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FUNCTIONALLY GRADED $MOSI_2$-AL_2O_3 TUBES FOR TEMPERATURE SENSOR APPLICATIONS

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ABSTRACT

$MoSi_2$ and Al_2O_3 are thermodynamically stable elevated temperature materials whose thermal expansion coefficients match closely. Composites of these materials have potential for applications such as protective sheaths for high temperature sensors. $MoSi_2$-Al_2O_3 functionally graded tubes were fabricated using advanced plasma spray-forming techniques. Both continuously-graded and layered-graded tube microstructures were synthesized. The characteristics of the graded microstructures and the features of the graded mechanical properties of these tubes will be discussed.

INTRODUCTION

Using platinum coatings on alumina (Al_2O_3) sheaths for thermocouples is a widely used practice in the glass industry. Protection of the thermocouple wires and alumina (Al_2O_3) sheathing is necessary to avoid corrosion and dissolution of the temperature-sensing unit. The cost associated with providing platinum coatings on the Al_2O_3 sheath material can be prohibitively high when taking into consideration the infrastructure needed at the glass plants to maintain and secure an inventory of available platinum. There are also issues associated with improving the performance of the platinum coated Al_2O_3. The failure rate of the thermocouples can be as high as 50%. The U.S. glass industry has been in search of alternative materials that can replace platinum and still provide the durability and performance needed to survive in an extremely corrosive glass environment.

Investigations by Y.S. Park et al [1] have shown that molybdenum disilicide ($MoSi_2$) has similar performance properties in molten glass as some refractory materials that are currently being used in glass processing applications. Molybdenum disilicide is a candidate high temperature material for such applications because of its high melting temperature (2030°C), relative low density (6.24g/cm^3), high thermal conductivity (52 W/mK), a brittle to ductile transition near 1000°C, and stability in a variety of corrosive and oxidative environments [2,3]. Additionally, the cost of $MoSi_2$ is significantly lower as compared to platinum coatings.

Plasma spraying has been shown to be a very effective method for producing coatings and spray formed components of $MoSi_2$ and $MoSi_2$ composites [4]. Investigations on plasma spray formed $MoSi_2$-Al_2O_3 composite gas injection tubes were shown to have enhanced high temperature thermal shock resistance when immersed in molten copper and aluminum [5]. The composite tubes outperformed high-grade graphite and SiC tubes when immersed in molten copper and had similar performance to high-density graphite and mullite when immersed in molten aluminum. Energy absorbing mechanisms such as debonding (between the $MoSi_2$ and Al_2O_3 layers) and microcracking in the Al_2O_3 layer contributed to the composites' ability to absorb

thermal stresses and strain energy during the performance test (shown in Figure 1). Molybdenum disilicide and alumina are chemically compatible and have similar thermal expansion coefficients [6,7].

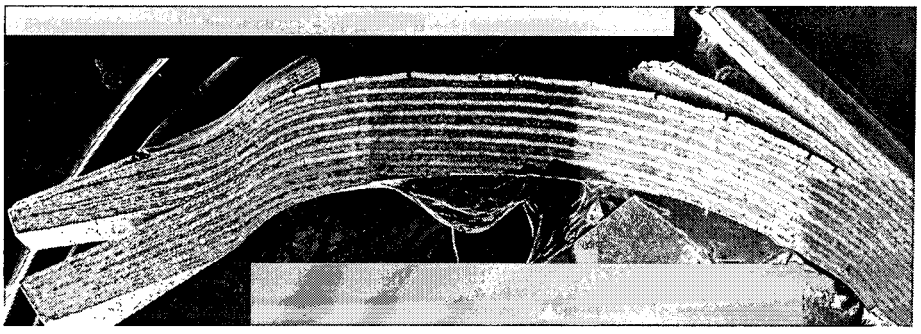

Figure 1. Four-point bend test beam after testing at 1400°C. Extensive debonding at the $MoSi_2/Al_2O_3$ interface and cracking within the Al_2O_3 was observed [5].

