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Synthesis of ZrAlN coatings with thermal stability at high temperature

LI Dejun

College of Physics and Electronic Information Science, Tianjin Normal University, Tianjin 300074, China
(email: dejunli@mail.tjnu.edu.cn)

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Abstract Dry machining will result in elevated temperatures at the tool surface (800—1000℃). So, coating materials that can provide protection for cutting tools at these temperatures are of great technological interests. ZrAlN coating is proposed to possess high-temperature stable structural and mechanical properties due to the addition of the alloying element. ZrAlN coatings were grown using a dc reactive magnetron sputtering. The XRD and nano indenter were employed to investigate the effects of reaction gas partial pressure and substrate bias on structural and mechanical properties, as well as high-temperature stability. The ZrAlN coating, when deposited under optimum conditions (–37 V substrate bias and 2×10^{-5} Pa N_2 partial pressure), showed smooth surface with thermal stable hardness. Its internal stress was relaxed from 2.2 to 0.7 GPa after annealing. Formation of Al_2O_3 and ZrO_2 crystalline phases should be related to thermal stability of the coatings.

Keywords: ZrAlN coating, magnetron sputtering, thermal stability.

Hard coatings have been successfully used for the protection of materials and particularly to enhance the life of cutting tools since 1970s. Both the technological process of their production and their properties, i.e. hardness, wear and oxidation resistance, however, are continuously being improved. Important milestones in the development of hard coatings briefly show the clear efforts (1) to decrease the temperature T at which hard coatings are formed and (2) to improve the properties of hard coatings, particularly to increase the hardness and oxidation resistance. During high-speed machining, the temperature of the tool tip can reach 1000℃. Therefore protective coatings should be stable at such high temperatures[1,2]. Over the last few years, several new coating systems have been developed[3—9].

ZrN has been studied increasingly as a hard coating [10]. In application, however, its poor oxidation resistance causes instability in structure and property at high temperature. ZrAlN coating might be able to solve this problem, because it is proposed to possess high-temperature stable structural and mechanical properties due to the addition of the alloying element. Addition of Al to the ZrN to form ZrAlN may improve the thermal stability due to the formation of an oxidation resistant layer, which may limit oxide growth and oxygen diffusion. It is beneficial for the thermal stability of the coating. Recently, some studies focus on the effects of Al content on phase change and microhardness of ZrAlN coating [11]. However, few reports on its thermal stability can be found in recent literatures. In this work, our aim is focused on this model grown in a dc reactive magnetron sputtering chamber. The X-ray diffraction (XRD) and indentation analysis were employed to investigate the effects of reaction gas partial pressure and substrate bias on structural and mechanical properties, as well as high-temperature stability before and after annealing.

1 Experimental

A dc magnetron sputtering chamber with ZrAl alloy target was used to synthesize ZrAlN films. The vacuum chamber was evacuated to a base pressure lower than 6.6×10^{-4} Pa. Sapphire substrates were used for this research. Prior to deposition, the substrates were cleaned sequentially in ultrasonic baths of acetone and isopropyl alcohol, and then sputter cleaned for 10 min in pure argon plasma at 3.3 Pa. During deposition, the total pressure, consisting of argon and nitrogen, was set at 0.8 Pa with independent partial-pressure/flow controls.

XRD was used for long range order structural analysis of the coatings. XRD was carried out using a SCINTAG XDS 2000 PAD V diffractometer, operated at 40 kV and 40 mA, with CuK_α radiation at 1.54 Å. The scans were done with different X-ray tube power, since the satellite peaks intensity changes over 5—6 orders of magnitude. Therefore, each scan was carried out with at least one peak overlapped, and then combined with other peaks.

A Nano Indenter XP was used to measure hardness and elastic modulus of the coatings. A Berkovich indenter, which is a three-sided pyramid and provides a sharply pointed tip, was used for this machine. In the indentation test, different maximum loads were used for different samples, in order to keep the maximum penetration depth within 10%—15% of the film thickness for minimizing substrate effects. Twenty indentations were utilized for each load with two successive indents at 25—30 μm apart. The root mean square (rms) surface roughness was determined from a sampling area of 1 μm×1 μm by A Nanoscope III AFM manufactured by Digital Instruments.

