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Title: SYNTHESIS AND DESIGN OF SILICIDE INTERMETALLIC MATERIALS

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1998 ANNUAL PROGRESS REPORT
ADVANCED INDUSTRIAL MATERIALS (AIM) PROGRAM

"SYNTHESIS AND DESIGN OF SILICIDE INTERMETALLIC MATERIALS"

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INTRODUCTION:

The overall objective of this program is to develop structural silicide-based materials with optimum combinations of elevated temperature strength/creep resistance, low temperature fracture toughness, and high temperature oxidation and corrosion resistance for applications of importance to the U.S. processing industry. A further objective is to develop silicide-based prototype industrial components. The ultimate aim of the program is to work with industry to transfer the structural silicide materials technology to the private sector in order to promote international competitiveness in the area of advanced high temperature materials and important applications in major energy-intensive U.S. processing industries.

The program presently has a number of developing industrial connections, including a CRADA with Johns Manville Corporation targeted at the area of $MoSi_2$-based high temperature materials and components for fiberglass melting and processing applications. We are also developing an interaction with the Institute of Gas Technology (IGT) to develop silicides for high temperature radiant gas burner applications, for the glass and other industries. With Combustion Technology Inc., we are developing silicide-based periscope sight tubes for the direct observation of glass melts. With Accutru International Corporation, we are developing silicide-based protective sheaths for self-verifying temperature sensors which may be used in glass furnaces and other industrial applications.

SUMMARY OF TECHNICAL PROGRESS: October 1997-June 1998

CRADA with Johns Manville Corporation:

The kinetics of corrosion of plasma sprayed and extruded $MoSi_2$ materials were investigated in molten alkali borosilicate glass under static and dynamic conditions at 1000-1550 °C for 0.5-1510 hours. The corrosion behavior was compared to zirconia, alumina, yttria, mullite, yttria-alumina garnet (YAG), alumina-zirconia-chrome-silica refractory (AZCS), YAG-molybdenum disilicide composites, zirconia-molybdenum disilicide composites, molybdenum, niobium, and a molybdenum-5 wt.% titanium alloy. The corrosion rates were evaluated by measuring dimensional changes above, at, and below the molten glass line. It was shown that the $MoSi_2$ materials were generally superior in performance to the other refractory materials with the exception of MgO stabilized zirconia and AZCS, which were superior to $MoSi_2$ at the glass line, but exhibited relatively similar corrosion rates above and below the glass line.

The mechanisms of corrosion were investigated. The corrosion behavior was evaluated by measuring dimensional changes above, at, and below the molten glass line and through microstructural studies using transmission and scanning electron microscopy and x-ray diffraction. The mechanisms of corrosion vary with location in or above the glass melt due to changes in the activity of oxygen and the propensity for dissolution of Si. It was demonstrated that above the glass line $MoSi_2$ forms a relatively protective layer of silica. Below the glass line, Si depletion through dissolution leads to the development of a protective Mo-rich layer comprised of Mo_5Si_3 and discontinuous Mo oxides, Mo particles, and crystalline SiO_2. At the glass line neither a protective silica layer nor Mo-rich layer forms due to the combined effect of rapid dissolution of SiO_2 and simultaneous vaporization of Mo products caused by the locally high oxygen activity. Thus, the rate of corrosion of pure $MoSi_2$ at the glass line is comparatively rapid. Although the mechanisms are different, the corrosion rates above and below the glass line were relatively similar. Dynamic glass corrosion tests demonstrated that the corrosion rates were independent of glass flow rate, suggesting that the processes are not rate limited by cation or anion transport through the melt. A phenomenological model was developed that describes the overall processes of corrosion at each of the three locations.

Interaction with Institute of Gas Technology:

The testing of a suite of materials in a gas radiant tube furnace facility was performed at IGT during the period of 10-27 March 1998. The materials, in the form of rectangular bend bar-type specimens, were placed at three locations inside and outside of the IGT radiant burner U-tube. The specimens inside the U-tube were exposed to the combustion gas environment. The specimens outside the U-tube were exposed to an endothermic environment. The test ran for 339 hours.

The materials tested by IGT were the following:

- Plasma sprayed $MoSi_2$ (73 samples)
- Plasma sprayed Mo_5Si_3 (61 samples)
- SCRB210 SiC (101 samples)
- $MoSi_2$ "C" hot pressed discs (32 samples)
- $MoSi_2$-A10/SiC hot pressed composites (32 samples)
- $MoSi_2$-E10/Si_3N_4 hot pressed composites (32 samples)
- IC221M – A1 thru A24 (24 samples provided by ORNL)
- FA386M2 – B1 thru B24 (24 samples provided by ORNL)
- IC438 – C1 thru C13 (13 samples provided by ORNL)

The test conditions were the following. The nominal air flow and natural gas flow to the radiant burner U-tube at high fire conditions was 3030 SCFH and 300 SCFH, respectively. The low fire rates were 780 SCFH of air and 75 SCFH of natural gas. The average temperatures of the specimens inside the U-tube were approximately 15-30 °F hotter than that of the furnace temperature once the furnace was equilibrated. There were peak temperatures as high as 1925 °F during startup. At high fire conditions, the average temperature of the samples on the outside of the burner (carburizing side) was approximately 1830 °F when the furnace was pressurized with nitrogen, and approximately 1815 °F in the endothermic atmosphere. At low fire conditions, the temperature varied between 1845 °F and 1815 °F in the nitrogen atmosphere and 1835 °F to 1805 °F in the endothermic atmosphere.