For thermocouple applications that require immersion of the thermocouple directly into molten glass, $MoSi_2$ coatings on Al_2O_3 protective sheaths will need to be optimized in order to perform in both a high-temperature (>1300°C) oxidizing environment (above the glass line) in addition to performing in the highly corrosive molten glass environment (below the glass line). We are currently evaluating the potential use of a graded coating of Al_2O_3 to $MoSi_2$ to enhance the performance of the $MoSi_2$ coating in molten glass. The graded microstructure of the coating will reduce the residual stresses that can develop during the spray deposition process, which can cause cracking and spallation of the coating limiting the coatings' lifetime. Preliminary results will be presented on the methodology used to produce the plasma sprayed $MoSi_2$-Al_2O_3 graded composites and on the microstructure and mechanical behavior.

EXPERIMENTAL PROCEDURES

Use of conventional plasma spraying equipment allows the flexibility of producing a variety of $MoSi_2$-Al_2O_3 microstructures, including laminate and graded structures. The plasma spraying equipment used for producing the graded structures included a Praxair Surface Technologies SG100 plasma torch and two Model 1264 powder feed hoppers. The plasma torch was mounted on a Fanuc S10 6-axis robot. A Technar DPV 2000 in-flight particle analyzer was used to measure the temperature, velocity and particle distribution of the $MoSi_2$ and Al_2O_3 particles as they exited the plasma torch. A computer control system was used to monitor and control the processing gases and the powder hoppers dispensing rate. Figure 2 shows an example of the computer control logic that was used to control the powder hopper rotation speed needed to produce the $MoSi_2$- Al_2O_3 graded structure. In this figure, pure Al_2O_3 (Powder 2) is first deposited at a powder hopper rotation speed of 0.8 rpm. After an initial period of depositing pure Al_2O_3, $MoSi_2$ (Powder 1) is gradually introduced into the plasma torch by increasing the powder hopper rotational speed for $MoSi_2$ and decreasing the rotational speed for Al_2O_3. The powder hopper speed for $MoSi_2$ subsequently reaches 0.8 rpm and the Al_2O_3 powder dispensing speed goes to zero. Pure $MoSi_2$ is then deposited on the outside diameter of the tube. Argon was used for the plasma generating gas (40 standard liters per minute, slm) and as a carrier gas for the $MoSi_2$ and Al_2O_3 powders (1 to 4 slm). A Mikron TH 4104 infrared camera was used to measure and display the temperature of the substrate. A POCO™ graphite tube (12.7mm OD, 9.5mm ID) was used as the substrate for the deposition spray trials.

To determine the mechanical behavior of the graded $MoSi_2$-Al_2O_3 structures, C-rings were machined from the material deposited on the graphite rods. C-ring samples were wire electro-discharge machined (EDM) out of the sprayed tube samples. The C-rings had an OD of 25.93 mm, an ID of 12.8mm and a width of 10.76 mm. The critical $b/(r_o-r_i)$ ratio was 1.64, within the required range of 1 to 4. The C-ring samples were tested in diametrical compression using a hydraulic Instron test frame (Type 1331 with an 8500 Plus controller and a 10kN load cell), at a crosshead speed of 0.125 mm/min (strain rate ~ 0.316×10^{-4} s^{-1}). Machine compliance was corrected using a standard Al_2O_3 sample of known stiffness. All of the samples were machined and tested in accordance with ASTM Standard C 1323-96. Twelve samples for each composite tube were tested. Four samples of monolithic plasma sprayed $MoSi_2$ and Al_2O_3 were tested and used for comparison. A Weibull statistical approach [8] was used to obtain the strength distributions in the coated and uncoated samples. While the standardized student-t test [8] employing the normal or gaussian frequency distribution is often used in statistical analysis, there is no theoretical or experimental justification for using it in problems involving fracture. Use of a normal distribution is often inappropriate in analyzing fracture problems with plasma-sprayed ceramic materials because of the presence of multiple flaw populations. The Weibull distribution is more appropriate (and conservative) in this scenario because it does not require that the flaw population be normally distributed.

