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High Temperature Stability, Interface Bonding, and Mechanical Behavior in β-NiAl and Ni_3Al Matrix Composites with Reinforcements Modified by Ion Beam Enhanced Deposition

Progress Report

for the period June 1, 1992 - May 31, 1993

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INTRODUCTION

Research funded by the U. S. Department of Energy office of Basic Energy Sciences, under grant # DE-FG02-85ER45205 entitled "Softening Mechanisms and Microstructural Instabilities During High Temperature, Low Cycle Fatigue of Ni, Ni_3Al and their Metal Matrix Composites" was renewed in 1991 under the title "High Temperature Stability, Interface Bonding, and Mechanical Behavior in NiAl and Ni_3Al Matrix Composites with Reinforcements Modified by Ion Beam Enhanced Deposition", for the three-year period beginning June 1, 1991. The following report summarizes activity and progress made during the second year under the latter title.

Progress Summary: June 1, 1992 - May 31, 1993

MODIFICATION OF REINFORCEMENTS FOR ALUMINIDE MATRIX COMPOSITES

Experimental Work Completed

Fiber Coatings. Initial study of diffusion bonded composites using Sumitomo, FP and PRD-166 fibers in a pure niobium (T_m = 2468 °C) matrix has been undertaken to evaluate the potential for niobium to act as a ductile compliant-layer. This data will help separate residual radial compression effects from chemical bonding and roughness effects on the interfacial shear strength, and help clarify previous results using Ni+Al reactive-binary coatings. Initial interfacial shear strength measurements on Nb-coated polycrystalline fibers are underway.

Tensile Strength of Coated Fibers. The stress state of sputter-deposited films on ceramic fibers affects their tensile strength: coated and uncoated FP fibers have been tested in a UTS load frame at .135 mm/s, and found to have strength and Young's modulus values of 1.31 GPa and 240 GPa for uncoated FP fibers; and 1.47 GPA and 168 GPa for IBED processed FP fibers. Therefore, the coating slightly increases tensile strength (presumably by altering surface flaw geometries), and has an approximate rule-of-mixtures effect on the elastic modulus.

We have also observed the presence of matrix-grain-boundary imprints on otherwise smooth fiber surfaces after diffusion bonding cycles (the fibers having been removed electrolytically from as-bonded matrices) which suggests that the as-consolidated tensile strengths are will also be sensitive to processing conditions. The latter effects may be mitigated by the presence of an adherent ductile coating, forming the innermost film of a multilayer, as discussed further below.

Interfacial Shear Strength Measurements. Push-Out Tests on Sumitomo and FP Fibers in nickel aluminide matrices have been repeated to clarify earlier measurements showing large increases in ISS associated with the Ni+Al bi-metallization. The general trend of the previous work has been confirmed, but the true magnitude of the effect has been shown to be more modest than suggested by the early data. For uncoated FP fibers in NiAl, the average interfacial shear strength was measured at 42 ± 15 MPa, whereas for an NiAl matrix with the FP#1 modified fibers, having a 200nm oxide layer, a 1 µm Al layer, and a 0.66 µm Ni layer, this value rose to 75 ± 20 MPa. NiAl with the FP#3 modification (150nm oxide layer, 1 mm layer Al, .66 mm Ni) had an average interfacial shear strength of 68 ± 18 MPa. Some confirmation of our hypothesis, that surface roughness is largely responsible for the observed difference, comes from measurements on 10 µm diameter Sumitomo ALTEX fibers, which are significantly smoother than the FP material. The smooth ALTEX fibers showed ISS levels of 22 ± 17 MPa. The substantial scatter in this data is partly due to nonuniform specimen thickness, and is not unusual in the available push-out techniques. Fiber surface roughening experiments have been begun, to systematically asses the effect of fiber roughness on the fiber-matrix adhesion. Uniform roughness was observed in an SEM investigation of Sumitomo fibers given several minutes exposure to boiling phosphoric acid. This technique has thus been found to be useful for producing uniform, but variable, surface roughness for assessment of the contribution of this parameter to the overall ISS level.

Contact Lithography. Alignment of fibers in composite tensile specimens within channels pre-etched by contact lithography, has been successfully used to lessen breakage of the larger diameter SAPHIKON fibers during diffusion bonding.

