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CERAMIC MATRIX COMPOSITES BY MICROWAVE ASSISTED CVI

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Chemical vapor infiltration (CVI) processes for producing continuously reinforced ceramic composites are reviewed. The potential advantages of microwave assisted CVI are noted. Recent numerical studies of microwave assisted CVI are then reviewed. These studies predict inverted thermal gradients in fibrous ceramic preforms subjected to microwave radiation and suggest processing strategies for achieving uniformly dense composites. Comparisons are made to experimental results obtained using silicon based composite systems. The importance of microwave-material interactions is stressed. In particular, emphasis is placed on the role played by the relative ability of fiber and matrix to dissipate microwave energy. Results suggest that microwave induced inverted gradients can in fact be exploited using the CVI technique to promote inside-out densification.

Introduction

Materials for many high temperature applications such as heat exchangers and turbine engines require high temperature strength, chemical stability, thermal shock resistance, hardness, abrasion resistance, low thermal expansion coefficient, and low density. Continuous fiber reinforced ceramic matrix composites are candidate materials for such applications. These materials typically consist of a fibrous backbone, or substrate, whose void spaces are filled with a "matrix" material. The chemical composition of the matrix may or may not be the same as that of the fibers. Manufacturing techniques differ primarily in the way matrix materials are infiltrated into the porous substrate. Infiltration may involve molten liquids, sol-gels, polymeric materials, powders, or vapors. Most of these techniques require final densification steps, e.g. sintering, involving matrix shrinkage. Consequently, large and undesirable stresses can develop if the matrix shrinks around non-shrinking fibers.

CVI is an attractive technique for introducing matrix materials since it avoids stressing the fibrous backbone during processing. In addition, relatively low temperatures are used which limits unwanted chemical attack on the reinforcement. Densification of composites by CVI involves reactant gas transport through the porous substrate followed by chemical vapor deposition reactions and product gas removal. A central issue in successful CVI is avoiding preferential deposition in the substrate's outer regions, which results in pore blockage, non-uniform composite density, and/or high residual porosity.

The use of electromagnetic radiation, in particular microwaves, in CVI processing is the subject of this paper. Advantages in using microwave energy in CVI are the ability to couple energy directly into the substrate and the possibility of heating the substrate volumetrically. Coupling energy directly into the substrate should increase energy efficiency, compared to resistively heated furnaces.

Volumetric heating, together with heat losses at the surfaces due to radiation and convection, gives rise to "inverted" thermal gradients. With the internal region of the substrate hot, cool reactant gases penetrate inward prior to the onset of the deposition reaction. Consequently, deposition can occur from the inside-out. Inside-out densification should minimize premature pore closure in outer regions, resulting in more spatially uniform, high density composites. Decreases in processing time are also expected using forced flow or pulsed pressure operations where deposition reactions are not transport limited. A cold wall reactor will also minimize unwanted deposition on the walls and fixtures thereby saving on reactant costs and minimizing waste production. In addition, microwaves could be used to induce a vapor phase glow discharge, enhancing the deposition kinetics.

In addition to the usual reaction engineering issues associated with CVI, such as balancing reaction and transport rates, the effective use of microwave energy in fabricating ceramic composites requires that attention also be given to applicator/cavity design and to microwave-material interactions. Composite production by CVI involves maintained heating and managed thermal gradients in a sample whose effective dielectric properties change as the matrix is deposited. Reliable diagnostics will be required for on-line process control. Microwave-material interactions must also reflect both the bare substrate and the matrix material, which typically have different dielectric properties. The effects of interfacial coatings between the fibers and matrix on microwave processing must also be considered. Plasma chemistry will also play a role in the process if glow discharges are induced. Thus, it appears that microwave assisted CVI may embody the entire range of technical problems encountered in microwave processing of ceramic materials. Progress made in addressing each of these issues is discussed below. The paper is arranged as follows. A review of conventional CVI processes is given first. Then microwave assisted CVI is discussed. Both numerical and experimental results are highlighted. The paper concludes with a brief discussion.

Conventional CVI

Conventional CVI processes, using resistively heated furnaces, may be either isothermal or involve intentionally imposed thermal gradients. Matrix deposition may be reaction rate limited, diffusion limited, or may rely on forced and/or pulsed reactant flows. Isothermal reaction rate and diffusion-limited CVI processes are now in commercial operation and can be used to fabricate complex shaped parts. However, these processes are inherently slow. Deposition in the outer regions of the preform typically leads to non-uniform composite density and blockage of pores. Achieving uniform infiltration can require several weeks to months of processing time, often with intermittent diamond machining to reopen closed pores. The resulting materials may still contain 15 to 25% residual porosity.