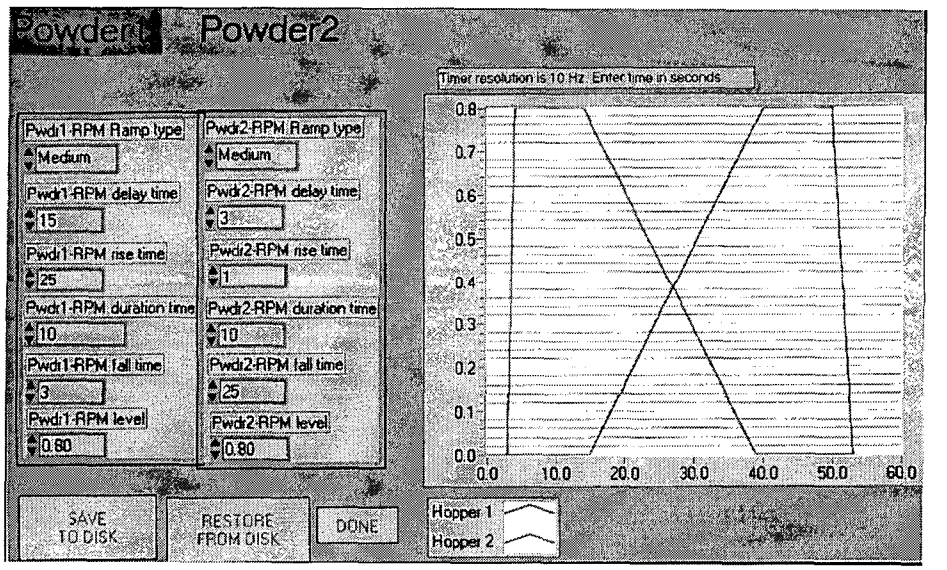

Figure 2. Computer based control system used to control the powder hopper dispensing rate for producing the $MoSi_2$-Al_2O_3 graded structures. Powder 2 is Al_2O_3 and Powder 1 is $MoSi_2$.

RESULTS

Macrographs of two types of $MoSi_2$- Al_2O_3 graded composites produced by plasma spraying are shown in Figure 3. The white phase is the Al_2O_3 and the dark phase is $MoSi_2$. Figure 3a, shows a layered and graded microstructure where the cross-section of the sample consists of discrete individual layers that have been graded from Al_2O_3 to $MoSi_2$. Figure 3b, shows the cross-section of a continuously graded structure where pure Al_2O_3 was first deposited on a graphite rod followed by increasing amounts of $MoSi_2$ until pure $MoSi_2$ is deposited on the outside diameter of

the tube. An example of a typical microstructure produce in the graded region between the $MoSi_2$ and the Al_2O_3 is given in Figure 4. A layered type of microstructure is produce when individual molten particles are flattened as they impact the substrate or previously deposited material.

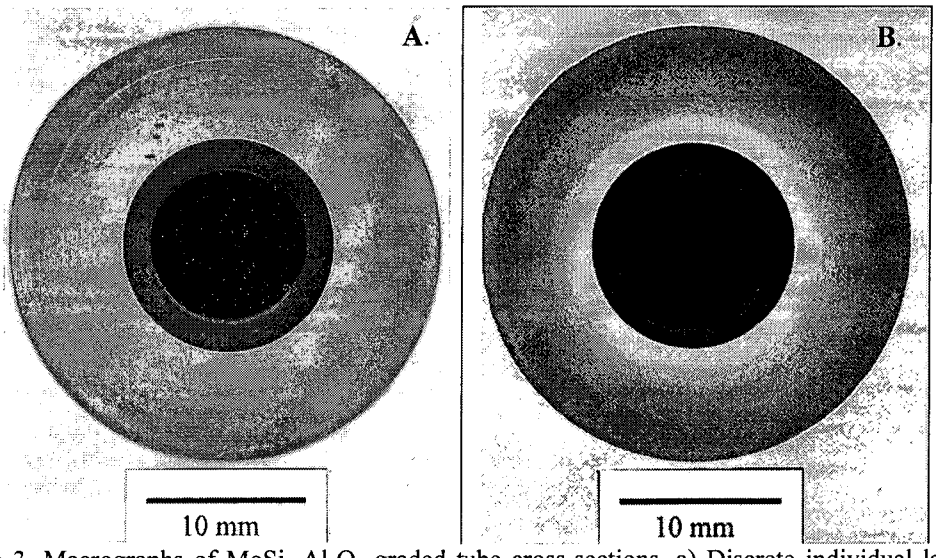

Figure 3. Macrographs of $MoSi_2$-Al_2O_3 graded tube cross-sections. a) Discrete individual layers that have been graded from Al_2O_3 to $MoSi_2$ and b) continuously grade structure from pure Al_2O_3 on the inside diameter of the tube to pure $MoSi_2$ on the outside diameter of the tube.

