A STUDY OF THE CODEPOSITION OF $TiCl_4$, BCl_3 AND METHYLCHLOROSILANES ON CARBON IN A HOTWALL TUBULAR REACTOR

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ABSTRACT

Development of CVD/CVI processes for the deposition of graded and dispersed phases of TiB_2 and SiC is currently under investigation in our laboratory. For these deposits it is essential to determine the chemical microscopic structure in order to characterize a successful reactor operating procedure, product, or the product's mechanical and oxidation properties. A study was made to determine which reactor conditions could be used for deposition and which chemical analytical techniques are most appropriate to characterize film processing. A brief comparison between established analytical methods is made and the preliminary experimental results of the study are presented.

INTRODUCTION

The addition of interstitial borides to silicon carbide and carbon has been suggested as a means to improve the physical properties and oxidation resistance of composite materials when they are used as structural and thermal elements (1,2). One such boride is titanium diboride (TiB_2) which is extremely hard (3500 $kgfmm^{-2}$) and can improve thermal properties such as thermal stress resistance (1,2). Titanium diboride also oxidizes at relatively low temperatures (~350° C) and forms solid solutions of titanium and boron oxides at the surface before appreciable C and SiC oxidation begins (3). These solutions act to seal cracks and provide a barrier through which oxygen must diffuse thus slowing the oxidation rate of the underlying strata. Thus mixtures of SiC and TiB_2 have the potential for good mechanical properties and an active mode of oxidation protection. There is however a problem with respect to the mismatch in thermal expansion coefficients of C, SiC and TiB_2. For example, the thermal expansion coefficient of TiB_2 is nearly twice that of SiC (7.5×10^{-6} vs. 4.7×10^{-6} /^{o}C). Therefore on heating and cooling, stress may build causing cracking or spallation. One method to alleviate or minimize stress is to fabricate the mixture as a graded or dispersed phase and/or design to the appropriate loading during use (4-6).

Although the chemical vapor deposition (CVD) of SiC and TiB_2 have been studied there is less experimental information available with respect to the feasibility of depositing graded

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deposits and dispersed phases of TiB_2 and SiC. The objective of this study was to determine the feasibility of obtaining TiB_2/SIC coatings and infiltrates by CVD/CVI. In this paper preliminary work will be presented which represents the results from screened reactor operating conditions for deposition and studying the most fruitful analytical techniques to characterize the deposits. In particular two substrates for deposition were of interest, carbon/carbon honeycomb cells and woven carbon fabric.

BACKGROUND

The chemical vapor deposition/infiltration of a single component as a coating is not a simple phenomenon. This can be further complicated when the substrate is a porous network such as a woven fabric. In the case of deposition where the feedstock contains a number of reactants, a greater number of potential solid reaction products may form and therefore the composition and distribution of deposit may be difficult to control or even obtain. For example, when a feedstock containing $TiCl_4$, BCl_3, and DDS (dichlorodimethylsilane) is used to deposit SiC and TiB_2, a typical thermodynamic analysis shows that TiB_2, $TiSi_2$, C, SiC, and B_4C can also be products at equilibrium.

Thermodynamic equilibrium need not always be attained; kinetic, mass transfer, and even morphological effects may also intercede and determine composition and distribution of the deposit. Because of these complications, determination of the chemical microscopic structure of the deposit becomes of paramount importance to characterize a successful reactor operating procedure, product, or the product's mechanical and oxidation properties. It is important to characterize a number of properties of the films and relate them to the overall thermal and structural performance. Because it is our goal to develop processes for depositing graded or dispersed phases it is important to use analytical techniques which are surface sensitive. In order to determine the uniformity of film growth and identify impurity phases throughout the films a technique is needed which allows quantitative depth profiling. It is also desirable to do quantitative imaging of the fiber infiltration region in order to understand the infiltration process. There are a number of analytical techniques which are applicable to these problems; careful selection is necessary in order to avoid ambiguous results.

