Microstructure and mechanical properties of Ti–Si–N coatings

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A series of Ti–Si–N coatings with 0 < Si < 20 at.% were synthesized by inductively coupled plasma assisted vapor deposition. Coating composition, structure, atomic short-range order, and mechanical response were characterized by Rutherford backscattering spectrometry, transmission electron microscopy, x-ray absorption near-edge structure spectroscopy, and instrumented nanoindentation. These experiments show that the present series of Ti–Si–N coatings consists of a mixture of nanocrystalline titanium nitride (TiN) and amorphous silicon nitride (a-Si:N); i.e., they are TiN/a-Si:N ceramic/ceramic nanocomposites. The hardness of the present series of coatings was found to be less than 32 GPa and to vary smoothly with the Si composition.

I. INTRODUCTION

Nanostructured ceramic coatings are being investigated for a number of macro- and microscale surface engineering applications.^{1–3} The mechanical properties and tribological characteristics of ceramic/ceramic nanocomposite coatings have been observed to depend systematically on coating composition, offering the potential of designing coatings for specific applications.⁴ Understanding the dependence of the mechanical response on the nanoscale structure goes to the heart of coating design. Despite much current activity in the synthesis and mechanical characterization of nanostructured ceramic coatings, conflicting results reported in the literature have yet to be resolved. In the titanium carbide/amorphous hydrocarbon (TiC/a-C:H) nanocomposite coating system, both the presence⁵ and absence⁶ of a pronounced hardness peak around 40 at.% Ti have been reported. In the Ti-Si-N coating system, coating hardness ranging from 40 to 80 GPa has been reported in the composition range of 2-20 at.% Si,^{7,8} significantly exceeding the hardness of crystalline B1-TiN.9 Whether all ceramic nanocomposites exhibit such superstrengthening is of significant interest, and critical experimental evidence needed to verify these findings should include detailed structural and mechanical characterization on the same set of specimens.

This paper reports the results of such an experimental study on a series of Ti–Si–N coatings with 0–20 at.% Si. Coating composition, structure, and atomic short-range order surrounding Ti and Si atoms were probed by combining Rutherford backscattering spectrometry (RBS),

transmission electron microscopy (TEM), and x-ray absorption near-edge structure (XANES) spectroscopy. Coating mechanical response was measured by instrumented nanoindentation. Our results show that the present series of Ti–Si–N coatings consists of a nanometer-scale mixture of crystalline titanium nitride (TiN) and amorphous silicon nitride (a-Si:N). The hardness of the present series of Ti– Si–N coatings was found to be less than 32 GPa and to vary smoothly with the Si composition.

II. EXPERIMENTAL

Deposition of Ti-Si-N coatings was carried out in a hybrid chemical vapor deposition (CVD)/physical vapor deposition (PVD) tool. This tool combines a 13.56-MHz inductively coupled plasma (ICP) with four balanced magnetron cathodes.¹⁰ The two facing Ti (99.99%) cathodes were operated at the same current, as were the two facing Si (99.99%) cathodes. Si(100) wafers of 2-in. diameter were used as substrates. The Si substrate surface was etched in a pure Ar ICP at a constant bias voltage of -100 V, followed by immediate deposition of a Ti-Si-N layer in an Ar (99.999%)/N2 (99.999%) mixture. During deposition, the substrates were rotated continuously at the center of the deposition zone, and subjected to a constant bias voltage of -50 V. Ar and N₂ gas input flow rates were fixed at 10.0/1.1, and the total pressure was kept at approximately 1.8 mtorr during all depositions. By fixing the Ti cathode current at 1.0 A and systematically raising the Si cathode current, Ti-Si-N coatings were deposited with increasing Si composition.

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No intentional substrate cooling or heating was applied during deposition. Separate substrate temperature measurements made by attaching type K thermocouples to a sacrificial substrate showed that the substrate temperature was approximately 250 °C during deposition. A heteroepitaxial B1-TiN/Si(111) specimen¹¹ and an a-Si:N/ Si(100) specimen were also prepared for comparison.

