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Magnetron sputter deposition of hafnium nitride coating on high density graphite and niobium substrates

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Abstract

Hafnium nitride (HfN) is a refractory compound considered to be a suitable material for reaction barriers. The present paper deals with the preparation of HfN thin films by reactive magnetron sputtering on high density (HD) graphite and niobium substrates. Deposition process parameters have been optimised with Si(100) substrate in order to get HfN coating of 3 μm thickness. The optimised parameters were used to deposit HfN on HD graphite and on niobium substrates. The results showed that HfN coating with a thickness of 2.8 μm was successfully deposited on HD graphite and niobium substrates. The presence of HfN was confirmed by glancing incidence X-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS). XRD studies on HfN coating on Si(100), HD graphite and Nb substrates showed nanocrystalline grains of size 130, 55 and 46 Å, respectively. The surface morphology of HfN coating on HD graphite and niobium by atomic force microscope (AFM) and scanning electron microscope (SEM) showed that nanoparticles are getting agglomerated into clusters. The HfN coating on niobium substrate exhibited good adhesion compared to that on HD graphite as studied by microscratch test. The thermal stress generated in the sputter deposited HfN coating on HD graphite and niobium substrates were calculated by analytical formula for thermal stress. The tensile and highly compressive stresses observed in the HfN coating on niobium and HD graphite, respectively, indicated a lower adhesive strength of the coating on the later than that of the former.

Keywords: A. Films; B. Electron microscopy; D. Nitrides

1. Introduction

High density graphite and niobium are suitable materials for high temperature application such as in aeronautic and nuclear industry. These materials are widely used for high temperature applications because of their high melting point, strength and resistance to thermal shock and chemical attack. Hafnium nitride has unique combination of properties such as high melting point 3387 °C (3660 K), high hardness (16.3 GPa), high thermal conductivity (21.7 W/m K), high thermal stability and chemical inertness [1]. Therefore, HfN coatings can be effectively used as diffusion barriers. Apart from this HfN has potential applications in the field of hard wear-resistant coatings, microelectronic devices, field emission cathodes, optical thin films, etc. Plasma sprayed HfN coating on niobium crucible has been developed and tested by Idaho National Laboratory, USA, to verify the crucible's compatibility with salt and uranium [2]. Their tests (five times) in cathode processor indicated no degradation to the niobium crucible or its HfN coating and the uranium ingot released successfully. Huang and Gallegos [3] showed that Ta, W and Ta—2.5 wt% were embrittled when exposed to liquid U at 1200 °C (1473 K) with intergranular penetration of U, while V and Nb showed ductile behaviour. Therefore, HfN coatings on vanadium and niobium could be candidate materials for uranium melting applications.

HfN coatings have been prepared by plasma spraying, PVD and CVD process and these films are sputter deposited by many researchers. Compared to other methods magnetron sputtering has the advantage of producing nanocrystalline, high quality, and low impurity thin films at high deposition rates [4]. Reactive magnetron sputtering

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is quite successful in low temperature deposition of stoichiometric high melting point transition metal nitride thin films. Magnetron sputter deposited coatings outperform the coatings produced by other techniques and produce high performance [5]. Moreover, nanocrystalline materials with their large number of grain boundaries result in improved properties under complex loads and aggressive environments [6]. Therefore, nanocrystalline HfN coatings deposited by reactive magnetron sputtering on HD graphite and niobium substrates with good adhesion have been proposed in the present study to achieve improved performance coupled with longer life.

Hafnium nitride coatings were prepared via very high rate reactive sputtering by Sproul [7] in an Ar–N_2 atmosphere. Stoichiometric HfN thin films were deposited by Gotoh et al. [8] by direct RF magnetron sputtering of HfN target. In the present study, HfN thin films were deposited initially on Si(100) substrate by reactive DC/RF magnetron sputtering and the optimised parameters were utilised to obtain dense and adherent nanocrystalline HfN coating of 3 μm thickness on HD graphite and niobium substrates. The paper discusses the deposition and characterisation of coatings by XRD, SEM, AFM, XPS, microscratch test and calculation of thermal stress by an analytical model.

2. Experimental details

2.1. Magnetron sputtering and visual examination

HD graphite disc samples of 12 mm diameter × 5 mm thickness and niobium samples of size 6 × 6 × 2 mm were prepared with desired surface finish. The samples were polished up to diamond finish and cleaned before coating. The parameters were carefully chosen to obtain nanocrystalline spherical deposits of 3 μm thickness by DC/RF magnetron sputtering. The parameters used for HfN coating on Si(100), high density graphite and niobium substrates by DC/RF magnetron sputtering technique (Excel Instruments) at IIT Roorkee are tabulated in Table 1. Pure Hf target of 99.99% purity was used with N_2 flow rate of 10 sccm, while Ar + N_2 (80:20) flow rate was 12 sccm + 3 sccm. The coated samples were visually inspected after coating and any changes observed were noted.

2.2. Characterisation by XRD, SEM, AFM and XPS

The crystallographic characteristics of the films were studied using XRD to confirm the phases present after deposition using Cu-Kα radiation (λ = 0.1542 nm). XRD was carried on the films deposited on Si(100), Nb and HD graphite substrates corresponding to the parameters optimised for 3 μm thickness as shown in Table 1. XRD was carried out in normal mode (Bruker AXS, D8 Advance) and also by glancing incidence mode (Philips X'pert). The XRD patterns obtained were compared with the standard JCPDF database [9] and PDF-2 codes of the compounds observed were provided in square brackets.

Si(100) substrate placed along with graphite and Nb samples was used for measuring the thickness of the coating deposited. Cross sections of the coated samples were prepared by fracturing Si substrate and observed in SEM to determine the thickness of the coating. The surface morphology and compositional analysis of HfN coated HD graphite and niobium samples were carried out using FE-SEM (FEI, Quanta 200F) attached with EDX.

