Chemical Vapor Deposition of Ta_2O_5 Corrosion Resistant Coatings

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Abstract

Silicon carbide and silicon nitride heat engine components are susceptible to hot corrosion by molten Na_2SO_4 which forms from impurities present in fuel and the environment. Chemically vapor deposited Ta_2O_5 coatings are being developed as a means to protect components from reaction with these salts and preserve their structural properties. Investigations to optimize the structure of the coating have revealed that the deposition conditions dramatically affect the coating morphology. Coatings deposited at high temperatures are typically columnar in structure; high concentrations of the reactant gases produce oxide powders on the substrate surface. Ta_2O_5 deposited at low temperatures consists of grains that are finer and have significantly less porosity than that formed at high temperatures. Samples of coatings which have been produced by CVD have successfully completed preliminary testing for resistance to corrosion by Na_2SO_4.

Introduction

Silicon carbide and silicon nitride materials have undergone extensive development in recent years for use in a wide variety of applications such as heat exchangers, hot gas cleanup systems, and advanced heat engines. In these types of systems, ceramics will be susceptible to hot corrosion in the form of attack by molten salts such as Na_2SO_4 formed from NaCl present in the atmosphere and sulfur impurities in the fuel.[1] Long term exposure

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to these types of conditions has been shown to degrade the properties of structural ceramics.[1-5]

Exposed surfaces of silicon-based ceramics oxidize at high temperatures to form a layer of silica which serves to inhibit further oxidation of the ceramic.[6] As described by others,[3,7-9] this silica layer can react with the molten salt to form a sodium-silicate liquid phase at temperatures above approximately 800°C, the eutectic temperature in the sodium-silica system.[10] As a result, the ceramic loses its protective layer and degradation of the ceramic occurs.[2,7,8]

Due to the nature of the service conditions under which these ceramic components are expected to perform, it becomes necessary to protect them from corrosion. Coatings are currently being developed which may protect SiC and Si_3N_4 components from salt-induced corrosion.

Background

In 1986, GTE Laboratories initiated a program to develop a coating system which would protect SiC and Si_3N_4 heat engine components from both corrosion and contact stress damage. The development of such coatings is difficult because a mismatch between the coefficient of thermal expansion (CTE) of the coating and that of the substrate can cause the coating to crack or spall. To resolve this problem, the coating system shown in Figure 1 was developed by GTE to accommodate the stresses caused by the difference in CTE.[11] Initially, an AlN coating was deposited onto the substrates. During the chemical vapor deposition (CVD) process, chemical interactions produced a SiAlON-type compound which provided adherence to the substrate. The coating was then compositionally graded from AlN to $Al_xO_yN_z$ to Al_2O_3 + ZrO_2. Due to the absence of sharp interfaces and the gradual increase in thermal expansion from the interface to the outer Al_2O_3 + ZrO_2 protective coating, residual stresses in the coating were minimized, providing a coating system which should survive in the thermal environment found in heat engines.

GTE Laboratories' coating system seemed appealing for several years.[12,13] However, thermal cycling of their coatings produced cracks, severely degrading their ability to protect components from oxidation. As a result, the developers of this coating system concluded that the difference in thermal expansion between SiC or Si_3N_4 and the Al_2O_3 + ZrO_2 coating is too great to develop an adherent, crack-free coating.

Candidate Protective Coatings

Several criteria must be met in order for a material to provide corrosion protection. The first and most obvious requirement is the ability of the coating to resist reaction with an aggressive salt layer. It must also have a CTE that is much closer to that of SiC and Si_3N_4. More closely matched CTE's would overcome the problem of adherence as well as minimize noncatastrophic cracking which would allow molten salt to penetrate the coating and result in a loss of corrosion protection. The material must also be a stable oxide. This requirement will make the coating inherently oxidation resistant. Additionally, considerations for weight and cost must also be taken into account.

Carbon/carbon composites are well known to have potential for use in the aerospace industry. In these high temperature applications, however, they must be protected from oxidation. Yet these composites are also known to have very low thermal expansion coefficients. As a result, after twenty years of investigation, no oxidation resistant coatings have been found that are capable of surviving the dramatic thermal cycles typical of aerospace environments. These investigations did, however, identify several materials with low CTE's that could be useful as coatings to protect SiC and Si_3N_4. These materials are listed in Table 1.

