J. Coat. Technol. Res., **7** (3) 403–407, 2010
DOI 10.1007/s11998-009-9225-x

BRIEF COMMUNICATION

Microstructure and mechanical properties of hafnium carbide coatings synthesized by reactive magnetron sputtering

Guanqun Li, Geyang Li

Abstract Hafnium carbide coatings with different carbon contents were synthesized in Ar–C_2H_2 mixture by reactive magnetron sputtering. Energy-dispersive X-ray, X-ray diffraction, scanning electron microscopy, atomic force microscopy, and nanoindentation were employed to characterize their microstructure and mechanical properties. The effects of C_2H_2 partial pressure on the composition, phase, microstructure, and mechanical properties of the coatings were investigated. The results show that hafnium carbide coatings can be synthesized at a low partial pressure of C_2H_2. The single-phase HfC coating with columnar crystal and favorable mechanical properties is obtained when the proportion of C_2H_2 partial pressure is only about 3.0% in the mixture, and the highest hardness and modulus are 27.9 and 255 GPa, respectively. The coating contains metal Hf and HfC phases and obtains low hardness under lower C_2H_2 partial pressure. When the C_2H_2 partial pressure is higher, the hardness and elastic moduli of acquired amorphous coatings decrease significantly.

Keywords Hafnium carbide, Hard coatings, Microstructure, Mechanical properties, Magnetron sputtering

Introduction

The transition metal nitrides with high hardness play important roles in surface engineering.[1,2] The successful application of titanium nitride coating started the ''golden revolution'' in the field of cutting tools in the 1970s, which powerfully promoted the development of the automation and mass production in the manufacturing industry. Other nitride coatings, such as chromium nitride,[3] zirconium nitride,[4] and titanium aluminum nitride,[5] with distinguished properties came forth. The emergence of these materials provided a wider range of selection to meet different machining requirements. Compared with nitrides, carbides also have many excellent properties and especially higher hardness. However, the development of these promising materials is limited due to their relative complicated structures and synthesis process. Until now, only a few carbide coatings such as titanium carbide and titanium carbon nitride[2] have been investigated and used in cutting tools.

Hafnium carbide coating has high hardness, excellent wear resistance, good resistance to corrosion, and low thermal conductivity, which are ideal characteristics for use in high-temperature applications.[6] However, until now scant researchers concentrated on HfC coatings. It was reported by Ferro et al.[7] that the hardness of pulsed laser ablation deposited HfC coatings depended on the coating thickness. It reached the highest hardness of 29 GPa when the coating thickness was about 650 nm. In the research of Teghil et al.,[8] HfC coating was synthesized with the same method as Ferro. Their results showed the microstructure of the HfC coating was a kind of columnar crystal, and the hardness was during 18–29 GPa, which was compared with the bulk of HfC. However, neither investigated the detailed relations among the composition, microstructure, and mechanical properties of the coatings.

In this article, a series of hafnium carbide coatings with different carbon contents were synthesized by reactive magnetron sputtering, and the effects of different C_2H_2 partial pressures on the composition, phase, microstructure, and mechanical properties of the coatings were investigated.

G. Li, G. Li (✉)
State Key Laboratory of Metal Matrix Composites,
Shanghai Jiao Tong University, 200240 Shanghai, PR China
e-mail: gyli@sjtu.edu.cn

Experimental details

A series of hafnium carbide coatings with different carbon contents were synthesized by reactive magnetron sputtering on ANELVA SPC-350 multi-target magnetron sputtering system. The 3-in. diameter hafnium target (99.9% in purity) was controlled by the radio frequency cathode. Mirror polished stainless steel substrates were ultrasonically cleaned in acetone and alcohol and then mounted on the substrate holder in the chamber. The distance is 5 cm between target surface and the substrate. When the background pressure reached below 1.0×10^{-3} Pa, Ar (99.999% in purity) and C_2H_2 (99.9% in purity) were separately introduced into the chamber. The total pressure of the mixture ($P_{Ar+C_2H_2}$) was kept at 6.0×10^{-1} Pa while C_2H_2 partial pressure ($P_{C_2H_2}$) varied from 5.0×10^{-3} to 3.0×10^{-2} Pa. During the deposition, the target power was kept at 150 W and the deposition time was 45 min for each sample. No heating and deliberate bias voltage were applied to the substrates.

