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INVESTIGATIONS INTO THE JOINING OF $MoSi_2$ TO 316L STAINLESS STEEL

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ABSTRACT

The partial transient liquid phase (PTLP) joining and low temperature brazing techniques were applied in joining $MoSi_2$ to stainless steel 316L alloy. Exploratory studies were carried out on various interlayer materials. The mechanical, physical, and chemical compatibilities between various interlayers, brazing material, and the substrate materials were investigated. The effect of the thermal expansion mismatch between various components of the joint on the overall joint integrity was also studied. This paper outlines some of the preliminary findings of the joining processes as applied to $MoSi_2$ and stainless steel 316L.

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 [1,6].

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 and non-ferrous alloys. 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 other refractory metals. The large thermal expansion mismatch coupled with the necessity of using high joining temperatures (in the case of refractory brazes) result 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.

In this work, $MoSi_2$ was joined to 316L stainless steel, a typical industrial material, utilizing a variety of interlayers and brazes. Desirable interlayer properties included a CTE intermediate to the $MoSi_2$ and the 316L, sufficient ductility, and adequate oxidation resistance. Interlayers investigated in this study included Ni, Ni-10Fe, Ta, and Nb. This variety of interlayer materials allowed for exploration of the effects of the above properties on final joint integrity. Brazing materials were chosen to allow for low to intermediate temperature joining. A silver-copper eutectic (Cusil™, Wesgo Inc., Belmont, CA 94002) was chosen as one typical industrial braze. Aluminum was also investigated as a braze owing to its low melting temperature. Additionally, aluminum can act as a transient phase because of its reactivity with $MoSi_2$ and the interlayer materials.

Transient liquid phases have been investigated as a method to join at low temperatures while allowing for eventual formation of a refractory joint [7]. The advantages of utilizing transient liquid phases is the fact that the brazing or joining operation can be carried out at relatively low temperatures. The low melting phase eventually reacts with one or more components of the joints and transforms into a more refractory material. This technique has the advantages of low joining temperatures and high refractoriness upon completion of the joining process.

Following is a summary of the results of our prelimanary experiments on the joining of $MoSi_2$ to 316L stainless steel.

2. MATERIALS USED

$MoSi_2$ powder was obtained commercially (Cerac, Inc., Milwaukee, WI 53201) and hot pressed into billets with densities greater than 95% of the theoretical density. Stainless steel 316L was in the form of discs with a diameter of 15.8 mm and a thickness of 2.4 mm (Metal Samples, Inc., Munford, AL 36268) for joint chemistry investigations, and also as 12 mm x 12 mm x 12 mm blocks for use as mechanical test specimens. Foils of 125 and 250 μm thicknesses of 99.9% pure Ni, Nb and Ta were obtained commercially (Aldrich Chemical, Inc., Milwaukee,

WI 53233; Alfa Aesar, Ward Hill, MA 01835-9953). Ni-10Fe interlayers were produced by rolling to a final thickness of 500 μm. Braze materials were 50 μm thick silver/copper eutectic foil (Cusil™), subsequently rolled down to 20 μm, and 8 μm 99.9% Al foil. A plot of the CTE's of all joining materials is given in Figure 1.

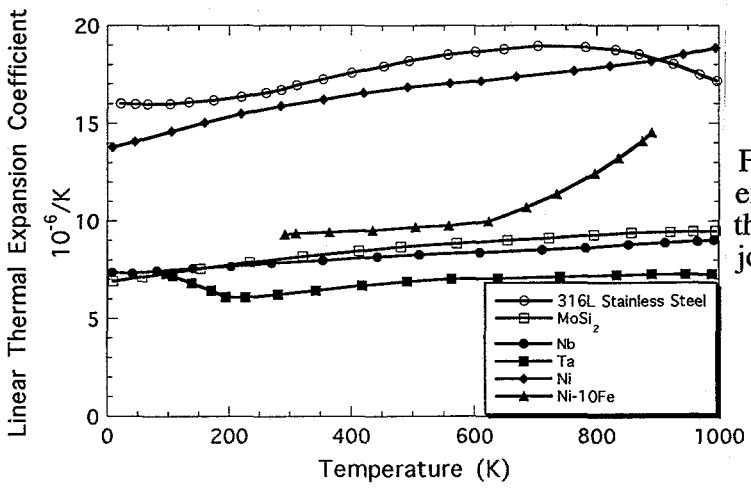

Figure 1. Thermal expansion coefficients of the interlayers used in the joining experiments.