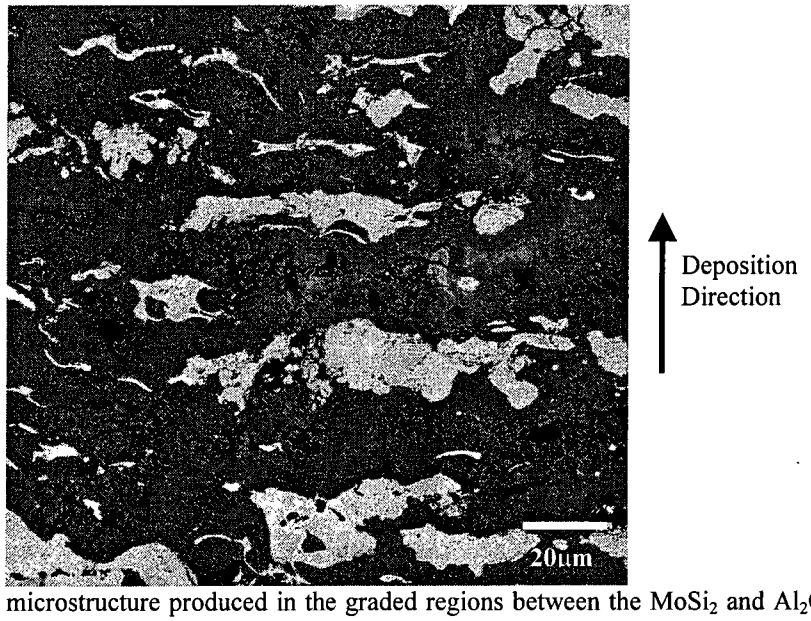

Figure 4. A typical microstructure produced in the graded regions between the $MoSi_2$ and Al_2O_3. Light areas are Al_2O_3 and dark areas are $MoSi_2$.

Residual stresses can occur in plasma sprayed deposited material as a result of quenching stresses that occur when individual particles are rapidly cooled upon impacting the substrate surface, differential thermal contraction between the deposited material and substrate and volume changes associated with any solid state phase transformation [9]. Residual stresses can give rise to deformation of the coated work piece and can result in spalling and cracking of the coating. In addition, various types of coating performance indicators such as adhesion strength, resistance to thermal shock under thermal cycling and erosion resistance are strongly influenced by the nature of the residual stresses. At elevated temperatures (> 1000°C), $MoSi_2$ goes through a brittle to ductile transformation [2] and can accommodate some of the residual stresses that occur during the deposition process and also during high temperature use of the material. Combining $MoSi_2$ with Al_2O_3 can enhance the high temperature performance of Al_2O_3 protective thermocouple sheaths by improving the poor thermal shock behavior of Al_2O_3.

THERMAL AND MECHANICAL PERFORMANCE

The mechanical behavior of the FGMs was evaluated using C-ring tests. Probability of failure at a given strength was obtained using Weibull analysis. Figure 5 shows the strength distribution plots for the layered and continuous FGMs. Both the continuous and layered FGM microstructures were found to exhibit similar mean Weibull strengths (~70 MPa). However, the spread of the data for the continuously graded material was smaller (hence a larger Weibull slope; 13.38 for the continuously graded samples, versus 7.635 for the layered graded samples). Interestingly, the fracture energy of the FGMs (qualitatively determined from the area under the load-displacement plot of the C-ring tests) was observed to be significantly higher (~3 times) than that of monolithic Al_2O_3 or $MoSi_2$ (monolithic Al_2O_3-285 J/m^2, monolithic $MoSi_2$-496 J/m^2, continuously graded $MoSi_2/Al_2O_3$ composite-766J/m^2, layered and graded $MoSi_2/Al_2O_3$ composite-955J/m^2. We are in the process of conducting independent fracture toughness tests to validate these preliminary observations and to determine if the graded microstructures exhibit R-curve behavior.