$3Al_2O_3 \cdot 2SiO_2$ (mullite) is a material that has a CTE very close to that of SiC and it has performed reasonably well in corrosion tests, corroding somewhat more severely than Al_2O_3 but surviving significantly better than SiC.[5] Mullite's corrosion resistance is dependent on the absence of free SiO_2, which is readily attacked by sodium-containing salts.[2,7,8] Because of its corrosion resistance and low CTE, mullite is currently being investigated as a material for high temperature cross-flow filters that are exposed to sodium contaminants.[14]

Al_2TiO_5 also has a CTE that is quite low. It is currently being investigated as a protective coating for carbon/carbon composites and as a corrosion resistant material for turbine engine components.[15] Problems, however, do exist for this material. Its CTE is very anisotropic, causing significant microcracking in monolithic structures. As with GTE Laboratories' coating system, this would obviously destroy the integrity of the coating and allow both oxygen and sodium to attack the components which it is designed to protect. Additionally, Al_2TiO_5 tends to absorb water and could degrade significantly if it were exposed to an environment containing as little as ten per cent moisture at high temperatures.

There is not a great wealth of information known about $ZrTiO_4$ or $HfTiO_4$. However, investigations have shown the thermal expansion coefficients of these materials to be quite low.[15-17] $ZrTiO_4$ and $HfTiO_4$ crystallize in orthorhombic structures which are free of transformations.[18,19] The structures formed by the titanate phases provide significant advantages over the destructive phase transformations experienced by ZrO_2 and HfO_2. Having stable crystal structures, the titanate phases do not require stabilizers which could be leached out of the structure.

Even less is known about $Ta_2O_5 \cdot 6ZrO_2$ and $Ta_2O_5 \cdot 6HfO_2$. Both materials are reported[15] to have low thermal expansion coefficients and each has potential for good corrosion resistance, making them promising candidates. The lack of knowledge of these materials, as well as the possible complexity in obtaining exact stoichiometries for $Ta_2O_5 \cdot 6ZrO_2$ and $Ta_2O_5 \cdot 6HfO_2$ and avoiding the production of homologous phases, pose potential problems concerning the ease with which they may be deposited.

On the other hand, the ease with which Ta_2O_5 can be deposited has already been demonstrated.[20,21] Additionally, phase equilibria studies of the Ta_2O_5-Na_2O system have shown that no liquid phases are present below 1625°C, as shown in Figure 2.[22] Formation of either of the sodium tantalate phases at typical application temperatures that are 300 to 500°C below the liquidus temperature would seem unlikely.[23]

In order to protect SiC and Si_3N_4 components, the candidate coating must also prevent the oxygen present in a combustion atmosphere from diffusing through the coating to the surface of the component. Since oxygen can diffuse through most oxides at a significant rate, another barrier to oxygen must be established. This can be provided by the native silica layer which coats silicon-based ceramics. Silica is relatively impervious to oxygen, and it should prevent oxidation of the component. However, if the silica layer should either react with or diffuse into the protective coating which is deposited on top of it, its effectiveness to stop oxygen penetration would likely be destroyed. Although phase equilibria for the system Ta_2O_5-SiO_2 does not appear to be well established, the available data shows that no liquid phases exist below 1550°C.[24] As in the formation of any intermediate sodium tantalate phases, no solid state reactions are expected at temperatures 200 to 400°C below the liquidus temperature. To ensure compatibility between the silica layer and the protective Ta_2O_5 coating, long-term testing will need to be performed.

Experimental Procedure

Chemical vapor deposition of Ta_2O_5 on SiC substrates has been performed using the experimental setup shown in Figure 3. This system is contained in a quartz tube which is sealed at both ends with stainless steel end caps. The substrate is heated inductively by heating a graphite susceptor with a radiofrequency generator. Corrected substrate temperatures in the range of 1000 to 1300°C are measured using an optical pyrometer by sighting through a window in the end cap. In the first stage of the reactor, chlorine gas is passed over tantalum metal in a chlorinator electrically heated to approximately 600°C, producing $TaCl_5$ via

$$2Ta + 5Cl_2 = 2TaCl_5.$$

The addition of O_2 through a separate inlet tube causes the gases to react at the substrate via

$$4TaCl_5 + 5O_2 = 2Ta_2O_5 + 10Cl_2$$

to produce an adherent Ta_2O_5 coating on the substrate.