Obtaining quantitative and representative depth profiles can be relatively time consuming and costly by any means, especially when studying complicated mixtures with complex surface morphology or large variations in grain size. Before undertaking a detailed quantitative analysis it is important to do a preliminary screening of surface morphology of a sample and a quick elemental survey analysis to be sure that the film possesses the characteristics of interest. SEM can be used to determine film thickness, grain size and surface morphology and, if equipped with the proper EDX, the same instrument can be used to establish the presence of B, C, Si and Ti (in our laboratory, a survey analysis is obtained using laser ablation/mass spectrometry). If one of these elements is undetected or a large amount of Cl or O has been deposited in the film it is clear that the deposition process has failed and no further analysis of the sample is required. Samples may also be eliminated if the grain size is large relative to the total film thickness or large globular features are present. The ideal graded (or dispersed) film will contain small grains of similar size and uniform lateral dispersion so that the gradient is perpendicular to the surface and not in a radial direction from the nucleus of a large structure. This preliminary sample characterization is essential in order to select a suitable analytical technique for quantitative depth profiling of the films.

The available depth profiling techniques can be divided into two groups which include those that look at sample cross sections and those that use sputter etching to remove layers of material. We are currently investigating the advantages of six of the most promising analytical

techniques with capabilities for quantitative depth profiling of matrix level species. These include EDX and WDX (energy and wavelength dispersed xray analysis), EELS (electron energy loss spectroscopy), XPS (xray photoelectron spectroscopy), AES (Auger electron spectroscopy) and SALI (surface analysis by laser ionization). Each technique has its own advantages and disadvantages in terms of depth and lateral resolution as well as the amount of sample preparation required for analysis. A comparison of techniques with respect to limitations is summarized in Table 1.

The main disadvantage of the cross sectioning techniques (EDX, WDX, EELS and AES) is that TiB_2 and SiC are very hard and often porous so they may be difficult to cross section and require extensive polishing to ensure that no significant contamination remains in the pores. EELS presents an additional problem in that thin cross sections are required (~100 nm or less). However, this added inconvenience may be warranted for our "best" films because the same transmission electron microscope used for EELS can also be used to obtain selected area diffraction patterns with better than 200 Angstrom resolution (theoretically). This would allow line scans to be used to measure concentration gradients as well as crystal structure throughout the film.

One pitfall to avoid in using cross section line scans is that the small beam sizes (1 micron diameter or less) used for these techniques can result in observation of local concentration effects which are not characteristic of the entire film. This can be avoided by obtaining multiple line scans and/or by choosing samples in which all of the grains appear to be similar in size. If there is a non-homogeneous distribution of grain sizes it is preferable to use a sputter depth profiling technique (with a 50 to 150 micron beam diameter) which would help to average out these effects.

Table 1. Techniques for quantitative in-depth analysis.

Method	Limitations	Depth (or lateral) Resolution
EDX (CS)	1,2,3,4	~0.5-3 um
WDX (CS)	1,2,3	~0.5-3 um
EELS (CS)	2,3	<20 nm
AES (CS)	2,3	<20 nm
AES (SP)	5,6	*
XPS (SP)	5,6	*
SALI (SP)	5	*
SALI (CS)	2,3	~20 nm

CS=cross sectioning; SP=sputter profiling
* Depth resolution limited by surface morphology and preferential sputtering effects.
1. Can't be used on thin films (<1 to 3 microns)
2. Sample prep required (cross sectioning and polishing)
3. Line scans can result in observation of local effects uncharacteristic of the entire film.
4. Possible signal interference between B and C requiring deconvolution of spectra for proper quantification.
5. Sputter effects must be eliminated or accounted for. Any sputter etching technique will probably require sample rotation. Sample charging may also be a problem with high ion beam currents required for sufficient sputter rates.
6. May observe only the "altered layer" making data interpretation more difficult or impossible.

Due to the sampling volume (1 to 3 micron in diameter) of EDX and WDX, these techniques are excellent for very thick films but will not give good depth resolution in films of ~3 microns or less. SALI, EELS and AES cross sections can give resolution on the order of ~20 nm (or better) but for very thin films it is generally preferable to use a sputter etching technique. Sputter profiling is simpler because there is no sample preparation required and the data acquisition time is similar. Sputter profiling techniques such as Auger, XPS or SALI can provide depth resolution on the order of 5 nm (dependent on sputter depth) when used on very smooth surfaces. Of course the materials studied here do not have smooth surfaces and depth resolution will be limited by surface roughness, grain size and preferential sputtering effects.