The surface morphology and surface roughness analysis of HfN coated HD graphite and niobium samples were carried out using scanning probe microscope (NT-MDT, Ntegra). The samples were analysed using Si tip in semicontact mode operated by tip scanning under ambient air condition.

X-ray photoelectron spectroscopy (SPECS, Germany) was carried out on coated surfaces with Al-Kα radiation (1486.71 eV). XPS spectra were obtained with pass energy of 12 eV, base pressure of around 10^{-9} mbar and binding energy reference to C 1s is 285 eV.

2.3. Microscratch test

The adhesion of the coating to the substrate was studied using microscratch test (CSM instruments, Reverest). The test was carried out at progressive loading of 20 N to a distance of 3 mm with a Rockwell C indenter with the tip radius of 200 μm as per the ASTM standard [10]. Optical and SEM examination of the scratch tracks was used to evaluate the damage features.

Table 1
Experimental parameters of the magnetron sputter deposition process.

Coating	Substrate	Working distance (cm)	Temperature °C (K)	Time (min)	Gas used	Base pressure (Torr)	Power (W)	Sputtering Pressure (mTorr)	Coating thickness
HfN	Si(100)	5	300 (573)	90	N_2	3×10^{-6}	(RF) 125	15	200 nm
HfN	Si(100)	4	300 (573)	120	N_2	2×10^{-6}	(RF) 150	15	700 nm
HfN	Si(100)	4	300 (573)	120	Ar + N_2	2×10^{-6}	(DC) 150	15	7.2 μm
HfN	Si(100)	4	300 (573)	50	Ar + N_2	2×10^{-6}	(DC) 150	15	3 μm
HfN	Nb	4	300 (573)	50	Ar + N_2	2×10^{-6}	(DC) 150	15	3 μm
HfN	HD graphite	4	300 (573)	50	Ar + N_2	2×10^{-6}	(DC) 150	15	3 μm

2.4. Analytical model for thermal stress

Tsui and Clyne [11] have used an analytical model for calculating the residual stress in progressively deposited coatings for the planar geometry configuration. By combining their analytical model and Stoney's equation for tension of metallic films, the thermal stress in thin coating can be obtained as [12]

$$\sigma_f = \frac{E_{ef}\int_{T_r}^{T_d}(\alpha_s-\alpha_f)dT}{1+4(E_{ef}/E_{es})(h/H)} \quad (1)$$

where $E_{ef}=E_f/(1-\nu_f)$, $E_{es}=E_s/(1-\nu_s)$, h, H, α_f, α_s, ν_f, ν_s, T_r and T_d are effective Young's modulus of the coating, effective Young's modulus of the substrate, coating thickness, substrate thickness, thermal expansion of coefficients of the coating, thermal expansion of coefficients of the substrate, Poisson's ratio of the coating, Poisson's ratio of the substrate, room temperature and deposition temperature, respectively [13].

The thermal stress generated in sputter deposited HfN coating was analysed using Eq. (1). Two types of substrates, i.e., HD graphite and niobium of 3 mm thickness and HfN coating of thickness 3 μm on the top of the substrate surface were considered for the study. The deposition temperature of 300 °C (573 K) and uniform temperature of 25 °C (298 K) were used as reference temperature and uniform temperature, respectively for the calculation and other values used for the analysis are shown in Table 2 obtained from literature [14–18].

Table 2
Properties of coating and substrate materials.

Property	HfN	Nb	Graphite
Thermal expansion at 20 °C ($\times 10^{-6}$/°C)	6.9	7.3	4.0
Poisson's ratio	0.35	0.38	0.1
Young's modulus of elasticity, GPa	450	103	7

3. Results and discussion

3.1. Magnetron sputtering and visual examination

Hafnium nitride coating deposited on high density graphite and niobium samples by magnetron sputtering technique was uniform. Table 1 summarises the parameters used for the deposition of HfN. It is clear from the table that high deposition rate was obtained when $Ar+N_2$ gas was used compared to the low deposition rate with pure N_2. This could be due to extensive target poisoning, i.e., extensive nitriding of target with N_2. The HfN coating on HD graphite exhibited a dark grey colour, while the HfN coating on niobium exhibited a bluish grey colour. When reactive sputtering for the deposition of transition nitride films is used, the colour of the films can be widely changed by the sputtering conditions, such as the nitrogen partial pressure, flow ratio of Ar/N_2, total gas pressure, substrate bias, substrate temperature, etc. [19] and the colour of some of the transition nitrides depends strongly on the nitrogen flow rate. Sproul [7] reported that as more and more nitrogen is admitted into the chamber, the colour of HfN coating varied from metallic to a very light gold colour to a rich gold and finally to a brownish colour.

The SEM cross section micrographs of HfN coating on Si(100) substrate placed along with niobium and high density graphite substrates are shown in Fig. 1a and b, respectively. The thickness of HfN coating on Si(100) substrate placed along with niobium substrate was found to be 7.02, 7.11, 7.08, 7.11 and 7.09 μm at different locations, and the average thickness is 7.08 μm for 2 h of deposition time (Fig. 1a). The time of deposition was reduced to 50 min; therefore, the thickness was around 2.8 μm for the niobium substrate. Similarly, the thickness of the HfN coating on Si(100) substrate placed along with HD graphite substrate was found to be 2.81, 2.81, 2.83, 2.84 and 2.86 μm at different locations, and the average

