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Oxidation and Corrosion of Ceramics and Ceramic Matrix Composites

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Nathan S. Jacobson

NASA Glenn Research Center

Cleveland, OH 44135

Phone: 216-433-5498

FAX: 216-433-5544

e-mail: nathan.s.jacobson@grc.nasa.gov

Elizabeth J. Opila

Cleveland State University

NASA Glenn Research Center

Cleveland, OH 44135

Phone: 216-433-8904

FAX: 216-433-5544

e-mail: opila@grc.nasa.gov

Kang N. Lee

Cleveland State University

NASA Glenn Research Center

Cleveland, OH 44135

Phone: 216-433-5634

FAX: 216-433-5544

e-mail: Kang.N.Lee@grc.nasa.gov

Introduction

Ceramics and ceramic matrix composites are candidates for numerous applications in high temperature environments with aggressive gases and possible corrosive deposits. There is a growing realization that high temperature oxidation and corrosion issues must be considered. There are many facets to these studies, which have been extensively covered in some recent reviews [1,2].

The focus of this paper is on current research, over the past two years. In the authors' view, the most important oxidation and corrosion studies have focused on four major areas during this time frame. These are (I) Oxidation of precursor-based ceramics. (II) Studies of the interphase material in ceramic matrix composites. (III) Water vapor interactions with ceramics, particularly in combustion environments. (IV) Development of refractory oxide coatings for silicon-based ceramics. In this paper, we shall explore the most current work in each of these areas.

Oxidation of Precursor Derived Ceramics

Precursor-derived ceramics in the system Si-B-C-N are promising new candidates for high temperature applications. Some of the outstanding properties attributed to these materials include thermal stability of the amorphous phase to temperatures as high as 1900°C [3], a stage III

creep rate below detectible measurement levels [4], and the lowest reported oxidation rates of any non-oxide material known to date [3].

Much of the work on these materials is focused on processing routes from ceramic-precursor materials [5]. Descriptions of oxidation behavior to date are based on a limited number of high temperature exposures in air. It is proposed [3,6] that a thin amorphous dual layer oxide which forms on SiBN_3C when exposed in air at high temperatures is responsible for the excellent oxidation resistance of this class of materials. Secondary neutral mass spectroscopy (SNMS) [3] as well as Energy Dispersive Spectroscopy (EDS) [6] show that the outer layer is composed of silica containing some boron and carbon, while the inner layer is a B-N phase containing some silicon and oxygen. Thermochemical calculations show that BN can exist in equilibrium with SiO_2 at low oxygen partial pressures [7] which is consistent with the SNMS and EDS observations. Oxidation rate constants determined from oxide thickness measurements for SiBN_3C powder oxidized in air at temperatures between 1000 and 1600°C are reported to be slightly lower those found for CVD Si_3N_4 in oxygen [6]. Care must be taken in comparing oxidation rates obtained at different oxygen partial pressures. For example, the rate of oxide formation on SiBN_3C ($k_p = 3.4 \times 10^{-2}$ (micrometers)²/h based on a 1.3 micrometer film grown in 50 h at 1500°C in air [3]), is not slower than SiC and Si_3N_4 as claimed. Pure CVD forms of SiC and Si_3N_4 yield oxidation rates of 9.5×10^{-2} and 1.1×10^{-1} (micrometers)²/h respectively at 1500°C in oxygen [8]. Oxidation rates of SiBN_3C would be expected to be about 1.6×10^{-1} (micrometers)²/h at an

oxygen partial pressure of 1 atm. At lower temperatures, SiBN_3C oxidation rates are comparable to CVD Si_3N_4 but lower than CVD SiC . Clearly these oxidation rates for SiBN_3C are very low, but entirely comparable to pure Si_3N_4 in this temperature range.

The work of Nickel and coworkers [7,9-10] is the first systematic work to assess the oxidation behavior of these materials. In an excellent summary [7] Nickel raises some of the key issues for the Si-C-B-N system. Thermal stability of the nitrogen in the base material is an issue. In addition, because these materials are silica formers the following problems of silica stability are expected to be equally detrimental for the Si-B-C-N materials: active oxidation, impurity dominated passive oxidation, water-vapor interactions, and hot corrosion. In addition, boria is very volatile at high temperatures especially in water vapor. These issues must be examined with careful experimental studies.

