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NASA Technical Memorandum 105430

## Plasma Etching a Ceramic Composite

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Prepared for the  
24th Annual Convention of the International  
Metallographic Society  
Monterey, California, July 29–August 1, 1991

The NASA logo, consisting of the word "NASA" in a bold, sans-serif font with a stylized "A".

# PLASMA ETCHING A CERAMIC COMPOSITE

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## SUMMARY

Plasma etching is found to be a superior metallographic technique for evaluating the microstructure of a ceramic matrix composite. The ceramic composite studied is composed of silicon carbide whiskers ( $\text{SiC}_w$ ) in a matrix of silicon nitride ( $\text{Si}_3\text{N}_4$ ), glass, and pores. All four constituents are important in evaluating the microstructure of the composite. Conventionally prepared samples, both as-polished or polished and etched with molten salt, do not allow all four constituents to be observed in one specimen. As-polished specimens allow examination of the glass phase and porosity, while molten salt etching reveals the  $\text{Si}_3\text{N}_4$  grain size by removing the glass phase. However, the latter obscures the original porosity. Neither technique allows the  $\text{SiC}_w$  to be distinguished from the  $\text{Si}_3\text{N}_4$ . Plasma etching with  $\text{CF}_4+4\%\text{O}_2$  selectively attacks the  $\text{Si}_3\text{N}_4$  grains, leaving the  $\text{SiC}_w$  and glass in relief, while not disturbing the pores. An artifact of the plasma etching reaction is the deposition of a thin layer of carbon on  $\text{Si}_3\text{N}_4$ , allowing  $\text{Si}_3\text{N}_4$  grains to be distinguished from  $\text{SiC}_w$  by back scattered electron imaging.

## INTRODUCTION

The need for more efficient propulsion systems requires materials to operate at increasingly higher temperatures in oxidizing environments. Ceramics are a leading candidate to provide high temperature strength and oxidation resistance. A major problem with ceramics is their low fracture toughness, which leads to brittle catastrophic failures. A method of increasing the toughness has been to introduce interfaces to deflect a propagating crack. One material system being studied is a ceramic composite composed of  $\text{SiC}_w$  in a matrix of  $\text{Si}_3\text{N}_4$ . The  $\text{SiC}_w$  provide the interfaces to deflect the crack tip (ref. 1).

The fabrication of  $\text{SiC}_w/\text{Si}_3\text{N}_4$  matrix composites involves several variables; i.e., whisker morphology and volume fraction, glass composition and volume fraction, consolidation temperature and pressure. Metallography plays a critical role in the evaluation of the effects of these variables on the composite. Metallography provides the ability to observe porosity,  $\text{Si}_3\text{N}_4$  grain and  $\text{SiC}_w$  size, percent glass and distribution of the phases. Correlation of microstructural

information with mechanical property data can be used to modify fabrication processes to further improve mechanical properties.

In metallography, etching is the critical step in revealing a material's microstructure. Etching is performed by selective removal of material from a specimen by a chemical reaction. Different features in the microstructure react at different rates, providing topographic relief observable by optical and electron microscopy (ref. 2). An etchant commonly used on  $\text{Si}_3\text{N}_4$  has been molten salts (e.g., potassium hydroxide, KOH, used at 673 K). The molten salt dissolves the intergranular glass phase that surrounds each  $\text{Si}_3\text{N}_4$  grain, allowing the grains to be observed.

Plasma etching is a dry etching technique developed for the fabrication of microelectronics in the late 1960's (refs. 4 to 7). The technique uses an electric discharge excited by a radio frequency source to produce chemically reactive fragments from an appropriate gas in a vacuum of 0.001 to 2 torr. The fragments react with the specimen creating volatile products which are pumped away. For silicon based materials the gas used is  $\text{CF}_4$ , which breaks down to  $\text{CF}_x$  and reacts with Si to form  $\text{SiF}_y$  (gas) (ref. 4).