Coating composition was measured by RBS. TEM was performed using a JEOL JEM2010 (Tokyo, Japan) instrument operated at 200 kV. XANES spectroscopy was performed at the Double Crystal Monochromator (DCM) beamline of the synchrotron facility at the Louisiana State University Center for Advanced Microstructures and Devices (LSU CAMD). Both Ti and Si K-edge spectra of the Ti–Si–N specimens were recorded in the total electron yield mode. Photon energy selection was provided by a Ge(220) and an InSb(111) double-crystal monochromator at the Ti K-edge and Si K-edge, respectively. Two to five spectra were acquired consecutively from each specimen and averaged. Further details on RBS, TEM, and XANES techniques have been presented elsewhere.^{12,13}

Instrumented nanoindentation was carried out on a Hysitron triboscope interfaced to a Digital Instrument Dimension 3100 atomic force microscope (AFM). A Berkovich diamond indenter was used. The instrument load frame compliance and indenter tip area function were calibrated with a vendor-supplied fused silica specimen assuming a contact depth (h_c) independent elastic modulus. The calibration load range was $100-13000 \mu N$, corresponding to an indenter contact depth range of $8 < h_c < 220$ nm. Indentations on Ti–Si–N/Si specimens were carried out at multiple loads ranging from 13000 to 200 μ N, with multiple indents performed at each load. The Oliver/Pharr analysis procedure was followed to extract values of the indentation modulus, $E_{ind} = E/(1 - E)$ ν^2), where E and ν are respectively Young's modulus and Poisson's ratio, and the hardness, H, from the experimental load versus displacement curves.¹⁴ Coating surface profiles were examined in the contact AFM mode with the Berkovich indenter tip, and the average roughness of the as-deposited coatings was determined to be approximately 2 nm, independent of the Si composition.

III. RESULTS AND DISCUSSION

RBS spectra showed compositional uniformity as a function of depth within the Ti–Si–N layer and impurity levels below the detection limit of approximately 1 at.%. The N composition ranged between 52 and 56 at.%. Figure 1 shows the measured Ti and Si compositions as a function of the Si cathode current. The average Si composition increases monotonically from <1 to approximately 20 at.% with increasing Si cathode current from <0.1 to 0.3 A. The composition of the a-Si:N specimen was measured at 55 \pm 5 at.% N, which is close to the



FIG. 1. Coating composition measurements by RBS: Si and Ti compositions of a series of Ti–Si–N coatings in atomic percent as a function of the Si cathode current.

value of 57 at.% of pure Si_3N_4 . The density of the a-Si:N coating is approximately 3.3 g/cm³ based on RBS and crosssectional TEM measurements of coating thickness. Thickness for the present series of Ti–Si–N coatings ranged from 110 to 130 nm, according to cross-sectional TEM.

Cross-sectional selected area electron diffraction patterns (SADPs) were taken from the Ti-Si-N coatings with Si compositions ranging from 0.3 to 19.3 at.%. All crystalline diffraction signatures from the coatings can be indexed to a cubic structure with lattice parameters of 4.22-4.23 Å, close to the 4.24 Å or bulk B1-TiN.¹⁵ Figures 2(a) and 2(b) show cross-sectional highresolution images of the coatings. At 0.3 at.% Si [Fig. 2(a)], the coating consists of columnar-like nanocrystalline grains, approximately 5 nm in width and >10 nm in height. Individual grains appear to be dislocation free, and most grain boundaries appear to be atomically sharp. At 19.3 at.% Si [Fig. 2(b)], the coating consists of narrower columnar-like nanocrystalline grains, 2–5 nm in width and >10 nm in height. Amorphous regions now separate these nanocrystalline grains. Again, individual grains appear to be dislocation free, and the nanocrystalline/amorphous interfaces appear to be atomically sharp. A plan-view high-resolution micrograph of the 19.3 at.% Si coating is shown in Fig. 2(c), showing 2–5-nm grains separated by amorphous regions several nanometers in thickness. Dislocations are visible at boundaries between individual nanocrystalline grains due to misorientation between grains. All diffraction and imaging results show that the only crystalline phase present within this series of Ti-Si-N coatings is consistent with B1-TiN and that any other phase present within these coatings is amorphous in structure.

