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# Use of Metallic Glasses in Molybdenum Disilicide-Stainless Steel Joining

*Rajendra U. Vaidya, Partha Rangaswamy, Richard G. Castro, John J. Petrovic, and Darryl P. Butt*

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**The successful use of a cobalt-based metallic glass in joining molybdenum disilicide ($MoSi_2$) to stainless steel 316L was demonstrated. The cobalt-based metallic glass (METGLAS™ (Allied Signal Inc., Parsippany, NJ) 2714A) was found to wet the $MoSi_2$ and stainless steel surfaces and provide high-quality joints. The joining was completed at 1050 °C for 60 min. Postbrazing metallographic evaluations coupled with quantitative elemental analysis indicated the presence of a Co-Cr-Si ternary phase with CoSi and $CoSi_2$ precipitates within the braze. Brazing conducted under these process parameters was found to provide interfacial joint strengths in the range of 60 to 80 MPa.**

**Keywords** metallic glasses, brazing, molybdenum disilicide, push-out tests

## 1. Introduction

Molybdenum disilicide ($MoSi_2$) is a potential high-temperature structural material owing to its excellent oxidation resistance, high melting temperature, a brittle-to-ductile transition near 1000 °C, and stability in a variety of corrosive and oxidative environments.[1–5] Some potential uses for $MoSi_2$ include furnace components, gas burners and ignitors, gas injection tubes, and high-temperature nozzles.[1,2,6]

In order for $MoSi_2$ to be used in many of the aforementioned applications, it must first be joined to other materials, in particular ferrous alloys (stainless steels). However, direct bonding of $MoSi_2$ to most metals is difficult due to the large differences in the coefficients of thermal expansion (CTE) between $MoSi_2$ and metals. The large thermal expansion mismatch coupled with the necessity of using high joining temperatures (in the case of refractory brazes) results in large residual stresses and can lead to joint failure upon cooling. Low-temperature brazing techniques and the use of ductile interlayers of intermediate CTE can alleviate the problem of large thermal stresses developed upon cooling from the bonding temperatures.

A number of recent studies[7,8] have demonstrated that these interlayers can successfully reduce the residual stresses in ceramic-metal systems and act as a buffer to accommodate the thermomechanical mismatch. Furthermore, we have demonstrated[9] that the use of interlayers can successfully reduce the residual stresses in $MoSi_2$-stainless steel joints. However, the addition of the interlayers adds to the cost and complexity of the joining process. The interlayer materials commonly employed are expensive metals and alloys based on nickel, niobium, and tantalum. Furthermore, many of the brazes employed in these joining operations can have large amounts of precious metals such as gold and silver, and the cost of the joining process can get exorbitant. These precious metal-based brazes also have limited high-temperature capabilities.

Metallic glasses are amorphous metal alloys that are produced by a continuous rapid solidification process that produces thin (0.001 to 0.0025 in.) foils. Cooling rates of up to one million degrees centigrade per second permit the foils to be made directly from the molten state, bypassing the formation of the crystalline structure. It is this random or glassy atomic structure that gives these alloys their unique mechanical properties. Metallic glasses are stronger, harder, and more ductile than the metals from which they are derived.[10,11] The ribbons can be folded back onto themselves (zero bend radius) without fracturing. Metallic glasses can thus be formed to comply with complex joint geometries or punched to exact joint shapes. Metallic glasses, when used as brazing filler materials, devitrify during the heating segment of the brazing cycle. Devitrification is not detrimental to the melting characteristics of the metallic glass. Furthermore, the devitrified metallic glass can be ductile enough to serve as an interlayer in the joint and dissipate residual stresses generated during the cooling cycle.

From a practical standpoint, use of metallic glasses as brazing foils reduces the size of the brazement gaps as those used with brazing pastes and powders, to achieve complete filling of the braze cross section. The high flexibility and ductility of these amorphous foils allows them to be used as a preplaced preform. These metallic glasses also melt over a narrow temperature range (during transient heating). The result is less erosion of the base materials being joined, lower sensitization of the base materials due to the shorter brazing times, absence of organic solvents (as with brazing pastes), and a more uniformly brazed joint. Furthermore, these foils have a significantly smaller amount of surface oxide film, unlike the gas-atomized powders used in filler brazes. These surface oxides prevent fusion of individual particles and result in nonuniform melting. The use of metallic-glass foils bypasses this problem.