The use of plasma etching for revealing the microstructure of a sialon was first reported in 1983 (ref. 8). Since then, others have used plasma etching to reveal the microstructure of  $\text{Si}_3\text{N}_4$  (refs. 9 to 11). In these materials, the  $\beta$ -sialon or  $\text{Si}_3\text{N}_4$  are selectively removed, with the glass phase remaining in relief, thus revealing the microstructure. Only one reference was found on plasma etching a ceramic composite ( $\text{SiC}/\text{Si}_3\text{N}_4$ ) (ref. 13). Plasma etching was used to remove  $\text{Si}_3\text{N}_4$ , thereby isolating the glass phase for chemical analysis in the transmission electron microscope (TEM). The purpose of this paper is to evaluate the use of plasma etching in revealing the microstructure of a  $\text{SiC}_w/\text{Si}_3\text{N}_4$  matrix composite by examination in the scanning electron microscope (SEM).

## EXPERIMENTAL

The  $\text{SiC}_w/\text{Si}_3\text{N}_4$  composite used for the plasma etching studies was formulated to yield a fully dense composite containing 10 percent  $\text{SiC}_w$  and 14 percent glass by volume. Premilled  $\text{Si}_3\text{N}_4$  powder was blended in hexane with  $\text{SiC}_w$ , and  $\text{Ce}_2\text{O}_3/\text{SiO}_2$  sintering aid. The homogeneous blended slurry was then pressed into a 5.1-cm diameter by 0.7 cm thick disk which was dried, and then sintered at 2413 K for 4 hr under 2.5 MPa nitrogen overpressure. The bulk density of the disk was  $3.31 \text{ g/cm}^3$  (immersion method). The disk was then sectioned to provide specimens for the plasma etching studies.

Metallographic preparation consisted of mounting the specimen in a two part epoxy, followed by vacuum degassing, and curing for 12 hr. The subsequent grinding/polishing steps that were used are listed in table I.

Etching of the specimens was performed by two methods; molten salt or plasma etching. Etching with molten KOH was performed as outlined in figure 1. The specimen was removed from the epoxy mount, wrapped in platinum wire and immersed in molten KOH at 673 K for 10 to 15 sec. Plasma etching was performed using the system shown in figure 2. The mounted sample is placed in the vacuum chamber and evacuated to 0.1 torr. The sample is preheated using nitrogen at 0.2 torr and plasma RF power of 100 W for 10 min. Next, etching is performed using  $\text{CF}_4+4\%\text{O}_2$  at 0.3 torr and plasma RF power of 100 W for 2 to 5 min.

Specimens were sputter coated with palladium and examined in a SEM using back scattered electron imaging and an accelerating voltage of 20 kV. TEM specimens were prepared by conventional techniques. A 3 mm disk was ultrasonically drilled from a 0.5 mm thick section, ground on both surfaces with 15 and 3  $\mu\text{m}$  diamond to a thickness of 140  $\mu\text{m}$ , and dimpled from each side to a thickness of less than 20  $\mu\text{m}$ . Final thinning was performed by ion milling to perforation using argon at 5 kV and 12° incidence angle. Electrical conductivity of the specimen was achieved by evaporation of approximately 10 nm of carbon onto one surface. The specimen was examined in the TEM at an accelerating voltage of 120 kV. After examination in the TEM, the specimen was affixed to a glass slide with small drop of carbon paint and plasma etched as described above, with a preheat of 5 min and an etch of 2 min. The specimen was removed from the glass slide and re-examined in the TEM. Electron energy loss spectroscopy (EELS) was performed to obtain chemical information.

## RESULTS

Back scattered electron imaging of the as-polished composite allows the identification of three microstructural features (fig. 3). The white phase is the  $\text{CeO}_2$  rich glass phase as determined by x-ray energy dispersive spectroscopy (XEDS), the black areas are regions of porosity, and the gray phase is  $\text{SiC}_w$  or  $\text{Si}_3\text{N}_4$ . Measurement of the size and shape of the gray phase is possible, but  $\text{SiC}_w$  and  $\text{Si}_3\text{N}_4$  can not be differentiated due to their identical average atomic number ( $\text{SiC}:(14+6)/2=10$ ;  $\text{Si}_3\text{N}_4:(3*14+4*7)/7=10$ ).

Molten salt etching removes the intergranular glass leaving the  $\text{SiC}_w$  and  $\text{Si}_3\text{N}_4$  grains in relief (fig. 4). Back scattered electron imaging again can not differentiate  $\text{SiC}_w$  from  $\text{Si}_3\text{N}_4$ . The white particles were identified by XEDS as contamination from the platinum crucible during etching. Obtaining reproducible etching results is difficult as shown by the influence an additional 5 sec had on the depth of etching on a second specimen (fig. 4(b)).

