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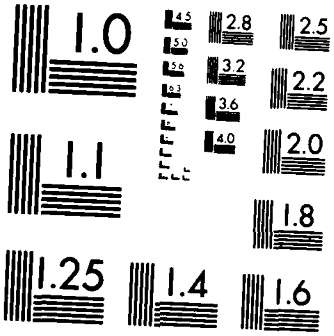

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VACUUM PYROLYSIS COATINGS FOR CERAMIC ALLOYS

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The effectiveness of vacuum pyrolysis coatings in improving oxidation resistance and mechanical properties of sintered SIALON substrates was investigated. The substrates were prepared at Martin Marietta Laboratories and the vacuum pyrolysis was performed at NADC by reacting nitrogen gas and hexamethyldisilizane on substrates heated to temperatures between 590°C and 710°C. No coating was produced at the low temperature.

Characterization and mechanical testing of the substrates was performed at Martin Marietta Laboratories. The high resolution SEM mode of the STEM was

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used to determine coating thickness and morphology. Coatings produced were 0.25-, 0.5-, 0.7-, and 1- μm thick. Surface analytical Auger/XPS techniques were used to identify chemical components of the film and to reconfirm thickness. The coatings contain silicon, carbon, nitrogen, and oxygen. The carbon probably exists in the coating in two forms, silicon carbide and graphite. The oxygen and nitrogen probably are bound to the silicon either as SiO_2 and Si_3N_4 or as Si_2N_2O. The large amount of carbon in the coating indicates that SiC and graphite are the major constituents of the film and SiO_2 and Si_3N_4 are only minor constituents. X-ray diffraction of the coatings revealed no peaks other than those from the substrate, indicating that the coatings may be amorphous.

Biaxial flexure testing was performed on coated and uncoated SIALON on samples at two temperatures. At room temperature, the mean flexure strength for the 0.25- μm-coated samples and their controls was 31.6 ksi and 32.4 ksi respectively, both with a standard deviation of 3 ksi. For 1- μm thick coatings, the mean room temperature strength for coated samples and their controls was 37. ksi and 36.0 ksi respectively, both with a standard deviation of 8 ksi. At 1400°C, with 1 μm thick coatings, the coated samples and their controls showed a mean flexure strength of 33.7 ksi and 34.2 ksi, respectively, both with a standard deviation of 3 ksi. Thus, there was no significant improvement or degradation in flexure strength as a result of these coatings for films as thick as 1 μm.

In samples exposed to 1400°C in air, both coated and uncoated samples show a new X-ray diffraction peak at $d = 4.07$ Å, which corresponds to the 101 peak for low, or α, cristobalite (a form of SiO_2). The relative intensity of this peak is higher for the uncoated samples than the coated samples by a factor of 1.7, indicating that the coatings do impart some oxidation resistance.

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I. INTRODUCTION

Refractory coatings, deposited by vacuum pyrolysis onto ceramic substrates, were investigated to assess their ability to protect the substrates in high temperature, high performance applications. The research program was designed to characterize the coatings and determine their effectiveness in this role. In ceramics, the practical strength is limited greatly by surface flaws.(1) Vacuum pyrolysis coatings have been shown to penetrate into grain boundaries and surface pores,(2) thereby reducing surface flaws and potentially increasing the mechanical strength of the substrates.

Coatings were produced on sintered SIALON substrates under various deposition parameters and using 2 different substrate surface preparations. The coatings were examined by optical and high resolution scanning electron microscopy (SEM) to determine their morphology, thickness, and adherence. Surface analytical Auger/XPS techniques were used to identify the chemical components of the film and film thickness. Biaxial flexure tests of coated and uncoated SIALON samples were performed at room temperature and 1400°C to determine the ability of the coating to fill surface defects and thus increase strength. X-ray diffraction and weight measurements were performed on coated and uncoated samples both prior to and after oxidation in stagnant air at 1400°C to determine the oxidation resistance of the coatings.

II. SUBSTRATE PREPARATION

A. MATERIALS

Samples were prepared from GTE SN402 amorphous Si_3N_4 (containing less than 1 w/o oxygen and less than 0.001 w/o Ca), Alpha Ventron Al_2O_3 (99.99%), and Atomergic Chemetal AlN (99.9%). The SIALON composition used was Si_3N_4 - 78w/o, Al_2O_3 - 14.5w/o, AlN - 7.5w/o. Ultra-high purity nitrogen was used for the sintering overpressure.