Although metallic glasses have been used as brazes in various metal-metal systems, there have been no studies in the literature demonstrating their use in ceramic-metal joining. In this study, we have demonstrated the feasibility of using a cobalt-based metallic glass in joining $MoSi_2$ to stainless steel

**Rajendra U. Vaidya, Partha Rangaswamy, Richard G. Castro** and **John J. Petrovic**, Materials Science and Technology Division, Los Alamos National Laboratory. Los Alamos, MN 87545; and **Darryl P. Butt**, Ceramatec, Inc., Salt Lake City, UT 84119.

alloy 316L. The process temperature and time for obtaining the optimum joints were determined. Detailed metallographic evaluations coupled with quantitative elemental analyses were conducted to determine changes in the chemistry at the brazed interface. Pushout tests were carried out to evaluate the joint strengths. Preliminary results of these studies are presented below.

## 2. Experimental

### 2.1 Materials

Commercial $MoSi_2$ Super Kanthal (Kanthal AB, Sweden) extruded injector tubes were used in the joining experiments. A typical composition of the material is given in Table 1. In addition to the elements listed in Table 1, traces of niobium were also detected in our material. The 12 mm diameter $MoSi_2$ tubes (with a 2.5 mm diameter hole in the center) were sliced 2.5 mm thick into disks and ground to −600 grit. The porosity in the $MoSi_2$, as determined by image analysis, was ~14 vol pct.

Stainless steel 316L was in the form of bar stock or disks (Metal Samples, Inc., Munford, AL). Composition of the stainless steel alloy used is given in Table 2. All of the stainless steel samples were polished (to −600 grit) and cleaned with acetone prior to joining. The disks had a diameter of 15.5 mm and a thickness of 1.5 mm. The bar stock material was machined in the form of rings, with an outside diameter of 19 mm and an inside diameter of either 12.05 or 12.10 mm. The thickness of the rings was 2.5 mm. The two different diameters were chosen to accommodate two different thicknesses of brazing foils (25 and 50 $\mu$m).

Four different metallic glasses were investigated in this study. Compositions of the metallic glasses used are given in Table 3. These metallic glasses were obtained from Allied Signal, Inc. (Parsippany, NJ). The metallic-glass ribbons had a nominal width of 50 mm and a thickness of 25 $\mu$m. The metallic-glass ribbons were cut to size using a pair of precision shears. All of the materials were ultrasonically cleaned in acetone followed by deionized water, prior to joining.

**Table 1 Composition of the $MoSi_2$ studied[12]**

| Element | Wt.% |
|---|---|
| Mo | 60.2 |
| Si | 35.6 |
| O | 3.1 |
| Al | 0.63 |
| Fe | 0.39 |
| Mg | 0.08 |
| Ca | 0.04 |
| C | <0.1 |
| B | <0.02 |

**Table 2 Composition of the stainless steel 316L studied[13]**

| Element | Wt.% |
|---|---|
| Fe | Bal |
| C | 0.03 |
| Mn | 2 |
| Si | 1 |
| Ni | 10–14 |
| Cr | 16–18 |
| P | 0.045 |
| S | 0.03 |

### 2.2 Brazing Procedure

Two different experimental braze setups were used depending on the experiment to be performed and the shape of the stainless steel. For the disk-shaped samples, the brazing foil and substrates were arranged in a block/foil/block orientation, and the entire assembly was placed into a loading device consisting of two $Al_2O_3$ platens and four $Al_2O_3$ bolts. The $Al_2O_3$ bolts were hand tightened. This procedure ensured sufficient contact between the various components of the joint. The assembled $Al_2O_3$ jig was placed into a tube furnace, which was vacuum purged with ultra-high-purity Ar-6% $H_2$ gas (three times) at room temperature and again at 250 °C to remove oxygen and absorbed water from the furnace and brazing assembly. The furnace was then purged continuously with Ar-6% $H_2$ gas. The ultra-high-purity Ar-6% $H_2$ gas was gettered by passing it first through calcium sulfate at room temperature and then 99.9% pure copper at 650 °C. The joints were completed by heating the assemblies from 250 °C, at 5 °C/min, to the brazing temperature (which was 10 to 30 °C above the braze melting temperature and was held for times varying between 30 to 120 min before cooling at 2 °C/min to room temperature). A schematic of the experimental setup used can be seen in Fig. 1.