In some preliminary experimental work Nickel [9] finds thin scales in some cases and thick, bubbled scales in other cases, sometimes within the same sample. Nickel's work demonstrates some of the difficulties in characterizing the oxidation behavior of the Si-B-C-N materials. First, weight changes due to oxidation are small relative to those for SiC and Si_3N_4 for the same amount of material oxidized. For example when Si_3N_4 is oxidized 13g weight gain will be measured for every mole (60g) of SiO_2 formed due to concurrent nitrogen loss as a gas. For SiBCN_3 , however, only 2g weight gain will be observed for 95g of SiO_2 + $\frac{1}{2}$ B_2O_3 formed due to concurrent nitrogen and carbon losses as gases. In

addition, volatilization of boron can lead to very low mass gains even for thick oxide scale formation. These relatively low weight gains suggest much better lower oxidation rates than reality. Thus comparisons of oxidation rates on a weight basis alone are not valid. Careful microstructural analysis of oxide thickness and material recession must be conducted to compare oxidation rates to other silica-formers.

Second, porosity in the as-pyrolyzed materials leads to internal oxidation, again making interpretation of weight change results difficult. Statements about relative oxidation rates of porous materials are meaningless unless the porosity is characterized (percent porosity, pore size and distribution).

Third, complete removal of hydrogen during pyrolysis is needed or samples can be destroyed by release of residual gases on oxidation. Baldus et al. [11] propose that Si-H bonds are more prone to oxidation and must be eliminated for good oxidation resistance. This can be accomplished by pyrolysis at temperatures of at least 1450°C.

Finally, inhomogeneous materials are a problem, since oxidation properties can vary from region to region of material. As processing methods are optimized, homogeneous materials are expected to become more available, enabling systematic oxidation studies.

The Problem of Easily Oxidizable Phases in Composites

Fiber-reinforced SiC and Si₃N₄ have numerous desirable properties such as high fracture toughness, strength retention at high temperatures, good thermal conductivity, and light weight. However, nearly all proposed types of composites based SiC and Si₃N₄ contain some type of easily oxidizable second phase such as carbon or boron nitride (BN). To achieve the full potential of these materials, open cracks are permissible. Yet these very cracks provide hot-gas-paths to the readily oxidizable phases. Thus recent studies have focused on understanding the mechanism of the oxidation of this second phase in hopes of eventually mitigating the damage.

Carbon-fiber reinforced SiC is one leading candidate composite [12]. Carbon fibers are relatively inexpensive and stable in inert atmospheres to very high temperatures. However the oxidation of these fibers is a critical issue.

Initial studies of oxidation of carbon fiber reinforced SiC have been done by Lamouroux et al. [13]. At low temperatures the chemical reaction of oxygen with carbon is rate controlling, at intermediate temperatures diffusion through the crack is rate controlling, and at the highest temperatures the matrix is sealed with silica.

Recently, Halbig et al. [14] have examined the effect of oxidation on stressed C-fiber/SiC-matrix composites. These readily oxidize leading

to extensive oxidation in a stressed state. Specimens were stressed at 69 and 172 MPa from 350-1500°C. Only the specimens tested at 550°C and below showed time to failure of 25 hrs or more. The specimens tested at temperatures greater than 550°C showed time to failure of 17-142 minutes.

Analytical and finite element models are developed to model oxygen concentrations through a crack bridged by carbon fibers [15]. Qualitatively these predict a small change in oxygen concentration for the diffusion controlled cases and a large change in oxygen concentration for a reaction controlled case. Figure 1 illustrates these effects.