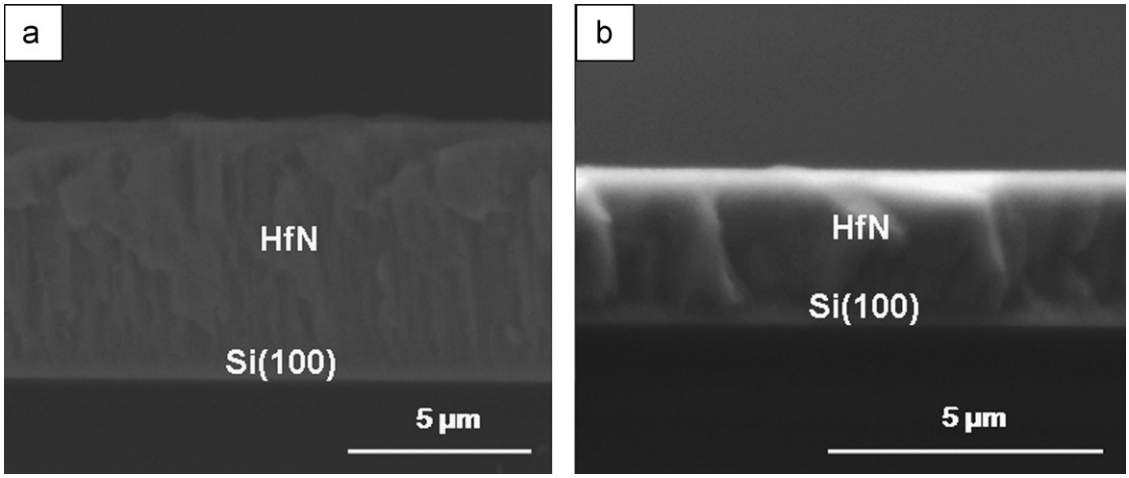

Fig. 1. Cross section micrograph of HfN coating on Si(100) placed along with (a) niobium and (b) HD graphite.

thickness is 2.83 μm (Fig. 1b). Thus, the parameters were optimised to obtain a coating thickness of around 3 μm.

3.2. Characterisation by XRD, SEM, AFM and XPS

3.2.1. GIXRD

XRD pattern of HfN coated on Si(100) is shown in Fig. 2a. On comparing the 2θ values of the coated sample with the standard XRD pattern of HfN [33-0592] three of the four peaks matched with the standard values. Thus, it was confirmed that HfN coating was obtained. The last peak for the 2θ value of 69.426° was matching with the substrate peak diffraction. The intensity of the HfN (200) peak was high compared to HfN (111) peak. This was due to the (200) texture which means that most of the planes on the surface have a (200) orientation. Yuan et al. [20] also obtained HfN with (200) preferred orientation when nitrogen flow rate ratio of 0.2 was used and by decreasing the flow rate ratio Hf_3N_2 film was obtained. Therefore, it is important to precisely control the nitrogen flow rate ratio to obtain stoichiometric HfN films of golden yellow colour. The crystal structure of HfN on Si(100) was FCC (NaCl structure with nitrogen atoms surrounded by six hafnium atoms in octahedral sites) and the lattice parameter of the structure was found to be 4.54 Å. Bulk and CVD HfN coatings have a lattice parameter of 4.52 Å, and sputter deposited HfN coatings have a lattice parameter of 4.55–4.58 Å depending on the nitrogen content [7]. GIXRD pattern of HfN coated on HD graphite and niobium is shown in Fig. 2b and c, respectively. GIXRD pattern of HfN coating on HD graphite showed a sharp high intense carbon peak [75-2078], while for the HfN coating on niobium it showed peaks of Nb [35-0789]. As with the Si(100) substrate, all the diffracted planes of the HfN were found corresponding to FCC structure. The lattice parameter of the coating using the same method as with the Si(100) substrate was determined and the lattice parameter was found to be 4.54 Å, while from the HfN(111) peak the lattice parameter was found to be 4.59 Å. Diffraction peaks corresponding to Nb was observed on coated sample with the lattice parameter of 3.3 Å which is less than the lattice parameter of HfN. The grain size determined using the Scherrer's equations for the HfN coating on Si(100) substrate was 131 Å. The grain size