Fracture surfaces for the continuously graded and layered FGMs are shown in Figure 6. The fracture surface exhibited extensive microcracking and roughening in the center portion of the C-ring. We believe that the increased toughening of the composite is a direct result of microcracking. Preliminary analysis has indicated the strength and toughness of these FGM tubes to be more than acceptable for the proposed applications.

Earlier studies conducted on $MoSi_2$ indicated that the oxidation of the $MoSi_2$ was acceptable below and above the glass line. However, the high corrosion rate at the glass line was unacceptable and the resulting glass-line oxidation provided a challenge in the development of thermocouple sheaths. The answers to some of these challenges lies in understanding the mechanisms involved in the glass corrosion process. Figure 7 is a schematic of a phenomenological model that describes the oxidation mechanisms occurring above, at and below the glass line for $MoSi_2$ in a borosilicate glass [1]. Above the glass line (air environment), a SiO_2 coating protects the $MoSi_2$ from continued oxidation. The protective SiO_2 layer is disrupted in the temperature range around 500°C and pesting of the $MoSi_2$ can occur. Below the glass line, molybdenum metal, oxides, and silicides form in a silicon-depleted layer. The silicon-depleted layer consists of a mixture of phases (Mo_5Si_3, Mo_3Si and Mo) that are stable due to low oxygen activity [1].

The high flux of molten glass at the glass line increases the oxygen activity, resulting in increased oxidation rates. The oxidation rate is further accelerated by the dissolution of the protective SiO_2 layer as a result of the convective flow of glass at the glass line. Efforts are underway to produce a protective $MoSi_2$ coating to eliminate the high corrosion rate at the glass line. We are currently pursuing composite coatings of $MoSi_2$ and higher viscosity glasses to minimize glass line corrosion rates.

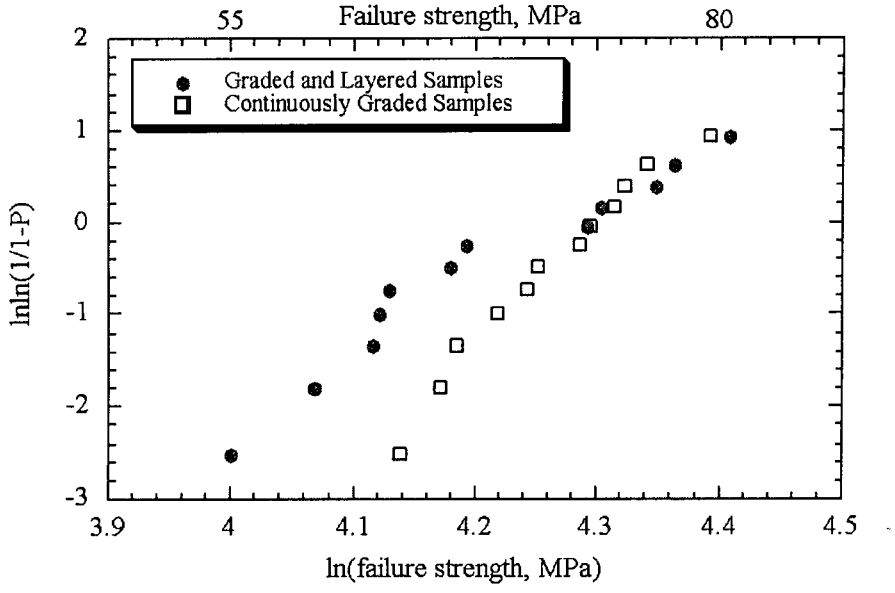

Figure 5. Results of C-ring tests performed on continuously graded and layered graded Al_2O_3-$MoSi_2$ coatings.