The samples inside the U-tube were exposed to higher combustion temperatures. The highest temperature observed was 2000 °F in the early stages of the test, and decreased to 1950 °F once the system equilibrated. The average temperature at all three internal sample holders was 1875 °F during the endothermic atmosphere and approximately 1890 °F when the furnace was pressurized with a nitrogen atmosphere. The temperature of the internal specimens was approximately 1872 °F with respect to an average furnace temperature of 1810 °F. Temperature swings of approximataely 75 °F were observed during high and low firing conditions.

The total operating time of the furnace was 339 hours, which included 210 hours in a nitrogen atmosphere and 129 hours in an endothermic atmosphere. The test was terminated at 339 hours due to the detachment of some of the specimen holders on the inside and outside of the radiant U-tube.

Initial visual test results showed significant degradation of plasma sprayed Mo_5Si_3 when exposed to both the combustion and the endothermic environments. Plasma sprayed $MoSi_2$ also showed significant degradation when exposed to the combustion environment, with an improved performance when exposed to the endothermic heat-treating environment. Minimal damage was observed for the rest of the samples tested.

Interaction with Combustion Tec Inc.:

We have been interacting with Combustion Tec Inc., to explore the development of a $MoSi_2$-based periscope sight tube, for use with their video monitoring system for viewing molten glass surfaces on the inside of glass furnaces. Techniques were developed to plasma-spray form a $MoSi_2$ tube approximately 6" in length and 1.5" in diameter. A fabricated $MoSi_2$ periscope sight tube was sent to Combustion Tec for performance testing. The performance test will require the insertion of the $MoSi_2$ tube into the glass melter which will cause a thermal shock condition of the tube from room temperature to approximately 1500 °C in a 30 second time period. Removal of the sight tube which occurs over a 5 second time period also provides a thermal shock condition.

Interaction with Accutru International Corporation:

We have been interacting with the Accutru International Corporation, to explore the development of $MoSi_2$-based protection sheaths for their self-verifying temperature measurement system. The Accutru self-verifying temperature measurement system allows for the in-situ calibration of a thermocouple while it is still in place in the high temperature environment. The use of the Accutru system to measure the temperature of molten glass baths and/or the temperatures inside of glass furnaces requires that the temperature sensor elements be protected by a sheath material which is resistant to these highly corrosive high temperature conditions. Our objective is to develop $MoSi_2$-based closed-end tubular protective sheaths by plasma-spray forming techniques, which will be compatible with Accutru sensor systems, and which can be tested in glass melting furnaces.

Interaction with Oxford University:

We have been interacting with Oxford University in the UK to explore the production of continuously reinforced SiC fiber-$MoSi_2$ matrix composites using a plasma spray monotape technology. Such SiC fiber-$MoSi_2$ matrix composites would possess high fracture toughness and thermal shock resistance.

$MoSi_2$ was successfully plasma sprayed onto SiC fiber monotape, with good penetration of the $MoSi_2$ around the SiC fibers. Damage to the SiC fibers as a result of the $MoSi_2$ plasma spraying process was observed to be minimal.

High Temperature Structural Silicides Conference:

An Engineering Foundation High Temperature Structural Silicides Conference was held on 25-29 May 1998 in Hyannis Massachusetts. The Conference had 50 attendees, from the U.S., Japan, China, U.K., Germany, and Sweden. The Conference Chairs were: A.K. Vasudevan, Office of Naval Research, J.J. Petrovic, Los Alamos National Laboratory, S.G.Fishman, Office of Naval Research, C.A. Sorrell, U.S. Department of Energy, and M.V. Nathal, NASA-Lewis Research Center.

The objective of the Conference was to assess the state-of-the-art of international materials research on High Temperature Structural Silicides. Forty-two technical presentations were given, in the areas of Materials, Mechanical Behavior, Atomic Mechanisms, Fabrication, Properties, and Applications. The refereed Proceedings of the Conference are to be published in the Journal of Materials Science and Engineering A in 1999.

TECHNICAL PROGRESS: July-September 1998

CRADA with Johns Manville Corporation:

Glass corrosion studies this quarter focused primarily on Mo_5Si_3 plasma sprayed coatings.
A static corrosion study was done at 1300°C for 1 hour. Dimensional analysis of the corrosion coupons is in progress. Due to the thin thickness of the coating and catastrophic oxidation of materials at and above the glass line as shown in Figure 1, a comparison of material loss could not be obtained. We are planning to compare material loss only below the glass line next quarter.

Figure 1 shows SEM morphologies of the plasma sprayed Mo_5Si_3 exposed at 1300°C for 1 hour. As shown in Figure 1, the glass line region split due to severe corrosion/oxidation at and above the glass line. The SEM microstructures and EDS analysis showed that Mo_5Si_3 oxidizes in the oxygen environment, forming mostly SiO_2 and Mo oxides (EDS showed mostly MoO_3). The approximate ratio of SiO_2 and Mo oxides under SEM was 50:50. As we reported previously, a protective, continuous SiO_2 oxide layer could not form on the surface of Mo_5Si_3 due to pesting of non-protective Mo oxide formation as products.