B. PROCESSING

The Si_3N_4 powders were first sieved through a 100-mesh screen to remove acicular α-phase crystals. The sieved Si_3N_4 powder was then combined with the Al_2O_3 and AlN powders and absolute ethanol to form a slurry and placed in an alumina ball mill for 1 hour. The powder was separated from the ethanol with a Buchner funnel, dried in a vacuum oven, and cold-pressed in a die at 6 kpsi to form pellets. The pellets were cold isostatically pressed at 40 kpsi, which results in a green density of about 1.35 g/cm^3, and then sintered under a N_2 overpressure.

The equipment used in the sintering studies is shown schematically in Fig. 1. Briefly, it consists of a 15-in.-diameter pressure chamber made of 3/4-in. stainless steel. The chamber contains feedthroughs for providing r.f. induction heating from a Lepel 200-kW unit, thermocouple leads, and viewing ports for making pyrometer measurements.

The sintering process involved two steps. A pellet was placed in a graphite crucible , packed in powder of similar composition, and presintered at 1650°C in the induction furnace under a nitrogen overpressure

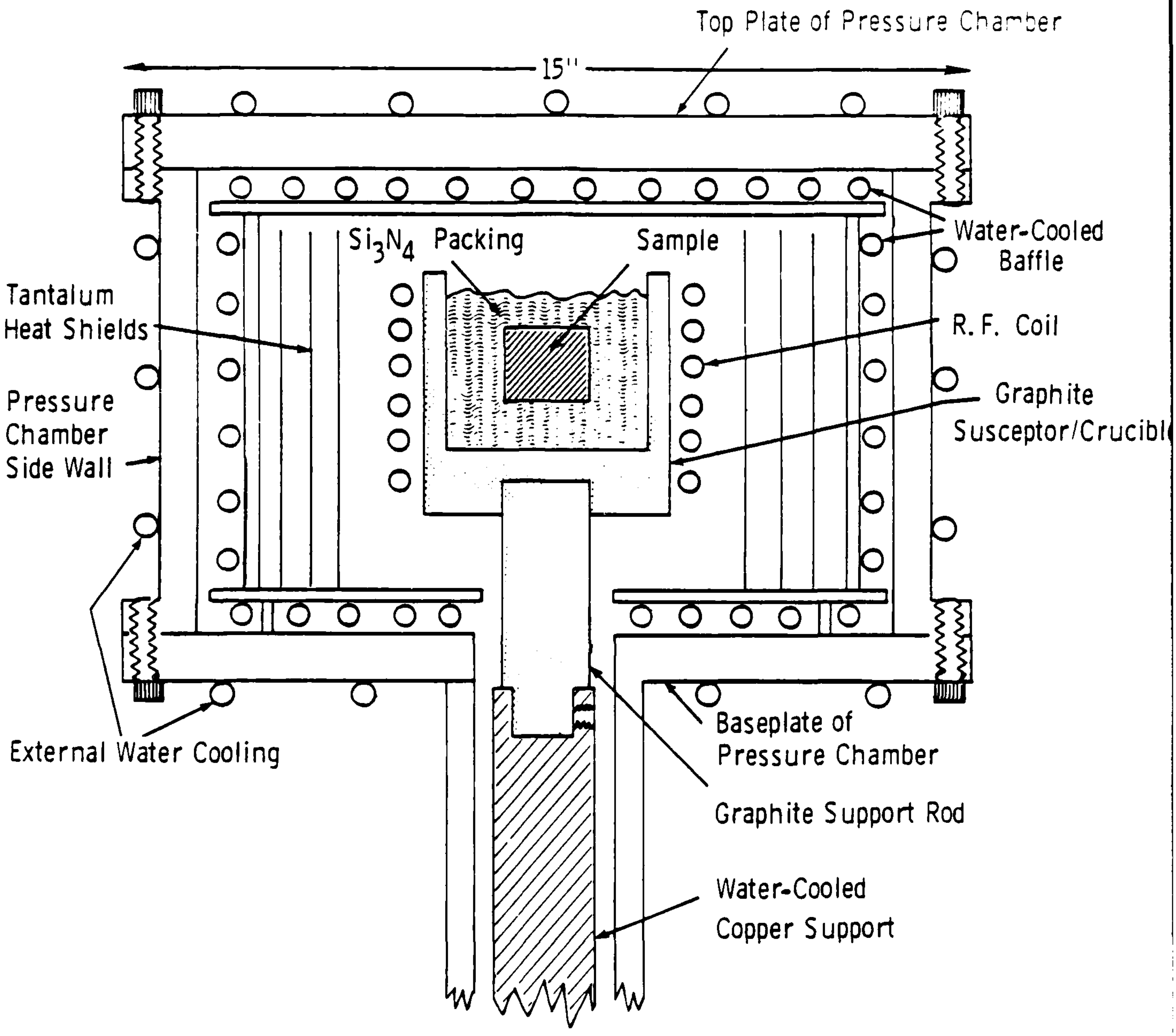

Figure 1. Internal structure of sintering chamber.

of 10 atm. Results of previous studies at Martin Marietta Laboratories showed that the packing powder and nitrogen overpressure improved sintering by reducing weight loss due to decomposition of the constituents in the presintering and sintering stages.(3) After presintering for 15 min, the specimen was removed and its weight and dimensions recorded. At the end of the second sintering step, performed by reheating to 1900°C under an N_2 overpressure of 2 atm for 15 min, the weight and dimensions were measured again and recorded.