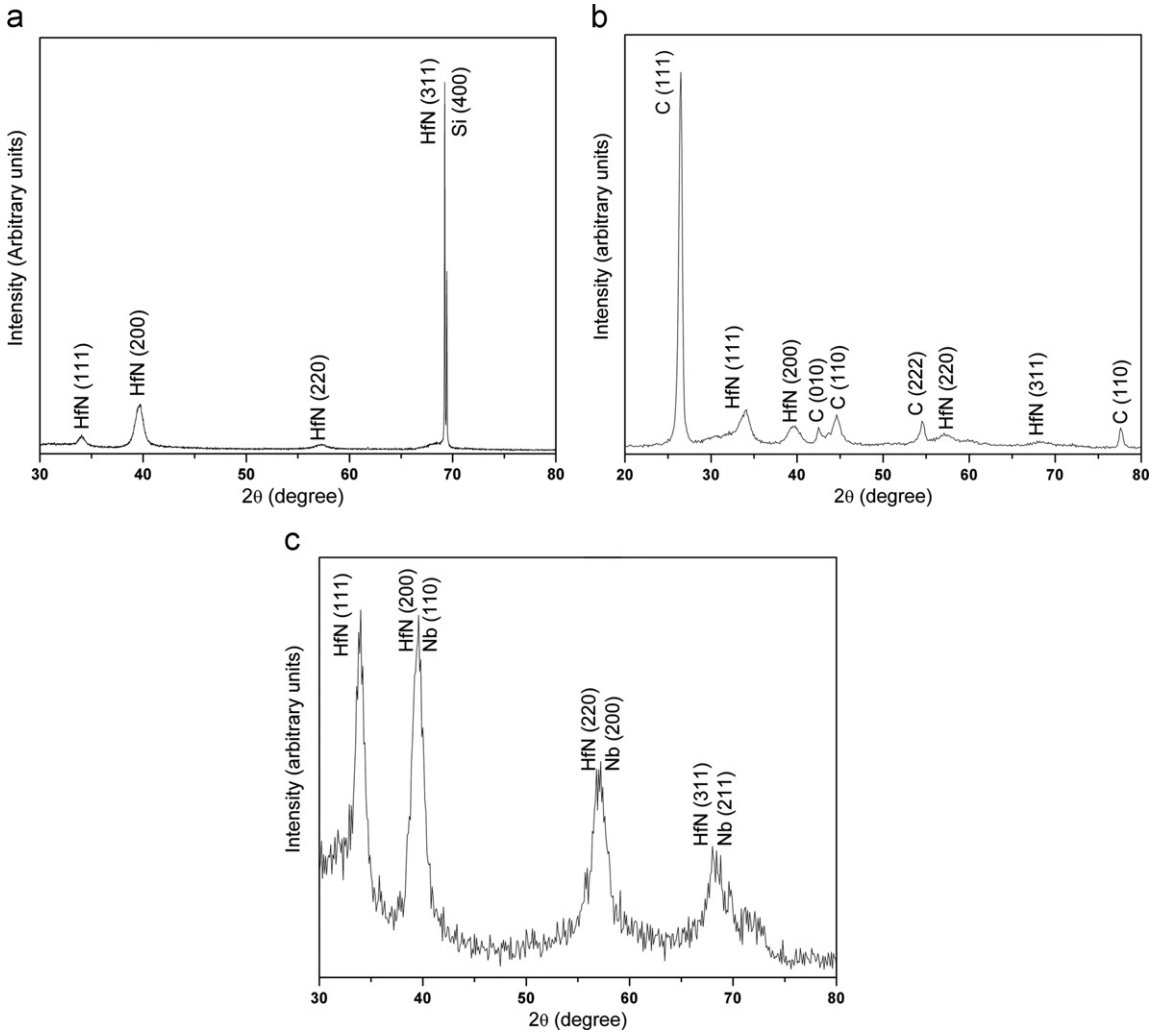

Fig. 2. (a) XRD pattern of HfN coated on Si(100), (b) GIXRD pattern of HfN coated on HD graphite and (c) on niobium.

determined for the HfN coating on HD graphite substrate and niobium were 55.1 Å and 46.4 Å, respectively.

3.2.2. SEM

Fig. 3a and b shows the SEM micrographs and corresponding EDX spectra of HfN deposited on HD graphite and niobium substrates, respectively. The figures show the uniform deposition of coating and the composition as analysed by EDX spectra, for HfN coated on HD graphite showed 96.56 wt% Hf and 3.44 wt% N. The composition of HfN coated on niobium as analysed by EDX showed 96.63 wt% Hf and 3.37 wt% N. In pure HfN, the nitrogen wt% is 7.3% which indicates that the HfN coating obtained has less nitrogen compared to theoretical stoichiometry. Owing to the error in EDX analysis particularly with light elements such as N and O, XPS analysis was carried out which is discussed in Section 3.2.4. Fig. 4a and b shows the surface morphology of nanocrystalline HfN coating on HD graphite and niobium, respectively, at high magnification. The deposited coatings showed the desired

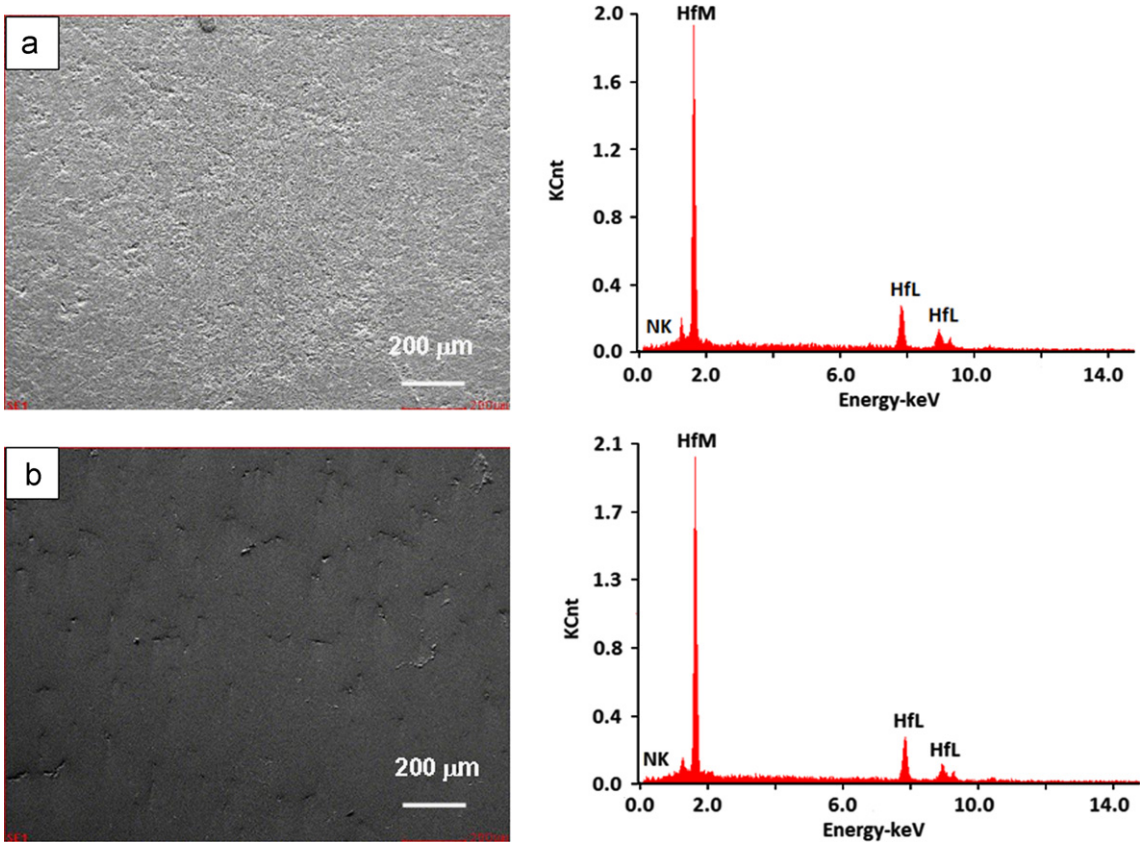

Fig. 3. SEM micrograph and corresponding EDX spectra of HfN deposited on (a) HD graphite and (b) niobium.