The severe corrosion at and above the glass line shown in Figure 1 also prevented the observation of microstructural changes below the glass line after the corrosion test. Thus, the microstructural changes occurring during the corrosion of Mo_5Si_3 will be focused only on corrosion taking place below the glass line.

Next quarter, we will also initiate corrosion studies of single crystal $MoSi_2$ and Mo_5Si_3 in the molten glass environments.

Institute of Gas Technologies Interaction:

We have continued investigations on the stability of molybdenum-based silicides in a combustion and endothermic heat-treating environment. The temperature history of the four-point bend samples varied depending on the location of the sample holders on the radiant U-tube. In general, the test samples on the interior of the U-tube (combustion environment) experienced a higher temperature than the samples on the exterior of the tube (endothermic environment). A summary of the temperature history observed during the furnace operation is given in Table 1.

Visual inspection of the four-point bend samples showed significant oxidation of the plasma sprayed Mo_5Si_3 when exposed to the combustion and endothermic environment. Plasma sprayed $MoSi_2$ also showed significant oxidation when exposed to the combustion environment with an improved performance when exposed to the endothermic heat-treating environment. The accelerated oxidation which was observed in the plasma sprayed materials was not present in the hot pressed $MoSi_2$ and the $MoSi_2$ composites. Analysis of these samples revealed the presence of both SiO_2 and Mo-oxides on the surface of the four-point bend samples. Differences in the oxidation behavior can be attributed to the loss of silicon during the plasma spray process which results in a molybdenum rich, silicon depleted material. As a result of this silicon loss, a large volume fraction of Mo_5Si_3 can be present throughout the $MoSi_2$ matrix, Figure 2. Mo_5Si_3 has been shown to have poor oxidation resistance at elevated temperatures. The observed catastrophic failure of the plasma sprayed Mo_5Si_3 in the combustion and endothermic environment also demonstrates the poor oxidation resistance of this material.

The surface morphologies of the materials were characterized by SEM and EDS. The morphologies are shown in Figure 3 for hot pressed $MoSi_2$, plasma sprayed $MoSi_2$, and $MoSi_2$ - Si_3N_4 composites. The EDS results in Table 2 show that all of the $MoSi_2$, Mo_5Si_3, and $MoSi_2$ - SiC, $MoSi_2$ – Si_3N_4 materials exhibit SiO_2 and Mo oxide formation from the molybdenum silicide and SiO_2 from the SiC and Si_3N_4 materials. The formation of products in the endothermic environment for each material will be characterized. To date, more Mo oxide formation in the combustion environment has been observed, due to the accelerated formation of Mo oxides/less formation of SiO_2 caused by the lower oxygen activities in the combustion environments as compared to pure air.

Due to severe oxidation of the plasma sprayed samples, four point bend testing after exposure to the endothermic and combustion environments was not possible. In addition, bend test samples which were adjacent to the plasma sprayed samples in the holders were also damaged/cracked as a result of the expansion which occurred during oxidation of the plasma sprayed samples. Four-point bend strength results of the silicide-based materials in the as-machined condition and after exposure to the endothermic and combustion environments are summarized in Table 3.

Test results indicated a 28% increase in strength of the $MoSi_2$/30SiC samples, from 341.5 MPa to approximately 438 MPa after exposure to both the combustion and endothermic environments. Investigations are currently being performed to determine the cause of the observed strength increase. Changes in the strength of $MoSi_2/30Si_3N_4$ samples were relatively small and were not statistically significant. The strength of the plasma sprayed (157.9 MPa) and hot pressed (153.8 MPa) $MoSi_2$ in the as-machined condition were similar but were below the strength levels of plasma sprayed Mo_5Si_3 (251.8 MPa).

Oxford University Collaboration:

Oxford University has successfully completed a 4-layer Sigma 1140+ fiber reinforced $MoSi_2$ and $MoSi_2$+SiAlON composite with excellent fiber spacing and minimal fiber damage. After heat treating at 1500 °C followed by furnace cooling, no matrix cracking was observed in the composites. Future investigations will focus on the use of a SCS-9 SiC fiber which has a carbon core. The Sigma 1140+ fiber has a tungsten core and is not suitable for high temperature applications above 1000 °C. A SiC coated SCS-9 fiber will also be evaluated to minimize interfacial reaction between the fiber and the $MoSi_2$ matrix. Consolidation of the continuous reinforced layered composite will be evaluated using hot isostatic pressing (HIP) and hot pressing. The physical and mechanical properties of the composite will be evaluated including the CTE of matrix, electrical conductivity, pesting and oxidation properties, interfacial strength, fiber tensile properties, bend strength, fracture toughness and creep properties. Consolidation of the composite material will be investigated at LANL.

