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Texture analyses of chemically vapor deposited coatings in the Ti-C-N system by wide film Debye-Scherrer X-ray diffraction technique

S. EROGLU[(1)] and B. GALLOIS

Department of Materials Science and Engineering, Stevens Institute of Technology, Hoboken, NJ 07030, U.S.A.

Abstract-Texture analyses were performed on the chemically vapor deposited monolithic TiN, TiC, TiC_xN_y coatings and graded TiN/TiC coatings by wide film Debye-Scherrer X-ray diffraction technique. The preferred orientations of the coatings were investigated as a function of coating thickness and input gas composition. The growth of TiN and TiC coatings was initiated as randomly oriented crystallites which subsequently grew into large columnar grains with a <110> preferred orientation. The textures of TiC coatings with the same thickness changed from the <110> orientation to the <100> orientation with decreasing hydrogen concentration in the gas phase. TiC_xN_y coatings exhibited a preferred orientation of <111> up to the CH_4/CH_4+N_2 ratio of 0.14 above which a strong <100> texture developed. The texture analyses on the graded TiN/TiC coatings showed that the TiC top layers were oriented in a <100> direction perpendicular to the sample surface.

1. Introduction

Coatings synthesized by chemical vapor deposition technique often exhibit a high degree of texture or preferred orientation. Preferred orientation affects coating properties such as hardness which, in turn, can influence the performance of the coatings [1]. For example, TiC coatings with a <100> texture exhibited better cutting performance than those with a <111> orientation [2].

Studies of textures in hard coatings deposited by chemical vapor deposition (CVD) technique [3-5] indicate that low index-planes such as (200), (220) and (111) tend to grow parallel to the substrate's surface. It is known that texture depends on the growth parameters such as deposition temperature, gas composition and substrate. There is, however, a lack of published information on the relationship between preferred orientation and CVD process parameters. The purpose of the present investigation was to systematically study the effect of deposition parameters on textures in the monolithic TiN, TiC, Ti_xN_y and graded TiN/TiC coatings by wide film Debye-Scherrer X-ray diffraction technique.

2. Experimental Details
2.1. Chemical Vapor Deposition

The depositions were carried out on polycrystalline graphite substrates in a computer-controlled hot-wall chemical vapor deposition reactor. The experimental conditions for chemical vapor deposition of TiN

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(1) *Address for correspondence: TUBITAK, Marmara Research Center, Materials Research Division, P.O. Box 21, Gebze-Kocaeli, Turkey*

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are described elsewhere [6]. All the deposition experiments were conducted at a total pressure of 10.7 kPa (80 torr) and a total flow rate of 670 sccm. In order to study the effect of hydrogen concentration on texture in TiC coatings grown at 1425 K, the hydrogen flow rate was varied from 100 sccm to 600 sccm at constant CH_4 (50 sccm) and $TiCl_4$ (20 sccm) flow rates. The total flow rate was maintained constant with argon. Details of the chemical vapor deposition of TiC and the properties of the graphite substrates are given in Ref. [7].

Ti(C,N) monolithic coatings with C/C+N ratio in the range 0-1 were grown at 1400 K by varying the CH_4/CH_4+N_2 ratio (X_{CH4}) in the input gas composition. Continously graded TiN/TiC coatings with parabolic, linear and exponentional composition profiles were also synthesized at 1400 K by using the methodologies described elsewhere [8].

2.2. Texture Analyses

Texture analyses were performed on a Read thin film camera of radius 5.0 cm. This camera is essentially a Debye-Scherrer X-ray diffraction camera equipped with a wide photographic film (18cmx13cm). Nickel-filtered copper radiation was used. The sample was held stationary at a given angle of incidence (generally 25°). The results obtained were checked and found to be in good agreement with those obtained by conventional X-ray diffraction technique [7].

The wide film Debye-Schrerrer x-ray diffraction technique is extremely useful for quickly obtaining an overview of the structure of the coatings such as texture. In this technique, the reflections from the planes parallel and inclined to the surface of the sample can be detected simultaneously, whereas in the case of the conventional diffractometer the reflections observed are from the planes parallel to the surface. It is especially well suited for studying coatings since a fixed small angle to the incident x-ray beam can be used to increase the path length of the x-rays through the coating [9].