Plasma etching selectively attacks the  $\text{Si}_3\text{N}_4$  leaving the  $\text{SiC}_w$  and glass in relief (fig. 5). Back scattered electron imaging reveals the  $\text{CeO}_2$  rich glass as the white phase. An atomic number difference between  $\text{Si}_3\text{N}_4$  and  $\text{SiC}_w$  is observed, with the  $\text{SiC}_w$  being lighter, and thus, apparently higher in average atomic number. As etching time is increased to 5 min, the contrast between  $\text{SiC}_w$  and  $\text{Si}_3\text{N}_4$  increases (fig. 5(b)). Examination of the specimen surfaces at higher magnification, using secondary electrons, reveals a mottled structure on the  $\text{Si}_3\text{N}_4$ , with the  $\text{SiC}_w$  and glass appearing unaffected (fig. 6). The longer etching time (5 min) removed more of the  $\text{Si}_3\text{N}_4$ .

TEM of an as prepared specimen shows the typical faulted structure of the  $\text{SiC}_w$ , an intergranular glass phase, and  $\text{Si}_3\text{N}_4$  grains containing dislocations (fig. 7(a)). After plasma etching for 2 min, examination of the exact same region shows the  $\text{SiC}_w$  and glass are intact, but the  $\text{Si}_3\text{N}_4$  is removed as evidenced by the absence of the dislocations (fig. 7(b)). The evaporated conductive carbon film is intact with a mottled deposit on it. Electron diffraction of the deposit showed an amorphous pattern and EELS shows carbon as the only element present (fig. 7(c)).

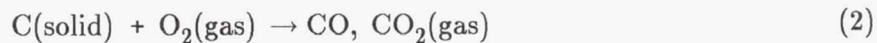
## DISCUSSION

Many problems exist with the conventional microstructural characterization techniques applied to  $\text{SiC}_w/\text{Si}_3\text{N}_4$  composites. Examination of both as-polished and molten salt-etched

surfaces with SEM does not reveal the complete microstructure of the  $\text{SiC}_w/\text{Si}_3\text{N}_4$  composite. Neither technique allow distinction between  $\text{SiC}_w$  and  $\text{Si}_3\text{N}_4$  grains in the SEM. Molten salt etching problems also include the requirement for the sample to be removed from the epoxy mount. This is necessary because the epoxy decomposes at 473 K and entrapped moisture can cause a small gas explosion, splattering molten salt. Etching of small delicate specimens cannot be performed because of destruction of the sample upon removal from the mount. Determining etching times is difficult because etching rate varies with the size of the sample. Larger samples have a higher heat capacity and require a longer etching time. Examination and handling of the sample is complicated when it is not in a uniform size mount, especially during observation with an inverted metallograph, where glass cover slips must be used to support the sample. Finally, if the sample is over-etched, it must be remounted for repolishing.

Plasma etching overcomes all of the problems discussed above. The temperature of the sample during plasma etching remains less than 358 K, using the etching conditions discussed. The epoxy mount can withstand temperatures to approximately 423 K, therefore the sample can remain in the mount. Another benefit of the lower etching temperature is the ability to partially etch a sample by simply covering a portion with adhesive tape (fig. 8). This is very useful for samples that might require unetched areas for electron microprobe studies.

The apparent atomic number difference between  $\text{SiC}_w$  and  $\text{Si}_3\text{N}_4$  is explained by the deposition of carbon during removal of  $\text{Si}_3\text{N}_4$ , as identified by TEM (fig. 7). A schematic drawing of a cross section of the composite surface is shown in figure 9. Although the chemical reactions that occur in the plasma etching process are not fully understood (refs. 6 and 7), the chemical reaction shown in equation (1) provides a basic understanding of the source for the carbon. Fragments of  $\text{CF}_x$ , generated by the  $\text{CF}_4+4\%\text{O}_2$  plasma, react with  $\text{Si}_3\text{N}_4$  to form volatile products of  $\text{SiF}_y$  and  $\text{N}_2$  which are removed by the vacuum pump, while carbon is deposited on the  $\text{Si}_3\text{N}_4$ . For the etching to proceed the carbon must be removed by reaction with the  $4\%\text{O}_2$  to form CO and/or  $\text{CO}_2$  (eq. (2)). The selective carbon deposition provided by the chemical reaction at the  $\text{Si}_3\text{N}_4$  surface provides a decrease in the apparent average atomic number of the  $\text{Si}_3\text{N}_4$ , while the  $\text{SiC}_w$  surface remains unetched (fig. 6).



