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MOLYBDENUM DISILICIDE MATERIALS FOR GLASS MELTING SENSOR SHEATHS

Author(s):

J.J. Petrovic, R.G. Castro, R.U. Vaidya, M.I. Peters, D. Mendoza, R.C. Hoover, and D.E. Gallegos

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MOLYBDENUM DISILICIDE MATERIALS FOR GLASS MELTING SENSOR SHEATHS

J.J. Petrovic, R.G. Castro, R.U. Vaidya, M.I. Peters, D. Mendoza, R.C. Hoover, and D.E. Gallegos
Materials Science and Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87545

ABSTRACT

Sensors for measuring the properties of molten glass require protective sensor sheaths in order to shield them from the extremely corrosive molten glass environment. $MoSi_2$ has been shown to possess excellent corrosion resistance in molten glass, making it a candidate material for advanced sensor sheath applications. $MoSi_2$-coated Al_2O_3 tubes, $MoSi_2$-Al_2O_3 laminate composite tubes, and $MoSi_2$-Al_2O_3 functionally graded composite tubes have been produced by plasma spray-forming techniques for such applications.

INTRODUCTION

The glass industry has a critical need for advanced sensors that can determine properties of molten glass such as temperature, viscosity, and chemistry. Because molten glass is a very corrosive high temperature environment, sensors placed in molten glass must be protected by sensor sheaths that are corrosion-resistant to molten glass. Materials that are presently used for direct exposure to molten glass are noble metals such as platinum, refractory metals such as molybdenum, and refractory ceramics such as AZCS (Alumina-Zirconia-Chromia-Silica).

For thermocouple protection sheaths, the glass industry currently uses either platinum tubes or platinum-coated alumina tubes for thermocouples that are inserted through the glass-air line. While platinum is a corrosion-resistant material above, at, and below the glass line, it is very expensive and its expense is a constraining factor on the extent of its use. Molybdenum sheaths can be employed for thermocouples that are completely immersed in molten glass, but not for thermocouples that traverse the glass-air line, due to the poor oxidation resistance of molybdenum. While refractory ceramics such as AZCS possess good molten glass corrosion-resistance above, at, and below the glass line, these materials are difficult to fabricate into long and narrow thermocouple protection sheath tubes. Additionally, AZCS has very low strength and can exhibit extensive plastic deformation at elevated temperatures.

$MoSi_2$-based materials show excellent molten glass corrosion-resistance both above and below the glass line. Unlike platinum, $MoSi_2$ materials are inexpensive and can be readily fabricated into protective sheath tubular geometries by industrial processes such as plasma spraying. In addition, the elevated temperature strength of $MoSi_2$ materials is significantly higher than that of the refractory ceramics. $MoSi_2$ is also electrically conductive, while the refractory ceramics are insulator materials.

Because of their combination of properties, $MoSi_2$-based materials constitute an important new class of materials for glass industry sensor sheath applications.

MOLTEN GLASS CORROSION RESISTANCE OF $MoSi_2$

The molten glass corrosion-resistance of $MoSi_2$ has been characterized in an alkali borosilicate glass (1). The corrosion behavior of $MoSi_2$ in comparison to the refractory ceramic AZCS is shown in Figure 1, for locations above, below, and at the glass-air line. The corrosion-resistance of $MoSi_2$ is similar to that of AZCS both above and below the glass-line, but at the glass-air line $MoSi_2$ has a lower corrosion-resistance than AZCS by approximately a factor of five.

