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GRAIN STRUCTURE AND GROWTH OF DISPERSED PHASE BN-ALN COATINGS
GROWN VIA CHEMICAL VAPOR DEPOSITION

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GARTH B. FREEMAN*, WOO Y. LEE**, W. J. LACKEY*, JOHN A. HANIGOFFSKY*, AND
KARREN L. MORE***

*Georgia Institute of Technology, Georgia Tech Research Institute, Atlanta,
GA 30332

**United Technologies, Research Center, East Hartford, CT 06108

***High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak
Ridge, TN 37831-6062

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ABSTRACT

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This paper discusses the variation in microstructures encountered during the separate depositions of boron nitride (BN) and aluminum nitride (AlN) as well as during the codeposition of BN-AlN dispersed phase ceramic coatings. This combination was chosen in order to take advantage of the self lubricating properties of hexagonal BN along with the hard, erosion resistance of AlN. Films were characterized using scanning and transmission electron microscopy (SEM and TEM), x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD).

A range of coating microstructures are possible depending on the conditions of deposition. The best films produced, in terms of hardness, density, and tenacity, were a fine mixture of turbostratic BN and preferentially oriented AlN whiskers aligned with the whisker axis perpendicular to the substrate surface as seen by both electron microscopy and x-ray diffraction.

INTRODUCTION

In recent years, specialized demands on materials have become particularly severe and the scientific community has responded by developing new material systems. It is of particular interest to develop advanced ceramic materials that possess both high temperature stability and strength which mitigate the natural brittle behavior of these materials. Dispersed phase ceramic composites are such systems which can show greatly improved strength and toughness while retaining excellent oxidation resistance. Relatively thin (1-100 μm) dispersed phase ceramic composite coatings are of significant interest because of the potential to engineer selected, superior mechanical and physical properties as a function of coating composition and microstructure. The process of chemical vapor deposition (CVD) has the advantage of being able to control the grain structure/composition via selection of reagents and optimization of process parameters including temperature, pressure, and flow rates.

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EXPERIMENTAL

The reaction for BN deposition was:

and similarly for AlN deposition:

The overall reaction for codeposition was initially assumed to be a combination of the two single phase reactions. A thermodynamic analysis of this system is discussed in detail elsewhere [1,2].

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The experimental CVD system consisted of a hot walled vertical geometry furnace with appropriate gas handling and pressure controls. Aluminum chloride (AlCl_3) was introduced into the system using a stainless steel vaporizer and a co-axial gas injector kept the ammonia, AlCl_3 and BCl_3 from reacting prematurely. In most experiments, a polycrystalline $\alpha\text{-Al}_2\text{O}_3$ substrate strip was either suspended vertically by molybdenum wire (vertical suspension geometry) or placed horizontally within the graphite cone (impinging jet geometry). The vertical suspension geometry was used in to provide information for understanding how the deposition behavior would be influenced by concentration boundary layers and the depletion of reagents along the flow direction while the impinging jet geometry was used to simplify the modeling. A more detailed description of these experimental systems is given elsewhere [3].

BN DEPOSITION

Boron nitride deposition proceeded via three different routes: homogeneous nucleation, and both amorphous and turbostratic heterogeneous nucleation. Coatings formed via homogeneous nucleation are very poorly adherent layers of roughly spherical submicron particles chained and clumped together. These particles nucleate in the gas phase and "fall" onto the substrate. In one run, an undesirable coating of B_2O_3 was seen, resulting from oxygen impurities introduced by reagent gases or vacuum leaks. Oxide islands (e.g., Figure 1), as identified by electron microprobe, were occasionally seen in other runs. The typical morphology of the heterogeneously nucleated BN is shown in Figure 2. The presence of amorphous and turbostratic BN phases were not differentiable via observation by SEM but were identified via XRD.

Examination of surface chemistry via XPS showed, typically, the presence of two different boron peaks: one corresponding to BN at about 190.3 eV and the other to a partially oxidized state at 192.3 eV easily differentiable from the peak position corresponding to B_2O_3 at 193.1 eV. This, and the semi-quantitative XPS data showing significant oxidation of the surface, was not consistent with electron microprobe data which confirmed the relative purity of the better BN coatings. This surface oxidation is thought to be a result of post deposition surface oxidation. Nonetheless, the XPS data proved to be extremely valuable for evaluation of the amorphous BN films during early processing runs.

Figure 1. SEM micrograph of boron oxide structure found on and in BN coating layer. Bar = $10\mu\text{m}$

Figure 2. SEM micrograph of typical BN coating layer morphology. Bar = $2\mu\text{m}$

AlN DEPOSITION

The deposition of AlN typically resulted in the formation of columnar whiskers oriented preferentially with the whisker axis oriented perpendicular to the substrate surface. By varying the conditions of deposition, the dimensions and forms of the AlN whiskers could be controlled. In Figure 3, two extreme forms of the whiskers grown on a graphite substrate are shown. These relatively large crystals were formed at high pressure and temperature (1127°C at 1 atm) where the conditions were favorable for fast growth and limited nucleation. By lowering the pressure and the temperature, significantly denser coatings of AlN were formed with the same preferential orientation of smaller single filament whiskers on Al_2O_3 substrates.