A different fixture was used for the ring-shaped samples (used in the pushout tests). The fixture consisted of an $Al_2O_3$ holder with a recess. The stainless steel ring, $MoSi_2$ tube, and brazing foil were arranged within this recess. The diameter of the recess was 19.1 mm. This diameter was selected so as to apply a constraint on the assembly during the heating cycle. The constraint would prevent excessive expansion of the stainless steel ring, thereby ensuring contact between the stainless steel, $MoSi_2$, and the metallic-glass foil during the brazing process. The heating cycle employed in the brazing process was identical to the ones described earlier. A photograph of the two fixtures used in the joining experiments can be seen in Fig. 2 and 3.

In conjunction with the joining experiments, wetting and spreading studies were also conducted by placing small (5 ×

**Table 3 Compositions (in wt.%) and melting points of the metallic glasses used**

| | Element | | | | | | |
|---|---|---|---|---|---|---|---|
| Brazing foil | Ni | Co | Cr | Si | Fe | B | P |
| MBF-20 | Bal | | 7 | 4.5 | 3 | 3 | ... |
| MBF-50 | Bal | | 19 | 7.3 | ... | ... | ... |
| MBF-60 | Bal | | ... | ... | ... | ... | 11 |
| METGLAS 2714A | 1 | Bal | | 15 | 4 | 14 | ... |

Melting points: MBF-20: 1024 °C, MBF-50: 1144 °C, MBF-60: 921 °C, and METGLAS 2714A: 1040 °C