Figures 3(a) and 3(b) show, respectively, Ti and Si K-edge XANES spectra of a number of the Ti–Si–N coatings. Pre-edge backgrounds have been removed, and



FIG. 2. High-resolution TEM images of the Ti–Si–N coatings: (a) cross-sectional image of the coating with 0.3 at.% Si; (b) cross-sectional image of the coating with 19.3 at.% Si; (c) plan-view image of the coating with 19.3 at.% Si.



FIG. 3. XANES spectra: (a) Ti K-edge spectra obtained from the Ti–Si–N coatings and from the B1-TiN specimen; (b) Si K-edge spectra from the Ti–Si–N coatings and from the a-Si:N specimen.

all spectra have been normalized to unit edge jump. The Ti K-edge and Si K-edge spectra of the B1-TiN/Si(111) and the a-Si:N/Si(100) specimens are also shown in Figs. 3(a) and 3(b), respectively. At all Si compositions, the Ti K-edge XANES oscillations exhibit a one-to-one correspondence with those of the B1-TiN specimen, indicating that the short-range order surrounding the Ti atoms within the Ti-Si-N coatings is predominantly B1-TiN like. As the Si composition increases, some amplitude decrease and broadening of the XANES oscillations are observed, suggesting somewhat increased disorder at the Si composition increases. The Ti K-edge XANES spectra are consistent with Ti atoms being incorporated into the Ti-Si-N coatings predominantly as B1-TiN and are also consistent with the TEM results showing a smaller TiN column width at larger Si concentrations. The Si K-edge XANES spectra display an overall resemblance to that of a-Si:N, possessing a pronounced white line around 1846 eV and one additional broad peak around 1860 eV. Appreciable differences do exist in the edge region of the coating spectra as compared to

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the a-Si:N specimen. The transition threshold starts at approximately 1838 eV for the Ti–Si–N coatings compared to approximately 1841 eV for the a-Si:N specimen, and it becomes more pronounced as the overall Si composition decreases. The peak of the white line also shifts gradually from 1845.3 to 1846.6 eV as the overall Si concentration decreases. The overall spectral resemblance to a-Si:N suggests that Si atoms incorporate into the Ti–Si–N coatings in an a-Si:N like environment, while differences in the edge and white line regions as compared to that of a-Si:N suggest that some Ti atoms are present within the first few coordination shells of Si, in addition to Si and N atoms.

Within a nanometer-scale mixture of B1-TiN and a-Si:N, the proximity of Si and Ti atoms can arise in two different ways. Some Ti atoms can be dissolved within the a-Si:N phase, or Ti atoms may preferentially bond to Si atoms across TiN/a-Si:N interfaces. The dissolution limit of Ti atoms within the a-Si:N phase under the present deposition conditions has not been determined. In the latter case, with decreasing Si composition, the fraction of Ti-Si bonds would increase because the surface to volume ratio of the a-Si:N phase increases. This is consistent with the observed gradual changes seen in the Si K-edge spectra as the overall Si composition decreases. Taken together, the Ti and Si K-edge XANES spectra of these Ti-Si-N coatings corroborate the TEM evidence, which indicates that they consist of a nanometerscale mixture of a B1-TiN phase and an a-Si:N phase; i.e., they are TiN/a-Si:N nanocomposites. The dispersion of nanocolumnar B1-TiN grains within an a-Si:N matrix is reminiscent of metallurgical rod eutectic structures, the formation of which may involve partitioning of Ti and Si atoms during growth.¹⁶