Thermal Cycling of NiAl-Al_2O_3 and Ni_3Al-Al_2O_3 Composites. Diffusion bonded NiAl-Al_2O_3 and Ni_3Al-Al_2O_3 composites were thermally fatigued at a temperature of 900 °C for 1500 and 3500 cycles (with a soak time of 8 minutes) in air. Specimens with fiber-ends exposed to the atmosphere, and with fiber-ends imbedded within the matrix, were cycled to assess the importance of pipe-diffusion routes in catastrophic oxidation phenomena. The object of the experiment was to determine the effects of interfacial wear and fast-diffusion paths along the fiber-matrix interface during thermal expansion of the two materials, and to assess the degree to which these processes could affect interfacial shear strength. Initial SEM investigations of exposed-end specimens broken in tension indicate that the fiber-matrix interface has weakened after 3500 cycles for the SAPHIKON fibers. The ALTEX, PRD-166 and FP fibers showed little, if any, degradation. Evaluation of the imbedded fiber experiments is currently in progress. Further studies are planned for higher temperature cycling, and construction of a furnace for 1300 °C operation is under way.

Particulate Coatings. In our most recent work we have evaporated Al_2O_3 directly from a pure oxide rod onto acoustically levitated silicon carbide particles using a specially constructed down-firing, rod-fed electron beam hearth. The films had very high intrinsic tensile stresses and poor adhesion properties, but reasonably good stoichiometry. Coatings with superior properties were subsequently produced using concurrent irradiation of the growing films with a 200 eV argon ion-assist beam at various ion/atom arrival ratios ranging between 0.1 and 0.5. Using these IAD methods, we have achieved high deposition rates, excellent adhesion, and significantly reduced intrinsic stress levels in these films. The assist-beam gun was also used to sputter-clean the substrate particles prior to application of the deposition flux. A sketch of a typical experimental setup is shown in Figure 1.

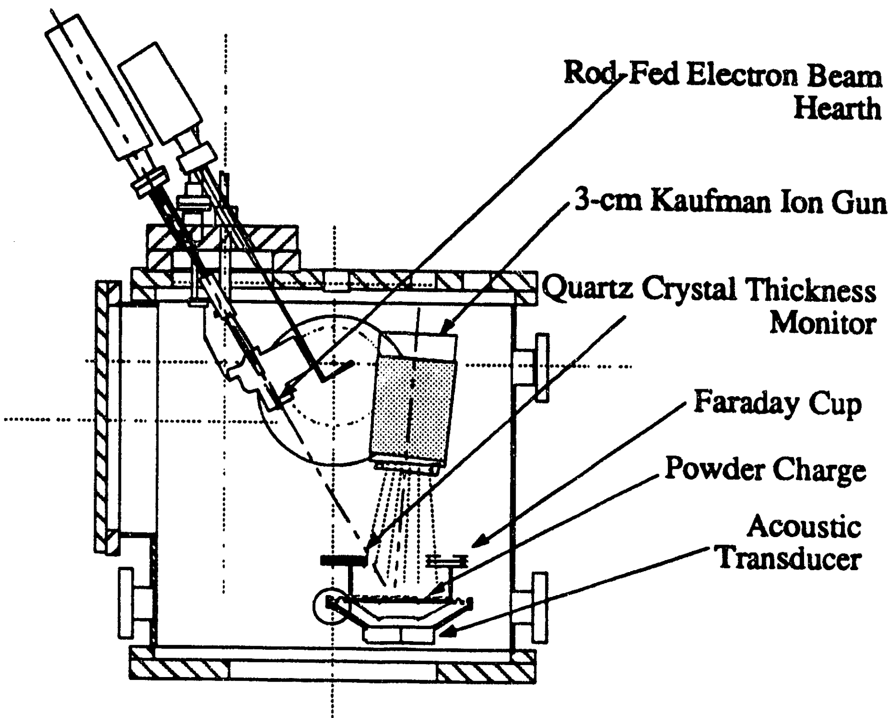

Figure 1. Schematic of Ion Beam Assisted Deposition setup for coating of particles

The magnitude of the intrinsic stress in the films was inferred from measurement of planar film stresses by determineing the change of curvature of a 25 mm diameter (100) silicon single-crystal wafer, situated adjacent to the charge canister during the deposition run, according to:

$$\sigma = \frac{E\,h^2 w}{3\,(1-\nu)\,x^2 t}$$

where $E/3(1-\nu)$ for Si is $7.2\text{x}10^{11}$ Pa, h is the wafer thickness, w is the change in curvature of the wafer, x is the length of the trace of the curvature, and t is the film thickness. Figure 2, below shows measured residual stress values plotted as a function of ion/atom arrival ratio.