The sintered samples were then cut with a diamond saw, ground to a thickness of approximately 1 mm, and polished. The polishing sequence generally was as follows: 20 μm grit, then 8 μm grit SiC, followed by polishing with Nalcoag 1030 (a colloidal silica polishing agent). In order to test the effect of different surface preparations on the adherence of the vacuum pyrolysis coating, a few samples were polished with the SiC grits alone. Since good adhesion was found in both cases, we chose the smoother surface finish to prepare the remaining specimens. After preparation the samples were sent to NADC where they were ultrasonically cleaned and then coated. The ultrasonic cleaning was found to improve coating adherence.

III. CHARACTERIZATION AND TESTING

A. MICROGRAPHY

Coating thickness, adherence, and morphology were studied by optical and scanning electron microscopy. Six batches of samples were coated at NADC. The first batch (six samples) coated at 690°C had a coating that was 0.25 µm thick and gained an average 0.45 mg per sample due to the weight of the coating. Although the coating was uniformly dispersed and adherent, its slight roughness indicated t it grew by island growth (Fig. 2a). Optical examination of a cr -section indicated good penetration of the coating into the pores (Fig

The second batch (five samples, 710°C) had a coating about 0.5 µm thick and an average weight gain of 0.94 mg. The third batch (5 samples, 590°C) did not form a coating and did not gain weight, probably because of the lower treatment temperature. The fourth batch (five samples, 705°C) had a coating thickness of 0.7 µm (Fig. 3a) and an average weight gain of 1.26 mg. The fifth batch (six samples, 705°C) showed a coating thickness of 1 µm (Fig. 3b) and an average weight gain of 1.83 mg (with the exception of 3 porous samples that showed an average weight gain of 4.57 mg).

None of the samples showed cracking or spalling of the coatings when they were initially examined. However, after several weeks, the samples with the 0.7-µm coating showed some cracking and spalling near the edges. This result may indicate residual stresses in the thicker coating that cause slow crack growth.(4) After mechanical tests, the 1-µm