The phase constituting hafnium carbide coatings was determined by X-ray diffraction (XRD) on the Dmax-2550/PC diffractor with Cu-K_α excitation radiation. The growth structure and chemical composition were characterized by the FEI SIRION 200 field emission scanning electron microscope (SEM) and the attached OXFORD INCA quantitative energy dispersive X-ray analysis (EDX), respectively. The surface morphology of the coatings was observed using the Nanoscope IIIa atomic force microscope (AFM).

Mechanical properties including Vicker's hardness (HV) and elastic moduli (E) of all coatings were measured on the Fischerscope H100 VP nanoindentor. In order to obtain reliable mechanical properties of the coatings, a maximum load of 20 mN was used for measurement based on a two-step penetration method[9] and the moduli were calculated with Oliver method.[10] The hardness and elastic modulus values for each sample were an average of at least 20 measurements.

Results and discussion

Composition and microstructure

The composition of hafnium carbide coatings acquired at different C_2H_2 partial pressures analyzed by EDX is listed in Table 1. The results show that the proportion of C_2H_2 partial pressure is very low in the synthesis of hafnium carbide coatings by reactive magnetron sputtering. When the C_2H_2 partial pressure is below 1.0×10^{-2} Pa, the carbon contents in the coatings are under 34.5 at.%. As the C_2H_2 partial pressure is between 1.5×10^{-2} Pa and 2.0×10^{-2} Pa, the carbon contents are between 48.5 and 56.9 at.%, which is nearly the stoichiometric ratio of HfC. Further increasing the C_2H_2 partial pressure to above 2.5×10^{-2} Pa, the carbon contents quickly increase to above 70 at.%.

The XRD patterns of hafnium carbide coatings with different carbon contents are shown in Fig. 1. In samples 1 and 2 with the carbon contents of below 34.5 at.%, there are two mixed phases of Hf and HfC in the coatings. The metal Hf peaks are very sharp while that of HfC is very low. A set of HfC peaks is found in the XRD patterns of samples 3 and 4 (about 50 at.% C). Not only the (111) peak is sharp, others such as (200), (220), and (311) are also clear but relatively lower, which shows that the coatings contain an inconspicuous (111) texture. Once the carbon contents are more than 70 at.% (samples 5 and 6), the peaks of HfC are gradually broadened, which indicates poor crystallization. Especially in sample 6, there is only a broadened (111) peak which shows the coating transformed to amorphous.

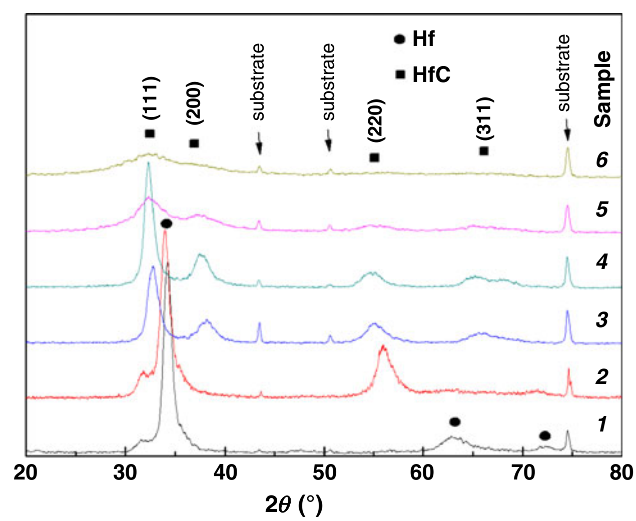

Fig. 1: XRD patterns of hafnium carbide coatings

Table 1: Composition of hafnium carbide coatings at different C_2H_2 partial pressure

Sample	1	2	3	4	5	6
$P_{C_2H_2}$ ($\times 10^{-3}$ Pa)	5	10	15	20	25	30
$P_{C_2H_2}/P_{Ar+C_2H_2}$ (%)	0.83	1.67	2.50	3.33	4.17	5.00
C (at.%)	22.9	34.5	48.5	56.9	71.0	85.1
Hf (at.%)	77.1	65.5	51.5	43.1	29.0	14.9

Further studying Fig. 1, it is discovered that the (111) peaks of HfC have the tendency to the lower angles with the increase of carbon contents, which may correspond to the enlarged lattice constants. In sub-stoichiometric HfC, the lattice constant is enlarged for the integrity of HfC lattice increases with addition of carbon contents; while in over-stoichiometric HfC the lattice constant increases due to carbon atoms being dissolved in the interstitial sites of lattice.