2 Results and discussion

The effect of substrate bias on coating properties was investigated. A series of ZrAlN coatings were deposited at a constant N_2 partial pressure of 2×10^{-5} Pa. Fig. 1 shows that the hardness of ZrAlN coatings increases slightly with the increase of substrate bias. High hardness induced by high substrate bias may be caused by the changed crystalline structure or the increased coating density due to high ion bombardment. However, the lower substrate bias leads to the smooth surface. Its roughness is only 1.38 nm at −35 V

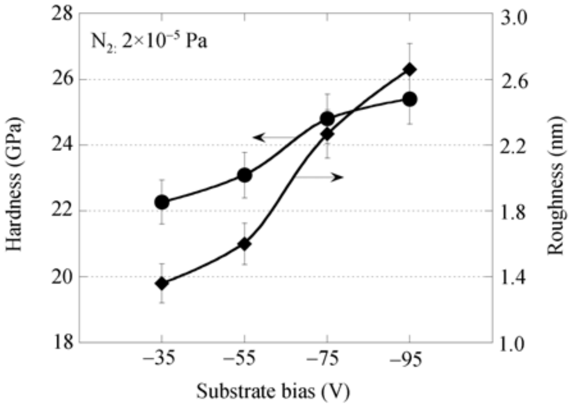

Fig. 1. The hardness and roughness vs. substrate bias.

substrate bias, which can produce a positive effect on tribiological properties of coatings. The internal stress of the coating also exhibits relatively lower values at lower substrate bias (Fig. 2), and their values continue to decrease after annealing. High compressive stress at high substrate bias due to increased momentum and flux of ion bombardment is the main reason for premature failure of the coatings.

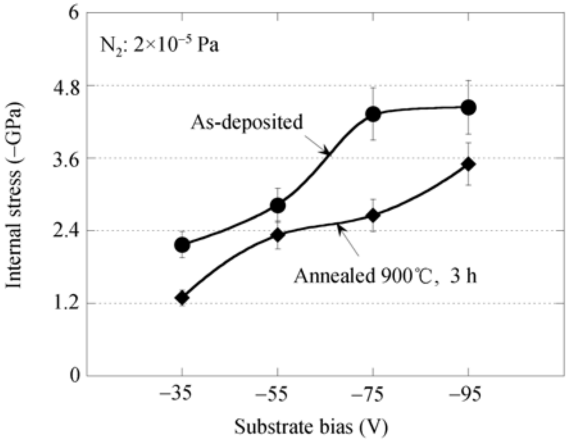

Fig. 2. The internal stress vs. substrate bias before and after annealing.

Fig. 3 shows the hardness of ZrAlN coatings as deposited at –37 V bias at room temperature and after annealing for 3 h as a function of N_2 partial pressure. The hardness of the coatings depends strongly on N_2 partial pressure. The maximum hardness of 22.5 GPa occurs at 2×10^{-5} Pa N_2 partial pressure, and its value is maintained after annealing at different temperatures. So, with proper control of N_2 partial pressure, we can synthesize ZrAlN coatings with good thermal stable hardness, although no apparent changes in elastic modulus can be observed in Fig. 4.

Internal stress of ZrAlN coatings before and after annealing at 900 and 1000℃ for 3 h as a function of N_2 partial pressure is shown in Fig. 5. Although the coatings exhibit a relatively higher compressive stress under lower N_2 partial pressure condition, its value

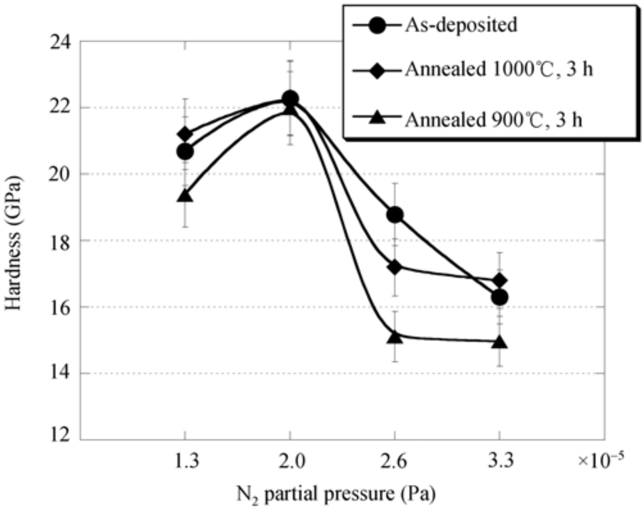

Fig. 3. The hardness vs. N_2 partial pressure before and after annealing. Substrate bias is –37 V.

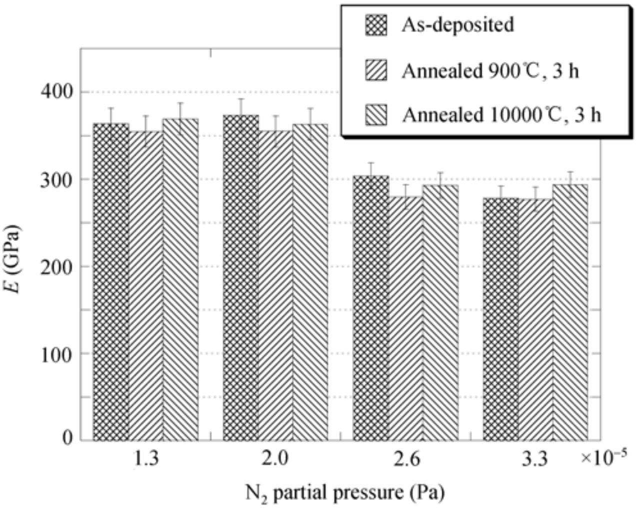

Fig. 4. The elastic modulus vs. N_2 partial pressure before and after annealing. Substrate bias is –37 V.