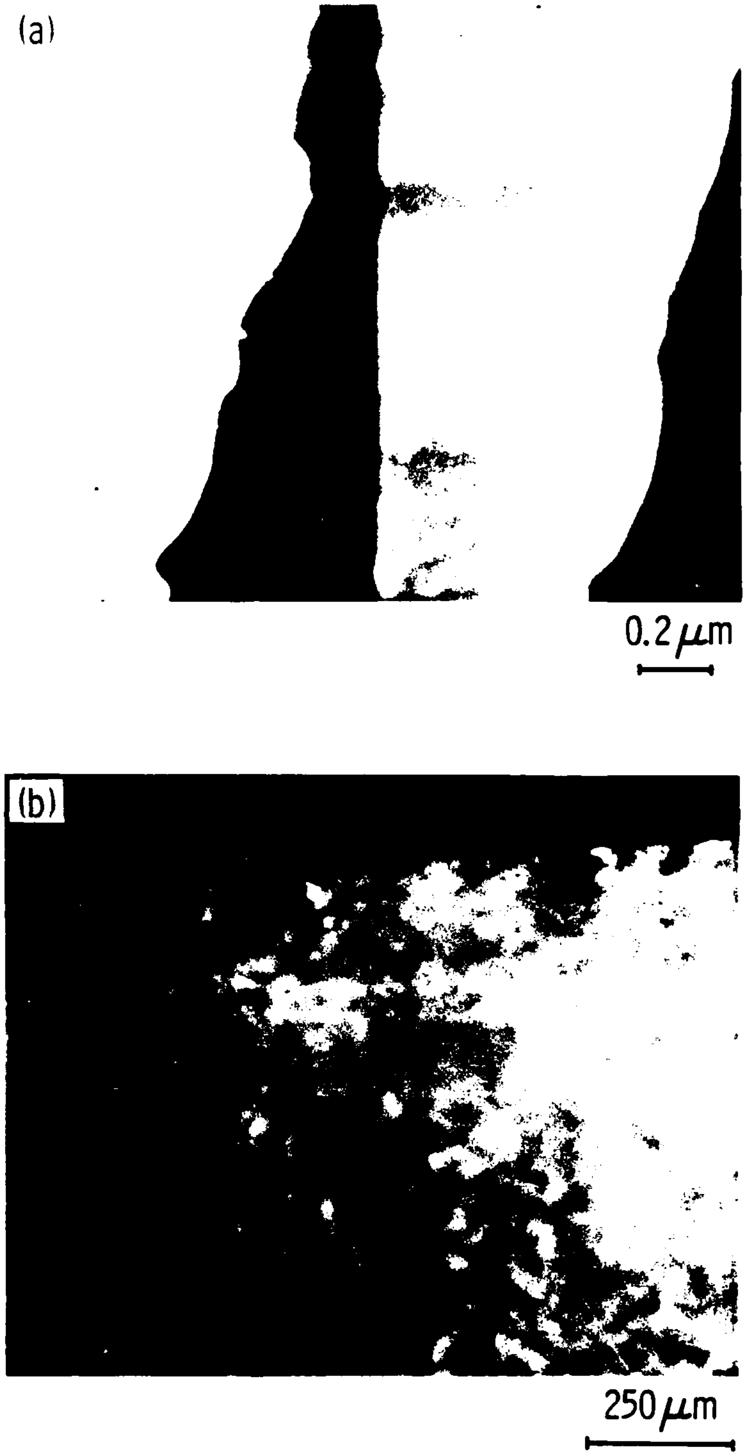

Figure 2. a) Stereo SEM micrograph showing cross-sectional view of a 0.25-μm-thick coating with translucent appearance, and b) optical cross-sectional view showing penetration of coating (the darker material) into pores of the substrate.