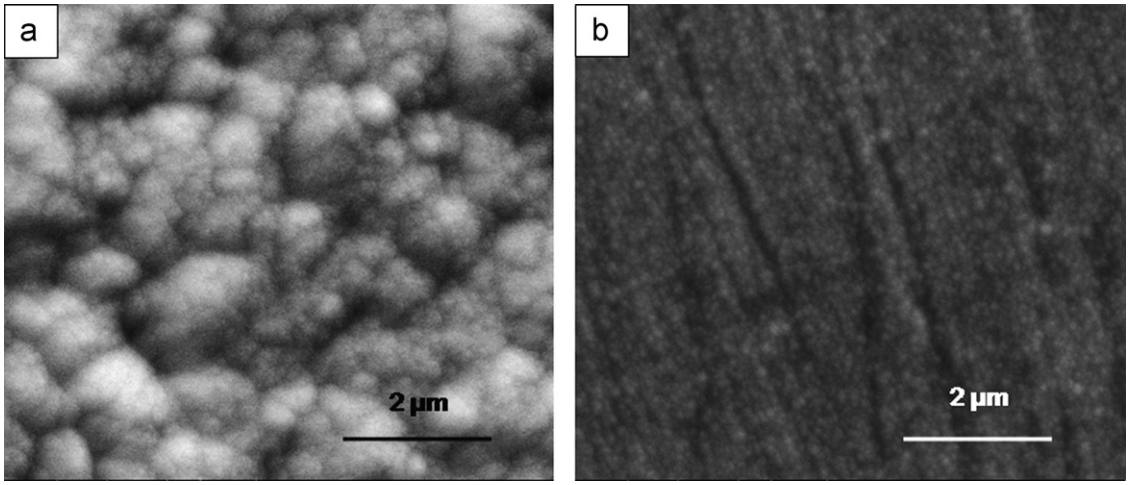

Fig. 4. Surface morphology of HfN coating deposited on (a) HD graphite and (b) niobium.

nanostructured spherical morphology of the coating as shown in the figure. From the surface morphology, it is found that particles are getting agglomerated into clusters. These agglomerated particles are much coarser on HD graphite compared to that on niobium substrate. The particles appear to be much finer on niobium substrate and there is not much agglomeration taking place. The grain size measurement of HfN coating on niobium from XRD was also found to be finer than that on HD graphite.

3.2.3. AFM

The AFM micrographs of HfN coatings on HD graphite and niobium are shown in Fig. 5a and b, respectively. The root mean square surface roughness values obtained using NT-MDT AFM software on high density graphite and niobium were 12.4 and 15.6 nm, respectively. The surface morphology of HfN coatings by AFM was also found to be similar to the SEM micrographs (Fig. 4). The particles are getting agglomerated into clusters on HD graphite compared to that on niobium substrate. The spherical morphology of the nitride particles obtained and agglomeration of particles into clusters (Figs. 4 and 5) on HD graphite could be attributed to the deposition parameters such as substrate temperature, pressure, target power, substrate bias and sputter current influence the growth process, surface diffusion, nucleation with other adatoms and agglomeration of growing particles [13]. The absence of such agglomeration on niobium substrate could indicate the effect of substrate and its roughness on the growth processes.

3.2.4. XPS

The XPS spectra from the HfN coated sample showed Hf, N, O and C peaks. Sputtering was carried out to remove carbon contaminated layer and high resolution spectra were recorded. High resolution XPS spectra (average of 10 scans) of Hf and N obtained from the surface of HfN coated sample are shown in Fig. 6. Perry et al. [21,22] studied the XPS spectra of HfN films of different stoichiometry, prepared by CVD, reactive sputtering and ion plating. The binding energy of N 1s from high resolution spectra is 399.4 eV (Fig. 6). Perry et al. [22] observed that the N 1s peak in HfN_x does not change in binding energy as the nitrogen content is varied. However, the relative height of the Hf 4f 5/2 and Hf 4f 7/2 peaks are reversed in the HfN films relative to Hf metal, due to overlap of N 2s

