraction peaks of the films shifted to small angles with an increase in the Zr/Ti molar ratio. Concurrently, the lattice constants of the films increased monotonically. The results suggest that the films were substitutional solid solutions of ZrN and TiN.



Figure 4. XRD patterns of the films.

Notably, the films exhibited certain textures. The preferred growth orientations of the films varied with an increase in the Zr/Ti molar ratio. When the Zr/Ti molar ratio in  $Ti_xZr_{1-x}N$  hard films was lesser than 40:60 or greater than 60:40, the films tended to grow in a preferred orientation on the (111) crystal plane, as shown in Figure 4 (1#, 2#, 3# and 7#, 8#). When the Zr/Ti molar ratio was approximately 40:60 or 60:40, preferred growth orientations in both the (111) and (220) crystal planes were observed, as shown in Figure 4 (4# and 6#). However, when the Zr/Ti molar ratio approached 50:50, the preferred growth orientation returned to the (111) crystal plane. Considering that the properties of the films were similar, we conclude that the Zr/Ti molar ratio is the only, or the most important, factor that influences the preferred growth orientation in the films.

The occurrence of texture in ternary nitride films, such as TiAlN, TiCrN, and AlCrN films, is a common phenomenon. The preferential growth orientations in films of FCC solid solutions vary with the deposition conditions or proportions of metal constituents, or both. Sometimes, the transformation of the preferential growth orientations is accompanied by the occurrence of a second nitride phase; for example, the hexagonal AlN phase in the TiAlN and AlCrN films [20–25]. For  $Ti_xZr_{1-x}N$  films, many studies show that the films deposited by ion plating tend to grow in the (111) crystal plane in a wide range of compositions. Examples of such films are the ones with a Zr/Ti molar ratio of 50:50 deposited by cathodic arc ion plating at bias voltages of 120–210 V at 450 °C [3], a molar ratio of 65:35 prepared at 40 V and 400 °C [2], a molar ratio of 66.5:33.5 prepared at 250 V [6], molar ratios from 24:76 to 40:60 prepared at 120 V and at 450–500 °C [4], and molar ratios of 80:20, 70:30, and 40:60 prepared by SCAE technology at 100 V [1]. These results show

that  $Ti_x Zr_{1-x}N$  films prefer to grow in (111) crystal planes because of low substrate bias voltage and low deposition temperature.

However, some inconsistent results regarding the preferred growth orientation of  $Ti_xZr_{1-x}N$  films have been reported [9,10]. In one study [10], a series of  $Ti_xZr_{1-x}N$  films with Zr/Ti molar ratios of 20:80, 40:60, 50:50, 60:40, and 80:20 was prepared by multi-arc ion plating at a very low bias voltage of 20 V and a high temperature of 600 °C. The research indicates that the preferred growth orientation of the films changed with composition. When the Zr/Zr+Ti molar ratio was very low (<20%), the films displayed the preferred growth orientation in the (111) crystal plane, similar to the TiN film. When the Zr/Zr+Ti molar ratio was between 20% and 40%, the preferred growth orientations were in both the (111) and (200) planes. When the Zr/Zr+Ti molar ratio was further increased, the film's preferred growth orientation was on the (200) plane, similar to the ZrN film. These results indicate that under certain deposition conditions, if the metal constituents of the nitride films have different preferred growth orientations, the preferred growth orientation of the alloy nitride films will change from one preferred growth orientation to the other and experience "double preferred growth orientations" within a certain interval Zr/Ti molar ratio [10]. Another study [9] on  $Ti_x Zr_{1-x}N$  films deposited by reactive sputtering technology showed that a TiN film had a preferred growth orientation in the (200) crystal plane, while ZrN had a preferred growth orientation in the (111) plane. When the Zr/Zr+Ti molar ratio in the films was between 34% and 45%, the preferred growth orientation was in the (111) and (200) planes. In the other Zr/Zr+Ti molar ratios (between 20% and 34% or between 45% and 67%), the films showed a preferred growth orientation in the (200) plane. Thus, it can be concluded that different deposition techniques and processes significantly influence the preferred growth orientation in  $Ti_x Zr_{1-x}N$  films. Furthermore, even if the same preparation technique is used, it is challenging to achieve the same deposition temperature and the same thickness and microstructure of the films because of the interaction between the deposition process parameters. For example, both the cathode arc current and the bias voltage influence the deposition temperature. Thus, maintaining the same deposition conditions and the same thickness and microstructure of the films are necessary to investigate the effect of the Zr/Ti molar ratio on the preferred growth orientations and the properties of the  $Ti_xZr_{1-x}N$  films.