decreases significantly with the increase of annealing temperature. We believe that this decrease is related to a combination of factors such as stress relaxation, interdiffusion and crystalline changing due to annealing. At higher temperature, surface atoms are more mobile because the higher thermal energy and defects trapped in the structure are easier to be annealed out, resulting in lower internal stresses. At high N_2 partial pressure, the coatings show a lower internal stress before and after annealing. However, its hardness is too low to use for the protective coatings to cutting tools.

As-deposited ZrAlN coating at 2×10^{-5} Pa N_2 partial pressure and –37 V substrate bias and one annealed at 900℃ for 3 h were characterized and compared. Fig. 6 shows $\theta/2\theta$ XRD patterns of those coatings. As expected, the coating before annealing shows a strong ZrN (111) preferred orientation and a weak ZrN (200) peak. After annealing, the

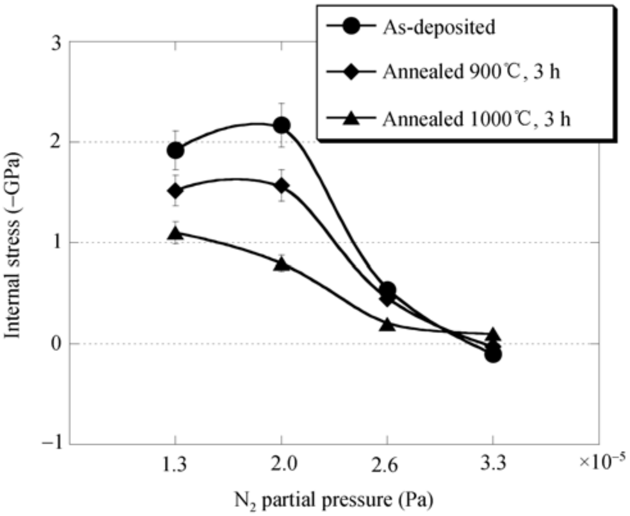

Fig. 5. The internal stress vs. N_2 partial pressure before and after annealing. Substrate bias is −37 V.

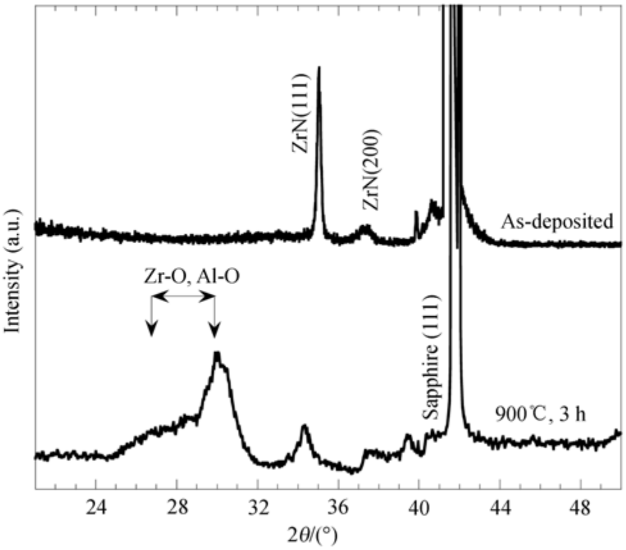

Fig. 6. XRD patters of ZrAlN coating prepared at −37 V substrate bias and 2×10^{-5} Pa N_2 partial pressure before and after annealing.

ZrN (200) peak almost disappears, and the ZrN (111) peak intensity decreases and the peak width increases, which means that the grain size of ZrN (111) gets smaller at high temperature. The result indicates the possibly reduced stress of the coating grains. Apparent Al_2O_3 and ZrO_2 peaks appearing in the structure after annealed at 900℃ should be responsible for that because its hardness almost kept constant at high temperature.

3 Conclusion

We have investigated the structural, mechanical properties and the high-temperature stability of ZrAlN coatings prepared at different substrate bias and N_2 partial pressure by dc reactive magnetron sputtering before and after annealing. These investigations showed that one can control the crystalline structure, hardness, internal stress and the smoothness of these coatings via the substrate bias and the N_2 partial pressure. Under −37 V substrate bias and 2×10^{-5} Pa N_2 partial pressure, one can obtain smooth ZrAlN coating with low internal stress. Its high-temperature stable hardness and internal stress relaxation after annealing are due to the formation of Al_2O_3 and ZrO_2 crystalline phases.

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