In contrast, isothermal forced-flow processes involve fixing the preform in a high temperature furnace while reactant gases are forced to flow through the fibrous structure under a pressure gradient. A related process, the forced-flow thermal gradient process, intentionally imposes a steep thermal gradient across the preform, which is held in a jacket cooled on one side.¹ Reactants enter at the cold side and are forced to flow toward the hot face where deposition occurs. The

forced-flow processes can result in a significant reduction in processing time (from weeks to days). However, they are generally limited to relatively simple preform geometries. Furthermore, since reactant gases must continually channel through the preform, full density cannot be attained and continuous open porosity remain after processing. Final densities approach 80-85% of the theoretical maximum.

Also available is the pulsed-pressure CVI technique for rapid and uniform delivery of reactants throughout a preform.² Here a processing cycle typically begins with the reactor and preform at operating temperature and evacuated of gases. Reactant gases are introduced rapidly until the desired pressure is reached. The system is then held static for a period of time during which deposition occurs. Products and unreacted precursors are then removed quickly to vacuum and the cycle is repeated. With several days processing time, this technique can yield composites of fairly uniform density, as deposition is not limited by reactant transport.

To varying degrees, the conventional CVI processes are subject to some or all of the following drawbacks: preferential deposition in the substrate's outer regions leading to pore blockage; long processing times; intermittent machining operations; non-uniform composite density; high residual porosity; and limitations on substrate geometry.

Microwave Assisted CVI

As noted above, a process exploiting electromagnetically induced thermal gradients, in conjunction with forced or pulsed flows, may offer several advantages over conventional CVI technologies. First, relatively short processing times should be possible. Second, constraints on preform geometry can be removed. Third, spatially uniform composites with high densities should be attainable. Fourth, machining operations to re-open closed pores should not be necessary since densification would occur from the inside-out. Establishing specific thermal gradients (e.g. inside out) may also involve "seeding" the center (or one side) of the substrate with a material which readily absorbs microwaves. Cool reactant gases then penetrate inward toward the hot region prior to the onset of the deposition reactions. Consequently, vapor deposition could occur preferentially in one region, e.g. from the inside-out, or from one side to the other. In this section, issues central to further development of microwave assisted CVI are reviewed.

Reactor Design. Construction of a microwave CVI reactor involves providing a controlled atmosphere within the microwave cavity and a means of reactant gas delivery and product gas removal. The microwave cavity may be either multi- or single mode. Multi-mode cavities are relatively inexpensive and easy to operate. Experimental CVI studies in multi mode cavities have relied on quartz bell jar assemblies as reactor vessels.^{3,4} At least with small volume multi-mode cavities, the distribution of electric field is generally not uniform despite the use of mode stirrers. However, as the dimensions of the cavity are increased, more uniform electric fields may be expected, a feature which may be important in scale up.

Single mode designs use internal tuning capabilities (stub and/or block tuners) which are varied until a resonant field is found. Single mode cavities are

more energy efficient and can localize heating. However, use of a single mode cavity during the densification of complex shaped substrates involving a matrix material different than the underlying reinforcement may require continual, non-trivial tuning schedules. Finally, the requirement of single mode cavities to have specified dimensions places limitations on scalability of the process. Although microwave assisted CVI in single mode cavities is under study,⁵ the subsequent discussion emphasizes results obtained in multi-mode cavities.

With either single or multi-mode reactors, monitoring and controlling the evolution of the thermal gradients during densification of the composite will require reliable diagnostics. Insertion of shielded thermocouples directly into the preform provides a means of measuring an average local temperature. However, due to the size of such probes, it may prove both impractical and inaccurate to insert numerous thermocouples to monitor thermal gradients. Optical measurement techniques such as IR pyrometers and fiber optics offer alternatives. Externally mounted optical pyrometers can be used to estimate temperatures at the preform center provided a correlation is developed relating internal temperature to that measured by the pyrometer. Our previous work has shown that fiber optic cables can be inserted directly into woven substrates and used to measure thermal profiles.³ However, if fiber optics are to be used in CVI reactor environments the long term effects of heat, hydrogen diffusion through the cable walls, and chemical attack must be assessed.