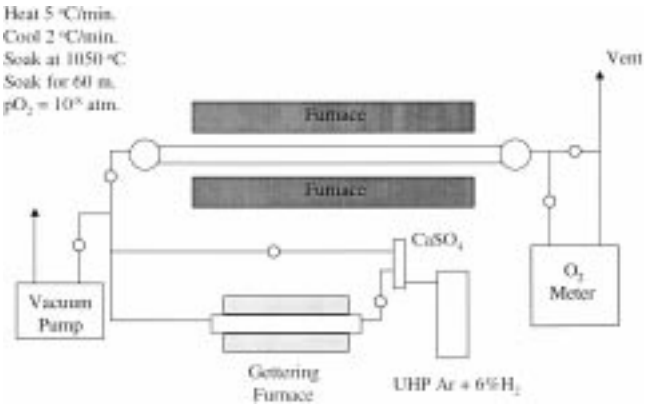



**Fig. 1** Experimental setup used for making the joints

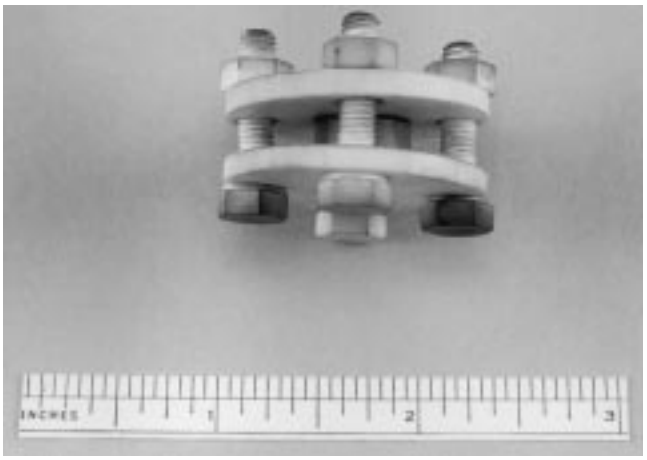


**Fig. 2** Fixture used in making the $MoSi_2$/stainless steel joints

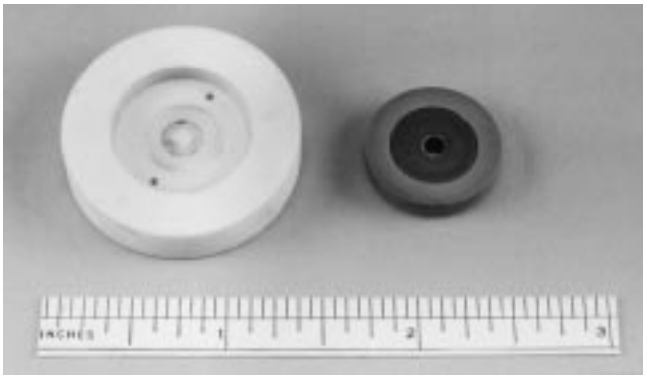


**Fig. 3** Fixture used in making the push-out test samples

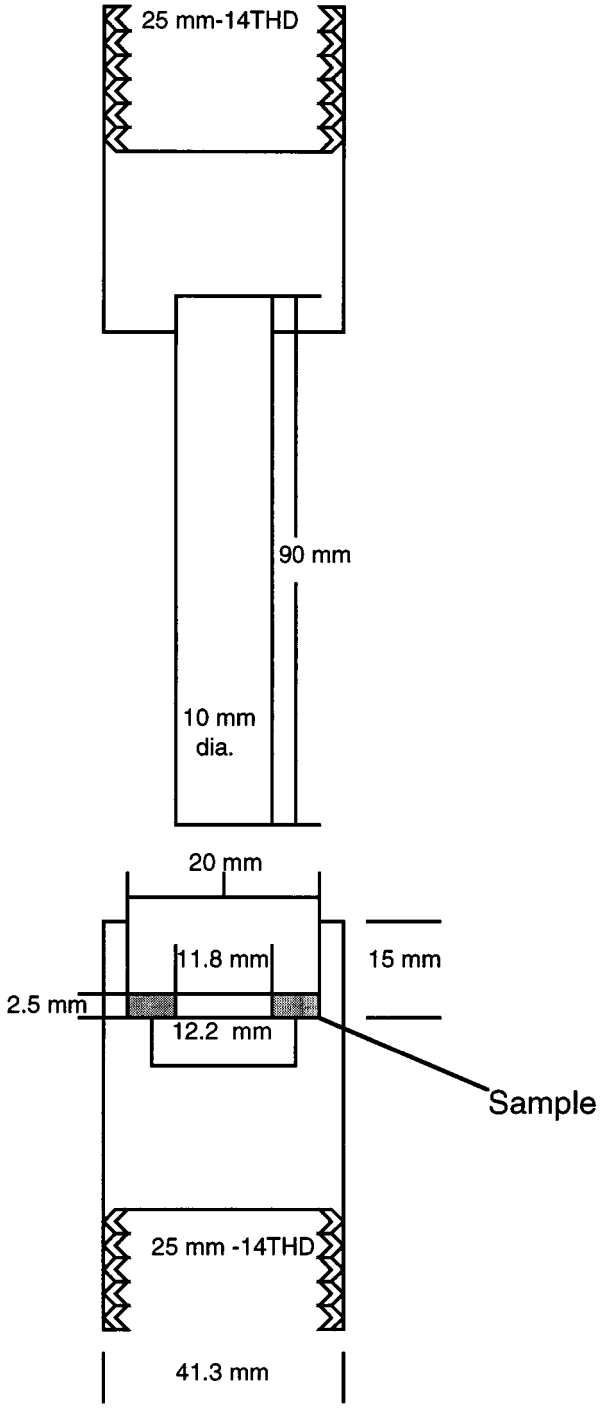



**Fig. 4** Schematic of the setup used in the push-out test

5 mm) pieces of brazing foil onto polished and cleaned surfaces of $MoSi_2$ and stainless steel 316L disks. These experiments were conducted in a tube furnace vacuum purged with Ar + 6% $H_2$, using conditions identical to those described above. The temperature and time of the furnace were varied depending on the foil used (10 to 30 °C over the melting point, 30 to 120 min of exposure time). The wetting experiments were primarily intended to provide information on the wetting characteristics of the brazing foils.

### *2.3 Joint Strength Measurements*

Ring-shaped samples were used to conduct a push-out test. A schematic of the setup used in the push-out test can be seen in Fig. 4. The sample thickness used in the push-out tests was 2.5 mm. The normal force applied to the $MoSi_2$ in the center

of the sample was balanced with the shear force at the $MoSi_2$-stainless steel interface, and the shear strength of the joint was evaluated therefrom. The maximum shear stress at the interface $\tau_{max}$ was evaluated using the equation

$$\tau_{max} = F_{max}/(2\pi dh)$$

where $d$ is the inside diameter of the stainless steel ring and $h$ is the height (or thickness) of the sample. The push-out tests were performed in an Instron (Canton, MA) machine using a crosshead speed of 0.05 mm/min.

It is important to note that the push-out test used was not a standardized test and was used for screening purposes only. The stresses developed at the interface may not be pure shear (may have a bending component).

## 3. Results and Discussion

Preliminary wetting studies carried out on the $MoSi_2$-stainless steel 316L system indicated that the nickel-based metallic glasses did not wet the stainless steel adequately. The nickel-based metallic glasses appeared to bead onto the surface of the stainless steel, and spreading of the braze was inadequate. The contact angle varied between 135 and 165°. Increasing the brazing time (or temperature) did not improve the wetting characteristics of the stainless steel by the nickel-based metallic glasses. The cobalt-based metallic glass proved to wet both the $MoSi_2$ and stainless steel and produce a brazed joint. The measured contact angles were between 25 and 45°.