3. Results and Discussion

3.1. Effect of Coating Thickness

Fig. 1 shows X-ray diffraction patterns of the TiN coatings deposited at 1300 K. The degree of preferred orientation in the coatings is inversely proportional to the length of the diffraction rings recorded on a photographic film. If certain (hkl) planes are oriented preferentially parallel to the substrate's surface, the (hkl) diffraction ring will exhibit a much higher intensity at its central portion in the form of a short arc, the length of which can be used as a qualitative indication of the sharpness of the preferred orientation in the coating. As can be seen in Fig. 1, the thinner coating (thickness 1.5 μm) exhibits continous diffraction rings while the coating with a thicknesses of 12 μm has discontinous rings with non-uniform intensities. With increasing coating thickness, the intensity of the (220) reflection increases near the equatorial plane of the diffraction pattern whereas the intensities of the (111), (200) and (311) reflections decrease. The thinner coating has a near random structure and thicker coatings have a <110> fiber texture or preferred orientation perpendicular to the plane of the coating. The sharpness of <110> orientation also increases with the coating thickness. The same trend was observed for the TiC coatings.

Texture studies indicate that the coatings at the beginning of the growth tend to have a nearly random structure, and that a <110> fiber texture develops as growth proceeds. This behavior can be explained by evolutionary selection theory [10]. The coatings are comprised of fine grains near the interface between the coating and the substrate. With increasing coating thickness, certain individual grains become greater in diameter, screening and suppressing less favorable grains. The

surface morphology of the coatings grown at 1300 K are shown in Fig. 2 as a function of thickness. The coating with a thickness of 1.5 μm has an acicular structure with a submicrometer grain size whereas the 12μm-thick coating exhibits larger grains with a size of the order of 3 μm.

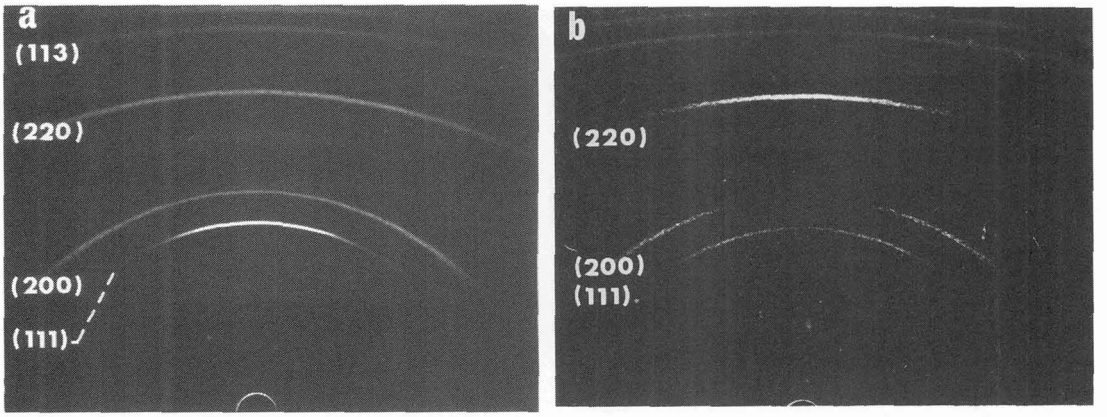

Fig. 1- X-ray diffraction patterns of the TiN coatings deposited at 1300 K as a function of thickness: (a)1.5 μm and (b) 12 μm. The (101) and (004) reflections originated from the graphite substrate.

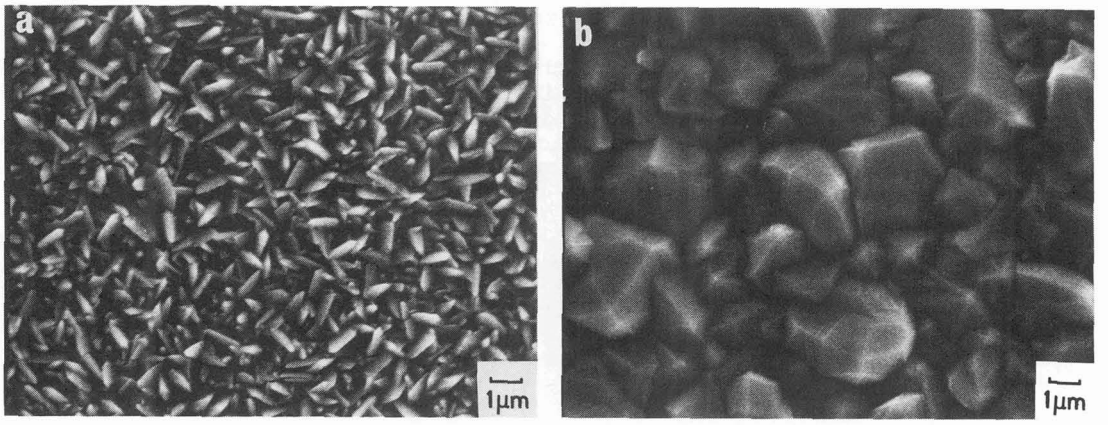

Fig. 2- Surface morphology of the TiN coatings with thicknesses of (a)1.5 μm and (b)12 μm grown at 1300 K.