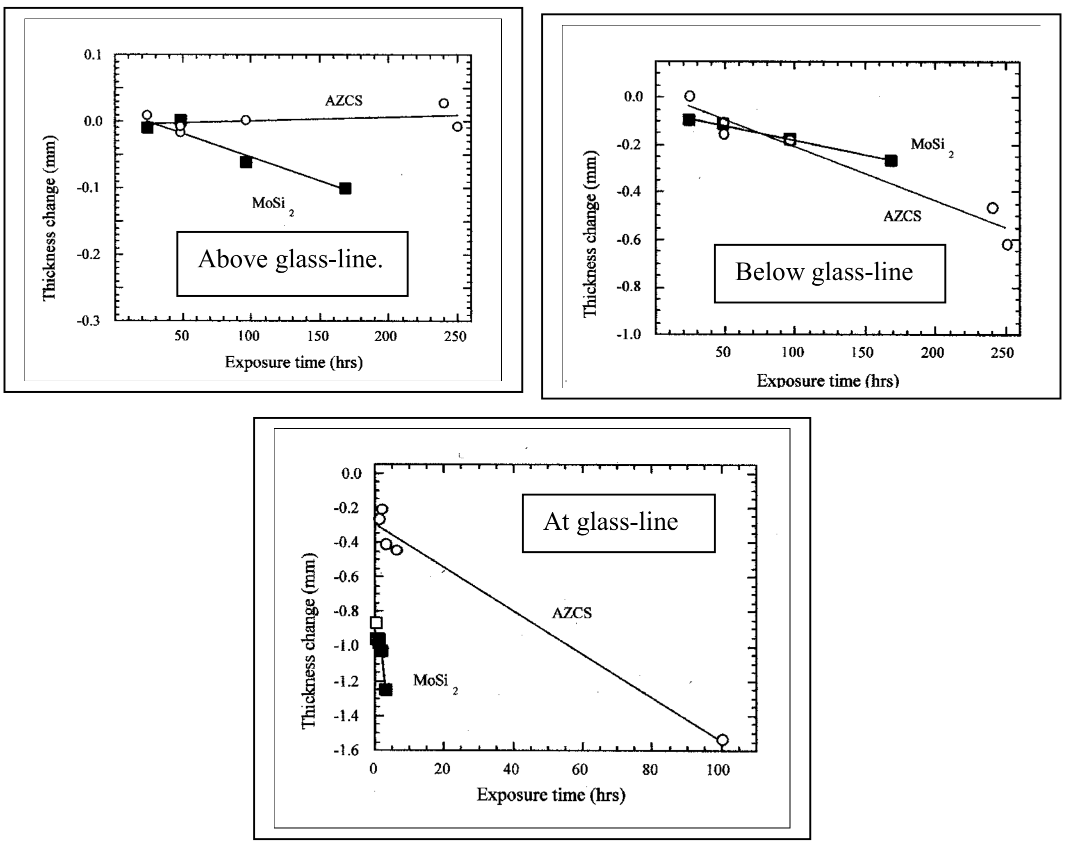


Figure 1: Molten glass corrosion of $MoSi_2$ above, below, and at the glass-air line (1).

Figure 2 shows the corrosion mechanisms that occur for $MoSi_2$ when it is immersed in molten glass. Above the glass-line a protective SiO_2 layer forms, while below the glass-line a complex multiphase protective layer is formed. However, at the glass-line no protective layer forms. Hence, the corrosion rate of $MoSi_2$ is maximum at the glass-line. For any material that is immersed in molten glass, the maximum corrosion rate occurs at the glass-line due to the increased chemical activity and mechanical convection at this location.

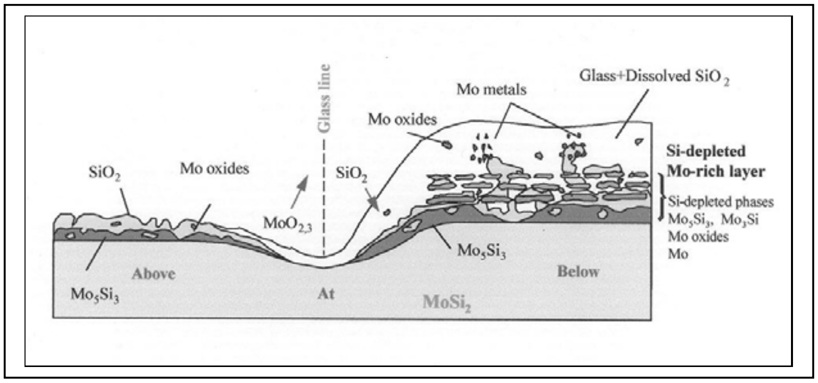


Figure 2: Corrosion mechanisms of $MoSi_2$ in molten alkali borosilicate glass (1).

$MoSi_2$-COATED Al_2O_3 TUBES

Sensor sheaths for glass furnace temperature sensors and for other types of furnace sensors such as video monitoring systems operating inside the glass furnace require a tubular geometry for the sensor sheath. $MoSi_2$-based tubes can be readily fabricated by plasma spray-forming (2). In this process, $MoSi_2$ or composites based on $MoSi_2$ are plasma sprayed onto graphite or alumina tubes.

$MoSi_2$ and Al_2O_3 constitute a good composite system for such applications, since these materials are thermodynamically stable with each other at elevated temperatures, and possess matching thermal expansion coefficients that minimize thermal stresses. $MoSi_2$-Al_2O_3 composites may exhibit improved thermal shock resistance, which is desirable for sensor sheath applications.

Advanced plasma spray techniques were employed to place $MoSi_2$ coatings on commercial Al_2O_3 tubes. A Miller thermal spraying system (SG 100 Gun and two Model 1264 programmable hoppers) coupled to a Fanuc robotic system (S-10), an in-flight particle analyzer (Technar DPV 2000), and an infrared camera (Mikron TH 5104) were employed to fabricate the $MoSi_2$-coated Al_2O_3 tubes.