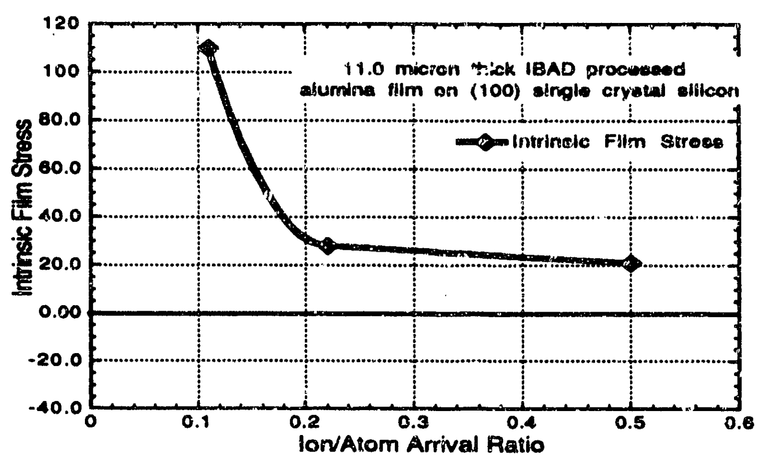

Figure 2. Residual stress in MPa measured on (100) silicon surveillance specimens as a function of Ion/Atom Arrival Ratio (I/A ratio) during deposition from an e-beam heated oxide rod source.

Significantly, the assist beam produced adherent films with reduced tensile stress levels. (Tensile stress on unassisted depositions caused film delamination and was therefore unmeasurably high.) However, the sought-after *compressive* residual stress has not yet been achieved, probably due to a combination of extrinsic stress contributions (due to differential thermal contraction from the deposition temperature) and an insufficiently high ion/atom arrival ratio. Since deposition rates were adequate for the maximum I/A ratio of 0.5, there appears to be ample room to increase the assist beam flux in future experiments.

Performance of the Diffusion Barriers.

Ion beam assisted depositions which produced 11 μm thick films on planar surveillance specimens gave film thicknesses on 60 μm diameter SiC powders of approximately 0.2 μm. The films were found to have a composition of approximately $Al_{37}O_{63}$ and were amorphous and electrically insulating in the as-deposited state. Annealing at 900 °C for 0.5 h. at $5x10^{-6}$ Torr produced unambiguous X-ray diffraction evidence of crystalline γ-alumina. Films on planar silicon substrates showed a columnar microstructure and were probably not fully dense. The latter result may be related to the relatively low substrate temperature used during deposition, inhibiting crystalline phase nucleation and interdiffusion. SEM observation of films on SiC particles revealed surface defects which have been tentatively associated with mutual-particle-impingement during deposition.

In diffusion bonding experiments with boron-doped Ni_3Al matrices subjected to compressive bonding at 40 MPa at 1100 °C for 1 hr, metallographic analysis showed that the diffusion barriers failed to prevent catastrophic particle-matrix reaction, probably as a result of film fracture during the initial stages of the diffusion bonding process, which can impose very high deviatoric stresses on the particles. In subsequent tests, the SiC particles in the diffusion couple were mixed with Ni_3Al alloy powders to make the stress state around the particles more hydrostatic, but with similar negative results.

Based on our observations we do not believe that the diffusion barriers failures are due to insufficient film thickness, but are rather a result of inadequate film quality related to tensile stress-state and defects such as porosity and film cracking. The deposition technique appears promising, but production of hermetic films on small particles with highly irregular surfaces has turned out to be more difficult than originally anticipated. Clearly, further refinement of the process will be required before competent diffusion barriers can be realized. We are currently experimenting with AlN coatings, reactively produced by both reactive evaporation (at P_{N_2}~0.1 mTorr), and by N^+ ion enhanced deposition from a metallic feedstock to the down-firing e-Gun.