Given the severity of the oxidation problem with carbon fiber reinforcements, some major composite design changes are needed. Lamouroux et al. [16] have suggested a matrix composed of a sequence of layers $B_4C_{1-x}/B_4C/B_4C_{1-x}/SiC$ layers to improve oxidation resistance via the following:

- a. Crack deflection by these layers generally creates a narrow, complex path for entering oxygen.
- b. Sealing of the crack occurs more readily due to borosilicate glass formation.

Their results do indicate improved performance over SiC matrices. However, point (b) must be discussed in more detail. Relative to pure silica, the lower viscosity borosilicate glass flows more easily and hence 'plugs' any porosity or cracks. Such an approach may be useful over the short term, but for long-term operation borosilicates tend to

lose the boria component due to vaporization of boria. This leaves behind pure silica. If a substantial number of cracks are filled with silica, then the composite is weakened.

Other composite architectures involve SiC fibers in SiC or Si₃N₄ matrices. Common SiC fibers become unstable at temperatures greater than about 1200°C and hence are not desirable. However stoichiometric SiC fibers have been developed and as their price decreases, composites of these fibers in a SiC or Si₃N₄ matrix are then feasible. In order for proper load transfer to the fibers, the fibers cannot bond to the matrix. Thus coatings which are non-reactive with the matrix are required. These fiber coatings, termed 'interphases', are of these three types [12]:

- (1) Thin layer (< 1 μm) of anisotropic pyrocarbon.
- (2) Layered refractory oxide--magnetoplumbite-type oxides and mica-type oxides.
- (3) Hexagonal boron nitride (BN).

There are a number of critical environmental issues to be addressed with each of these schemes. As discussed, carbon oxidizes and is completely removed as a gas. Models have been developed for this [17].

The concept of a layered refractory oxide seems attractive, but there are only a very limited number of these compounds available. Further, it has been pointed out that although these oxides may not oxidize further, they are poor protective coatings for SiC fibers [18]. Silica has the lowest known permeability to oxygen; anything else would show faster oxygen transport.

The third concept is hexagonal boron nitride. BN has a number of problems in an oxidizing environment [19,20]. Oxidation to $B_2O_3(l)$ starts at about $850^\circ C$. This $B_2O_3(l)$ reacts readily with water vapor to form various $H_xB_yO_z(g)$ species. Thus in a moisture containing environment, BN effectively volatilizes. Less crystalline forms of BN and high oxygen content BN appear to be more reactive with water vapor. These structural/impurity effects on reactivity are important and need to be explored further.

In a composite with BN fiber coatings, degradation can occur via two mechanisms, as illustrated in Figure 2. BN oxidizes to form $B_2O_3(l)$, which reacts with any available SiO_2 to form borosilicate glass, as shown in Figure 2(a). After longer times, the B_2O_3 is leached out of the borosilicate by reaction with water vapor. Alternatively, BN oxidizes to form $B_2O_3(l)$, which in turn is volatilized by reaction with water, as shown in Figure 2(b). More et al [21] have observed similar effects. They also find that oxygen-containing BN leads to SiC attack deeper within the composite.

The attack of BN interphases has also been modeled by several investigators [20, 22; Luthra and Meschter, private communication]. As discussed, BN volatilizes and leaves behind the anular region shown in Figure 2(b). Simultaneously the SiC fiber and matrix walls oxidize and this oxidation is enhanced by the presence of boron.

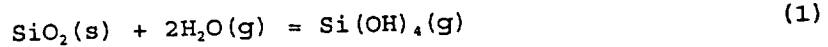
In summary, easily oxidizable second phases are a central issue with composites. By the very architecture of these materials, the second phases would be exposed to high oxygen potentials. In order for these composites to reach application, it is essential to address this problem.

Water vapor interactions with silicon-based ceramics

Silicon-based ceramics and composites are proposed for many applications in combustion environments. These environments contain substantial amounts of water vapor as a product of the combustion of hydrocarbon fuels. It has been shown that water vapor plays several roles in the degradation of silicon-based ceramics. The first effect is to increase the intrinsic oxidation rate of silicon-based materials relative to rates observed in dry oxygen or air. This effect is due to the higher solubility of water in the silica scale relative to oxygen. The increase in oxidation rates as a function of water vapor partial pressure has been quantitatively examined in several recent papers [23, 24]. It is generally agreed that the oxidation rate is proportional to $P(\text{H}_2\text{O})$ with a power law exponent of one. Results obtained experimentally with oxygen as a carrier gas should be corrected for the contribution of oxygen to the total oxidation process [Meschter, private communication].