Sets of experiments were statistically designed using a 2^n factorial method to efficiently find the optimal deposition conditions. X-ray diffraction (XRD) techniques were used to verify the composition of the coating. Coating morphology was characterized using scanning electron microscopy (SEM) and optical microscopy.

Coatings deposited by CVD underwent preliminary testing for corrosion by Na_2SO_4 using a solution of distilled water and Na_2SO_4. A drop of solution was applied to the top center face of a coated sample and dried in a drying oven, thus leaving only the salt on the coating. This was repeated until a Na_2SO_4 concentration of 10 to 20 mg/cm^2 was obtained. Corrosion testing was performed in a four inch diameter quartz tube furnace at 1000°C for 100 hours with a 200 sccm flow of air passing over the specimens. Samples were then analyzed using XRD and SEM techniques.

Results and Discussion

The morphology of the Ta_2O_5 coating was strongly dependent on the deposition conditions. The statistically designed experiments examined the effects of system pressure, argon gas flow rate, substrate temperature, and oxygen and chlorine gas flow rates. Initial experiments over a range of substrate temperatures and gas flow rates indicated that regardless of substrate temperature or gas flow rates, consistently denser deposits of Ta_2O_5 were being formed at pressures of approximately 6.67 kPa (50 Torr) and using 40 sccm of argon to dilute the reactant gases. As a result, pressure and argon flow were fixed at these two values during the investigation. Gas flows for oxygen and chlorine ranged from 8 to 20 and 1 to 5 sccm, respectively.

Substrate temperatures of 1300°C produced coating structures which contained large, columnar grains with considerable intergranular passages. This structure can be seen in the optical and scanning electron microscope photographs shown in Figure 4. Obviously, this coating could do little to protect SiC or Si_3N_4 from the corrosive environment found in heat engines. Liquid Na_2SO_4 could flow in between the columnar grains with ease, attack and dissolve the SiO_2 coating the ceramic component, and subsequently attack the component itself.

Ta_2O_5 which was produced with high concentrations of reactants - an oxygen to chlorine to argon ratio of 10 to 3 to 40 - produced powders on the substrate surface. These can be seen in Figure 5. Even though most of the powders adhered to the substrate well enough to be examined by microscopy, it is certain that they would not be able to withstand the high pressure combustion environment, loaded with abrasive particulates, found in an engine.

At lower temperatures and with more dilute concentrations of reactant gases, more coherent coatings have consistently been produced which contain more equiaxed grains. As shown in Figure 6, these coatings are very uniform and continuous in structure. Unlike the morphologies described previously, they likely would not allow molten salts a direct path to the substrate surface.

Additional work is currently underway to further optimize coating morphology. The aim of refinements to the Ta_2O_5 structure is to produce finer, more equiaxed grains. Reducing grain size would increase the diffusion path along grain boundaries to the substrate surface. If oxygen diffusion occurs along grain boundaries, a reduction in grain size would increase the time required for oxygen transport across the coating. Residual coating stresses due to anisotropy in the coefficient of thermal expansion would also be minimized with a reduction in grain size. Coating morphologies such as these promise to protect the ceramic components in heat engines.

Preliminary corrosion tests using 15 mg/cm^2 of Na_2SO_4 in contact with CVD deposited Ta_2O_5 demonstrated that no apparent reaction occurred between the coating and the molten salt. As shown in the upper left corner of Figure 7, the Ta_2O_5 coatings which were tested consisted mainly of columnar grains and whiskers. Despite the coating morphology, no interaction of the coating or substrate with the molten salt seems to have taken place. An examination of Figure 7 indicates that the Na_2SO_4 in the lower right corner melted upon heating past its melting point and wetted the surface of the Ta_2O_5 coating. At the end of the corrosion test, the salt simply recrystallized as a polycrystalline film on the coating surface. These results were confirmed by X-ray diffraction, which identified SiC and Ta_2O_5 as the phases present. To more completely determine the suitability of Ta_2O_5 coatings, however, additional work is needed to test and subsequently analyze specimens under similar conditions for up to 1000 hours.