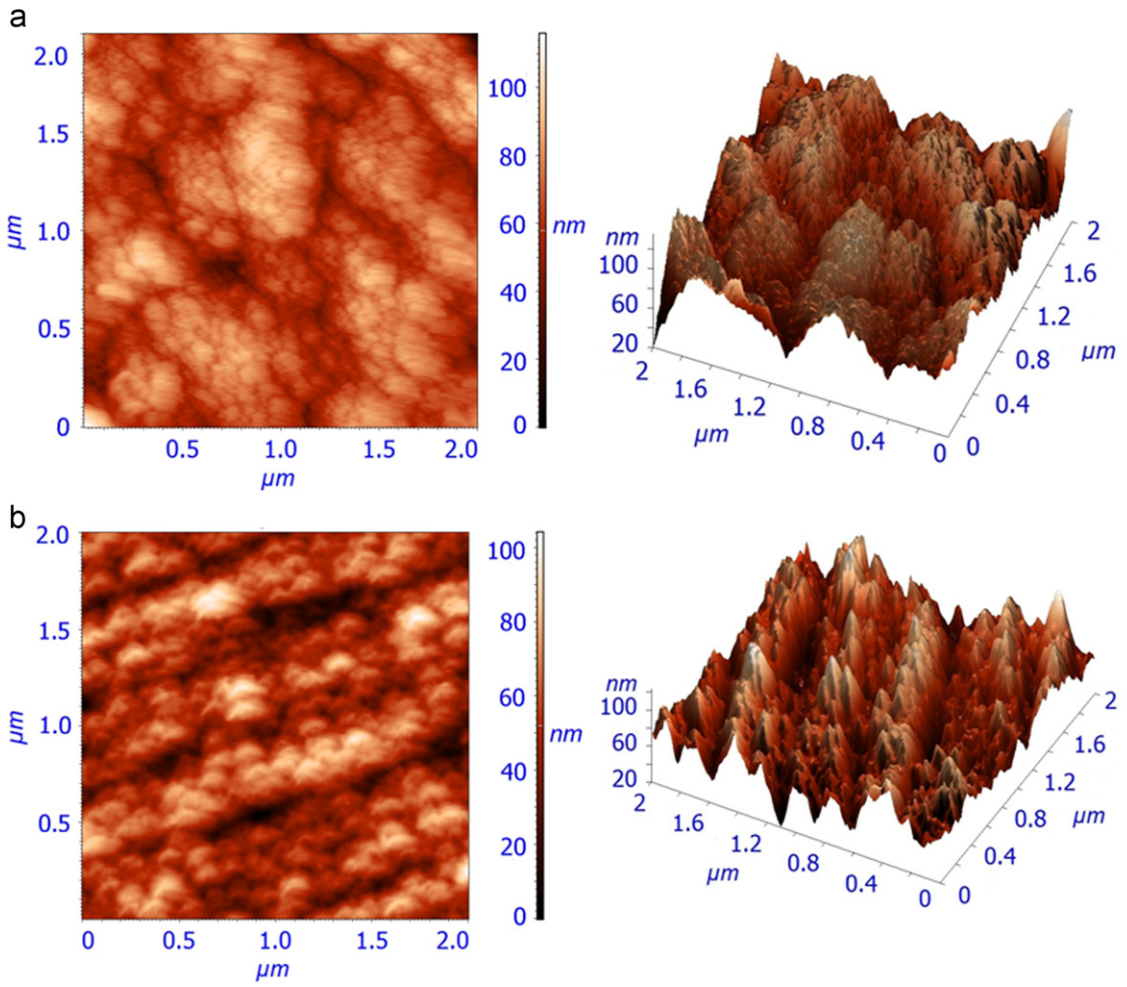

Fig. 5. AFM images of HfN coating on (a) HD graphite substrate and (b) niobium.

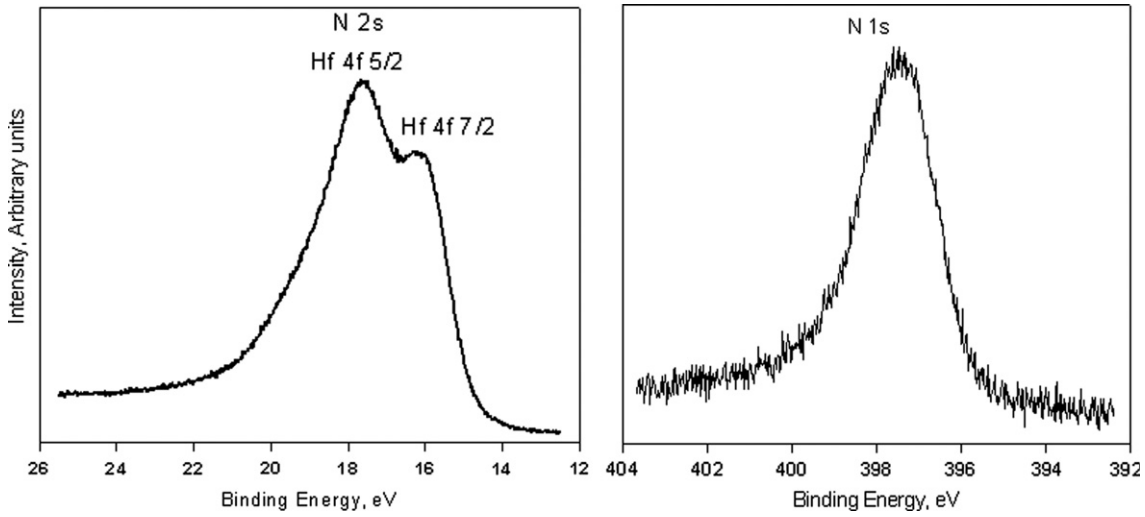

Fig. 6. XPS spectra of the Hf 4f and N 1s bands recorded from coated surface.

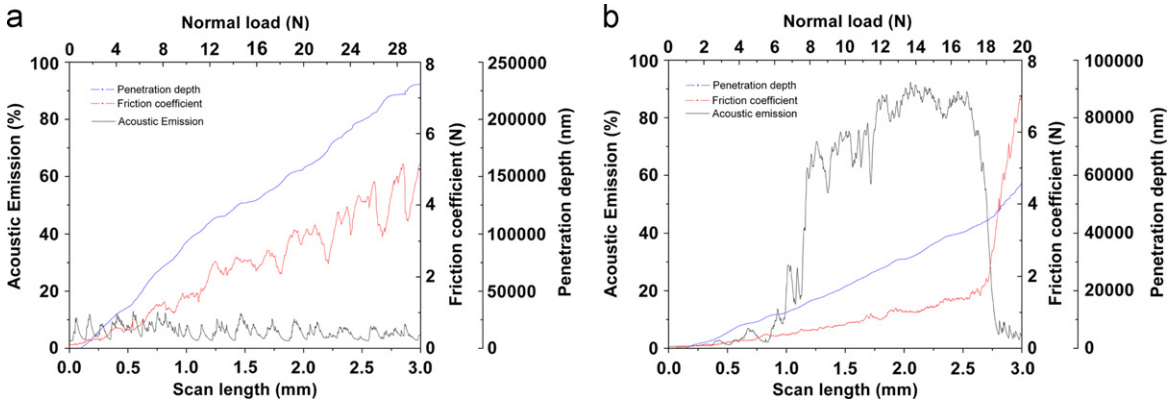

Fig. 7. Progressive load pattern of HfN coating (a) on HD graphite and (b) on Nb sample.