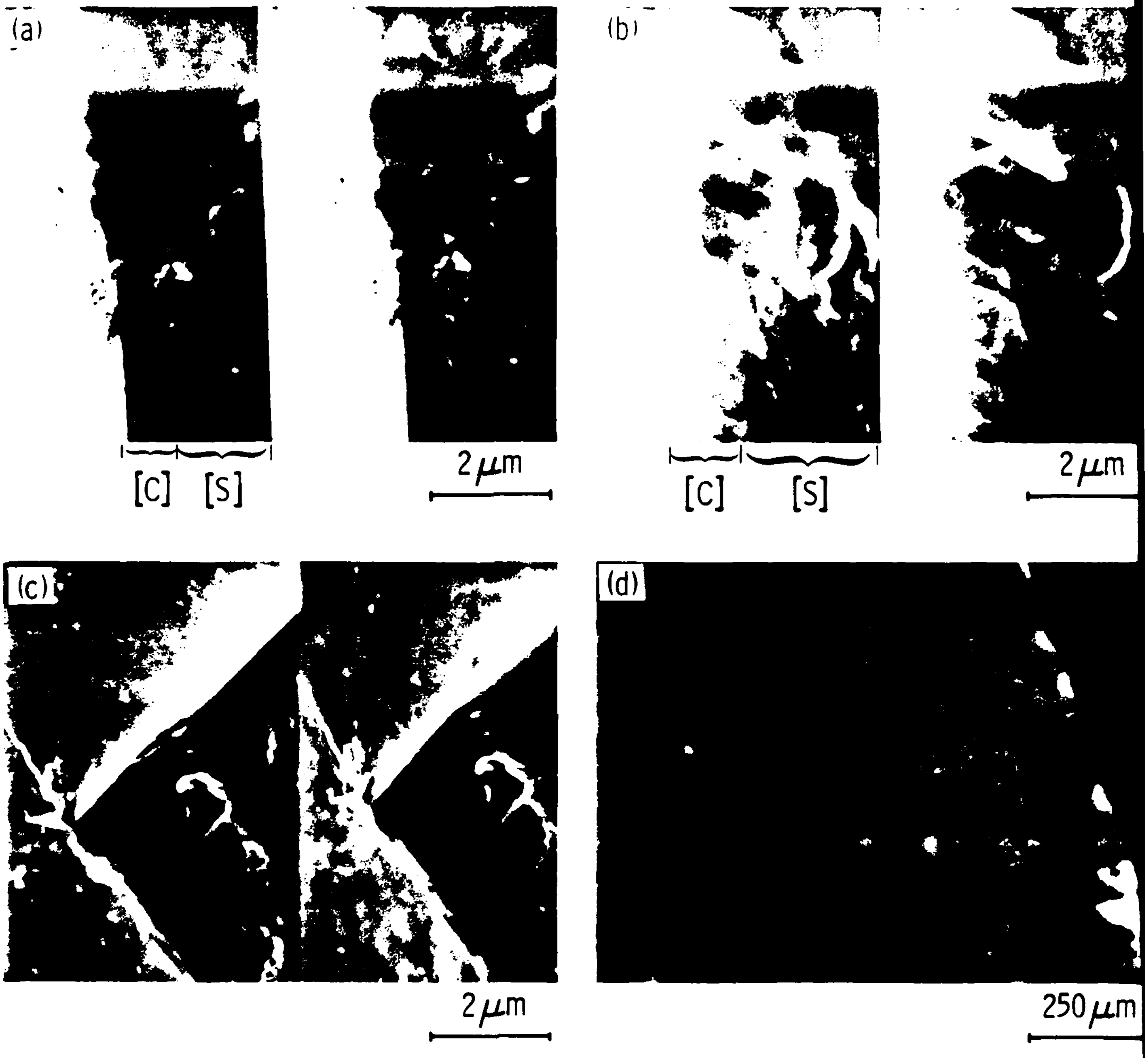

Figure 3. Stereo electron-micrographs showing: a) cross-sectional view of a .7-μm-thick coating [c] on the SIALON substrate [s]; b) cross-sectional view of a 1-μm-thick coating after 1,400°C flexure test; c) stereo top view of coating cracked during room-temperature flexure test. Bare substrate can be seen where coating has been removed; and d) top view optical micrograph of coated sample after room-temperature flexure test showing cracking in the coating and spalling on the right edge.

coated samples showed extensive cracking (Figs. 3c and 3d) although the others did not. Optical examination of those tested at 1400°C showed some crystallization that was either dendritic (Fig. 4a) or spherulitic (Fig. 4b) in form and bounded by cracks.

In general, there seems to be a good correlation between coating thickness and weight gain of ~ 1.80 mg/μm. In samples of greater porosity, the weight gain is higher probably due to filling in of pores.

B. CHEMISTRY

Several techniques were used to determine the chemistry of the coatings. Energy dispersive spectroscopy, which is capable of detecting elements of atomic weight greater than Na, revealed no contamination in this range. The XPS sputtered depth profile (Fig. 5) of the 0.25 μm coating showed that it contained silicon, carbon, oxygen and nitrogen. The amounts of silicon and carbon found in the coating were comparable and were more than double the nitrogen and oxygen. The N/Si ratio of the coating was only one third that of the substrate. The sputtering rate was 12 Å/min and the time to reach the coating-substrate interface was 220 min, giving a coating thickness of 2640 Å or approximately 0.26 μm.

The Auger line shapes of carbon indicate that it may exist in the coating in two forms; both as a carbide (probably SiC) and as free carbon. The oxygen and nitrogen probably are bound as either SiO_2 and Si_3N_4 or as Si_2N_2O.