The second effect of water vapor on silicon-based ceramics, which is of wide interest in the last few years, is the effect of volatility of

silica on material recession rates. Silica volatilizes by the following reaction:



High pressure burner rig studies showed linear recession rates of SiC and Si₃N₄ due to this effect [25, 26]. A parilinear kinetic model was developed to explain these results [26, 27]. It is shown that the linear volatility rate of silica and the linear recession rate of silica formers (k_1) have the following dependence:

$$k_1 \propto P_{\text{H}_2\text{O}}^2 \frac{v^{1/2}}{P_{\text{total}}^{1/2}} \quad (2)$$

This has been substantiated in a number of other burner rigs [28, 29] and land-based turbine environments [30-32]. It is very important when trying to simulate surface recession in turbine environments that a high gas velocity is used, in addition to a high partial pressure of water vapor. The volatility effect is barely discernable for a gas velocity of 4×10^{-2} m/s (50% water vapor/1 atm total pressure/1200 to 1400°C).

Recent work in a low velocity (5×10^{-4} m/s) high pressure (10 atm total pressure, 1.5 atm water vapor) rig has shown rapid degradation of silicon-based ceramics but by a different mechanism [31, 33-36]. In these low velocity conditions the volatility of silica is minimal. Because the water vapor partial pressure is high, oxidation is

enhanced, first, due to the high solubility of water vapor in silica as mentioned above, and second, these high oxidation rates generate large amounts of gaseous products [23]. The oxide scales become riddled with pores as the product gases accumulate. The oxidation rate is no longer controlled by solid state diffusion of oxidant through the silica scale. Instead, many short circuit paths through the pores are available for gaseous transport of the oxidant. Very thick oxide layers grow, however, they are non-protective and linear oxidation and recession rates are observed [33,35]. In the literature there are cases where the degradation of silicon-based materials in low velocity conditions are compared to degradation occurring in high velocity conditions [31,34,36]. It is important to recognize that the linear recession in low velocity and high velocity environments occurs by two entirely different mechanisms and simulations of turbine environments require high gas velocities for accurate prediction of surface recession.

The low velocity, high pressure rig is a useful tool, however, for other purposes. This type of rig is useful for simulating environmental damage internal to composites where gas velocity effects are not important. Another use for the high pressure low velocity rig is to screen materials which are needed as diffusion barriers to water vapor. Such materials may be needed as a barrier layer between silicon-based materials and environmental barrier coatings, which will be discussed in the next section.

At very high gas velocities experienced by turbine blades the model shown in Equation 2 above fails to account for recession occurring at the leading edge [32]. In addition, little oxide is found on the material surface [32, Opila, unpublished work]. The lack of surface oxide raises questions about the validity of applying Equation 2 under these conditions. A recent paper [37] maps out the pressure/velocity conditions where the parabolic model is applicable. Microstructural and recession data obtained under different pressure and velocity conditions are needed to complete this map.

Coatings

The use of silicon-based ceramic components in advanced gas turbine engines depends on the successful development of methods to prevent the volatilization of silica in water vapor. Application of external environmental barrier coatings (EBCs) is a promising approach to providing such a protection [38]. In addition such coatings provide protection against other forms of corrosion, such as deposit-induced corrosion.

Key issues that must be considered in selecting coating materials are as follows [39]: 1) The coating possesses environmental durability in water vapor. 2) The coating possesses a coefficient of thermal expansion (CTE) close to that of the substrate to minimize CTE mismatch stress. 3) The coating maintains a stable phase under thermal exposure. A volumetric change typically accompanies a phase transformation, disrupting the integrity of the coating. 4) The coating is chemically compatible with the substrate to avoid detrimental chemical reactions.