Conclusions

SiC and Si_3N_4 heat engine components are susceptible to hot corrosion by molten Na_2SO_4 salts which are formed from impurities in the engine's fuel and air intake. A number of oxides have been identified which may protect these components from corrosion. Among these, Ta_2O_5 was selected as one of the most promising candidates, and chemical vapor deposition techniques have been developed to deposit it onto SiC substrates. Depending on the deposition conditions, a variety of coating morphologies have been produced, and conditions have been identified which produce dense, continuous Ta_2O_5 deposits.

These conditions are being further optimized to produce a finer, more equiaxed microstructure. Additionally, preliminary corrosion tests with 15 mg/cm^2 of Na_2SO_4 at 1000°C showed no degradation of the CVD deposited coatings of Ta_2O_5.

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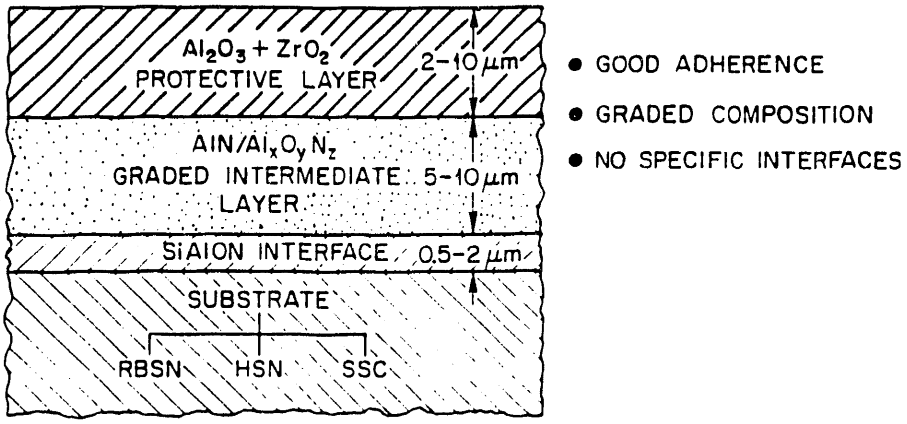


Figure 1
GTE's Protective Coating

Table 1
Refractory Oxides with Potential for Oxidation/Corrosion Protection

Compound	Density (g/cm^3)	CTE (x10^{-6}/°C)
Al_2O_3 *	3.97	8.0
$3Al_2O_3 \cdot 2SiO_2$	2.8	5.7
SiC *	3.21	5.5
$ZrTiO_4$	≈5	≈4
$HfTiO_4$	≈5	≈4
$Ta_2O_5 \cdot 6ZrO_2$	≈6	≈4
$Ta_2O_5 \cdot 6HfO_2$	≈6	≈4
Ta_2O_5	8.02	3.6
Si_3N_4 *	3.19	3.0
Al_2TiO_5	3.68	2.2
Carbon/carbon *	1.9	≈0