In general, both ZrN and TiN films prepared by cathode arc ion plating have preferred growth orientation in the (111) crystal planes at conventional bias and deposition temperatures [1,6,26–28]. When the Zr/Ti atom ratio is relatively small or large, the fewer atoms of the substituting metal element do not influence the lattice parameters of the nitride. When the Zr/Ti or Ti/Zr molar ratio approaches 1:1, more defects and a larger lattice distortion are produced due to the difference in atomic radius and electronegativity of the two metals. The preferred growth orientation in the (111) crystal plane observed in ZrN and TiN films is difficult to maintain. A higher index of the crystal plane is selected during growth, and then preferential growth orientations in two crystal planes occur. When the Zr/Ti or Ti/Zr molar ratio is approximately 1:1, the preferred growth orientation of the Ti<sub>x</sub>Zr<sub>1-x</sub>N hard film returns to the (111) crystal plane because of short-range ordering in the ZrN and TiN solid solution.

Using Vegard's law, the idealized lattice constant of substitutional solid solutions can be calculated without considering the effect of lattice distortion [29]. The difference between the film's lattice constant measured via XRD and that calculated using Vegard's law can reflect the intensity and density of lattice distortion and lattice defects, respectively. The largest difference in lattice constant occurred when the Zr/Ti molar ratio was approximately 40:60 or 60:40 within the studied composition range, as shown in Figure 5. This result is consistent with the appearance of preferential growth orientations in two crystal planes. When the Zr/Ti molar ratio was approximately 50:50, the difference in the lattice constants decreased slightly. This means that the lattice distortion is less severe, and the strengthening due to the distortion with a Zr/Ti molar ratio of 50:50 may be expected to decrease slightly compared with that of Zr/Ti molar ratios of 40:60 or 60:40.



Figure 5. Lattice constant of the films obtained from the experiments and calculations using Vegard's law.

#### 3.4. Hardness

The hardness variation in the films with increasing Zr/Ti molar ratio is shown in Figure 6. When the Zr/Ti or Ti/Zr molar ratio was much lesser than 50:50, the hardness of the films was low and tended to be close to the hardness value of ZrN or TiN. When the Zr/Ti or Ti/Zr molar ratio gradually approached 50:50 and was between 21:79 and 70:30, the hardness of the hard films was relatively high, up to approximately 30 GPa. The maximum values of hardness, 32 and 31 GPa, correspond to the Zr/Ti molar ratios of 40:60 and 60:40, respectively. Notably, when the Zr/Ti molar ratio was approximately 50:50, the hardness of the films decreased slightly, and an inflection point in the hardness value curve was observed. These results can be attributed to the phase structure of the films. The two maximum hardness values correspond to the compositions with Zr/Ti molar ratios of 40:60 and 60:40. These compositions also correspond to the preferred growth orientations in two crystal planes and the difference in the lattice constant obtained from the measurements and Vegard's law.



Figure 6. Hardness of the films.

The relationship between the composition and hardness of  $Ti_xZr_{1-x}N$  films has been discussed in other related studies. The hardness of films increases monotonically with increasing Zr/Zr+Ti molar ratios from 6:94 to 18:82 to 35:65 [7]; however, the hardness increases significantly with decreasing Zr/Ti molar ratios from 2.9:1 to 1.8:1 [2]. The hardness of the films also increases monotonically with decreasing Zr/Ti molar ratios from 4.9.1 to 1.8:1 [2].

80:20 to 60:40 to 40:60 [1]. In summary, the dependence in hardness values of the films with Zr/Zr+Ti molar ratio is parabolic [10]. A quasi-parabolic trend was also observed in the present study, as shown by the colored dashes in Figure 6, with a maximum hardness value corresponding to the Zr/Ti molar ratio of 40:60 but an inflection point at the Zr/Ti ratio of 50:50.

## 4. Conclusions

- 1. The surface and cross-sectional morphologies and the deposition rate of  $Ti_xZr_{1-x}N$  films with varying Zr/Ti molar ratios were similar when the deposition conditions such as  $N_2$  gas flow and maintaining the total arc current at 110 A during evaporation of any two of the Ti, Zr, and TiZr targets were maintained.
- 2. The FCC structure of the films was retained while the lattice constant increased monotonically with increasing Zr/Ti molar ratio, consistent with Vegard's law.
- 3. The preferred growth orientations of the films were affected by their composition. When the Zr/Ti molar ratio was 40:60 or 60:40, the films showed preferred growth orientation in the (111) and (220) crystal planes; however, at other compositions, the films exhibited a preferred growth only in the (111) crystal plane. A symmetrical distribution in the preferred growth orientation relative to the Zr/Ti molar ratio 50:50 was displayed.
- 4. The films exhibited a quasi-parabolic hardness distribution. The maximum hardness was observed at a Zr/Ti ratio of 40:60. An inflection point with a small reduction in hardness occurred at a Zr/Ti ratio of 50:50, after which the hardness increased as Zr/Ti ratio increased from 40:60 to 60:40.

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