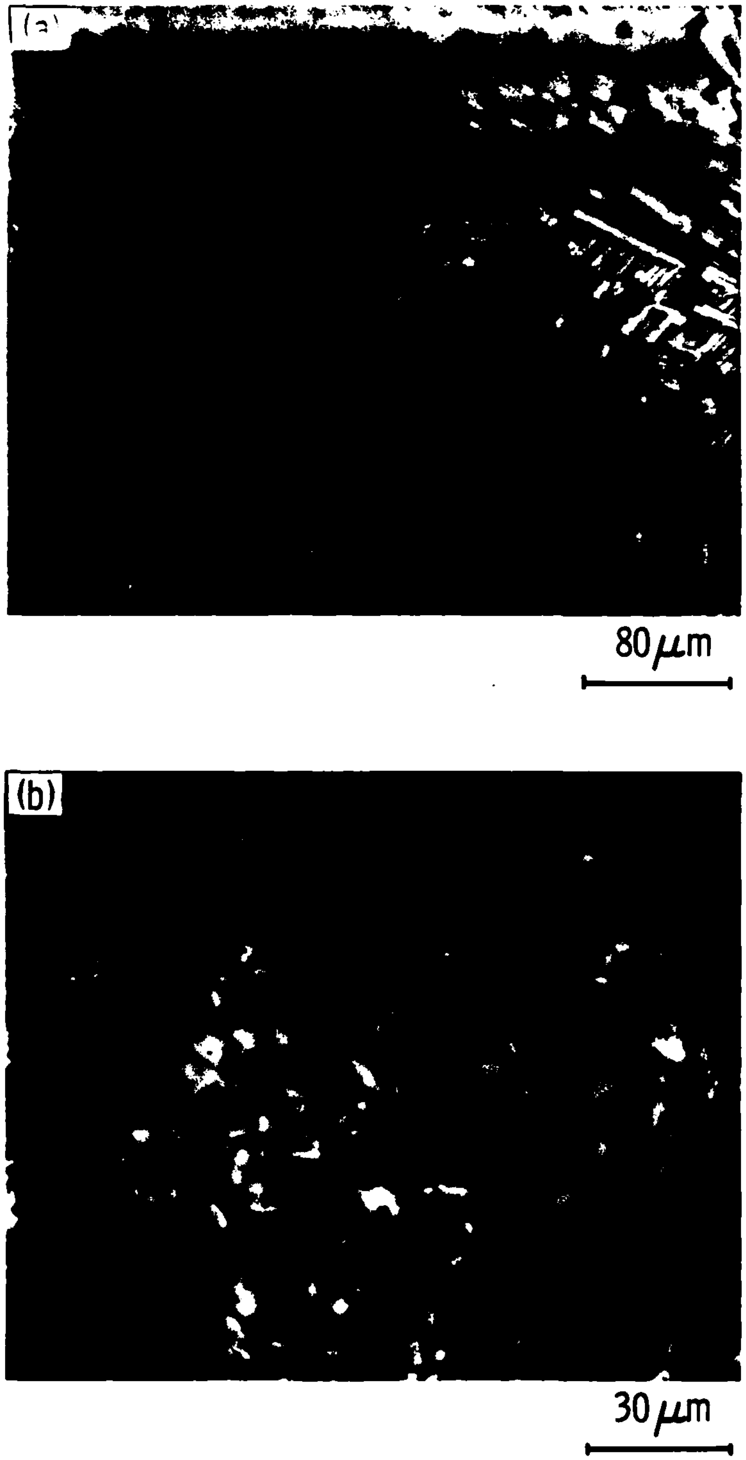

Figure 4. Optical micrographs of coated samples held at 1400°C for 15 minutes exhibiting: a) dendritic crystallization, and b) spherulitic crystallization.