5) A low elastic modulus is desirable to enhance the compliancy of the coating under stress.

Previous coatings research primarily focused on silicate coatings because of their chemical compatibility with Si-based ceramics and CTEs ($3 - 5 \times 10^{-6}/^{\circ}\text{C}$) comparable to that of Si-based ceramics ($\sim 4 \times 10^{-6}/^{\circ}\text{C}$) [40-41]. These silicates include mullite, zircon, barium alumino-silicate (BAS), calcium alumino-silicate (CAS), cordierite, and barium-strontium alumino-silicate (BSAS). One key drawback of silicate coatings is the phase instability. Conventionally plasma-sprayed silicates typically deposit as an amorphous or a metastable phase. A phase transformation in subsequent thermal exposures can result in severe cracking or delamination [41]. Therefore, a thorough understanding of phase stability as a function of temperature and a careful control of processing parameters are necessary to minimize detrimental phase transformations. Besides the phase instability, some silicates have a relatively high silica activity and consequently will suffer a selective vaporization of silica in high pressure, high velocity water vapor environments [38,42]. This is illustrated in Figure 3 for mullite. BSAS is another silicate that has recently been identified as a promising EBC candidate [36,43-44]. It has a low silica activity (< 0.1), a low CTE ($\sim 4 \times 10^{-6}/^{\circ}\text{C}$), and an excellent resistance to cracking. The key drawback is its chemical incompatibility with Si-based ceramics. It can develop a reaction zone, when in contact with Si-based ceramics, and pores can also develop with certain Si-based substrates, such as melt-infiltrated SiC/SiC composites (MI).

Although a single layer coating possessing all key requirements for successful coating is most ideal, such a coating has not been identified yet. The next best option appears to be duplex or multilayer coating systems, consisting of multiple coating layers with each layer possessing one or more of the key requirements. A duplex coating of mullite and BSAS is a good example where the mullite provides the bonding and chemical compatibility, while BSAS provides the environmental protection [43-44]. In such a system, mullite is analogous to the metallic bond coat in conventional TBCs while BSAS is analogous to the YSZ top coat. Multilayer coating design with a compositional grading is an option when there is a large CTE mismatch between the constituent layers. Current state-of-the art EBC consists of two bond coats (silicon and modified mullite) and a top coat (BSAS) (Fig. 4) [36, 43-44]. The silicon bond coat provides a further improvement in the adherence and the modified mullite exhibits much improved crack resistance compared with the early mullite coating. In a high pressure burner rig exposure, uncoated MI exhibits weight loss due to silica volatilization, while EBC-coated MI exhibits fairly constant weight, demonstrating the effectiveness of EBCs in preventing silica volatilization (Fig. 5).

Non-silicate oxide ceramics in general possess superior environmental durability and phase stability in combustion environments. However, traditional high temperature refractory oxides, such as zirconia, alumina, and yttria, have CTEs higher than that of silicate ceramics by a factor of at least two. Consequently, these coatings readily crack and spall under thermal cycling. Multilayer coating systems consisting

of a low CTE silicate bond coat, such as mullite, and a refractory oxide top coat, such as zirconia, have demonstrated some promise [39,42]. As indicated earlier, compositional grading should help reduce the CTE mismatch stress between the bond coat and the top coat. More detailed work, analytical and experimental, needs to be done to fully understand the benefits as well as the limitations of the multilayer coatings concept to better design the coating. Non-silicate, low CTE oxide ceramics need to be explored as well. Such a coating may eliminate the need for a silicate bond coat.

EBCs for CMCs is an emerging area of technology and excellent opportunities for further development are on the horizon. Future coatings research should be directed to thorough characterization and understanding of current EBCs, development of improved coating design concepts, further exploration of low CTE ceramics, development of other processing techniques [45,46], and development of life modeling.

Conclusions

Four major areas of ceramic corrosion research have been discussed. The oxidation of precursor-derived ceramics requires systematic experiments with rigorous analyses. Oxidation of ceramic composites focuses the easily oxidizable phases—both in terms of oxidation modeling and mitigating oxidation effects. In the area of water-vapor effects, the emphasis is on modeling and further extension to actual combustion environments. Research in protective coatings is directed at the development of refractory oxide coatings for protection against water vapor volatility of silica.