## CONCLUSIONS

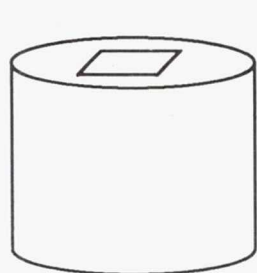
The microstructure of a  $\text{SiC}_w/\text{Si}_3\text{N}_4$  matrix composite is revealed by plasma etching with  $\text{CF}_4+4\%\text{O}_2$ . All four microstructural constituents:  $\text{Si}_3\text{N}_4$  grains,  $\text{SiC}_w$ , pores, and intergranular glass are distinguishable in one specimen. The selective deposition of carbon on  $\text{Si}_3\text{N}_4$  allows the  $\text{SiC}_w$  to be imaged by back scattered electrons. Ability to keep the specimen in the mount allows examination of small, delicate specimens and facilitates imaging on an inverted metallograph. Partial etching saves time when both unetched and etched specimens are required for analysis.

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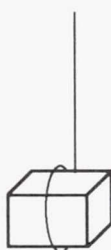
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TABLE I.—METALLOGRAPHIC PREPARATION

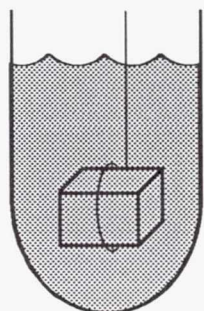
Step	Diamond abrasive, $\mu\text{m}$	Lubricant	Time, min	Comments
Grinding (fixed abrasive)	115	Water	Until planar	
	65	Water	1	
	20	Water	1	
Lapping (nonfixed abrasive)	6	Alcohol	6	Iron/copper disk
	6		9	Plastic disk
Polishing (slurry)	6		3	Hard synthetic cloth
	3		2	
	1		2	
Final polishing (vibratory)	0.5	Oil	16 hr	High nap synthetic cloth



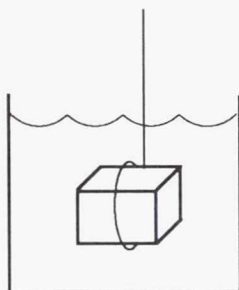
(a) Mounted and polished specimen.



(b) Specimen removed from mount and wrapped in Pt wire.



(c) Specimen immersed in molten KOH at 673 K for 10 to 20 seconds.



(d) Specimen ultrasonically cleaned in water.

Figure 1.—Schematic diagram of steps involved in molten KOH etching.

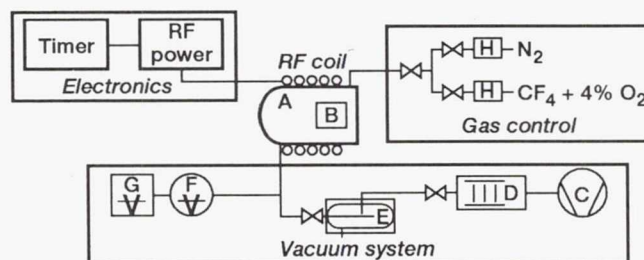


Figure 2.—Schematic diagram of plasma etching system. (a) Vacuum chamber. (b) Specimen. (c) Mechanical vacuum pump (fomblin oil). (d) Sorption trap. (e) Liquid nitrogen trap. (f) Thermocouple gauge. (g) Vacuum read out. (h) Flow meter.