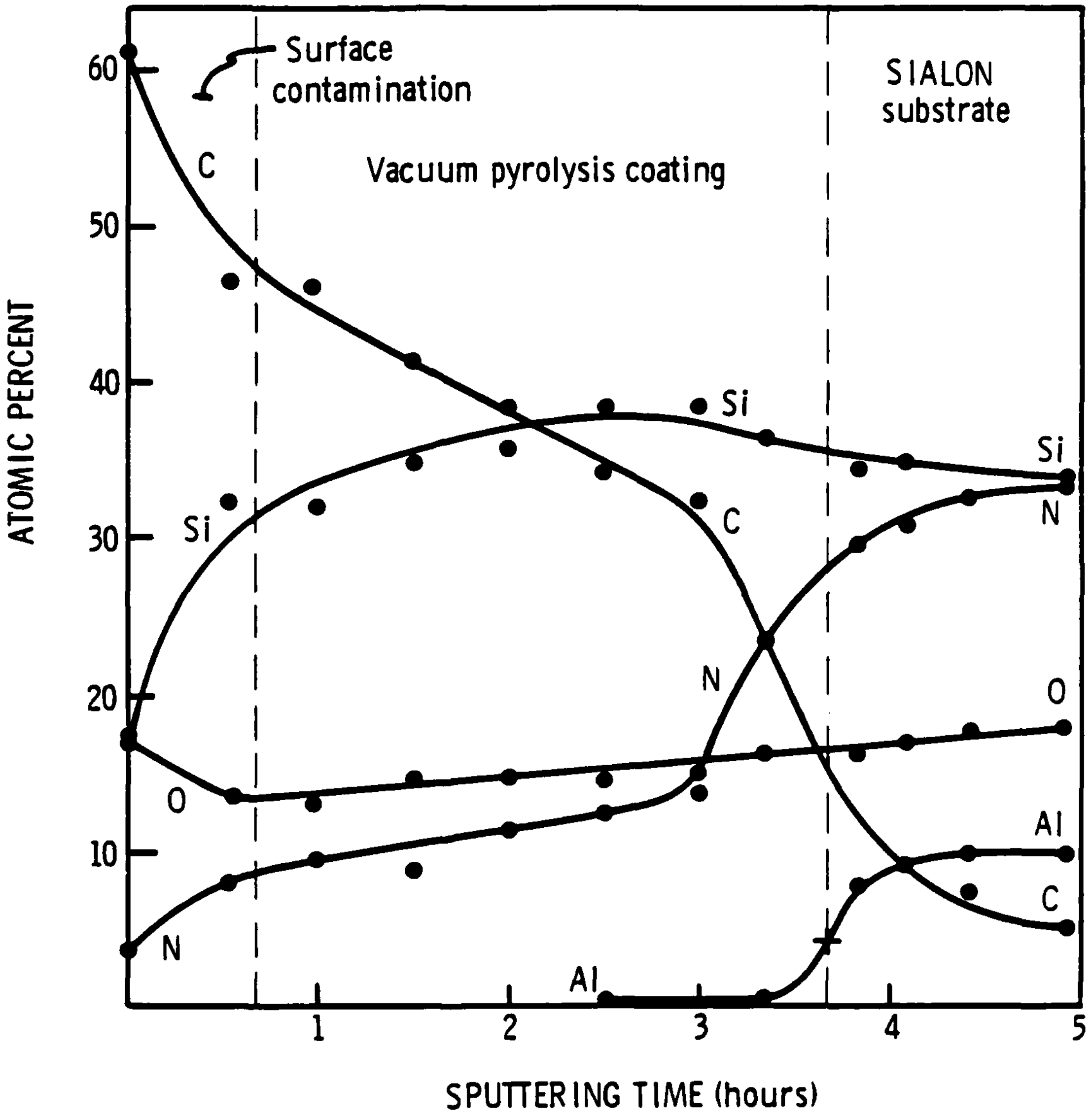

Figure 5. Depth profile showing that the coating (0.26-μm) is carbon rich and nitrogen poor in comparison with the SIALON substrate.

The high carbon and low oxygen and nitrogen values indicate that SiC and elemental carbon are the major constituents of the film and SiO_2 and Si_3N_4 are only minor constituents.

X-ray diffraction on the as-received coated samples only showed peaks that corresponded to β ($Si_{6.x}Al_xO_xN_{8-x}$) and x phase ($Si_2N_2O.4 Al_2O_3$) from the SIALON substrate, which agrees with the results of a previous study.(5) In X-ray diffraction on a coated graphite sample, all peaks were accounted for by the graphite substrate. Thus, the coatings are either amorphous or too thin to produce detectable diffraction peaks. After oxidation at 1400°C for 1 hour, both coated and uncoated samples show a new diffraction peak at $d = 4.07$ Å, which corresponds to the 101 peak for low, or α, cristobalite (a form of SiO_2). This peak was also found for the samples that had been held at 1400°C for 15 minutes. The relative intensity of this peak to the SIALON β 110 peak after a 15-minute and a 1-hour oxidation respectively is 0.26 and 0.27 for the coated samples. In the uncoated sample, 15-minute and a 1-hour oxidation lead to a relative intensity of 0.50 and 0.40 respectively. The oxidation peak for the uncoated samples in both cases is relatively higher by an average factor of 1.7. Thus the coatings do appear to afford some measure of oxidation resistance.