DOE/OIT Glass Call 99 Proposal:

A Proposal entitled "Molybdenum Disilicide Composites for Glass Processing Sensors" was submitted to the DOE/OIT Glass Lab Call 99 in June 1998. We proposed a program to develop strong, tough, and thermal shock resistant molybdenum disilicide hybrid composite tubes by plasma spray-forming techniques which can be employed for a variety of advanced sensors and controls for the glass industry. LANL will test these tubes as protective sheaths for the advanced temperature sensors being developed for the glass industry by the Accutru International Corporation and as periscope sight tubes for closed-circuit video glass furnace sensors marketed by Combustion Tec. Inc. Research performed at LANL has shown that $MoSi_2$ materials are highly resistant to corrosion in molten glasses and their performance in molten glass is similar to the refractory ceramic AZS which is widely used in the glass industry. $MoSi_2/Si_3N4$-SiC fiber composites possess the mechanical characteristics necessary for applications inside glass furnaces where thermal stresses and thermal shock conditions require materials that can standup to these severe mechanical requirements. Preliminary studies have established the feasibility of plasma spray-forming both $MoSi_2/Si_3N_4$ particulate reinforced composites and $MoSi_2$/SiC fiber composites. $MoSi_2$-oxide laminate tube geometries have also been produced by plasma spray-forming, and are also under consideration for glass industry sensor applications.

Our Proposal was selected for funding by DOE/OIT. These activities have commenced in October 1998. There will be a 50% cost sharing each year from our industrial partners Accutru International Corporation, Combustion Tec Inc., Plasma Process Inc., and Exotherm Inc. In

FY1999, we will establish and optimize plasma-spray forming techniques for $MoSi_2$-oxide laminate composite and $MoSi_2/Si_3N_4$-SiC fiber hybrid composite tube geometries and evaluate the composite mechanical properties and corrosion resistance in molten glasses. In FY-2000, we will fabricate prototype composite temperature sensor sheath and periscope sight tubes and perform preliminary tests in glass melting furnaces in association with Accutru and Combustion Tec. In FY-2001, we will demonstrate an Accutru glass furnace temperature measurement sensor system and a Combustion Tec closed-circuit glass furnace video monitoring system which use composite tubes as critical components for dramatically improved glass sensor performance.

Facility Upgrades:

A Fanuc S-10 industrial robot was purchased and installed in the thermal spray booth at LANL. The robot has 6-axis of motion and will be capable of spraying long (~ 36") sheathing tubes for glass processing sensors. An acceptance test and training course on the operation of the robot was done on September 28-29, 1998 at LANL. An SG-100 plasma spray torch has been mounted on the robot arm and a demonstration has been performed on coating Al_2O_3 thermocouple tubes with $MoSi_2$. The robot will be used to support the dèvelopment of $MoSi_2$-based glass processing sensors.

PUBLICATIONS:

Journals:

1. J.J. Petrovic, M.I. Pena, I.E. Reimanis, M.S. Sandlin, S.D. Conzone, H.H. Kung, and D.P. Butt, "Mechanical Behavior of $MoSi_2$ Reinforced-Si_3N_4 Matrix Composites", J. Am. Ceram. Soc., 80, 3070-3076 (1997).

2. H. Kung, Y.C. Lu, A.H. Bartlett, R.G. Castro, and J.J. Petrovic, "Structural Characterization of Combustion Synthesized $MoSi_2$-Si_3N_4 Composite Powders and Plasma Sprayed $MoSi_2$-Si_3N_4 Composites", J. Mater. Res., 13, 1522-1529 (1998).

3. J.J. Petrovic and A.K. Vasudevan, "Key Developments in High Temperature Structural Silicides", accepted for publication in Materials Science and Engineering A, 1999.

4. K.K. Chawla, J.J. Petrovic, J. Alba, and R. Hexemer, "Phase Identification in Reactively Sintered Molybdenum Disilicide Composites", accepted for publication in Materials Science and Engineering A, 1999.

5. A.M. Baker, P.S. Grant, R.G. Castro, and H. Kung, "Preliminary Characterization of a Plasma Sprayed $MoSi_2$/Sigma SiC Fibre Monotape", accepted for publication in Materials Science and Engineering A, 1999.

6. Y. Park, D.P. Butt, R. Castro, J. Petrovic, and W. Johnson, "Durability of Molybdenum Disilicide in Molten Alkali Borosilicate Glass", accepted for publication in Materials Science and Engineering A, 1999.

7. Y. S. Park, R. G. Castro, K. J. Hollis, J. J. Petrovic, and D. P. Butt, "Corrosion of Molybdenum Disilicide Materials in Molten Alkali Borosilicate: I, Kinetics and Comparison to Other Refractories" submitted to *J. Am. Ceram. Soc.*, 1998.

8. Y. S. Park, R. D. Field, J. J. Petrovic, and D. P. Butt, "Corrosion of Molybdenum Disilicide Materials in Molten Alkali Borosilicate Glass, II: Microscopy and Mechanisms," submitted to *J. Am. Ceram. Soc.*, 1998.

9. S.D. Conzone, D.P. Butt, and A.H. Bartlett, "Joining $MoSi_2$ to 316L Stainless Steel", J. Mater. Sci., 32, 3369-3374 (1997).

10. R.U. Vaidya, P. Rangaswamy, M.A.M. Bourke, and D.P. Butt, "Measurement of Bulk Residual Stresses in Molybdenum Disilicide/Stainless Steel Joints Using Neutron Scattering", accepted for publication in Acta Materialia, 1997.

11. R.U. Vaidya, A.H. Bartlett, H.H. Kung, and D.P. Butt, "Joining of $MoSi_2$ to Itself and Reactions with Aluminum Interlayers", accepted for publication in Journal of Materials Science Letters, 1997.