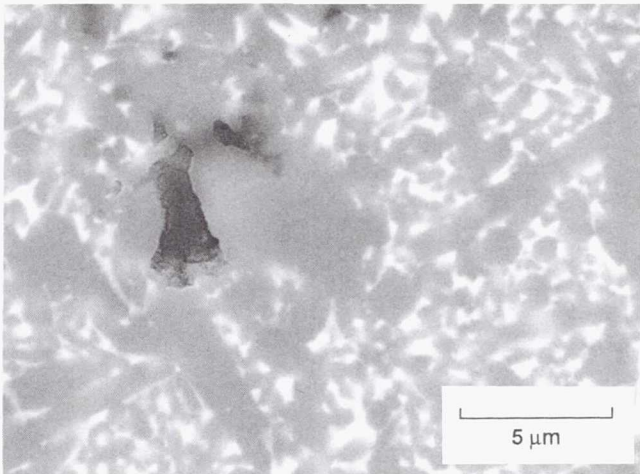
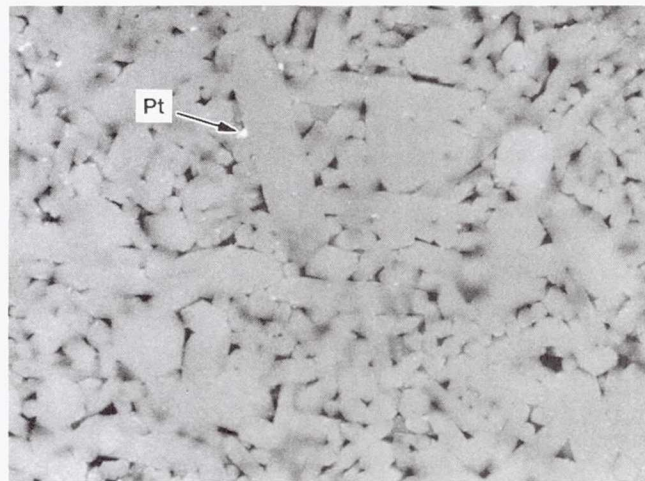
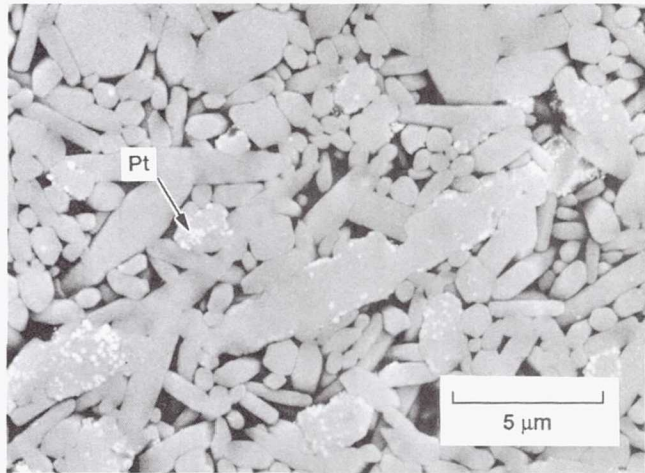


Figure 3.—Back scattered electron image of as-polished  $\text{SiC}_w/\text{Si}_3\text{N}_4$  matrix composite.



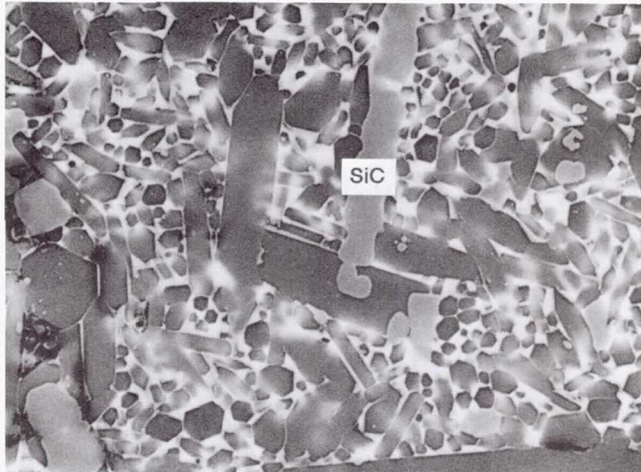
(a) Etched 10 seconds.