A photo of a $MoSi_2$-coated Al_2O_3 tube is shown in Figure 3. The Al_2O_3 was a commercially available closed-end tube (998 alumina from LSP Industrial Ceramics Inc.) with an OD of 12.7 mm and an ID of 9.53 mm. The tube was coated with a 2 mm thick coating of $MoSi_2$, over a 450 mm length of the tube, including the closed end. A cross-section of the coated tube is also shown in Figure 3.

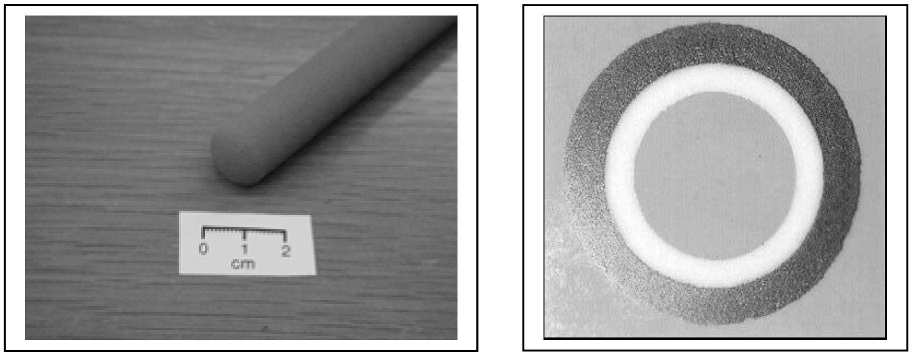


Figure 3: $MoSi_2$-coated Al_2O_3 closed-end tube. Tube cross-section is also shown.

$MoSi_2$-Al_2O_3 LAMINATE COMPOSITE TUBES

Figure 4 shows the cross-sections of laminate $MoSi_2$-Al_2O_3 tubes that were fabricated by plasma spraying alternate layers of $MoSi_2$ and Al_2O_3 onto a graphite tube mandrel (the graphite mandrel is subsequently removed by oxidation).

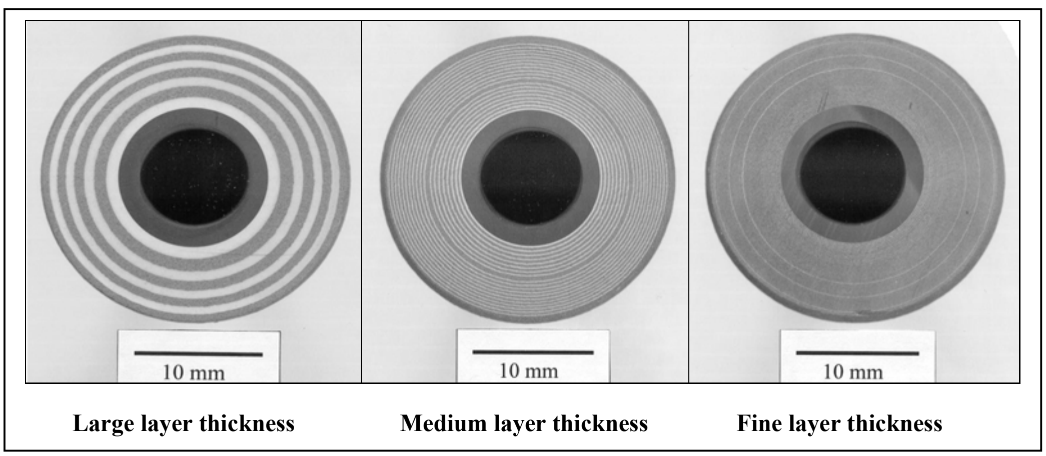


Figure 4: 50 vol.% $MoSi_2$-50 vol.% Al_2O_3 laminate composite tubes produced by plasma spray-forming. $MoSi_2$ is the dark phase and Al_2O_3 the light phase.

Tubes with three different layer thicknesses of 0.8 mm, 0.2 mm, and 0.08 mm were fabricated. The fabricated tubes were approximately 300 mm in length. Because of the thermal expansion coefficient match between $MoSi_2$ and Al_2O_3, no cracking due to thermal stresses has occurred in the tubes. $MoSi_2$-Al_2O_3 laminate composite bend strengths were in the range of 85-115 MPa and were observed to increase with decreasing layer thickness.

$MoSi_2$-Al_2O_3 FUNCTIONALLY GRADED COMPOSITE TUBES

Figure 5 shows the cross-sections of functionally graded $MoSi_2$-Al_2O_3 tubes fabricated by plasma spray-forming. Both continuously graded and layered graded tubes were fabricated. The strengths of these FGM tubes were approximately 70 MPa.