We were interested in determining the lowest temperature and time that could be employed to complete the braze. Therefore, we conducted a time-temperature study and brazed in the temperature range 1050 to 1080 °C (10 to 30 °C above the melting temperature, with brazing times varying between 30 and 120 minutes). The temperature-time experimental space is provided in Table 4. Our experiments demonstrated that excellent joints could be produced at 1050 °C using a 60 min hold, or at 1060 °C using a 30 min hold. Reducing the brazing time below 60 min at 1050 °C led to inadequate melting and spreading of the braze material. Increasing the brazing time beyond 60 min and/or temperature above 1060 °C led to extensive diffusion of the braze material into the $MoSi_2$.

Successful brazes were produced using either 25 or 50 $\mu$m thick (two foils) metallic glass. The actual thickness employed in a real application will be dictated by the geometry of the components to be brazed and the ease of incorporating different brazing foil thicknesses. Prior to application, a detailed residual stress analysis should be required and performed to determine if the brazing foil thickness has any effect on the residual stresses within the components of a particular joint assembly.

**Table 4 Experimental temperature-time space used in the experiments**

| | Temperature | | | |
|---|---|---|---|---|
| **Time (min)** | **1050 °C** | **1060 °C** | **1070 °C** | **1080 °C** |
| 30 | x | **X** | x | x |
| 60 | **X** | x | x | x |
| 90 | x | x | x | x |
| 120 | x | x | x | x |

x: all the conditions tested

**X**: conditions that produced the best joints

A scanning electron micrograph of the brazed joints (produced at 1050 °C for 60 min using two foils) can be seen in Fig. 5. Higher magnification backscattered images of the $MoSi_2$-stainless steel 316L joint can be seen in Fig. 6(a) and (b). What appears as a gap between the $MoSi_2$ and the braze is actually relief from the polishing (Fig. 5 and the elemental maps in Fig. 7). In reality, the interface between the braze material and both components of the joint, namely, the $MoSi_2$ and the stainless steel 316L, was continuous and defect free. As expected, various braze elements appeared to have diffused extensively into the $MoSi_2$. Iron from the metallic glass was saturated in a layer farthest from the interface. Detailed wavelength dispersive spectroscopic (WDS) analysis of the $MoSi_2$ adjacent to the braze also indicated Co diffusion into the $MoSi_2$. The bulk of the metallic-glass braze, which did not diffuse upon melting, was found to have crystallized.

The portion of the braze in the immediate vicinity of the $MoSi_2$ revealed the presence of $CoSi_2$ and a few CoSi precipates in a Co-Cr-Si ternary, indicating that chromium diffused from the stainless steel into the braze. A few Si- and Cr-rich regions were also detected in the braze. A Co-rich region (with traces of Cr) was located adjacent to the stainless steel. The grain boundaries of the stainless steel in the vicinity of the Co-rich region of the braze also appeared to be enriched with Cr. Various WDS elemental maps of the joint can be seen in Fig. 7(a) and (b).

The presence of the Co-Si intermetallic precipitates has some important significance on the application of this metallic glass in the $MoSi_2$-stainless steel joining process. These intermetallics have melting points that are significantly higher than that of the braze material (1480 °C for CoSi and 1326 °C for $CoSi_2$). The resultant braze microstructure is a composite consisting of hard intermetallic particles in a ductile ternary Co-Si-Cr matrix. Although we have not conducted any creep experiments, such a