When sputtering multicomponent/multiphase materials it is important to be aware that a number of sputtering effects (i.e. preferential or selective sputtering) can affect the results of a quantitative analysis (7). For example, differences in sputter yields for different atoms, phases and/or crystal orientations can cause sputter roughening of the sample surface. These effects can also alter the surface composition by depleting the surface of high yield species. Surface roughening due to varied grain orientation is dependent on the incidence angle of the ion beam and can be minimized by sample rotation during sputter etching. All of these sputtering effects will be studied in future work by comparison of the AES, XPS and SALI depth profiles.

A study is currently underway in our laboratory to determine which of the techniques are most compatible with studies of our film processing. Only some of the preliminary results of this study will be presented here.

EXPERIMENTAL APPARATUS AND PROCEDURES FOR CVD/CVI FILM PREPARATION

Samples for study were made in a small hot wall tubular reactor. The reactor was constructed of two annular quartz tubes heated in a resistance furnace (Fig. 1). The design is similar to that reported for the deposition of SiC (8). Carbon/carbon honeycomb cells * and plain weave carbon fabric** were used as substrates for deposition (9). Individual honeycomb cells were stacked on top of each other on a ceramic thermowell in the center of the reactor. The woven carbon fabric was cut into 1/2" strips and anchored in Grafoil disks at either end of the reactor tube. The feed manifold consisted of $TiCl_4$ and DDS liquids in separate bubblers, and H_2 and BCl_3 gas. The H_2 and BCl_3 flows were monitored with mass flow controllers***. The concentration of $TiCl_4$ and DDS in the gas were estimated by weighing the bubblers before and after a run.

In a typical run the system was purged with purified argon, evacuated, and backfilled and purged with H_2. With the H_2 flowing the reactor was heated to a setpoint temperature and maintained at that temperature for 15 minutes to attain thermal equilibrium before the $TiCl_4$, DDS and BCl_3 were admitted to the reactor. Typical run times were on the order of 2 to 10 hours. Nominal flow rates in all cases were approximately 300 cc/min. Nominal concentrations in the feedstock were 1% by vol. $TiCl_4$, 0-3% BCl_3, and 0-3% DDS. Temperature profiles as a function of setpoint temperature were measured with a traveling thermocouple in a central thermowell (Fig. 1). Runs were made at 0.3 atm and 1 atm pressure. The pressure was measured with a transducer. Local average deposition rates were estimated by weighing the substrates before and after a run and dividing by the length of time of the run and the original weight.

* Hexcel Corp., Dublin, CA
** Hercules Corp., Magna, Utah
*** Tylan Corp., Torrance, CA

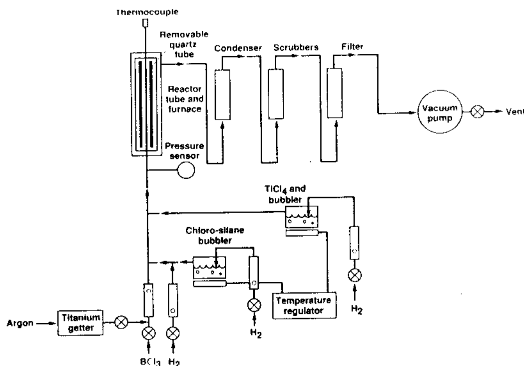

Figure 1. Schematic diagram of CVD/CVI reactor.

RESULTS AND DISCUSSION

Figures 2 and 3 display typical rate data for two experiments. In the Figures, the deposition rates are plotted versus distance from the furnace entrance. Each point on the curve represents the amount of material deposited on a sample of given dimensions located at the specified position in the reactor. Note that the reactor temperature profiles are overlaid on the rate data. SEM images of the films grown under these conditions indicate that the deposits were on the order of 10 to 100 microns thick. Clearly, a line scan (cross sectioning) technique is required for in depth analysis of these particular films. The EDX line scan method was chosen for the preliminary quantitative analysis because it has several distinct advantages over the others. Aside from being the least expensive of the techniques mentioned above, EDX uses very low electron beam currents (100 to 500 picoamps). Higher current ion or electron beams may cause charging in these samples. Although the samples should be electrically conductive, they don't always have the large smooth areas necessary for making good electrical contact with a sample stage.