* Included only as a reference and not as a potential coating

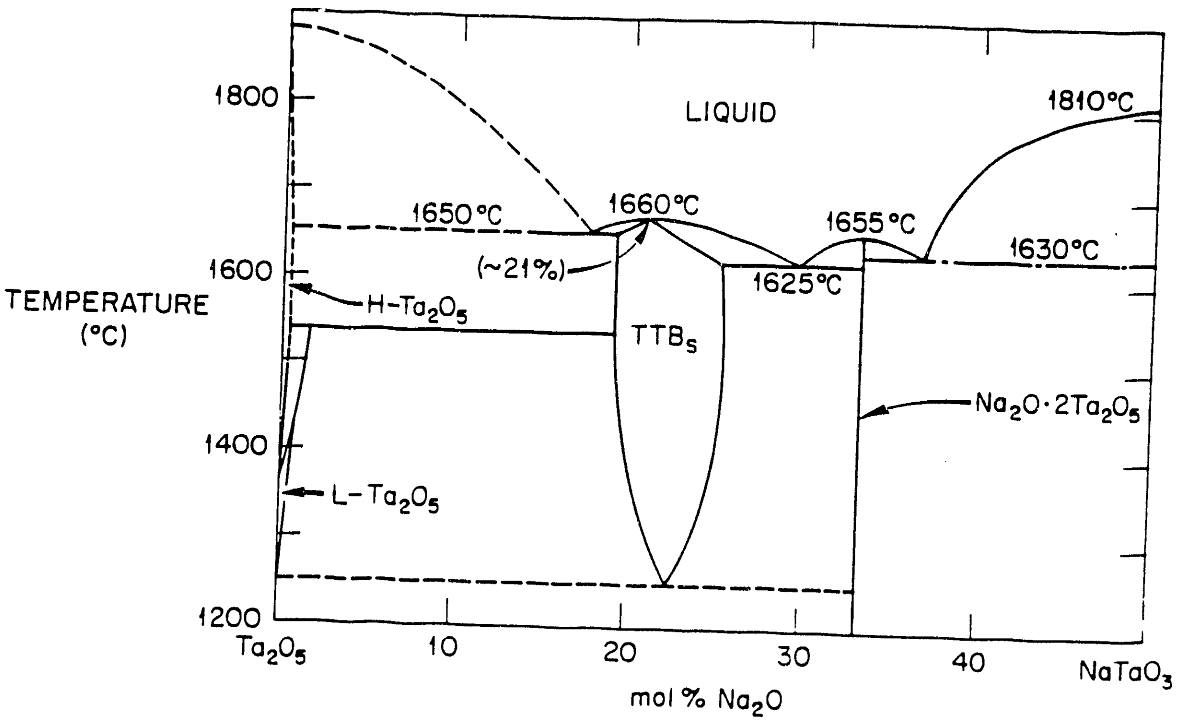


Figure 2