with Hf 4f 5/2 [21]. It is also reported that as nitrogen content increased the intensity of Hf 4f 5/2 appeared to increase relative to Hf 4f 7/2 [22]. As shown in Fig. 6, the peak at 16.2 eV corresponds to Hf 4f 7/2, and the peak at 17.58 eV corresponds to Hf 4f 5/2 and N 2s. In the present study, the Hf 4f 5/2 peak is more intense than the Hf 4f 7/2 which is in good agreement with the XPS spectra reported by Perry et al. [21,22]. In addition, it is reported that Hf 4f 5/2 (16.8–17.3 eV) and Hf 4f 7/2 (15.2–15.7 eV) core levels are moved steadily to lower binding energies as nitrogen is decreased [22]. The higher binding energies of Hf 4f 5/2 and Hf 4f 7/2 also indicate that nitrogen content in the film has not decreased. GIXRD pattern also did not show any evidence for the presence of metallic Hf. Therefore, it can be inferred from these results that the coating consists of HfN.

3.3. Microscratch test

A very simple, quick and easy tape test, to give qualitative information about the adhesion of the coating, was conducted on HfN coated samples and the results indicated poor adhesion of the coating on HD graphite. All the coating was taken off from the graphite substrate while no residue on the scotch tape was found from the Nb substrate by scotch tape test, indicating good adhesion of the coating on Nb substrate. From the results, it is clear that HfN coating on Nb has good adhesion compared to that on HD graphite. The scratch test is the most widely used test to gain qualitative information on adhesion of the ceramic thin film coatings to the substrate and failure modes. Fig. 7a and b shows the frictional coefficient, acoustic emission signal and penetration depth measured and recorded during the progressive load scratch test process for HfN on HD graphite and niobium substrate, respectively. From the scratch test performed, many critical loads (C_L) can be defined according to the shape of the pattern and the visual aspect of the scratch.

As observed from the tape test, the adhesion of the HfN coating on HD graphite was poor and no critical load can be determined even before 1 N. Earlier studies on TiN, ZrN and Ti–Si–N coatings also showed poor coating

adhesion on HD graphite [23]. The poor coating adhesion on HD graphite may be due to the low sputtering power and deposition temperature. In order to get improved coating adhesion, HD graphite samples should be prepared with desired roughness and the parameters of deposition need to be optimised. From the niobium sample scratch test, the results are more interesting. Four critical loads were determined from the acoustic emission data. The first critical load around 3 N is corresponding to the first damage. These damages are minor cracks that appear as light blue in colour as shown in the optical micrograph of Fig. 8a. The second critical load around 4 N corresponds to big acoustic emission due to bigger cracks as shown in Fig. 8b. The third critical load recorded at 7 N, corresponds to a recovery spallation at the border of the scratch track as shown in Fig. 8c. The last critical load around 19 N corresponds to the substrate being exposed as shown in Fig. 8d. A rapid increase of the friction coefficient is noticed at 19 N critical load (Fig. 7b). This is mainly due to the contribution of the substrate at this critical load. The scratch test was repeated at three different locations and similar results were obtained.

Fig. 9a shows the SEM micrograph of the scratch track on HD graphite and on Nb sample. The SEM micrograph from HD graphite shows adhesive failure of the coating at lower load with gross spallation. For the Nb sample the events taking place at critical loads L_{C1} and L_{C4} are interesting. The events occurring at these critical loads