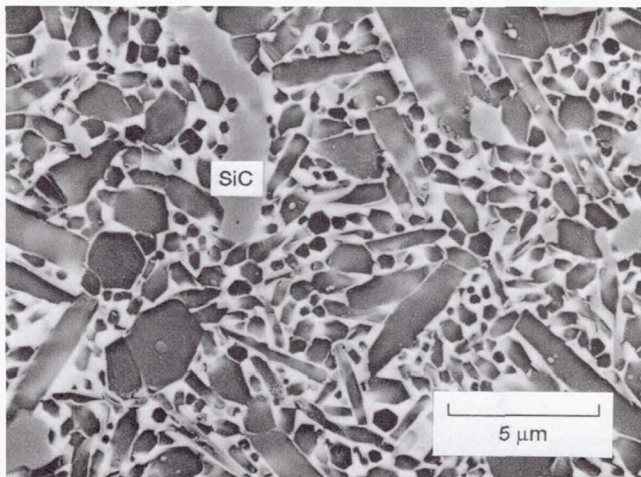
(b) Etched 15 seconds.

Figure 4.—Back scattered electron images of  $\text{SiC}_w/\text{Si}_3\text{N}_4$  composite following molten KOH etching at 673 K.



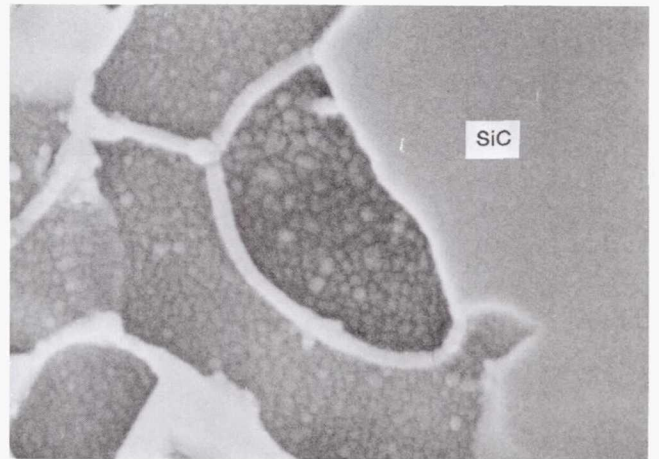


(a) Etched 3 minutes.

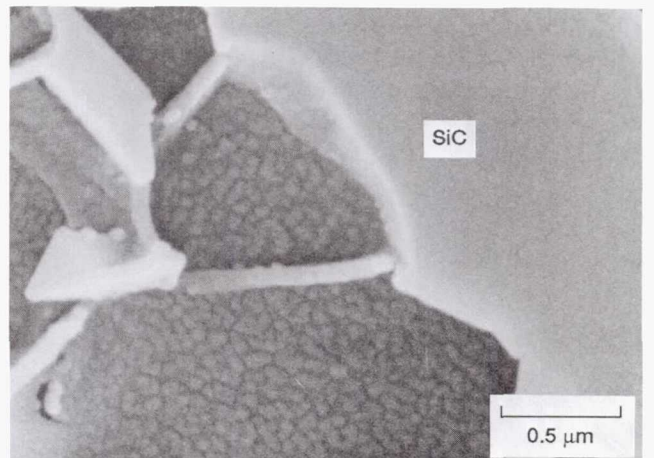


(b) Etched 5 minutes.

Figure 5.—Back scattered electron images of plasma etched  $\text{SiC}_w/\text{Si}_3\text{N}_4$  composite (10 minutes  $\text{N}_2$  preheat and  $\text{CF}_4 + 4\% \text{O}_2$  etch for times shown).

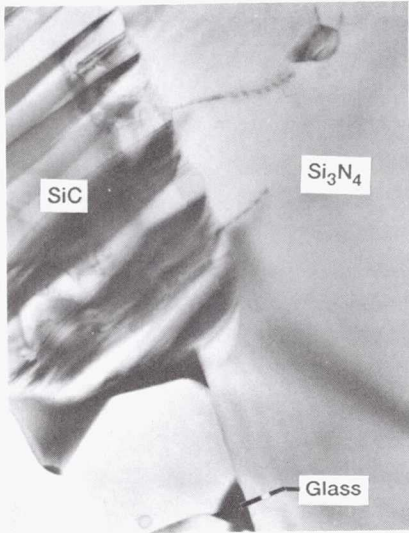


(a) Etched 3 minutes.