Other Publications:

1. J.J. Petrovic, "High Temperature Structural Silicides", Ceram. Eng. Sci. Proc., 18, 3-17 (1997).

2. D.E. Alman, J.A. Hawk, J.J. Petrovic, C.H. Henager, and M. Singh, "Abrasive Wear Behavior of $MoSi_2$-SiC Composites", pp. 51-61 in Wear of Engineering Materials, Ed. J.A. Hawk, ASM International, c. 1998.

3. R.G. Castro, R.U. Vaidya, A. Ayala, B.D. Bartram, D.E. Gallegoes and H.S. Kurek. "Evaluation of Molybdenum-Based Silicides in a Combustion and Endothermic Environment" to be published in the proceedings of the United Thermal Spray Conference, Dusseldorf, Germany, March 17-19, 1999.

4. R.U. Vaidya, A.H. Bartlett, S.D. Conzone, and D.P. Butt, "Investigations into the Joining of $MoSi_2$ to 316L Stainless Steel", in Ceramic Joining, Eds. I. Reimanis, C. Henager Jr., and A. Tomsia, pp. 63-74, American Ceramic Society, Westerville, OH, c. 1997.

5. Y.S. Park, D.P. Butt, K.J. Hollis, R.G. Castro, and J.J. Petrovic, "Viability and Degradation of Molybdenum Disilicide Materials in Molten Glass Environments", Proceedings, 22nd Cocoa Beach Conference on Composites, Advanced Ceramics, Materials and Structures, American Ceramic Society Engineering Ceramics Division, January 1998, Cocoa Beach, Florida.

6. R.G. Castro, K.J. Hollis, H.H. Kung, and A.H. Bartlett, "Molybdenum Disilicide Composites Produced by Plasma Spraying", Proceedings, 15th International Thermal Spray Conference, 25-29 May 1998, Nice, France, Vol. II, pp. 1199-1204.

7. J.J. Petrovic, "Ceramic-Silicide Composites", to be published in the Proceedings of the World Ceramics Congress, 14-19 June 1998, Florence, Italy.

PRESENTATIONS:

Invited Presentations:

1. J.J. Petrovic, "Key Developments in High Temperature Structural Silicides", Keynote Presentation, Engineering Foundation High Temperature Structural Silicides Conference, 25-29 May 1998, Hyannis, Massachusetts.

2. K.K. Chawla, J. Alba, J.J. Petrovic, and R.L. Hexemer, "Phase Identification in Reactively Sintered Molybdenum Disilicide Composites", Engineering Foundation High Temperature Structural Silicides Conference, 25-29 May 1998, Hyannis, Massachusetts.

3. J.J. Petrovic, "Ceramic-Silicide Composites", World Ceramics Congress, 14-19 June 1998, Florence, Italy.

Other Presentations:

1. Y.S. Park, D.P. Butt, K.J. Hollis, R.G. Castro, and J.J. Petrovic, "Viability and Degradation of Molybdenum Disilicide Materials in Molten Glass Environments", 22nd Cocoa Beach Conference on Composites, Advanced Ceramics, Materials and Structures, American Ceramic Society Engineering Ceramics Division, January 1998, Cocoa Beach, Florida.

2. A.M. Baker, P.S. Grant, R. Castro, and H. Kung, "Preliminary Characterization of Plasma Sprayed $MoSi_2$/Sigma SiC Fibre Monotapes", Engineering Foundation High Temperature Structural Silicides Conference, 25-29 May 1998, Hyannis, Massachusetts.

3. Y.S. Park, R.G. Castro, K. Hollis, J.J. Petrovic, and D.P. Butt, "Durability of Molybdenum Silicide Materials in Molten Alkali Borosilicate Glass", Engineering Foundation High Temperature Structural Silicides Conference, 25-29 May 1998, Hyannis, Massachusetts.

4. R.G. Castro, H. Kung, K.J. Hollis, and J.J. Petrovic, "Applications of Molybdenum Disilicide Composites Produced by Plasma Spraying", Engineering Foundation High Temperature Structural Silicides Conference, 25-29 May 1998, Hyannis, Massachusetts.

5. R.G. Castro, K.J. Hollis, H.H. Kung, and A.H. Bartlett, "Molybdenum Disilicide Composites Produced by Plasma Spraying", 15th International Thermal Spray Conference, 25-29 May 1998, Nice, France.

6. R.G. Castro, J.J. Petrovic, D.P. Butt, K.J. Hollis, H.H. Kung, and Y. Park, "Durability of $MoSi_2$ in High Temperature Industrial Applications", DOE/OIT Advanced Industrial Materials Annual Meeting, 23-25 June 1998, Jackson Hole, Wyoming.

7. J.J. Petrovic, R.G. Castro, D.P. Butt, K.J. Hollis, and Y. Park, "Advanced High Temperature Materials for Glass Applications", DOE/OIT Glass Industry Project Review, 12-13 August 1998, Argonne, Illinois.

HONORS AND AWARDS:

1. J.J. Petrovic was a Co-Organizer of the Engineering Foundation High Temperature Structural Silicides Conference, 25-29 May 1998, Hyannis, Massachusetts.

PATENTS/DISCLOSURES:

None.

LICENSES:

None.

INDUSTRIAL INPUT and TECHNOLOGY TRANSFER:

Johns Manville Corporation:

We have a CRADA with Johns Manville Corporation to develop $MoSi_2$-based materials for fiberglass processing.