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Figure Captions

Figure 1. Cross section illustrations of the oxidation patterns at two stages of oxidation of carbon fiber tows for reaction controlled and diffusion controlled kinetics. The microstructures with fibers parallel to and perpendicular to the page are from stressed oxidation until failure. The dark gray areas are where a fiber was consumed from oxidation and the black areas are voids. (from [13] reprinted with permission of the American Ceramic Society).

Figure 2. Micrographs of composites with one edge ground off and exposed to oxidized gases. The top photo (courtesy of Q. Nguyen) shows borosilicate formation and the bottom photo shows volatilization due H-B-O(g) specie formation (from [19] reprinted with permission of the American Ceramic Society).

Figure 3. Mullite plasma-sprayed on substrate heated at 1200°C after cyclic exposure in high-pressure burner rig (50h, 1230°C, 6h cycles, 6 atm, equivalence ratio = 1.9, $V_{gas} = 2000$ cm/sec) [44].

Figure 4. Modified mullite/BSAS-coated melt-infiltrated SiC matrix with SiC fibers SiC after cyclic exposure in water vapor furnace (200h, 1300°C, 2h cycles, 90% H₂O/O₂, 1 atm) (adapted from [44]).

Figure 5. Weight change of coated and uncoated MI after cyclic exposure in high-pressure burner rig (1200°C, 6h cycles, 6 atm, equivalence ratio = 0.78, $v_{gas} = 2000$ cm/sec) [44].