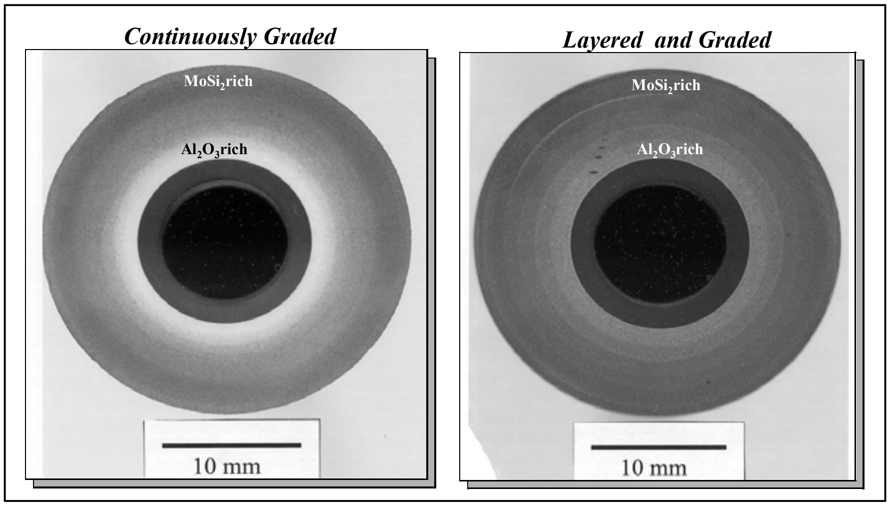
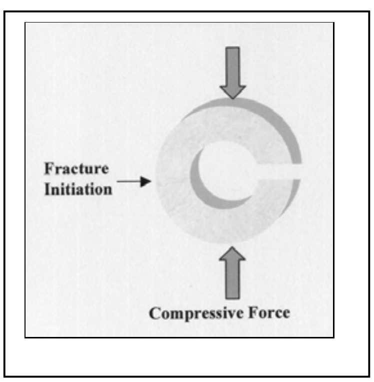


Figure 5: Continuously graded and layered graded $MoSi_2$-Al_2O_3 composite tubes produced by plasma spray-forming.

The $MoSi_2$-Al_2O_3 functionally graded materials exhibited interesting load-displacement curves when mechanically loaded in C-ring test specimen configurations as shown in Figure 6.



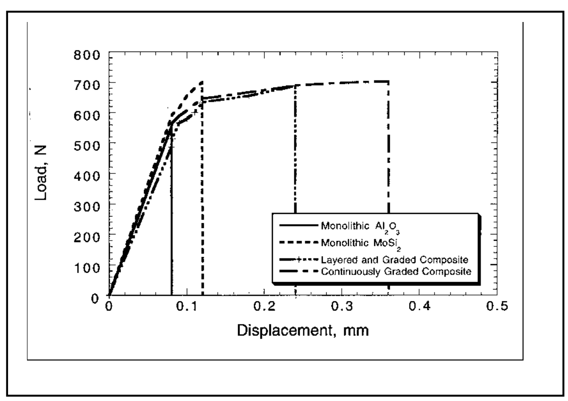


Figure 6: C-ring mechanical test load-displacement curves for $MoSi_2$-Al_2O_3 functionally graded composite tubes.

Monolithic $MoSi_2$ and Al_2O_3 tubes showed relatively low work-of-fracture values (the work-of-fracture is the area under the load-displacement curve). The value for $MoSi_2$ was 496 J/m^2, while that for Al_2O_3 was 285 J/m^2. In distinct contrast to these monolithic values, the layered graded composite showed a work-of-fracture of 766 J/m^2, while the continuously graded $MoSi_2$-Al_2O_3 composite showed a work-of-fracture of 955 J/m^2.

The substantial increase in the work-of-fracture of the functionally graded $MoSi_2$-Al_2O_3 composites in comparison to the work-of-fracture values of monolithic $MoSi_2$ and Al_2O_3 correlated with fracture surface observations. In the functionally graded composites, fracture initiated from the outside $MoSi_2$ region of the tube and then proceeded into the graded two-phase structure. As it did so, the fracture surface transitioned from smooth to rough, indicating significant crack deflection and greater energy absorption during the fracture process through the graded microstructure.

SUMMARY

$MoSi_2$ is a material that is resistant to molten glass corrosion. This makes it a candidate material for sensor protection sheaths, such as thermocouple sensors, that are immersed in molten glass. Advanced plasma spray techniques were employed to produce tubular sheaths configurations. $MoSi_2$-coated Al_2O_3 tubes, $MoSi_2$-Al_2O_3 laminate tubes, and $MoSi_2$-Al_2O_3 functionally graded tubes were fabricated. Functionally graded tubes exhibited significantly higher work-of-fracture values than monolithic tubes.

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