Ta_2O_5-Na_2O Phase Diagram

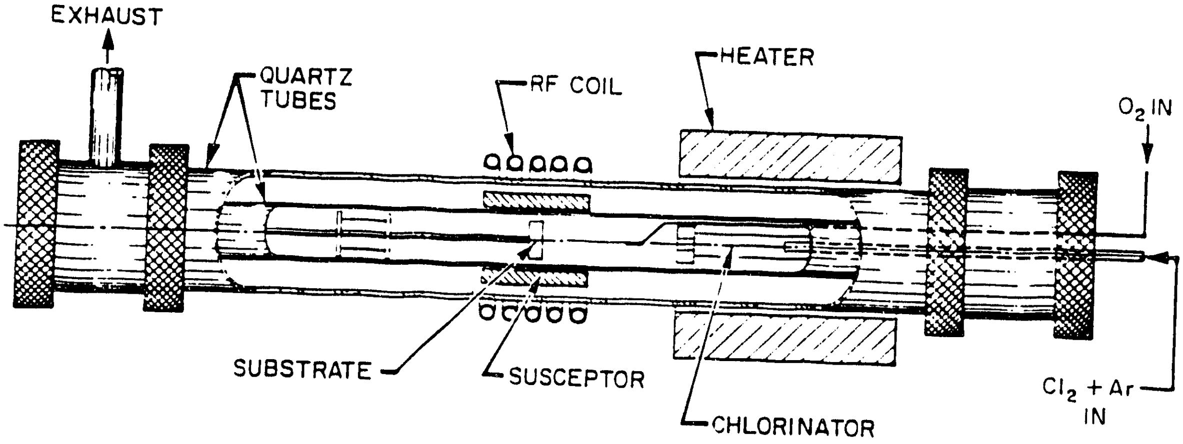
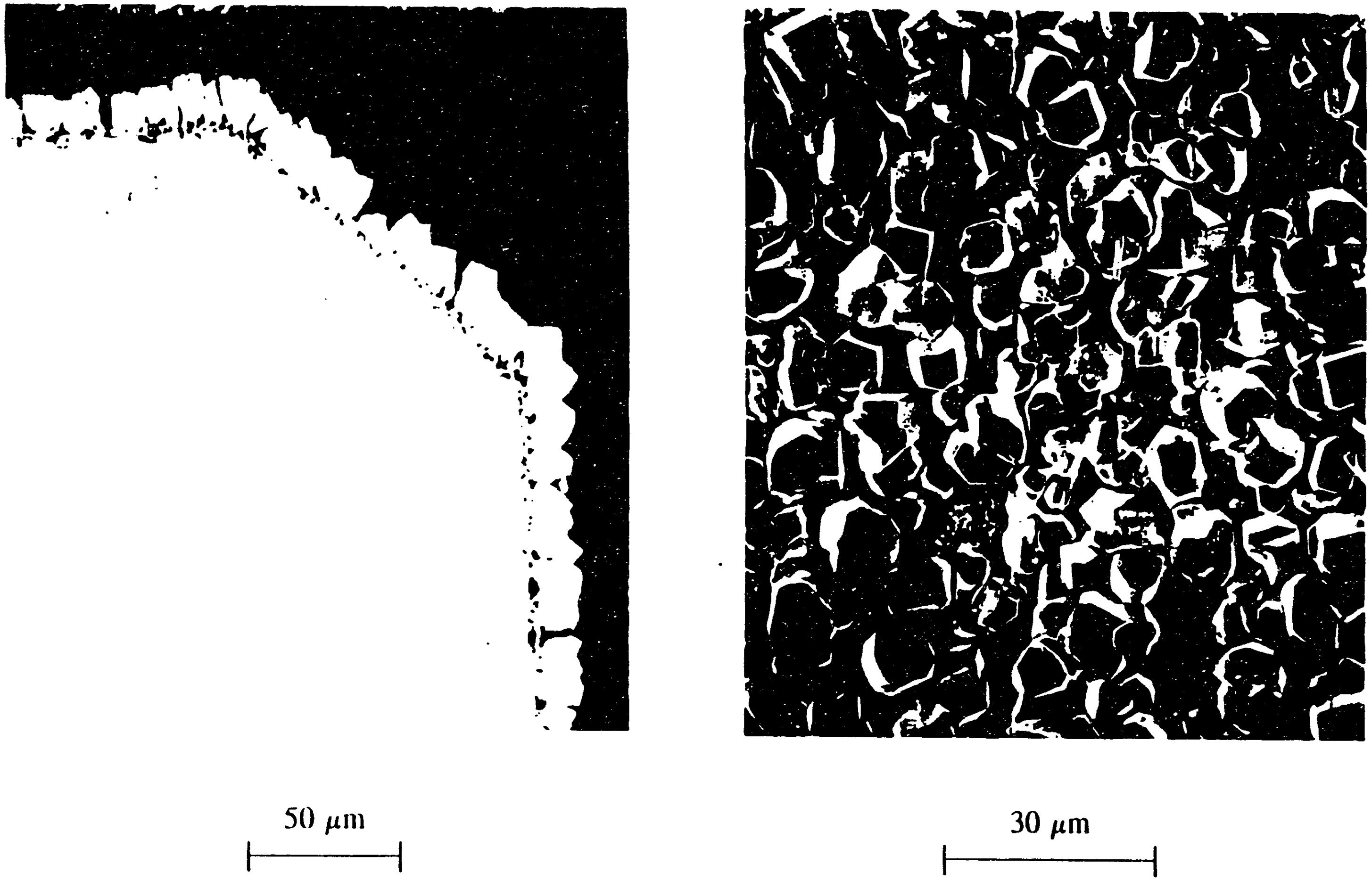