From these observations, it can be concluded that there is a competition between differently oriented grains. As growth proceeds, more and more grains are overgrown by adjacent crystals and the number of grains extending to the surface decreases progressively. Only those crystals with a <110> growth orientation perpendicular or nearly perpendicular to the substrate surface survives, whereas grains with other orientations are gradually buried.

3.2. Effect of Input Gas Composition

Texture in TiC coatings is greatly influenced by the hydrogen flow rate in the range 600-100 sccm. The growth rate of the TiC coatings is not affected, however, by the hydrogen concentration in the input gas

composition [7]. The thickness of the coatings was measured to be around 8 μm. The sharpness of the <110> preferred orientation observed in the TiC coatings decrease with decreasing hydrogen flow rate up to 200 sccm at which point a slight <311> orientation is observed. Above that, the coating has a high <100> preferred orientation. Fig. 3 shows the X-ray diffraction patterns of TiC coatings grown at hydrogen flow rates of 100 sccm and 400 sccm.

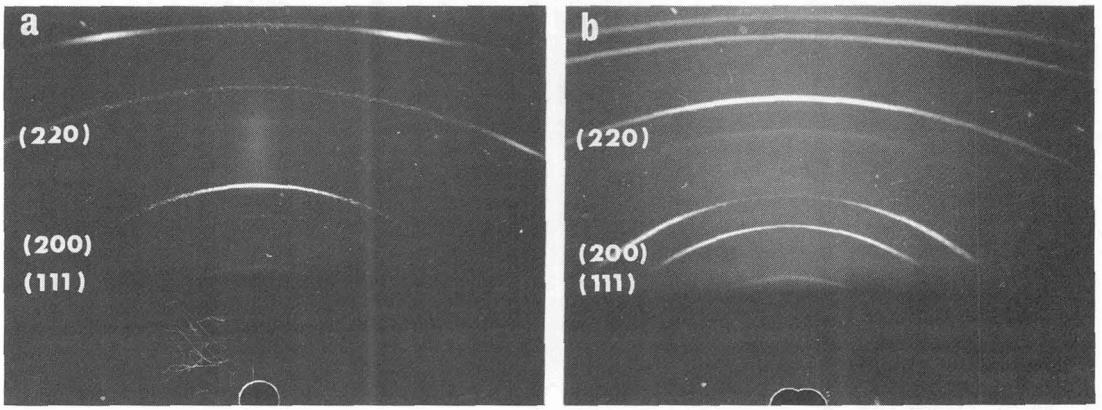

Fig. 3- X-ray diffraction patterns of TiC coatings grown at hydrogen flow rates of (a) 100 sccm and (b) 400 sccm.

The texture studies on monolithic TiC_xN_y coatings reveal that as the CH_4/CH_4+N_2 ratio in the gas phase increases, the preferred orientation observed in the <111> direction at low methane concentrations changes to the <100> direction. The transition ratio (X_{CH4}) was determined to be 0.14. The sharpness of the <100> orientation increases with increasing CH_4/CH_4+N_2 ratio. Fig. 4 shows some of the diffraction patterns of the