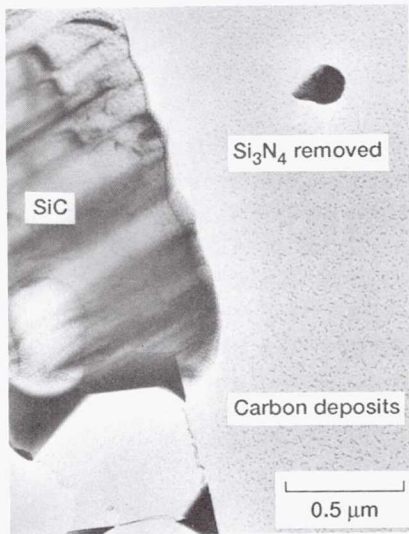


(b) Etched 5 minutes.

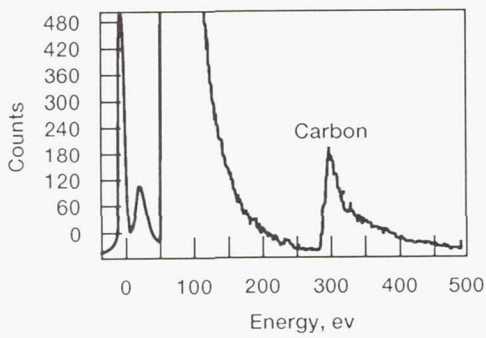
Figure 6.—High magnification secondary electron micrographs after plasma etching.



(a) As prepared.

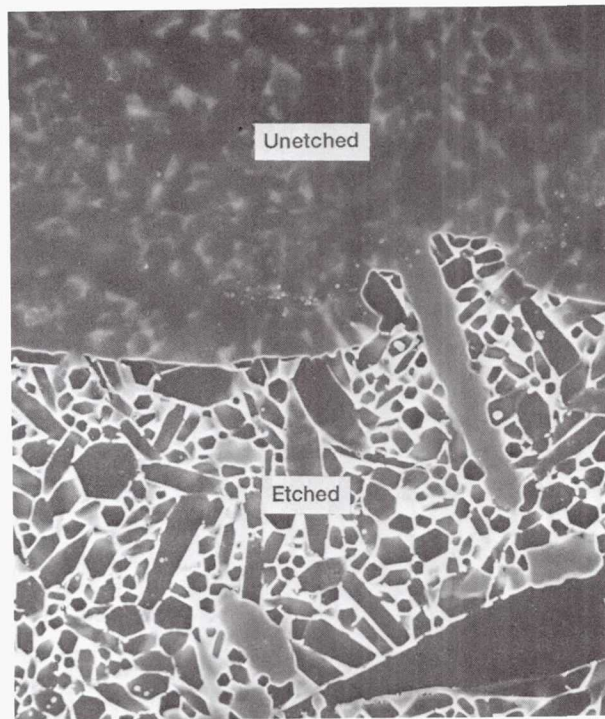


(b) After plasma etching 2 minutes.

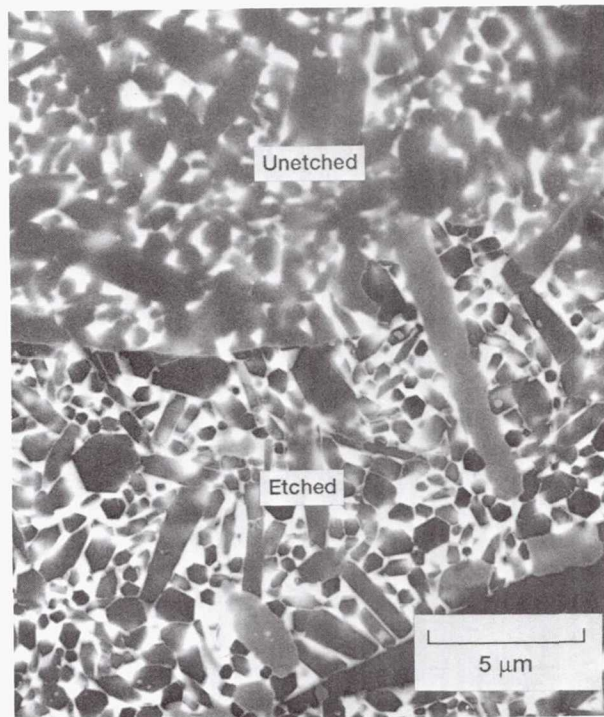


(c) Electron energy loss spectrum of deposits.

Figure 7.—TEM bright field of SiC<sub>w</sub>/Si<sub>3</sub>N<sub>4</sub> matrix composite.