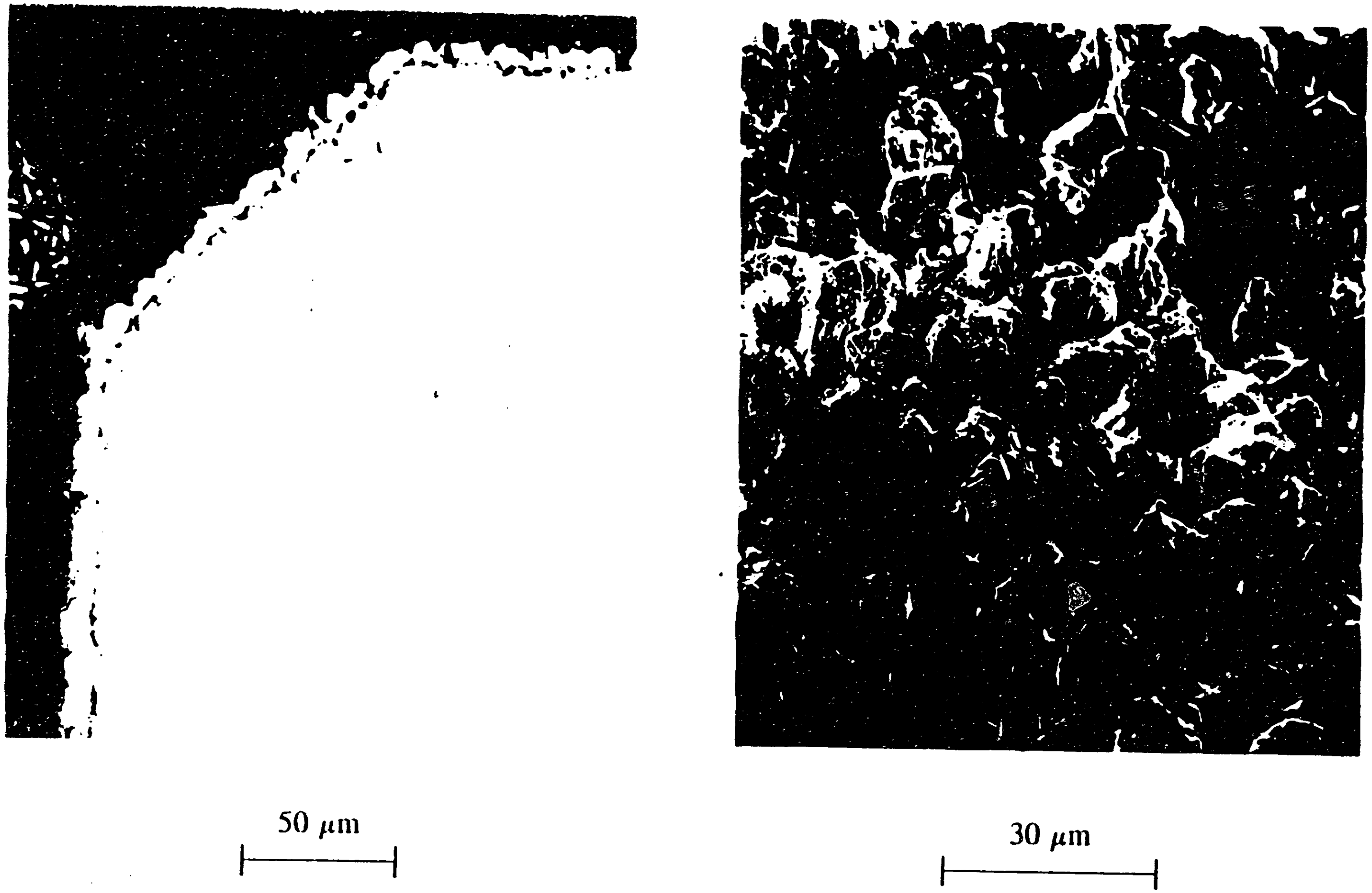
Figure 3
Schematic of CVD Reactor



(a) Photomicrograph of a section through the Ta_2O_5 coating and SiC substrate, as polished