An additional consideration in reactor set-up is how to position preforms. For substrates consisting of three dimensional weaves, positioning is not expected to be a major problem since they are free standing net-shape preforms. For lay-ups of two dimensional cloths, a means must be provided by which the lay-up can be compressed and held in place. Care must be used in selecting materials for any fixtures. To minimize adverse effects of the fixturing on electric field distribution, low loss materials such as quartz and silicon nitride should prove preferable to materials which are more microwave absorbant (e.g. graphite).

Numerical Results. Numerical studies of microwave assisted CVI have predicted both inverted thermal gradients and inside-out densification. While these modeling exercises provide qualitative insight, thus far they have not explicitly included details of the microwave-material interactions. Following discussion of the models, the central role played by the effectiveness of both reinforcement and matrix in dissipating the microwave energy will be highlighted.

The earliest study, published by Gupta and Evans,⁶ considered a cylindrical pore CVI model together with volumetric microwave heating. The effective electrical and thermal properties were considered to be independent of the degree of infiltration. The electric field within the preform is described by a phasor, leading to a standing wave with boundaries defined by the preform dimensions. This description allows for spatial variation in temperature due to localized high field concentrations. Further establishment of temperature gradients came from heat losses at the surface due to convection. At power densities of a few watts per square meter, temperature gradients of several hundred degrees per centimeter were obtained for preforms 1.5 cm thick. Inside out densification, leading to rapid infiltration and higher densities was demonstrated. The use of multiple frequencies

as a means of minimizing the effects of preform dimension on heating efficiency was also explored.

In another simulation,⁷ a preform structure consisting cylindrical fibers randomly oriented in space was considered. Volumetric heating by either microwave or RF radiation was explored. While variations in the effective electrical properties of the preform with degree of infiltration were accounted for, volumetric heating was described by a constant rate of heat generation. Thus, the possibility of "hot spots" due to high field concentrations was ignored. A 1.0 mm fiber bundle was heated with power densities approaching 10^9 watt/cm³ yielding gradients on of 300°C/mm. Temperature profiles were established by varying the convective heat transfer coefficient. Again rapid inside-out infiltration with increased densities was demonstrated. The effect of different power levels was also explored. While the magnitude of the temperature gradients remain similar with increasing power, the overall temperature increases. At lower power levels, uniform infiltration from inside-out occurred. At increased power levels, preferential deposition begins in regions near the surface of the preform rather than at the center. Consequently, depletion of the reactant necessary for further infiltration leads to low densities in the preform interior. In subsequent work,⁸ the effect of pulsing the power between the high and the low levels was investigated. Improved densities over those obtained at a constant high power was suggested. By adjustment of the duty cycle between the high and low power levels, uniform densities comparable to those obtained at constant low power was possible in a third of the processing time. In practice, the effects of cyclical thermal stress as well as the potential for variations in matrix phase, composition, and morphology needs to be addressed. For example, in the reaction of methyl trichlorosilane to SiC, preferential deposition of carbon at high temperatures or deposition of silicon at low temperatures, could lead to an undesirable two phase matrix. Alternatively, the effect might be exploited to intentional produce a two phase composite matrix material.

The proposed models differ fundamentally in their treatment of both the CVI and microwave heating aspects of the problem. At the present stage of development an understanding microwave heating effects is probably the least understood aspect of the problem. Additional insight could be provided by further simulations. The simple description of the field as a phasor⁶ can be useful in gaining information on heating in single mode cavity reactors. However, the lack of adjustment to the electrical properties with degree infiltration limits the quantitative validity of the model. The assumption of a constant heat generation rate^{7,8} is good for the small one mm fiber bundle used in the computer experiment. For larger samples, the potential for hot spots may preclude the direct use of this model. Neither model considers the temperature dependence of the dielectric properties and its effects on the evolution of thermal gradients. These properties lead to commonly encountered problems in microwave processing, e.g. thermal runaway, and will have to be included. The use of effective electrical properties, especially at intermediate degrees of infiltration, represents a further difficulty. Microwave interactions with dense regions of the composite differ from interactions with porous regions. This effect will certainly play a role in maintaining desirable thermal gradients. Despite the preceding criticism, the models provide guidance in developing processing schemes and further demonstrate the potential of microwave assisted CVI.