(a) Secondary electrons.



(b) Back scattered electrons.

Figure 8.—Partial etching of SiC<sub>w</sub>/Si<sub>3</sub>N<sub>4</sub> matrix composite.

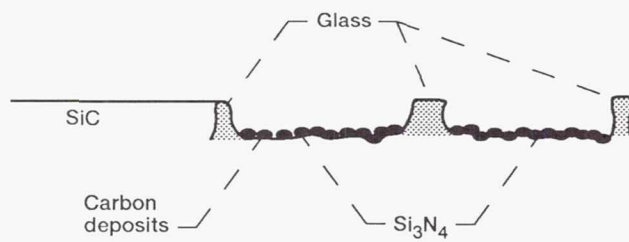


Figure 9.—Schematic cross-section of composite after plasma etching.

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<b>1. AGENCY USE ONLY (Leave blank)</b>		<b>2. REPORT DATE</b> 1992	<b>3. REPORT TYPE AND DATES COVERED</b> Technical Memorandum	
<b>4. TITLE AND SUBTITLE</b> Plasma Etching a Ceramic Composite			<b>5. FUNDING NUMBERS</b>  WU-505-63-5A	
<b>6. AUTHOR(S)</b> David R. Hull, Todd A. Leonhardt, and William A. Sanders				
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b>  National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191			<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  E-6846	
<b>9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)</b>  National Aeronautics and Space Administration Washington, D.C. 20546-0001			<b>10. SPONSORING/MONITORING AGENCY REPORT NUMBER</b>  NASA TM-105430	
<b>11. SUPPLEMENTARY NOTES</b>  Prepared for the 24th Annual Convention of the International Metallographic Society, Monterey, California, July 29-August 1, 1991. David R. Hull, NASA Lewis Research Center; Todd A. Leonhardt, Sverdrup Technology, Inc., Lewis Research Center Group, 2001 Aerospace Parkway, Brook Park, Ohio 44142; William A. Sanders, Analox Corporation, 3001 Aerospace Parkway, Brook Park, Ohio 44142. Responsible person, David R. Hull, (216) 433-3281.				
<b>12a. DISTRIBUTION/AVAILABILITY STATEMENT</b>  Unclassified - Unlimited Subject Category 27			<b>12b. DISTRIBUTION CODE</b>	
<b>13. ABSTRACT (Maximum 200 words)</b>  Plasma etching is found to be a superior metallographic technique for evaluating the microstructure of a ceramic matrix composite. The ceramic composite studied is composed of silicon carbide whiskers (SiC <sub>w</sub> ) in a matrix of silicon nitride (Si <sub>3</sub> N <sub>4</sub> ), glass, and pores. All four constituents are important in evaluating the microstructure of the composite. Conventionally prepared samples, both as-polished or polished and etched with molten salt, do not allow all four constituents to be observed in one specimen. As-polished specimens allow examination of the glass phase and porosity, while molten salt etching reveals the Si <sub>3</sub> N <sub>4</sub> grain size by removing the glass phase. However, the latter obscures the original porosity. Neither technique allows the SiC <sub>w</sub> to be distinguished from the Si <sub>3</sub> N <sub>4</sub> . Plasma etching with CF <sub>4</sub> +4%O <sub>2</sub> selectively attacks the Si <sub>3</sub> N <sub>4</sub> grains, leaving the SiC <sub>w</sub> and glass in relief, while not disturbing the pores. An artifact of the plasma etching reaction is the deposition of a thin layer of carbon on Si <sub>3</sub> N <sub>4</sub> , allowing Si <sub>3</sub> N <sub>4</sub> grains to be distinguished from SiC <sub>w</sub> by back scattered electron imaging.				
<b>14. SUBJECT TERMS</b> Plasma etching; Ceramic composite; Microstructure; Silicon nitride; Silicon carbide			<b>15. NUMBER OF PAGES</b> 12	
			<b>16. PRICE CODE</b> A03	
<b>17. SECURITY CLASSIFICATION OF REPORT</b> Unclassified	<b>18. SECURITY CLASSIFICATION OF THIS PAGE</b> Unclassified	<b>19. SECURITY CLASSIFICATION OF ABSTRACT</b> Unclassified	<b>20. LIMITATION OF ABSTRACT</b>	

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