TiB_2 is normally deposited at a much lower temperature than SiC. Because of the dramatic difference in temperature coefficients of these reactions, unless there is a special reactor design or operating characteristic the two reactions may not occur simultaneously at the same location making it difficult to obtain codeposition of TiB_2 and SiC simultaneously as a dispersed phase. The bimodal rate data in Figure 2 suggests this is the case. EDX analyses were executed on samples 6, 8 and 10. A spot quantitative analysis of sample #6 showed a stoichiometry of $TiB_{2.1}$ and sample #10 $SiC_{2.6}$. The estimated errors in atomic ratios were reported to be on the order of +/- 10%. The EDX line profiles confirm that TiB_2 is primarily formed at the lower temperatures at the entrance of the furnace (#6) and the SiC at the higher, (#10). No significant codeposition of TiB_2 and SiC occurs in any of these samples.

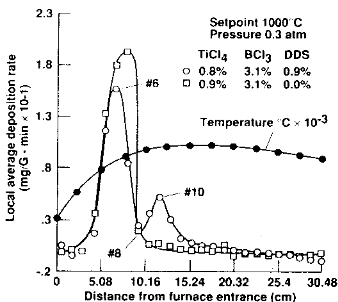

Figure 2. Deposition rate curves for single feedstock/temperature process.

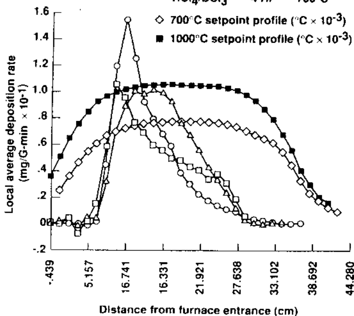

Figure 3. Deposition rate curves for alternating feedstock/temperature process.

Because the temperature coefficients of the reactions were so different and the results with honeycomb showed little codeposition, an alternating feedstock was considered to produce a graded deposit on the fabric strips. An alternating layer of SiC and TiB_2 was successfully deposited by varying feedstock compositions and the temperature levels of reaction. The rate curves for the independent and combined two step process are shown in Figure 3. Note that the combined rates do not add up to the sum of the independent rates. This may indicate that deposition on the SiC layer is not as efficient as on the substrate or that there is a reaction between gas phase species and the previously deposited material. The SEMS and EDX line profiles of the layers are shown in Figure 4. Even in the separate layers of TiB_2 and SiC, there is some gradient in composition. The two sides of the TiB_2 layer are richer in Ti than B; the SiC layer adjacent to the TiB_2 layer appears to be richer in Si than C but is fairly uniform further in depth. In these line profiles one can also trace the SiC coating around the carbon fibers in the tows in the fabric. Using similar procedures an attempt was made to intersperse small quantities of TiB_2 and SiC together to see if a graded and dispersed phase could be achieved. In this case, depositing small amounts of SiC and TiB_2 as a uniform layer was not entirely successful. Deposition generated a complex morphology. Voids and separation of layers were apparent in the SEMS. Different operating programs or methods may be required to consolidate the deposits with suitable mechanical and chemical properties.

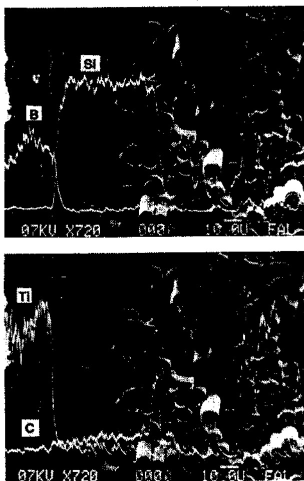

Figure 4. Overlay of SEM image and EDX line scans of Si, C, B and Ti.

CONCLUSIONS

A preliminary study to codeposit and/or produce graded deposition of TiB_2 and SiC was partially successful. Simultaneous codeposition did not appear to be possible in the present reactor design at the conditions studied. Alternating feedstocks and temperature levels did result in a multi-layered deposit. An attempt at simulating codeposition by this method resulted in a discontinuous film. Other reactor operating conditions or designs may prove more successful. The importance of selecting a proper analytical method is emphasized. A number of analytical methods to characterize deposition are summarized along with their limitations and approximate depth resolution.

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