(b) Scanning electron micrograph of the as-deposited Ta_2O_5 coating

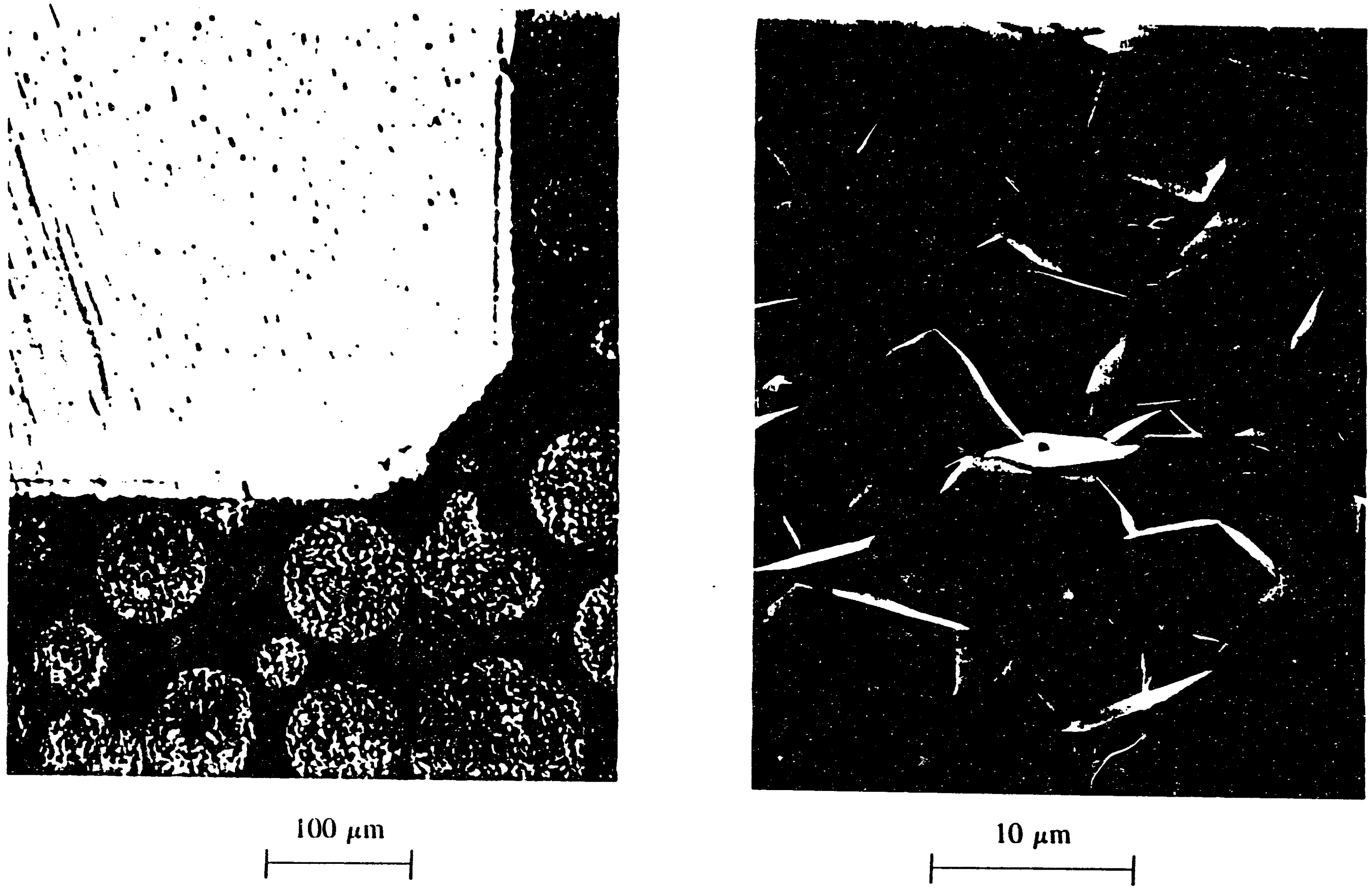
Figure 4
Coating Morphology Produced by High Deposition Temperatures



(a) Photomicrograph of a section through the Ta_2O_5 coating and SiC substrate, as polished

(b) Scanning electron micrograph of the as-deposited Ta_2O_5 coating

Figure 5
Coating Morphology Produced by High Reactant Concentrations



(a) Photomicrograph of a section through the Ta_2O_5 coating and SiC substrate, as polished

(b) Scanning electron micrograph of the as-deposited Ta_2O_5 coating

Figure 6
Coatings Produced Using Low Temperatures and Low Reactant Concentrations

Figure 7
Scanning electron micrograph of the Ta_2O_5 and Na_2SO_4 interface after corrosion testing

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