Institute of Gas Technology (IGT):

We are interacting with IGT to perform tests on $MoSi_2$-based materials in radiant gas combustion tube environments.

Exotherm Corporation:

We have been investigating the plasma spraying of advanced $MoSi_2$, Mo_5Si_3, and composite powders from the Exotherm Corporation.

Combustion Tec, Inc.:

We are interacting with Combustion Tec to develop a $MoSi_2$ sight tube for a glass furnace monitoring system, that can withstand 3000 °F at the glass furnace wall.

Accutru International Corporation:

We are interacting with Accutru International to develop $MoSi_2$-based composite protection sheaths for their self-verifying temperature measurement system for glass furnaces.

Plasma Process Inc.:

We are interacting with Plasma Process Inc. to transfer the plasma spray-forming technology which we have developed for $MoSi_2$-based materials and composites.

Oxford University:

We are interacting with Oxford University to examine the plasma spray fabrication of continuous SiC fiber-$MoSi_2$ matrix composites.

Table 1: Summary of the temperature history during furnace operations

4-point bend samples exposed to the endothermic environment, Ao, Bo and Co
• average temperature of the four-point bend samples on the outside of the U-tube (endothermic environment) were approximately 15 to 30 °C hotter then the furnace temperature. • the temperature of the samples were approximately 1000 °C when the atmosphere in the furnace was nitrogen and approximately 990 °C in the endothermic atmosphere. • the temperature varied from one location to another by approximately 25 °C depending on high or low fire conditions • the samples located in the A position had the highest temperature during the high fire operation and the lowest temperature during low fire conditions.
4-point bend samples exposed to the combustion environment, Ai, Bi, and Ci
• the samples located inside of the U-tube were exposed to higher temperatures of the combustion flame. The highest peak temperature recorded was approximately 1095 °C. • The average temperature at all three holders was approximately 1025 °C during the endothermic atmosphere and approximately 1030 °C when the furnace was under a nitrogen atmosphere. • The average temperature of the internal coupons was 1020 °C with respect to the average furnace temperature of 985 °C. • The temperature varied from one location to another by approximately 25 °C depending on the high/low firing operation. • The samples located in the A position had the highest temperature during high fire and the lowest temperature during low fire.

Table 2: EDS results from the outer surface of the specimens exposed in the combustion environments

S : Small intensity peak

Sample	Mo	Si	O	Fe	Ca	Al	S	Remarks
$MoSi_2$								
HPC C1-27	0	0	0					SiO_2/Mo oxides
HPC OC-29	S	0	0	0				Mostly SiO_2 (little Mo oxides)
PS C1-11	S	0	0	0				Mostly SiO_2 (little Mo oxides)
PS CO	0	0	0					SiO_2/Mo oxides
$MoSi_2$-Si_2								
OC-37		0	0				0	SiO_2 with S impurity
$MoSi_2$-SiC								
C1-37		0	0	S				SiO_2
$MoSi_2$-Si_3N_4								
C1-32	0	0	0	0	0			SiO_2/Mo oxides
OC-32	0	0	0		0			SiO_2/Mo oxides
SCRB-210								
C1-8		0		0	0		0	SiO_2 with impurities
OC-8		0	0		0		0	SiO_2 with Sulfur
Mo_5Si_3								
C1-PS	0	0	0					Mostly SiO_2 (little Mo oxides)
CO-19PS		0	0	0				SiO_2 with Fe(less Mo oxides)

Table 3: Four-point bend strength (MPa) of plasma sprayed (PS) $MoSi_2$ and Mo_5Si_3 and hot pressed (HP) $MoSi_2$, $MoSi_2$/30SiC and $MoSi_2$/30 Si_3N_4.

Condition	PS $MoSi_2$	PS Mo_5Si_3	HP $MoSi_2$	HP $MoSi_2$/30SiC	HP $MoSi_2$/30Si_3N_4
as-machined	157.29	251.86	153.8	341.5	462.3
combustion	oxidized	oxidized	broke	438.7	464.3
endothermic	oxidized	oxidized	broke	438.0	484.8