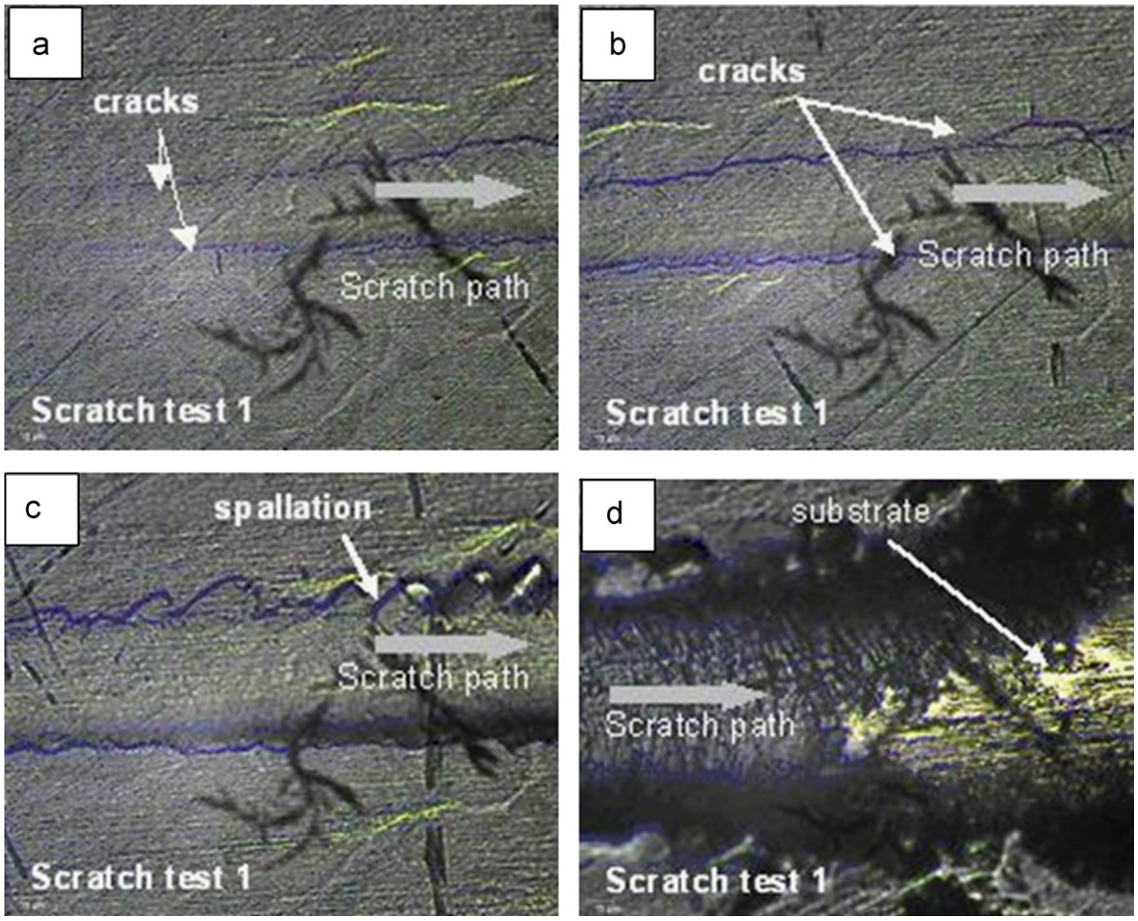

Fig. 8. Optical micrograph of the scratch tested HfN coated niobium sample at four different critical loads namely L_{C1}, L_{C2}, L_{C3} and L_{C4}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

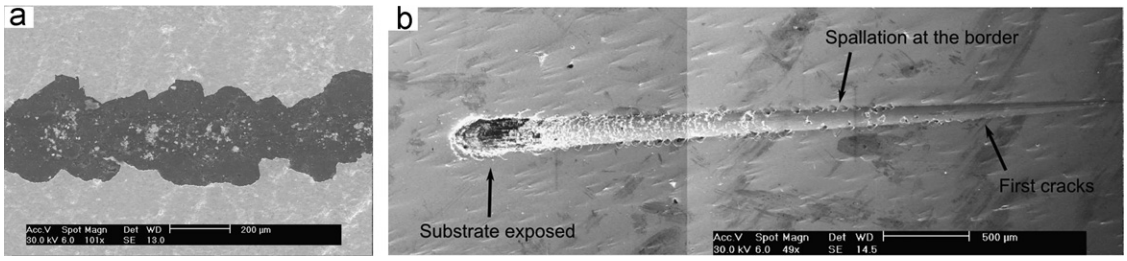

Fig. 9. SEM micrograph of the scratch track (a) on HD graphite and (b) on Nb sample.

are shown in Fig. 9b, L_{C1} that is around 3 N belongs to cohesive failure within the coating, whereas L_{C4} around 19 N belongs to adhesive failure, where the substrate is exposed. Even though the lattice parameter of Nb (3.3 Å) and HfN (4.52 Å) are different, the coating adhered well to the Nb substrate. Moreover the epitaxial condition for HfN with Nb as observed in Fig. 2c, could have been responsible for the improved adhesion of the coating on Nb and absence of such epitaxial condition for graphite (Fig. 2b) resulted in poor adhesion. Sproul [7] has reported that the critical load for magnetron sputtered HfN coating on tool steel varied linearly with thickness and the adhesion of the coating was excellent. However, further improvement in adhesion of HfN coating on Nb is necessary for longer life of the coating. It is reported that HfN layers showed a marked increase in adhesion when deposited at higher substrate temperature [24]. They also reported that the scratch showed cracking and flaking, and in the track, coating appears to fail in ductile manner still remaining bonded to the substrate. Fig. 8b also shows similar kind of failure of the coating.

3.4. Calculation of thermal stress

Thermal stress generates when the film was deposited above room temperature and upon cooling from the deposition temperature to room temperature. In general, the difference in the thermal expansion coefficients of the substrate and the film causes build up of thermal stress. In the present work, the thermal stress values calculated using Eq. (1) for HfN coating on HD graphite and niobium substrates are (−)0.4146 GPa (highly compressive) and (+)0.0763 GPa (tensile), respectively. Compressive stress builds up when heavy ions or energetic particles strike the coating in an accelerating manner, packing the atoms more tightly during deposition. On the other hand, tensile stress is generated due to the presence of microvoids in the coating, because of the attractive interaction of atoms across the voids. Hence, the compressive stress is responsible for compact coating and tensile stress for porosity in the coating.

Therefore, HfN coating deposited on HD graphite substrate was a compact film due to compressive stress but due to the poor properties of substrate, the adhesion was not good between the coating and substrate which was observed in the present study. On the other hand, HfN coating deposited on niobium substrate was a porous film due to tensile stress but the stress value was near to zero and, the adhesion between the HfN coating and Nb substrate was good as observed in the present study.

4. Conclusions

In the present study, HD graphite and niobium substrates have been coated with HfN using reactive magnetron sputtering process. The following are the important conclusions from the work carried out.

1. Optimisation of parameters were carried out on Si(100) to obtain nanocrystalline HfN of thickness 3 μm. XRD pattern of the coatings indicated the presence of HfN on HD graphite and niobium substrates with a FCC structure. The grain size of the coatings was found to be 55.1 Å and 46.4 Å on HD graphite and niobium substrate, respectively.
2. The surface morphology of coatings studied by atomic force microscope and scanning electron microscope indicated nanoparticles getting agglomerated into clusters on HD graphite and has a surface roughness of 12.4 nm for HfN coated on HD graphite and 15.6 nm for HfN coated on niobium.
3. XPS analysis with more intense Hf 4f 5/2 peak relative to Hf 4f 7/2 indicates that the coating consists of HfN and nitrogen content in the film has not decreased.
4. The adhesion on the HD graphite substrate was poor probably due to the low sputtering power and deposition temperature. For the niobium sample, two interesting critical loads were determined around 3 N and 19 N corresponding to cohesive failure and adhesive failure, respectively. The adhesion of the coating needs to be optimised by optimising the deposition parameters.
5. The thermal stress values obtained for HfN coating on HD graphite and niobium substrates are (−)0.4146 GPa and (+)0.0763 GPa, respectively, which means highly compressive stress with HD graphite substrate and tensile stress with Nb substrate.

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