Negligible AlN was found to form for simple Al-metal evaporation at P_{N_2}~10^{-5} Torr. Films made with P_{N_2}~$2x10^{-5}$ Torr, with concurrent irradiation by N^+ ions supplied at 250eV at an ion/atom arrival ratio of 0.5, are currently being analyzed. However, a planar AlN film, 0.6 μm thick, on a monolithic SiC substrate showed minimal reaction and interdiffusion in a diffusion-bonding test at 1200 °C. AlN has low-reactivity with SiC and NiAl, similar to that of Al_2O_3, but has a much lower thermal expansion coefficient (below, rather than above that of SiC) and will thus produce extrinsic stresses of opposite sign relative to the oxide. The oxide and the nitride thus form a good matrix for study of the coating-expansion-coefficient effects on ISS and fiber strength levels.

We currently experimenting with a prototype levitation system which uses a tubular quartz beam, fed through the chamber wall, which acts as an articulated member to transmit acoustical energy to the levitation fixture. In this way, we will be able to radiantly heat the levitated powders during deposition to temperatures limited only by the softening point of the quartz fixture components. A prototype device made from Pyrex has performed well and we anticipate reaching 1000-1100 K with the set-up fabricated from quartz. We expect that depositions at temperatures above $T_m/2$ for the deposit species will lead to films of sufficient quality to function well as diffusion barriers.

Laboratory Development Related to the Project

Development of Experimental Apparatus. A 3-kW rod-fed electron beam heated evaporation source has also been installed and brought into operation using both metallic and dielectric feedstocks. The gun is of special 30-degrees-down-firing design for coating levitated particulates. Because of this, the melt-pool dynamics are somewhat different than normally encountered, and optimum beam conditions have had to be established for each feed material by experiment.

A cyclic-oxidation/thermal-fatigue furnace, operable to 1050 °C and having a forced-air cooling chamber with an automated transfer device for cycling between high and low temperature zones, has been brought into operation. Thermal fatigue studies can now be performed in air, and the furnace can be used for isothermal studies of the effectiveness of diffusion barrier coatings deposited on reactive materials such as silicon carbide. Modifications for operation to 1200-1300°C are underway.

Custom-made grip components have been designed for the MTS 810/Centorr material testing system to allow testing of small button-head composite specimens having NiAl and Ni_3Al sheet matrices with various experimentally modified fiber reinforcements. The improvement will allow determination interfacial shear strength at service temperature by measuring the length distributions for fibers fractured during monotonic tensile deformation. A prototype set of inserts has been fabricated from Inconel which, if successful, will be executed in TZ-molybdenum or tungsten for use to 1400 °C.

An Orton PN 10017 Automatic Recording Dilatometer with a temperature range of 0 - 1000 C has been acquired (by donation from Ford Motor Co.), installed and calibrated. Initial thermal expansion measurements have been performed on both β-NiAl and γ- Ni3Al bulk specimens. Dilatometry measurements allow a direct and independent analyses of the fiber stress and matrix stress due to differences in thermal expansion as a function of temperature.

Acquisition of Materials. A quantity of SAPHIKON Single crystal Al_2O_3 (150μm and 75μm diameter) and Sumitomo ALTEX (10μm diameter) Al_2O_3 + SiO_2 fibers have been acquired. The latter have extremely fine grain size (50 nm) and excellent creep resistance at composite processing temperatures of 1400 °C. In addition, a quantity of DuPont PRD-166, 20 μm diameter, Al_2O_3 + ZrO_2, with surface roughness on the order of the .5μm grain size, has also been obtained.

The small diameter of the Sumitomo fibers allows easy room temperature determination of the interfacial shear strength (using the ITS fiber-pushout apparatus) while also allowing easy modification of the coating-fiber thickness ratio, providing needed confirmation of predictions made by compliant layer theory. The smoothness of these fibers minimizes the surface roughness effects on the interfacial shear strength, thus simplifying the interpretation of the data. The SAPHIKON fibers, on the other hand, will provide a realistic example of what is currently being pursued in the metal matrix composite community. Because of the single crystal nature of the SAPHIKON fiber, it provides a model system for determination of interfacial chemical reactions and surface roughness parameters. Additionally, the large diameter of the fiber allows fabrication of diffusion bonded couples with a larger volume fraction of reinforcement (~5%). Thus rules of mixtures for various properties can begin to be applied in analysis of mechanical properties measurements.

PUBLICATIONS ACKNOWLEDGING DOE SUPPORT

R. Schalek and D. S. Grummon, "Effect of Binary Reactive Fiber Surface Metallizations on the Fiber-Matrix Interfacial Behavior in Diffusion Bonded NiAl-Al_2O_3 and Ni_3Al-Al_2O_3 Composites", submitted to *Scripta Metallurgica*, February 1, 1993.

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