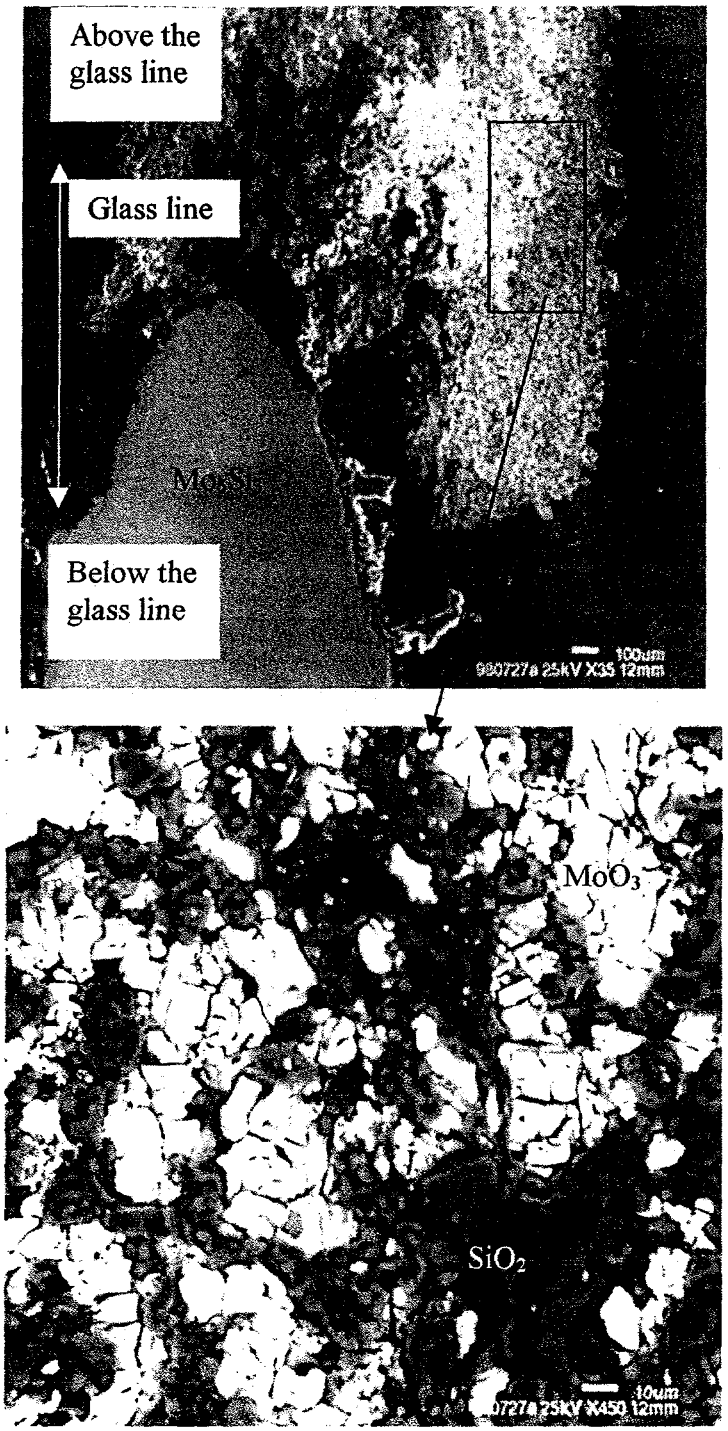


Figure 1. SEM observation of plasma sprayed Mo_5Si_3 near the glass line exposed at 1300°C for 1 hour. Top row shows near glass line showing severe corrosion/oxidation at the glass line and bottom row shows above the glass line morphology observed from the square regions showing SiO_2 and MoO_3 formation as products.

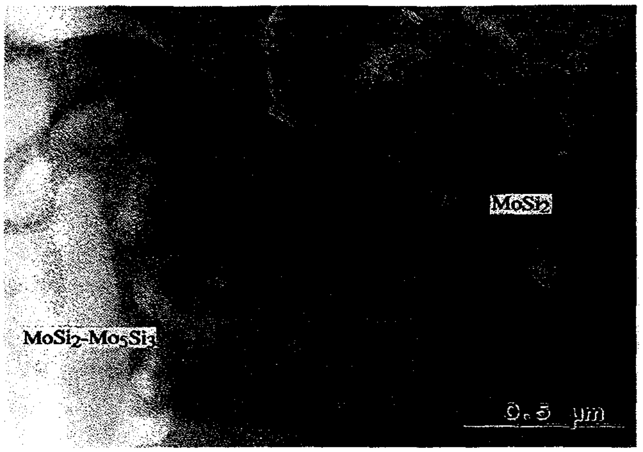
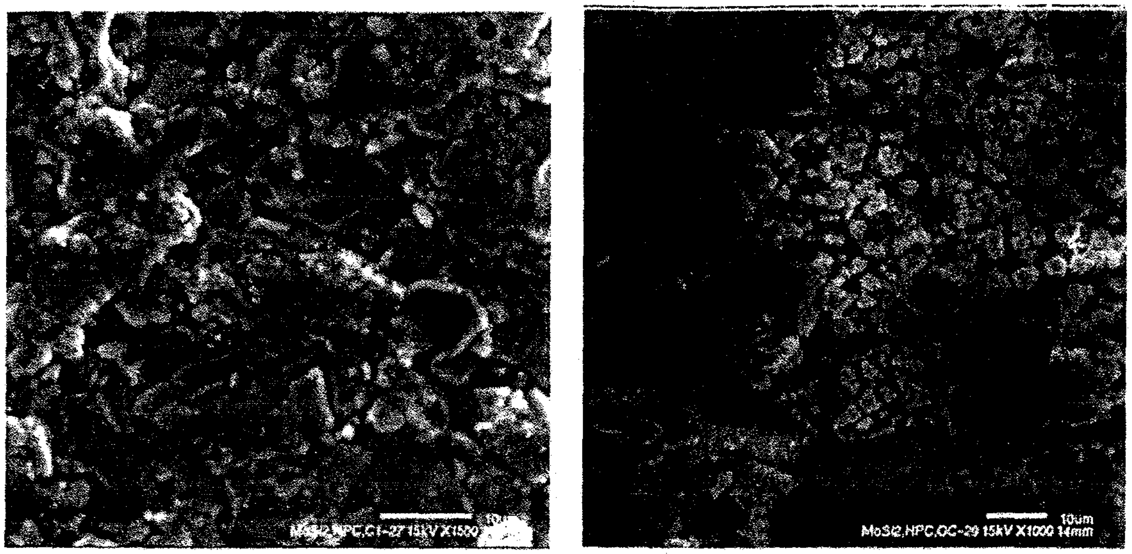
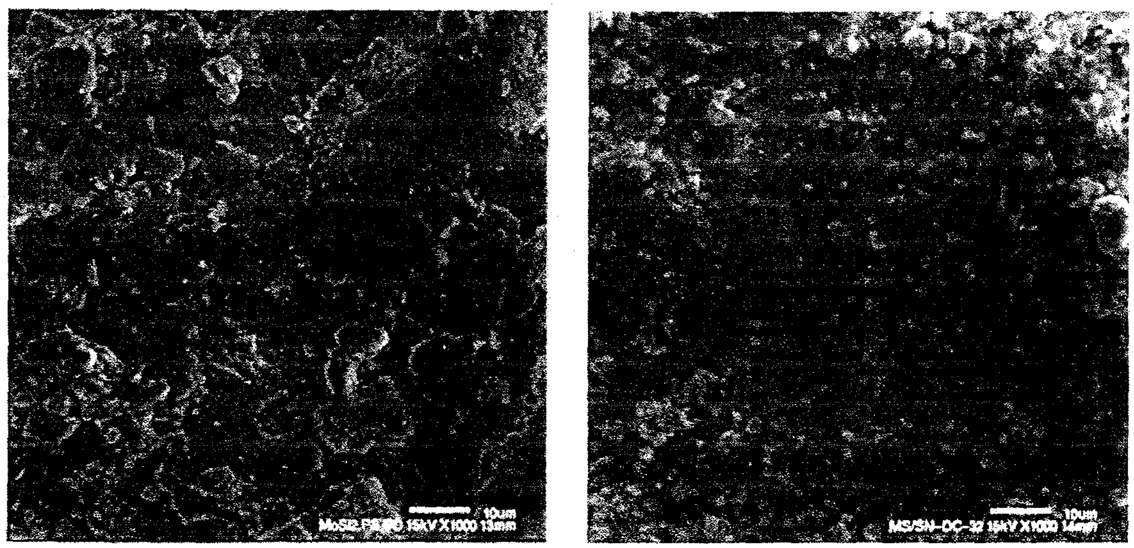