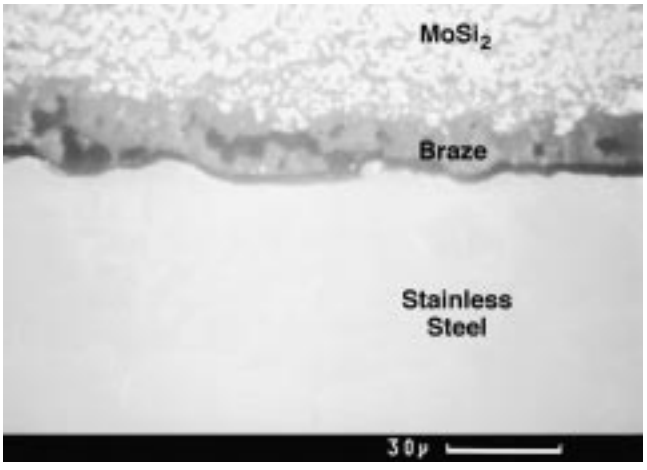
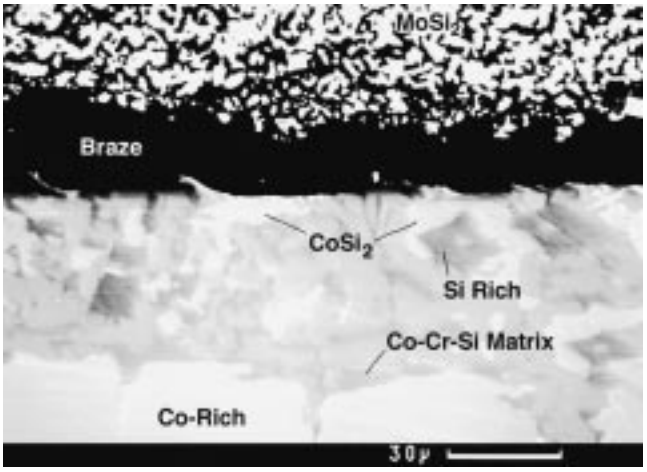


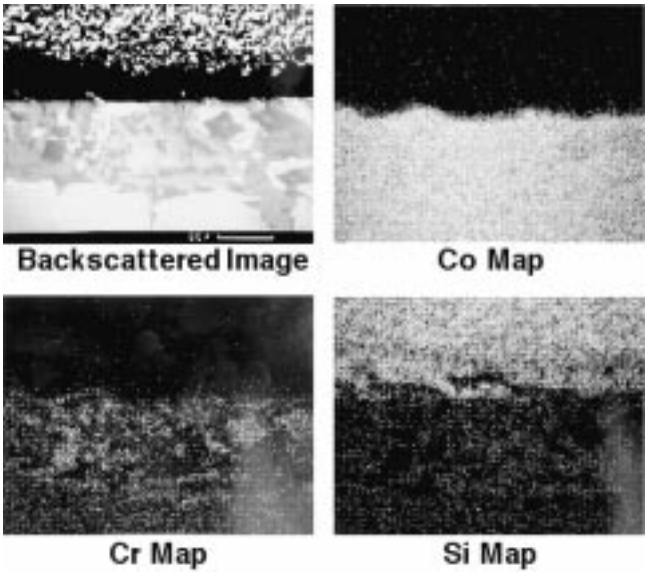

**Fig. 5** A scanning electron micrograph of the brazed joints produced at 1050 °C for 60 min



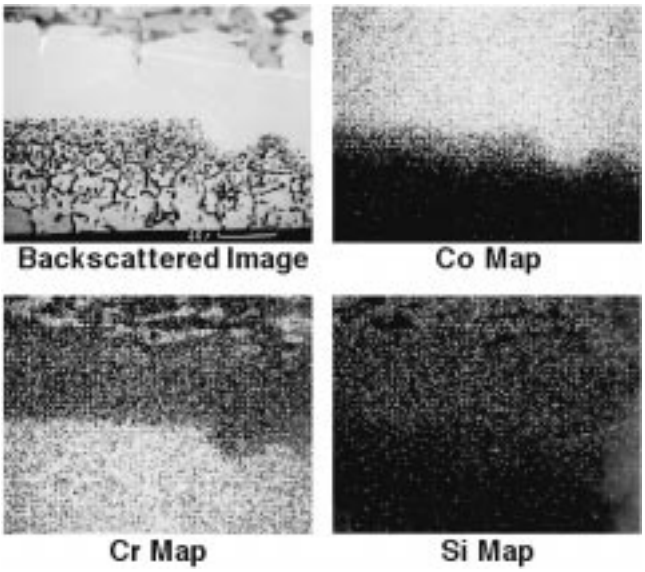

**(a)**


**(b)**

**Fig. 6** Backscattered images of the $MoSi_2$/stainless steel joints. (**a**) In the vicinity of $MoSi_2$. Note the various phases in the braze. (**b**) In the vicinity of the stainless. Chromium appears to have diffused to the grain boundaries of the stainless steel.




**(a)**




**(b)**

**Fig. 7** (**a**) and (**b**) Wavelength dispersive spectroscopic elemental maps for the various regions seen in Fig. 6(**a**) and (**b**)

microstructure is expected to provide excellent creep resistance. The presence of these precipitates also illustrates the "reactive" nature of the braze.