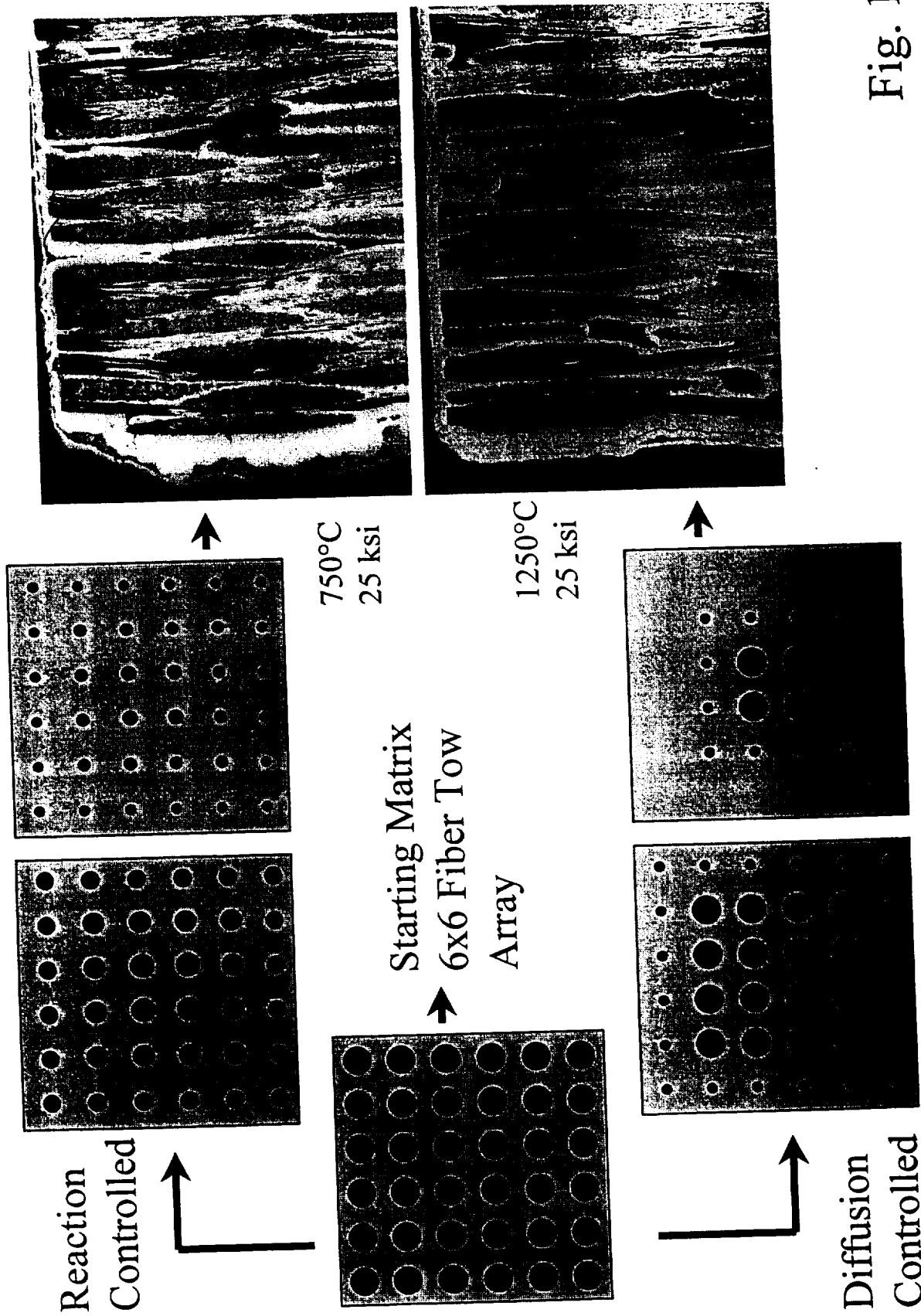


Fig. 1

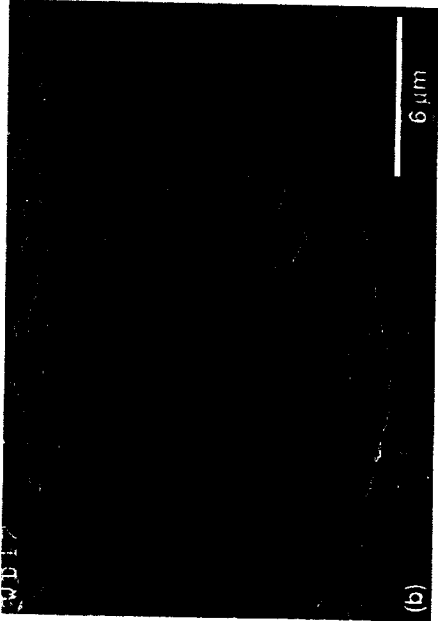
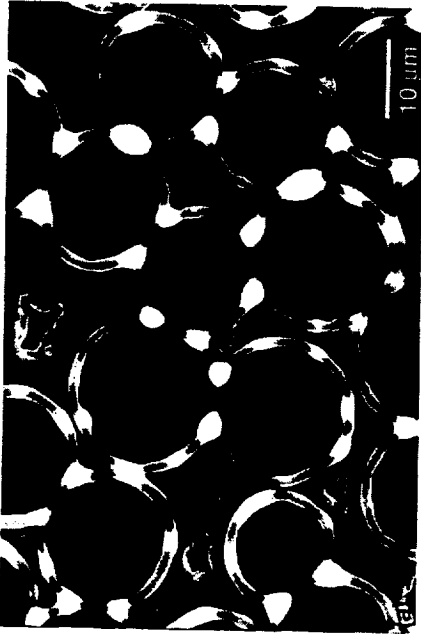