Microwave-Substrate Interactions. Heating a ceramic substrate with microwaves involves primarily two physical mechanisms. Conductive currents may flow in response to the oscillating electrical field, giving rise to an ohmic loss mechanism (i.e. Joule heating). With this loss mechanism, the conductivity of the material play a central role. If permanent dipoles exist in the material, orientation or dipolar loss mechanisms may also result. Although reinforcing filaments made of alumina, alumina-silicates, silicon carbide, and carbon are commercially available, this discussion concentrates on Nicalon™ (SiC) fibers, which were used in earlier experimental studies of microwave assisted CVI. These experiments,³ conducted in a multi-mode cavity, indicate that temperatures exceeding 1000°C can be maintained with 700 watts of input power in stacks of ceramic grade Nicalon™.

Nicalon™ filaments are formed by pyrolysis of polymeric SiC precursors. Atomic composition is reported as 35% Si, 55% C, and 10% O, while the microstructure consists of 2 nm β -SiC crystals with similarly sized C clusters embedded in an O-rich amorphous phase.⁹ The amorphous phase acts as broad grain boundaries of composition $\text{SiC}_{1-x}\text{O}_x$. Silicon NMR shifts attributable to C_2SiO_2 , CSiO_3 , and SiO_4 have been identified in the amorphous phase.⁹ Surface treatments using hydrofluoric acid and exposure to air at elevated temperatures indicate no change in the electrical properties of the filaments. The mechanism of microwave heating in Nicalon™ may well involve dipolar coupling in the amorphous phase. However, the dc conductivity (10^{-3} ohm-cm⁻¹) is in the range where Joule heating may also contribute.

Microstructural changes in the reinforcement occurring with extended heating may also affect microwave absorption. In the case of Nicalon™ short duration annealing experiments in nitrogen atmospheres at 1200-1300°C indicate that the SiC crystal size increases.¹⁰ Furthermore, it was reported that a small change in SiC crystal size, from 1.8 to 2.0 nm, can have significant impact on the conductivity. Growth of the SiC particles would presumably involve extraction of Si and C from the oxygen rich amorphous phase, and could affect microwave dissipation by both the dipolar and ohmic mechanisms. Microstructural changes occurring with long-term heat treatment in the range of 900-1000°C, where CVI is typically preformed, must also be considered. Our experiments show no appreciable change in the ability of ceramic grade Nicalon™ to absorb microwave energy following 30 hrs of heating (950°C) in a hydrogen atmosphere.

To have good composite toughness, it is essential that the reinforcing fibers debond and pull out from the matrix upon cracking. This process is usually facilitated by coating the fibers with an interfacial material which does not form a strong bond with the matrix. The two most popular choices are pyrolytic carbon and boron nitride. The effects of interfacial coatings on microwave absorption must be considered. Microwave heating experiments (in hydrogen atmospheres) using ceramic grade Nicalon™ coated with pyrolytic carbon suggest that the carbon coating affects the absorption of microwave energy. Uninsulated uncoated cloth heats readily with 700 W of power, whereas Nicalon™ cloth coated with 10-20 micrometers of pyrolytic carbon does not heat. However, with a small amount of porous, microwave transparent insulation it readily heats at the same power levels as the uncoated cloth. Based on the value of its conductivity (10^{-11} to 10^{-12} ohm cm⁻¹), boron nitride should be essentially microwave transparent.

Microwave-Matrix Interactions. Properties of the matrix material can have significant impact on absorption of microwave energy and on the evolution of thermal gradients. For example, when Joule heating mechanisms are prevalent, dissipation of microwave energy into heat goes as the electrical conductivity times the square of the local electric field strength. A high conductivity matrix suggests electrons in conduction bands suffer relatively few collisions and microwave energy is re-radiated from the surface. An extremely low conductivity implies little dissipation as heat and a large microwave penetration depth. Intermediate values correspond to regions where Joule heating may be important. Results obtained using silicon based matrix materials suggest that the ability of the matrix to absorb microwaves, relative to the fibers, can ultimately govern the composite evolution.

Microwave assisted CVI involving deposition of a β -SiC matrix is apparently a case where the reinforcement absorbs microwave energy better than the semiconducting matrix material. Deposition of β -SiC by reaction of methyl-trichlorosilane (MTS) in hydrogen initially proceeds with inside-out densification occurring.³ However, following deposition of a coating thickness on the same order of magnitude as the microwave skin penetration depth, the matrix apparently reflects the microwaves and a shift in modes occurs. As shown earlier, this in turn results in the evolution of complex heating and deposition patterns.³

By modifying reaction conditions a siliconized SiC matrix can be deposited from the MTS-hydrogen system.³ Deposition of a Si-rich SiC matrix is an example of a case where both the matrix and reinforcement dissipate microwave energy reasonably well. The extra Si serves to lower the conductivity of the matrix into a range where ohmic loss mechanisms are more effective. Previous results have shown that CVI then proceeds without development of the complex heating patterns seen with β -SiC deposition. Furthermore, regions of high composite density can be attained at the composite center as densification occurs from the inside out.