Figure 2 shows the cross-sectional fracture micrographs of coatings. Columnar crystals are found in the Hf and HfC coexisting coatings (Fig. 2a, sample 1). With the increase of carbon contents, more distinguished columnar crystals appear in HfC single-phase coating (Fig. 2b, sample 4). When the carbon content is more than 70 at.%, an amorphous fracture, the substitution of the columnar one, is observed (Fig. 2c, sample 6). This growth structure transformation of the coatings is related to the presence of the amorphous phase.

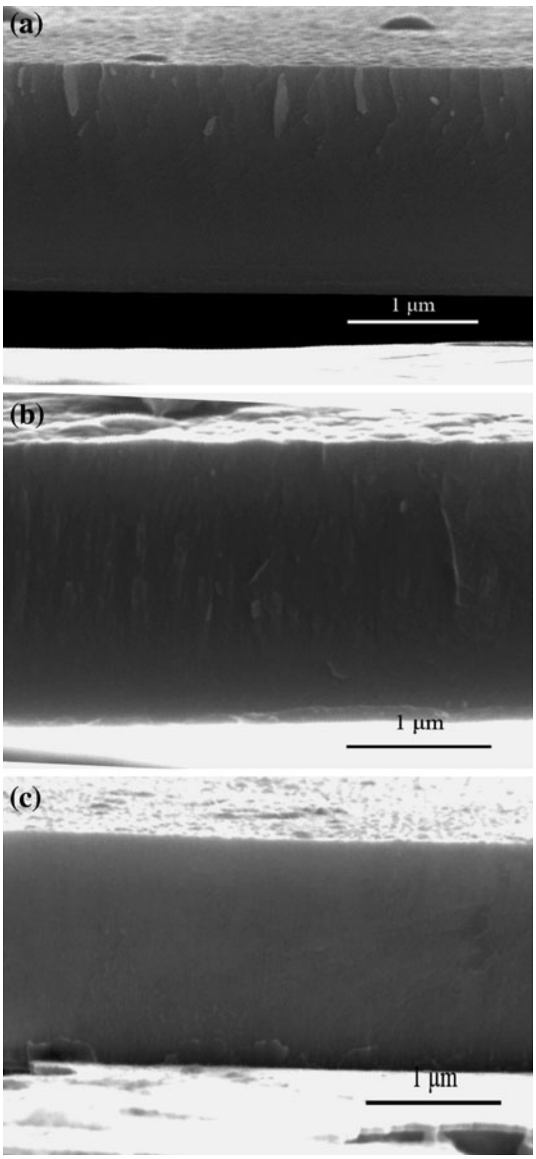

Fig. 2: Cross-sectional SEM images of hafnium carbide coatings: (a) sample 1, 22.9 at.% C; (b) sample 4, 56.9 at.% C; and (c) sample 6, 85.1 at.% C

Moreover, the SEM graphs suggest that with the increase of the carbon contents, the thicknesses of coatings show little change. It indicates that the deposition rate of coatings rarely depends on the proportion of C_2H_2 in the mixture. Although the proportion of C_2H_2 significantly influences the composition and growth structures, there is no ''target poison'' phenomenon in which the sputtering rate decreases significantly when the reactive gas partial pressure is high.

The surface morphology and the corresponding roughness (R_q) obtained from AFM are displayed in Fig. 3. In Fig. 3a, the compact cellular structure with a roughness of 7.15 nm is shown in the Hf and HfC coexisting coatings (sample 1). With the increase of carbon content, the single-phase HfC coating also shows a compact cellular structure and the roughness increases slightly to 8.19 nm in sample 4 (Fig. 3b). However, once the amorphous phase appears due to the excessive carbon content, the coating shows a smooth growth morphology with a roughness of only 4.56 nm in sample 6 (Fig. 3c).