The significance of the reactive nature of the braze material on the joint integrity and strength was evaluated using a push-out test. In particular, we were interested in determining the effect of the Co-Si precipitates and the Cr-enriched region in the stainless steel on the joint strength. A schematic of a shear stress-linear displacement plot obtained in a push-out test (samples had two foils) can be seen in Fig. 8. The interfacial shear stress was calculated by balancing the normal force exerted on the $MoSi_2$ over the sheared area at the joint interface. The peak stress in the plot corresponds to the peak load at which shear failure occurred in the joint. A corresponding load drop followed by a moderate increase in the load represents the friction in the sliding process. Once the two rings ($MoSi_2$ and stainless steel) have slid apart by 0.15 mm, the load drops monotonically. A total of five samples weretested. All of these samples were brazed according to the procedure outlined earlier and employed a brazing foil thickness of 50 $\mu$m. With the exception of one sample, all of the shear failure occurred in the braze material. The average shear stress was calculated to be 72.3 MPa. The interfacial shear stress values ranged from 60.3 to 83.1 MPa.

The sample, which was excluded from the statistics, exhibited compressive cracking in the $MoSi_2$. Calculations revealed that the normal stress on the $MoSi_2$ was on the order of 50 MPa, which is low for $MoSi_2$ (fracture strength between 150 to 200 MPa). We believe that this sample might have had either inherent defects or large residual stresses, which caused it to fail at this low stress.

Some of the features of the samples after the push-out test can be seen in Fig. 9(a) and (b). The cross section in Fig. 9(a) illustrates the ductile nature of the braze material even after the completion of joining, as evidenced by stretched-out regions in the braze. Failure within the braze was consistent in all the

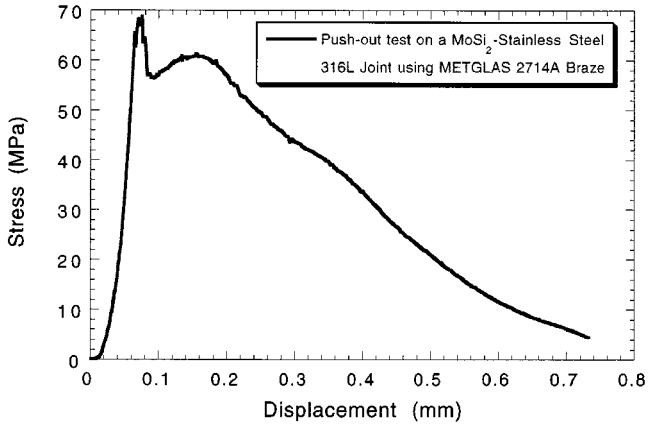



**Fig. 8** Schematic of a shear stress-linear displacement plot obtained in a push-out test

samples and occurred by circumferential cracking. Excellent bonding was retained between the metallic-glass braze and the two components of the joint ($MoSi_2$ and stainless steel). The integrity of these surfaces was maintained after pushout and can be seen in Fig. 9(b). Pushout primarily occurred by failure in the braze material.

Based on these studies, we can conclude that METGLAS 2714 A can be used to braze $MoSi_2$ to stainless steel. The joining process is reactive and results in the formation of intermetallic Co-Si precipitates in a ductile Co-Si-Cr matrix. Push-out tests have indicated adequate joint strengths and retained ductility within the braze after joining.

## 4. Conclusions

We were successful in joining $MoSi_2$ to stainless steel 316L alloy using a cobalt-based metallic glass (METGLAS 2714A). Time-temperature studies revealed that the best quality joints were obtained when the brazing was completed at 1050 °C for 60 min. Larger joining times and/or higher temperatures resulted in excessive diffusion of the braze material into the $MoSi_2$. The brazing process was reactive and resulted in the formation of intermetallic Co-Si precipitates in a Co-Si-Cr ternary. Such a microstructure is expected to provide excellent high-temperature creep resistance. Push-out tests carried out on brazed samples indicated an average interfacial shear strength of 72.3 MPa. In most of these samples, failure occurred within the braze. Failure of the braze was found to occur in a ductile manner.