Figure 4(a) shows hardness H versus indenter contact depth $h_{\rm c}$ as measured by nanoindentation for a Ti–Si–N coating with 9.5 at.% Si. The apparent hardness increases as h_c decreases, reaching a maximum between 13 nm < h_c < 18 nm, and decreases at smaller contact depths because indenter-specimen contact becomes elastic at smaller load levels. Values of E_{ind} and H obtained from indentations with $h_c < 18$ nm (approximately 15% of coating thickness), excluding those corresponding to elastic contact, were taken as being representative of the Ti-Si-N coating. A set of indentation data such as that shown in Fig. 4(a) was collected for each Ti-Si-N coating, and the same procedure was followed to extract coating modulus and hardness. Figure 4(b) displays the E_{ind} and H values for the present series of Ti-Si-N coatings versus the Si composition. H decreases with increasing Si composition and stays below 32 GPa over the entire composition range of 0–20 at.% Si. Hardness of the B1-TiN specimen obtained following the same procedure is approximately 22 GPa. The hardness of the present series of Ti-Si-N coatings is thus higher than that of the B1-TiN specimen but lower than the previously



FIG. 4. Instrumented nanoindentation: (a) apparent hardness of a Ti– Si–N coating with 9.5 at.% Si versus indenter contact depth; (b) hardness and indentation modulus of the Ti–Si–N coatings as a function of the Si composition; (c) load versus displacement curves for the Ti– Si–N coating with 6.4 at.% Si and for the B1-TiN specimen.

reported hardness values of 40–80 GPa.^{7,8} Figure 4(c) shows load versus displacement curves determined for a Ti–Si–N coating with 6.4 at.% Si. Load versus displacement curves for the B1-TiN specimen are also shown for comparison. At 1000- μ N maximum load, the loading curve



and the depth at peak load are not significantly different for the Ti–Si–N and B1-TiN specimens. The initial unloading stiffness for the Ti–Si–N specimen is less than that for B1-TiN, indicating a lower E_{ind} than B1-TiN. Figure 4(c) does indicate the presence of increased elastic recovery for the Ti–Si–N specimen as compared to B1-TiN.

The morphology of the present series of Ti-Si-N coatings, nanocolumnar TiN grains along the growth direction interdispersed within an a-Si:N matrix, is different from that previously reported, with equiaxed nanocrystalline TiN grains embedded within an amorphous matrix.^{7,8} Whether this morphological difference is responsible for the difference in observed mechanical response awaits further clarification. Complete segregation of B1-TiN and a-Si:N phases within the nanocomposite implies little dissolution of Si and Ti atoms within the TiN and a-Si:N phases, respectively. While the present TEM and XANES evidence suggests that few Si atoms are incorporated within the TiN phase, some Ti atoms may be dissolved within the a-Si:N phase. Whether the degree of phase separation would significantly influence the mechanical properties of two-phase ceramic nanocomposites deserves further investigation. It has been suggested that percolation of the a-Si:N phase is responsible for the reported enhancement of TiN/ a-Si:N mechanical properties.¹⁷ If one takes the density of the TiN and a-Si:N phases within the Ti-Si-N coatings to be respectively 5.4 and 3.3 g/cm³, the a-Si:N volume fraction increases approximately linearly with the Si composition, reaching approximately 0.45 at approximately 20 at.% Si. The percolation threshold for a-Si:N depends on the dimensionality of the microstructure, i.e., on the nanocrystalline TiN grain morphology, which remains to be determined.

VI. CONCLUSION

In summary, we have performed a detailed examination of the microstructure and mechanical properties of a series of Ti–Si–N coatings with 0–20 at.% Si. Structure and atomic short-range order studies show that these Ti–Si–N coatings are TiN/a-Si:N nanocomposites, with nanocolumnar TiN grains aligned in the growth direction interdispersed within an a-Si:N matrix. Instrumented nanoindentation measurements show that their mechanical properties vary smoothly with the Si composition. The measured hardness is below 32 GPa within the entire composition range.

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