Mechanical properties

Figure 4 shows the variation of hardness and elastic moduli of coatings with carbon content. The hardness and elastic modulus of the two-phase coating with 22.9 at.% C are only 8.3 and 160 GPa, respectively, due to the redundant metal hafnium phase in the coating. Increasing the carbon contents to 56.9 at.%, the single-phase HfC coating reaches the peak hardness and elastic modulus of 27.9 and 255 GPa. With the further increase of carbon content to more than 70 at.%, the hardness and elastic moduli of amorphous coatings drop significantly.

Conclusions

Hafnium carbide coatings can be synthesized by reactive magnetron sputtering in Ar and C_2H_2 mixture conveniently. The composition, phase, microstructure, and the corresponding mechanical properties of the coatings show the sensitivity to the partial pressure of C_2H_2. The single-phase HfC coating with columnar crystal and favorable hardness is obtained when the proportion of C_2H_2 partial pressure is only about 3.0% in the mixture. The most optimistic hardness and modulus are 27.9 and 255 GPa, respectively. The coating consisting of Hf and HfC phases obtains low hardness under lower C_2H_2 partial pressure. When the

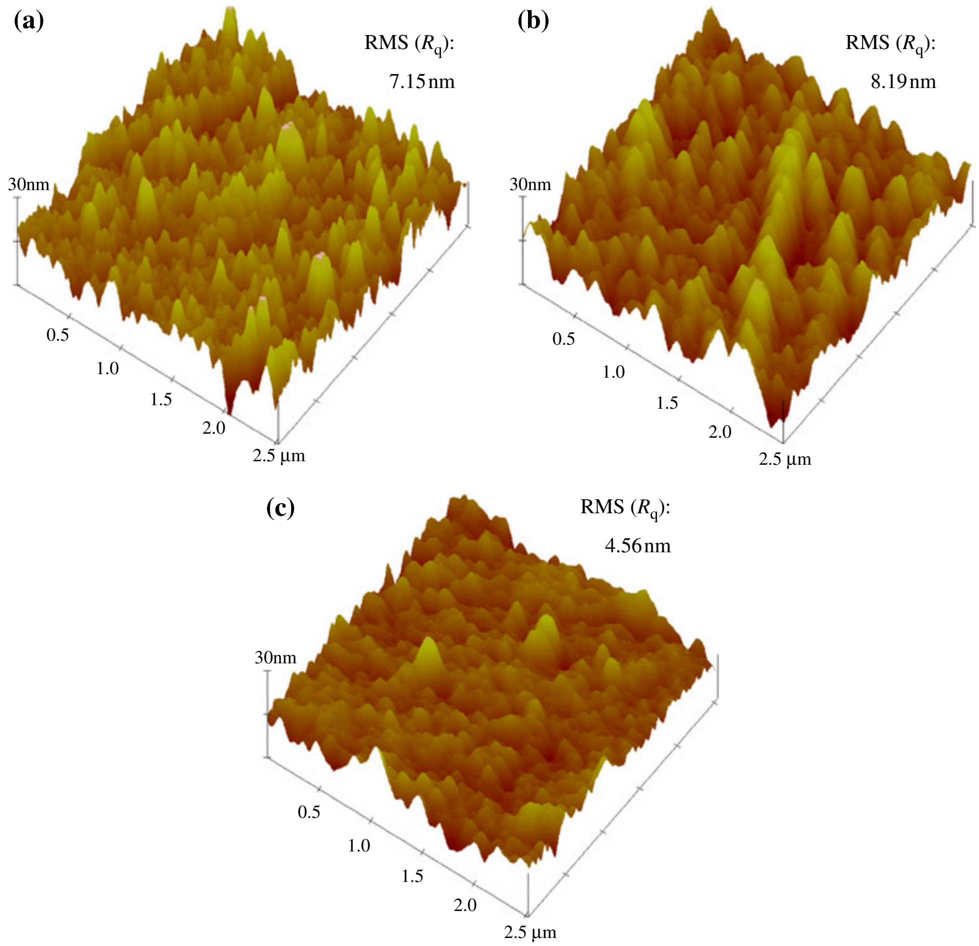

Fig. 3: AFM images of hafnium carbide coatings: (a) sample 1, 22.9 at.% C; (b) sample 4, 56.9 at.% C; (c) sample 6, 85.1 at.% C