Fig. 2

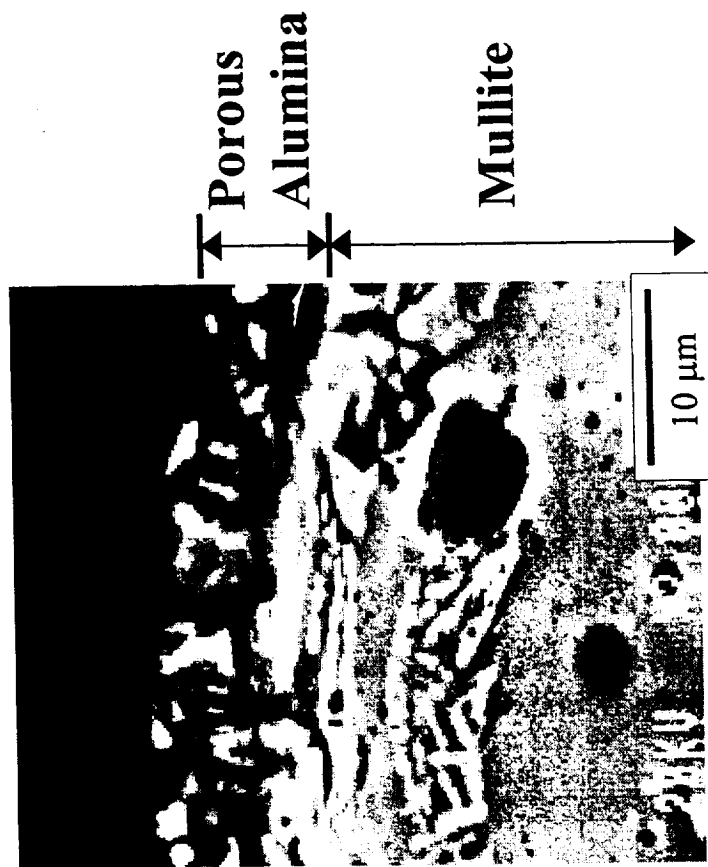


Fig. 3



Fig. 4

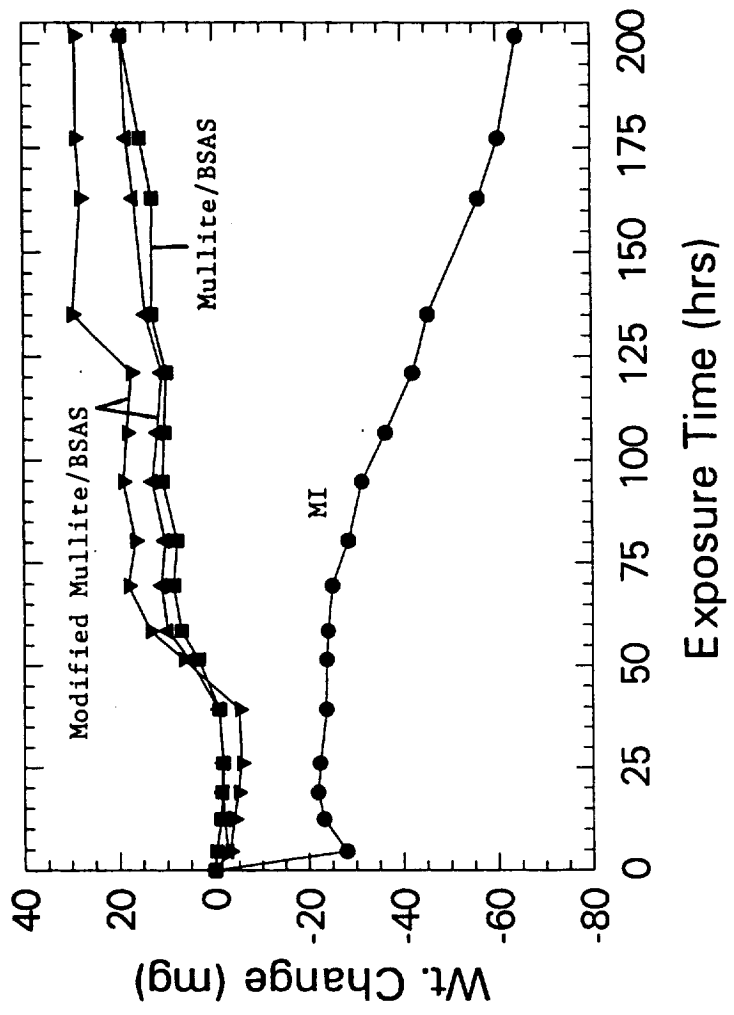


Fig. 5