Silicon nitride has a low conductivity (10^{-9} ohm-cm⁻¹) and is essentially microwave transparent. Deposition of Si₃N₄ is easily accomplished by reaction of silane and ammonia, in a hydrogen atmosphere. Deposition of Si₃N₄ by CVI into uncoated and insulated carbon coated ceramic grade Nicalon™ cloth stacks demonstrated inside-out densification.⁴ Figure 1 shows a stack of 10 carbon coated Nicalon™ cloths before and after the infiltration run. For the densified cloth shown in Figure 1, the initial weight was 6.46 gm while the final weight following 29.5 hrs of infiltration was 26.78 gm. The reactor configuration and preform fixturing were as previously described.⁴ Figure 2 shows a cross-section of Si₃N₄ infiltrated cloth stack, with a height of approximately 1 cm.

The infiltrated stacks had regions of relatively high porosity. The darker areas seen in the infiltrated stack shown in Figure 1 are indicative of this. This effect is thought to be the result of primarily non-uniform electric fields. However, cooling of certain cloth regions by the (cool) flowing gases may also contribute, as gas flow rates and patterns were not optimized. The stacks used in these experiments were loosely held in a microwave transparent ceramic receptacle. The initial preform porosity was high, on the order of 89%. While a significant amount of Si₃N₄ was deposited, the final porosity of the disc was still on the order of 60%. Although this density is too low for most applications, it should be noted that had the stack been compressed so that the initial porosity were in the range commonly

used for CVI (i.e. 40-45%), final densities in the range of 80-85% would have been achieved, given the amount of Si_3N_4 deposited. Densities in this range are competitive with existing conventional CVI processes for infiltrating disc shaped cloth lay-ups and are high enough for many applications. Furthermore, weight gains of this magnitude can be obtained in approximately 30 hrs using microwave assisted CVI. Such processing times are also competitive with existing forced flow technologies using conventional heating.

Discussion

The recent experimental and numerical studies demonstrate the viability of microwave assisted CVI as a process for the rapid fabrication of net shape ceramic matrix composites. The initial studies also serve to highlight the technical obstacles requiring further study. In addition to the usual concerns in CVI processing, such as, reaction chemistry, mass transport, preform structure and thermodynamics, many of the difficulties seen in microwave processing of ceramics also exist. Field homogeneity in multi-mode cavities, control schemes in single mode cavities, scale-up issues, thermal runaway, and microwave materials interactions will all have to be addressed. For example, for certain classes of materials in which microwave energy is dissipated by way of Joule heating, there appears to be an upper limit to the matrix conductivity for straightforward application of microwave assisted CVI. Deposition of the higher conductivity matrix materials (e.g. pure β -SiC) may require co-deposition of another phase to modify the matrix conductivity and maintain efficient microwave absorption. However, if the matrix effectively dissipates the energy of the electric field by way of other heating mechanisms (e.g. as in oxide ceramics), use of the CVI technique to densify the composite may proceed without difficulty.

The gross changes in material properties which occur as infiltration proceeds further complicates the process. Our experimental results indicate that spatial variations in porosity within the preform ranging from 10 to 70% can occur. Furthermore, given the limitations on the types of commercially available fibers, the electrical properties of the deposited matrix will invariably be different than those of the fiber. Processing schemes must deal with relative interactions of microwaves with fibers and matrix. Differences in these properties can be used to advantage as in the seeding a microwave transparent preform and its subsequent infiltration with a lossy matrix.

Finally, microwave assisted CVI processing schemes such as power or reactant pulsing offer the potential for further reductions in processing times with improved composite uniformity. Combination of both approaches may lead to further improvements and a means of developing new composite microstructures.