Figure 2: TEM micrograph of as-sprayed $MoSi_2$ showing the presence of a $MoSi_2$-Mo_5Si_3 eutectic.



Outer surface morphology of hot pressed $MoSi_2$ exposed inside of radiant U-tube(CI-27, left hand side) and outside of radiant U-tube(OC-29, right hand side)



Outer surface morphology of plasma sprayed $MoSi_2$ (left hand side) and $MoSi_2$-30% Si_3N_4 composite (right hand side) exposed outside of radiant U-tube

Figure 3: SEM observation of hot pressed $MoSi_2$, plasma sprayed $MoSi_2$, and $MoSi_2$ – 30% Si_3N_4 composites exposed at 1000-1020°C.

PROJECT SUMMARY

Advanced Industrial Materials (AIM) Program

PROJECT TITLE: Synthesis and Design of Silicide Intermetallic Materials

PHASE: FY-1998 **COMPLETION DATE:**

PERFORMING ORGANIZATION(S): Los Alamos National Laboratory (LANL)

PRINCIPAL INVESTIGATOR(S): J.J. Petrovic (505)667-0125, R.G. Castro (505)667-5191

PHASE OBJECTIVE: Conduct CRADA with Johns Manville Corporation on silicide materials for fiberglass processing. Interact with Combustion Tec Inc. and Accutru International Corporation to initially explore the use of silicides in glass processing sensors. Interact with the Institute of Gas Technology (IGT) to test silicide materials in gas radiant tube combustion environments. Develop the plasma spraying and plasma spray-forming of $MoSi_2$-based materials and composites.

ULTIMATE OBJECTIVE: To develop $MoSi_2$-based high temperature structural silicide materials with optimum combinations of properties for applications of importance to U.S. processing industries, and particularly the glass processing industry.

TECHNICAL APPROACH: Develop plasma spray and plasma spray-forming techniques for the fabrication of high fracture toughness, high thermal shock resistant $MoSi_2/Si_3N_4$-SiC fiber hybrid composites and $MoSi_2$-oxide laminate composites with high oxidation/corrosion resistance. Develop $MoSi_2$-based protection sheaths for molten glass and glass furnace high temperature sensors. Develop gas combustion-related applications for silicide materials

PROGRESS: Our CRADA with Johns Manville Corporation is continuing, with emphasis on corrosion of silicide materials in molten fiberglass. Silicide materials have been tested in a gas radiant tube combustion environment by IGT. A new effort involving Accutru International Corp. and Combustion Tec Inc. has begun which is targeted at developing high temperature protective sheaths for glass processing sensors.

Patents: -	**Publications:** 11	**Proceedings:** 7
Books: -	**Presentations:** 10	**Awards:** 1

ACCOMPLISHMENTS: The mechanisms of corrosion of $MoSi_2$ in molten fiberglass have been established. A protective silica layer forms above the glass line, while a protective complex molybdenum-rich layer forms below the glass line. No protective layers form at the glass line. Silicide materials were tested at IGT for 339 hours at temperatures in the range of 990-1030 °C in a natural gas combustion radiant tube furnace system.