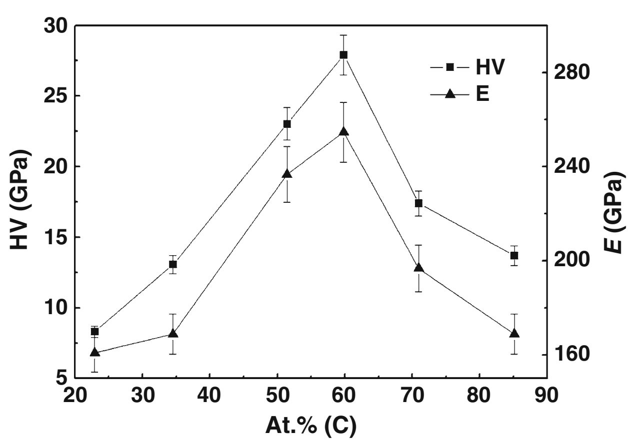

Fig. 4: Hardness and elastic moduli of HfC coatings as a function of atomic carbon content

C_2H_2 partial pressure is higher, the hardness and elastic moduli of acquired amorphous coatings decrease significantly.

Acknowledgments This study was supported by the National Science and Technology Supporting Item (no. 2008BAF32B06).

References

1. Sundgren, JE, Hentzell, TG, ''A Review of the Present State of Art in Hard Coatings Grown from the Vapor Phase.'' *J. Vac. Sci. Technol. A*, **4** (5) 2259–2279 (1986)
2. Robinson, GM, Jackson, MJ, ''A Review of Micro and Nanomachining from a Materials Perspective.'' *J. Mater. Process. Technol.*, **167** (2–3) 316–337 (2005)
3. Berg, G, Friedrich, C, Broszeit, E, Berger, C, ''Development of Chromium Nitride Coatings Substituting Titanium Nitride.'' *Surf. Coat. Technol.*, **86–87** (Part 1) 184–191 (1996)
4. Liu, F, Meng, YD, Ren, ZX, Shu, XS, ''Microstructure, Hardness and Corrosion Resistance of ZrN Films Prepared by Inductively Coupled Plasma Enhanced RF Magnetron Sputtering.'' *Plasma Sci. Technol.*, **10** (2) 170–175 (2008)
5. Derflinger, VH, Schutze, A, Ante, M, ''Mechanical and Structural Properties of Various Alloyed TiAlN-Based Hard

Coatings.'' *Surf. Coat. Technol.*, **200** (16–17) 4693–4700 (2006)

6. Krajewski, A, D'Alessio, L, De Maria, G, ''Physiso-Chemical and Thermophysical Properties of Cubic Binary Carbides.'' *Cryst. Res. Technol.*, **33** (3) 341–374 (1998)
7. Ferro, D, Barinov, SM, Rau, JV, Latini, A, Scandurra, R, Brunetti, B, ''Vickers and Knoop Hardness of Electron Beam Deposition ZrC and HfC Thin Films on Titanium.'' *Surf. Coat. Technol.*, **200** 4701–4707 (2006)
8. Teghil, R, Santagata, A, Zaccagnino, M, Barinov, SM, Marotta, V, De Maria, G, ''Hafnium Carbide Hard Coatings Produced by Pulsed Laser Ablation and Deposition[J].'' *Surf. Coat. Technol.*, **151–152** 531–533 (2002)
9. Tian, JW, Han, ZH, Lai, QX, Yu, XJ, Li, GY, Gu, MY, ''Two-Step Penetration: A Reliable Method for the Measurement of Mechanical Properties of Hard Coatings.'' *Surf. Coat. Technol.*, **176** (3) 267–271 (2004)
10. Oliver, WC, Pharr, GM, ''An Improved Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments.'' *J. Mater. Res.*, **7** (6) 1564–1580 (1992)