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References

1. T.M. Besmann, B.W. Sheldon, R.A. Lowden, and D.P. Stinton, "Vapor Phase Fabrication of Continuous Filament Ceramic Composites". *Science* Vol. 253: 1104 (1991).
2. K. Itoh, M. Imuta, A. Sakai, J. Gotoh, "Pulsed Chemical Vapor Infiltration of SiC to Three-Dimensional Carbon Fibre Preforms". *J. Mater. Sci.* 27, 6022 (1992).
3. D.J. Devlin, R.P. Currier, R.S. Barbero, B.F. Espinoza, and N. Elliot, "Microwave Assisted Chemical Vapor Infiltration". *Mater. Res. Soc. Symp. Proc.* Vol. 250: 245 (1992).
4. D.J. Devlin, R.P. Currier, R.S. Barbero, B.F. Espinoza, "Chemical Vapor Infiltration with Microwave Heating", *Ceramic Engineering and Science Proceedings*, Vol. 14, No 7-8, (1993).
5. P.S. Day, D.J. Skamser, M.S. Spotz, H.M. Jennings and D.L. Johnson, "Microwave-Assisted Chemical Vapor Infiltration" *Ceramic Engineering and Science Proceedings*, Vol. 14, No 7-8, (1993).
6. D. Gupta and J.W. Evans, "A Mathematical Model for Chemical Vapor Infiltration with Microwave Heating and External Cooling". *J. Mater. Res.* Vol. 6 No. 4: 810 (1991).
7. J.I. Morell, D.J. Economou, and N.R. Amundson, "A Mathematical Model for Chemical Vapor Infiltration with Volume Heating", *J. Electrochem. Soc.* Vol. 139, No 1, 328 (1992).
8. J.I. Morell, D.J. Economou, and N.R. Amundson, "Pulsed-Power Volume-Heating Chemical Vapor Infiltration". *J. Mater. Res.* Vol. 7, No. 9: 2447 (1992).
9. Y. Hasegawa, "Synthesis of Continuous Silicon Carbide Fibre", *J. Mater. Sci.* 24:1177 (1989); C. Laffon, et al., "Study of Nicalon-Based Ceramic Fibres and Powders by EXAFS Spectrometry, X-ray Diffractometry and Some Additional Methods" *ibid.* 24:1503 (1989); L. Porte and A. Sarte, "Evidence for a Silicon Oxycarbide Phase in the Nicalon Silicon Carbide Fiber", *ibid.* 24:271 (1989); Y. Maniette and A. Oberlin, "TEM Characterization of Some Crude or Air Heat-Treated SiC Nicalon Fibres", *ibid.* 24:3361 (1989), "Interphase Phenomena in Silicon Carbide Single Filament Composites", *ibid.* 25:3864 (1990); R.J. Day, V. Piddock, R. Taylor, R.J. Young, and M. Zakikhani, "The Distribution of Graphitic Microcrystals and the Sensitivity of their Raman Bands to Strain in SiC Fibers", *ibid.* 24:2898 (1989).
10. O. Chauvet, T. Stoto, and L. Zuppiroli, "Hopping Conduction in a Nanometer-Size Crystalline System: A SiC Fiber". *Phys. Rev. B* 46(13): 8139 (1992).



Figure 1. Cloth before and after infiltration.

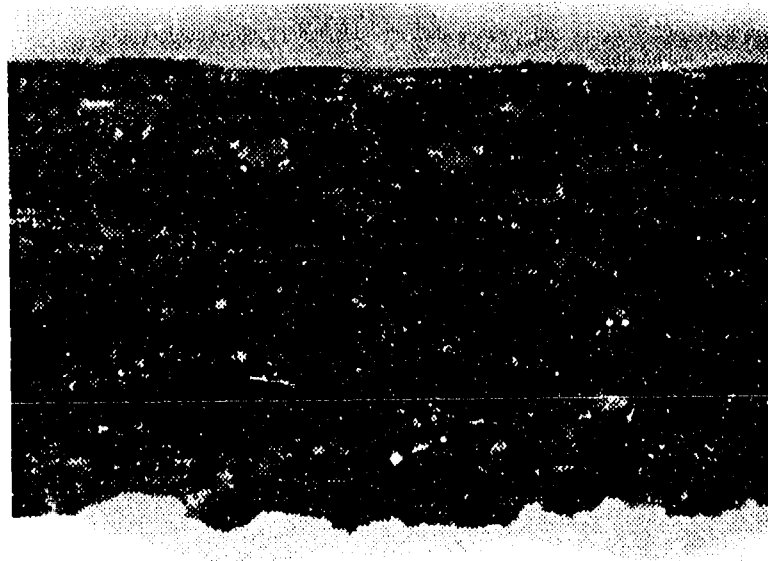


Figure 2. Cross-section of Si₃N₄ infiltrated cloth.