C. MECHANICAL PROPERTIES

Biaxial flexure strength tests were performed on both coated and uncoated control samples to determine whether the coating enhances the flexure strength of the substrate. With this test procedure, which we employed previously in a NASA contract "Solid State Studies in Ceramic

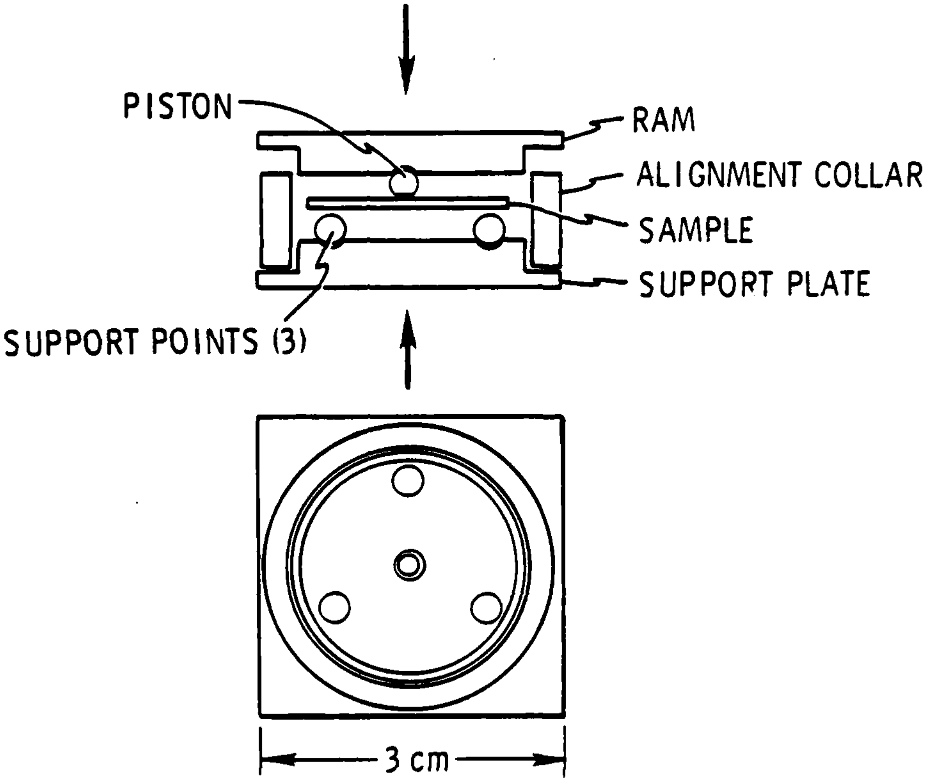

Figure 6. Schematic diagram of biaxial flexure test jig used to obtain flexure strength.

Alloys,"(5) we determined the fracture strength by applying a load to the center of a thin, round, plate-like specimen (approximately 1.5 cm in diameter and 1-mm thick) supported by three equally spaced balls located on a circle concentric with the load (Fig. 6). The advantage of this method over more conventional bend tests is that the results are unaffected by the edge condition of the specimen, thereby reducing scatter in the data.

Six SIALON substrates, having a 0.25-μm thick coating, and their controls were tested at room temperature. Eight samples, having a 1-μm thick coating, and their eight controls were tested at room temperature and 1400°C. The results of these tests are shown in Table I. It can be seen that the coatings afforded no significant improvement or degradation of flexure strength to the substrates.

TABLE I

Thickness of Vacuum Pyrolysis Coating (μm)	Test Temperature (°c)	Mean Biaxial Flexure Strength (ksi)	Standard Deviation
0.25	25	31.6	± 3
0.0 (control)	25	32.4	± 3
1.0	25	36.0	± 8
0.0 (control)	25	37.7	± 8
1.0	1400	33.7	± 3
0.0 (control)	1400	34.2	± 3

IV. CONCLUSIONS

Vacuum pyrolysis coatings have previously been found to increase abrasion resistance.(2) In this study they were shown to increase oxidation resistance of SIALON substrates. Besides good penetration into surface pores, the thin coatings (0.25 and 0.5 μm) showed good adherence and did not crack or spall off. The 0.7-μm coating did show crack growth on the sample edges after a period of several weeks and the 1-μm coating showed extensive cracking after mechanical testing. No improvement in flexure strength resulted from coatings at thicknesses of 0.25 or 1 μm either at room temperature or at 1400°C.

Further work would be required on this system before these coatings could be effectively utilized in high-performance applications. Specifically, it is evident that the coating process must be improved to reduce the carbon content and increase the nitrogen content so that the composition of the coating is closer to that of the substrate material.

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