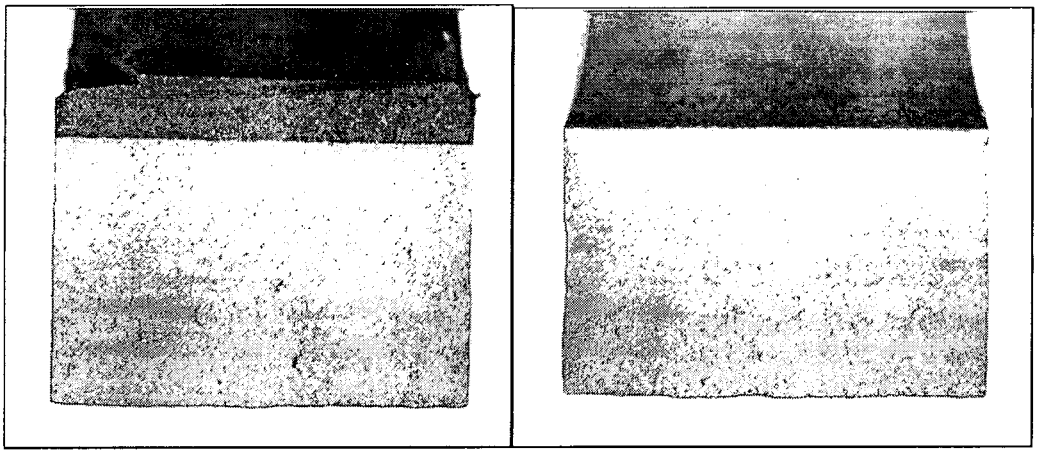

Figure 6. Macrographs of c-ring tests performed on Al_2O_3-$MoSi_2$ coatings sprayed on graphite substrates. a) Layered FGM b) Continuous FGM.

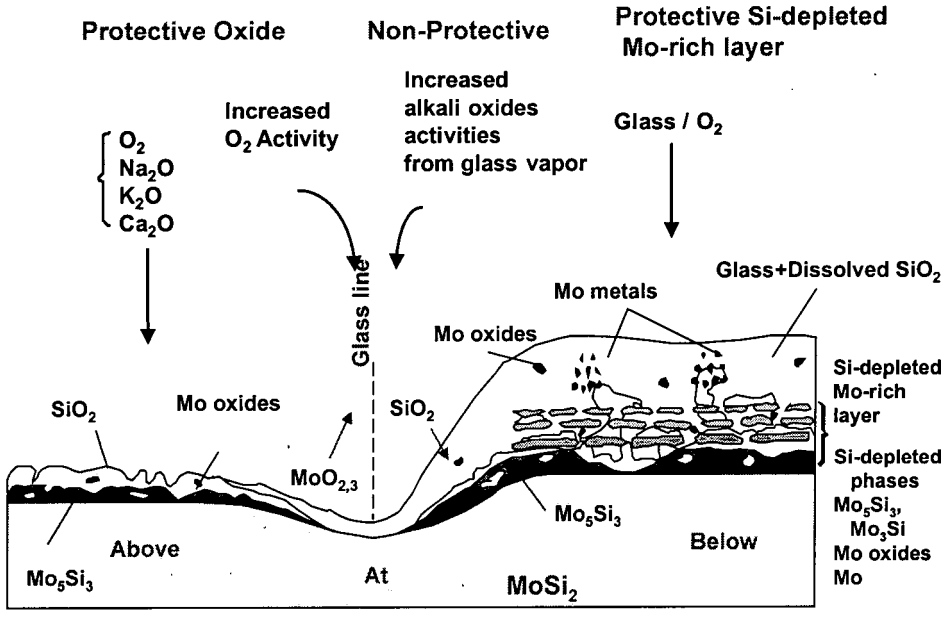

Figure 7. Schematic of model describing the oxidation of the FGM $MoSi_2$ coating above, below and at the glass line [1].

CONCLUDING REMARKS

We have demonstrated the use of conventional plasma spraying equipment in manufacturing $MoSi_2$-Al_2O_3 FGMs. The mechanical performance of these FGMs was superior to that of the monolithic materials. This was verified through C-ring tests. Although the molten glass corrosion behavior of the FGM coating is acceptable below and above the glass line, the corrosion rate at the glass line is higher than desirable. Processing of $MoSi_2$ based FGM composite coatings is ongoing and it will be determined if these new FGM coatings will reduce the glass-line corrosion.

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