Figure 3. Two different crystalline AlN structures formed in different regions on the same sample. A) Bar = 10 μm B) Bar = 4 μm

The high resolution XPS Al 1s spectra collected typically showed two peaks: an AlN peak at about 73.8 eV and an Al_2O_3 peak at about 74.5 eV. While electron microprobe shows small residual oxygen concentration, most of the oxide present in the surface spectra appear to be due to post processing oxidation.

BN-AlN MIXED PHASE DEPOSITION

The simultaneous deposition of mixed BN-AlN, while not a simple, first order combination of the two single phase reactions, was, nonetheless, qualitatively predictable from the single phase data. The codeposition of the two different phases seems to be competitive wherein the growth of one phase inhibits the crystalline growth of the other. The critical parameters, in terms of competitive crystalline formation are the temperature and the ratio of BCl_3 partial pressure to the sum of the BCl_3 and ACl_3 partial pressures. While, overall, the deposition rate was about an order of magnitude greater with the impinging jet geometry, about 200 $\mu\text{m/hr}$ versus 20 $\mu\text{m/hr}$ with the vertical suspension geometry, it is clear from the microstructural examination that there were often significant differences in coating thickness and composition as a function of position on the substrate for both geometries; within the stagnation region for the impinging jet geometry, the coatings are rather uniform as confirmed by electron microprobe data [4].

Figure 4 is an example of the often multilayer character of the coatings grown in the vertical suspension mode. While, in this case, there was no evidence for differing composition between the various layers, it is evident that there were distinct times at which the deposition/nucleation rates

changed sharply despite efforts to maintain constant deposition conditions. Other coatings exhibit no such layering. The sample shown in Figure 4 was one of three connected samples exposed during the same experimental run differing only in position (height in the furnace). X-ray photoelectron spectroscopic analysis showed distinct differences in surface composition of the three samples in that the B to Al atomic ratio varied from 1.2 to 3.6 relating, presumably, to differences in local reagent concentrations.

Figure 4. Layered mixed phase AlN/BN coating. Bar = 40µm

Figure 5. Dense, adherent mixed phase coating cross section. S - Alumina substrate, C - Coating. Bar = 40µm

While the structure shown in Figure 5 is indicative of the best coatings, other very different morphologies were also in evidence for some processing conditions. These samples included dense, brittle glassy coatings which were heavily cracked, multilayer coatings with starfish like crystalline phases dominating an outer layer, and fibrous coatings wherein the AlN whiskers were readily apparent even at fairly low magnification. It is of particular interest to note that the XPS examination of the latter samples often showed a large boron concentration on the surfaces with relatively low aluminum concentration despite the obvious presence of the AlN whiskers. This result implies that the AlN whiskers are coated with BN as is confirmed by higher magnification SEM and TEM examination (see Figures 6 and 7).

Figure 6. Low magnification TEM micrograph showing AlN (A) whiskers intermixed with BN (B) regions. Bar = 500nm

Figure 7. Lattice image of mixed phase BN-AlN coating. Note: A - AlN whisker, B - amorphous BN, and T - turbostratic BN. Bar = 4nm

X-ray diffraction could be used to monitor the crystallinity of the coating through identification of different phases, preferential crystalline growth directions and average crystallite sizes. An example of these results is shown in Figure 8. Analysis of the codeposited coatings by XPS show no peaks which were not present during single phase deposition. These data are consistent with the codeposition product being made up of two independent phases rather than including a single mixed aluminum-boron phase. This observed structure is consistent with the BN-AlN phase diagram.

Figure 8. X-ray diffraction pattern from mixed phase coating showing presence of turbostratic BN and preferentially oriented AlN on an alumina substrate.

Determination as to the relative quality of the deposited films was made via qualitative maximization of several different aspects including measured microhardness values, microscopic examination of coating density, and observation of coating tenacity (some coatings, for example, spalled within hours or days after deposition) and coating uniformity (as determined via optical and electron microscopy as well as direct observation). The processing parameters for the samples specifically cited in this paper are listed in Table 1.

TABLE 1 PROCESSING PARAMETERS							
SAMPLE	T(°C)	P(atm)	FLOW RATES (SCCM)				
			AlCl ₃	BCl ₃	NH ₃	H ₂	Ar
FIG 1,2	1100	0.2	—	10	50	—	400
FIG 3 ^A	1127	1.0	45	—	100	—	1900
FIG 4 ^B	900	0.2	15.8	10	50	—	1430
FIG 5	927	0.1	20	3	40	50	950
FIG 6,7	1127	0.2	15	10	50	—	1900
FIG 8	1127	0.2	5	10	5	—	1900
A - GRAPHITE SUBSTRATE (ALL OTHERS Al ₂ O ₃)							
B - VERTICAL SUSPENSION (ALL OTHERS IMPINGING JET GEOMETRY)							

CONCLUSIONS

The best coatings, in terms of hardness and tenacity, were composed of anisotropic AlN whiskers (submicron diameter and lengths up to several micrometers) coated with a mixture of turbostratic and amorphous BN. These coating compositions occurred in a fairly narrow processing range shown in Figure 8. In general, denser composites were formed at lower absolute pressures and higher temperatures.

Figure 9. Processing diagram showing crystalline structure of BN-AlN coatings as a function of deposition temperature and AlCl₃ and BCl₃ concentrations.

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