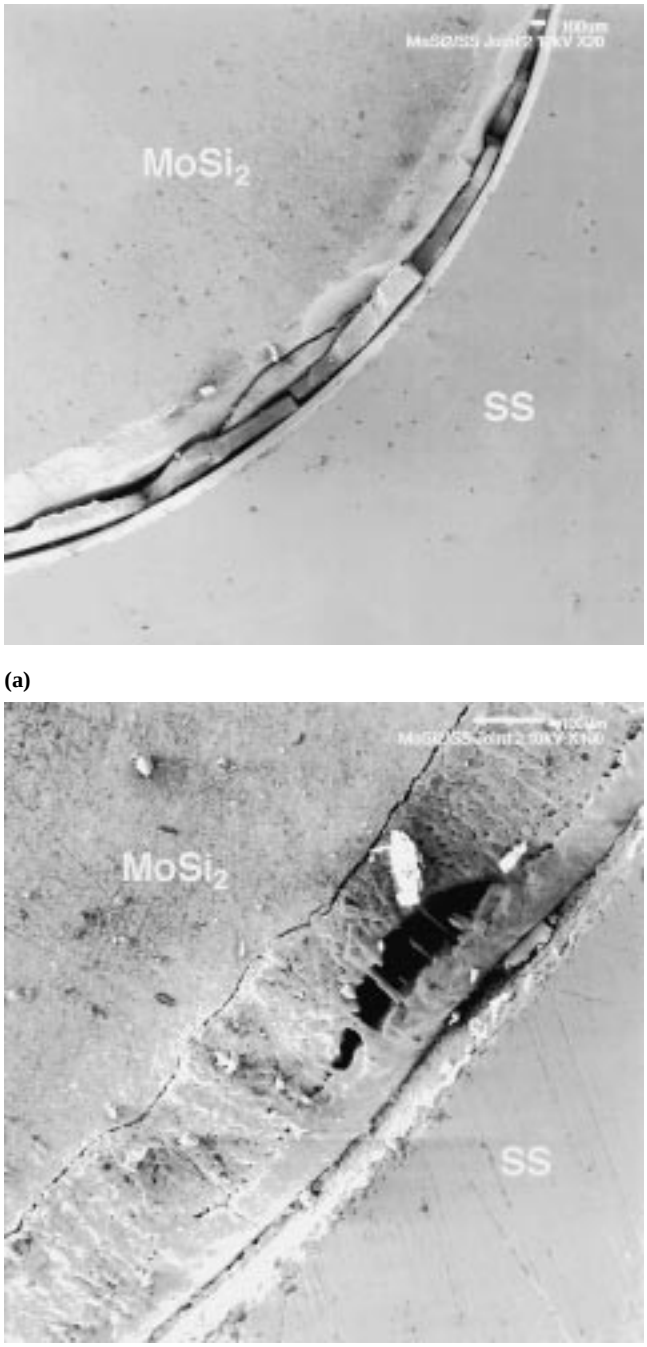



**Fig. 9** (**a**) and (**b**) Scanning electron micrographs of the samples tested in pushout

### References


1. J.J. Petrovic: *MRS Bull.*, 1993, vol. 18 (7), p. 35.
2. J.J. Petrovic and A.K. Vasudevan: *A. Mater. Sci. Eng.*, 1999, vol. A261, p. 1.
3. T.C. Chou and T.G. Nieh: *J. Mater. Res.*, 1993, vol. 8, p. 214.
4. D.A. Berztiss, R.R. Cerchiara, E.A. Gulbransen, F.S. Pettit, and G.H. Meier: *Mater. Sci. Eng.*, 1992, vol. A155, p. 165.
5. J.J. Petrovic: *Mater. Sci. Eng.*, 1995, vol. A192-A193, p. 31.
6. A. Bartlett, R. Castro, H. Kung, D.P. Butt, and J.J. Petrovic: *Ind. Heating, J. Thermal Technol.*, 1996, vol. 63, p. 33.
7. C.R. Hubbard, S. Spooner, S.A. David, B.H. Rabin, and R.L. Williamson: *Mater. Sci. Eng.*, 1996, vol. A211, p. 45.
8. R.U. Vaidya, D.P. Butt, S.D. Conzone, and A.H. Bartlett: *Ceram. Trans.*, 1996, vol. 77, p. 63.
9. R.U. Vaidya, P. Rangaswamy, M.A.M. Bourke, and D.P. Butt: *Acta Metall. Mater.*, 1998, vol. 46, p. 2047.
10. D.G. Ast and D. Kretinsky: *Mater. Sci. Eng.*, 1976, vol. 23, p. 241.
11. T. Matsumoto and R. Maddin: *Mater. Sci. Eng.*, 1975, vol. 19, p. 1.
12. Z.H. Lai, D.Q. Yi, and C.H. Li: *Scripta Metall. Mater.*, 1994, vol. 31 (7), p. 815.
13. *Metals Handbook*, Desk edition, H.E. Boyer and T.L. Gall, eds., ASM, Materials Park, OH, 1995, p. 15-3.