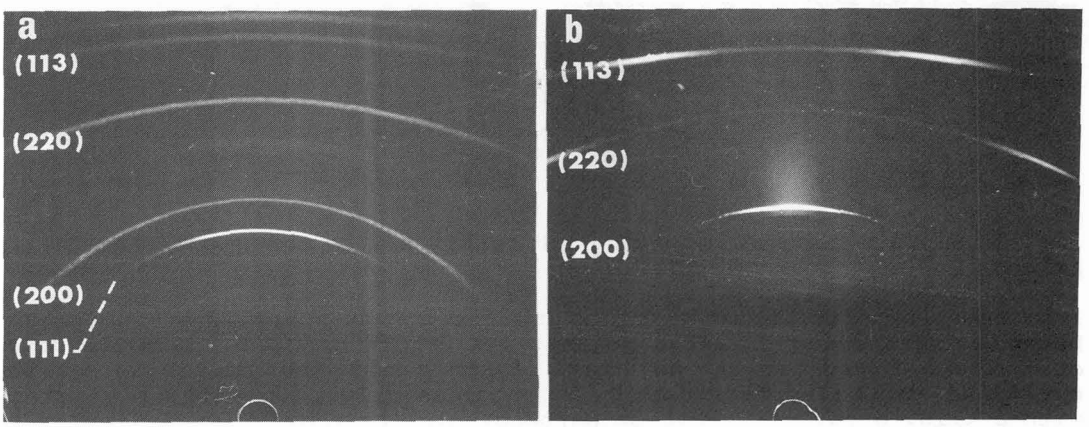

Fig. 4- X-ray diffraction patterns of the coatings grown at CH_4/CH_4+N_2 ratios of (a) 0.14 and (b) 0.74.

TiC_xN_y coatings. The coatings exhibit columnar grains, typical of preferrentially oriented coatings.

Surface morphologies of the graded TiN/TiC coatings consisted of uniformly distributed faceted square based pyramids as shown in Fig.

5(a). The cross-sectional view of the parabolically graded coating reveals that the growth starts with fine grains near the interface between the TiN layer and the substrate and develops into narrow columnar ones on which small grains are grown [Fig. 5(b)]. Above this zone, large columnar grains are observed. Texture analyses on the graded TiN/TiC coatings showed that the TiC top layers have a fiber texture of <100> orientation (Fig. 6). This texture was expected from the deposits with surface morphologies characterized by square-based pyramids with facets consisting of (111) planes.

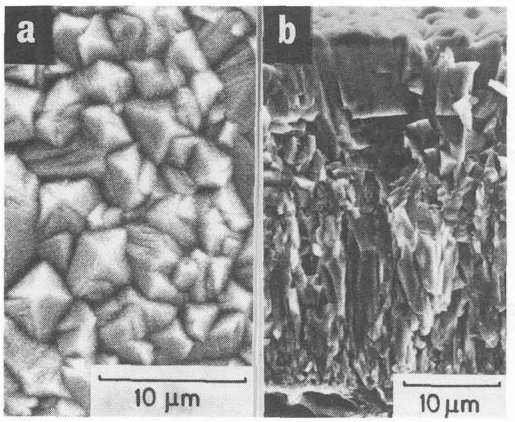

Fig. 5- Scanning electron micrographs of the graded coating with a parabolic composition profile:(a) Surface morphology and (b) cross-sectional view.

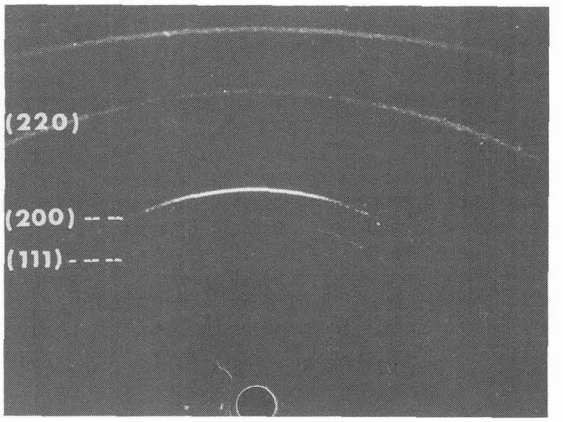

Fig. 6- X-ray diffraction pattern of the graded coating.

The textures in the coatings are greatly influenced by input gas composition, as the studies indicate. The source of the development of the textures might be related to the preferential attachment of gaseous species on crystal planes, thus poisoning or promoting the growth of certain crystallographic planes. It would be worthwhile to identify the gaseous species on the substrate's surface. Correlations of the adsorbed species with texture could lead to the understanding of the development of preferred orientation. Since preferred orientation is accompanied by columnar growth and since columnar grains are structurally weak, the determination of process conditions which prevent columnar growth would be invaluable.

4. Conclusions

Wide-film Debye-Scherrer X-ray diffraction camera technique was employed for the texture analyses of the chemically vapor deposited coatings in the Ti-C-N system. The growth of the TiC and TiN coatings was initiated as randomly oriented grains which then grew in a columnar mode. The grains with a <110> orientation suppressed the growth of grains of other orientations, as the growth proceeded. The TiC coatings tended to have a <100> texture as the hydrogen concentration decreased. TiC_xN_y coatings grown at low CH_4 concentration exhibited a <111> texture and a strong <100> texture developed in these coatings as the CH_4 concentration increased. The <100> texture was also observed in the top TiC layers of continuously graded TiN/TiC coatings.

Acknowledgements

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