3. EXPERIMENTAL PROCEDURES

A diamond wafering saw was used to cut rectangular specimens (5 mm x 5 mm x 3 mm and 12 mm x 12 mm x 12 mm) from the hot pressed billets of $MoSi_2$. The smaller samples were used for joint chemistry, while the larger samples were used for mechanical testing. The $MoSi_2$ specimens were polished to either a 600 grit finish or a 1 μm diamond finish using standard metallographic techniques. Similar sized samples and surface preparation techniques were applied to the stainless steel 316L. The as received Nb, Ni, Ta, Ni-10Fe, Cusil, and Al foils were cut to sizes slightly greater than the silicide and steel pieces. All materials were then ultrasonically cleaned in acetone followed by deionized water. After cleaning, the samples were dried at 150°C for 5 minutes.

Bonding was achieved using the block/interlayer/block assembly. Dimensions and a schematic of the loading assembly can be found elsewhere [8]. After arranging the foils and substrates in the block/interlayer/block orientation, 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. For those samples joined under a controlled atmosphere, the loaded Al_2O_3 press 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 bonding 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.

Joints in air were made by loading the Al_2O_3 press assemblies into a standard box furnace. For joints made using the Cusil braze, a ramp rate of 5°C/min. was used to heat the furnace to the joining temperature of 830°C (50°C above the 780°C Cusil eutectic). The temperature was then held at 830°C for times ranging from 10 min. to 1 h before cooling at 2°C/min. to room temperature. For joints made with the Al braze, similar ramps rates and times were used, with bonding temperatures ranging from 710 °C to 750 °C. After bonding, the specimens were characterized by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

Mechanical test specimens of approximate dimension 2 mm x 2 mm x 25 mm were electro discharge machined from the Cusil/Nb/Cusil and Cusil/Ni/Cusil joints. The tensile face of the beam was ground to a 600 grit finish, and the edges were beveled to prevent corner failures during mechanical testing. Four-point bend tests of the joined specimens were done at room temperature at a strain rate of $\approx 10^{-4}$ /s. Fracture surface and crack path investigations were done post-test.

4. RESULTS AND DISCUSSION

Following is a summary of the joints that were successfully made:
1. $MoSi_2$ /Cusil/Nb/Cusil/316L (controlled atmosphere)
2. $MoSi_2$ /Cusil/Ni/Cusil/316L (controlled atmosphere)
3. $MoSi_2$ /Cusil/Ni-10Fe/Cusil/316L (controlled atmosphere)
4. $MoSi_2$ /Al/Ta/Al/316L (controlled atmosphere)
5. $MoSi_2$ /Al/$MoSi_2$ (air and controlled atmosphere)

4.1 Joint Chemistry

4.1.1 Cusil/Nb/Cusil interlayer: Joints with Cusil/Nb/Cusil interlayers were dense and crack-free. Scanning electron micrographs of the diffusion zones produced at the 316L/Nb and $MoSi_2$/Nb interfaces are shown in Figure 2. At the 316L/Nb interface, gross segregation of the Cusil eutectic during bonding caused the formation of two Ag/Cu alloys rich in either Ag or Cu. These Ag (92-94 at%) rich and Cu (96-98 at%) rich alloys have approximate melting temperatures of 925°C and 1070°C, respectively.

Three major phases formed at the $MoSi_2$/Nb interface are also seen in Figure 2. As with the 316L/Nb interface, gross segregation of the Cusil eutectic composition during bonding caused the formation of a Cu/Ag alloy composed of 92-94 at% Ag, and a Cu/Si phase composed of 88-90 at% Cu. This Cu/Si phase is a peritectic composition with a melting point of 852°C. The Mo_5Si_3 phase formed near the interface as Si diffused out of the pure $MoSi_2$ to form the Cu/Si phase. Mo_5Si_3 is a refractory phase which has a melting temperature of 2180°C.

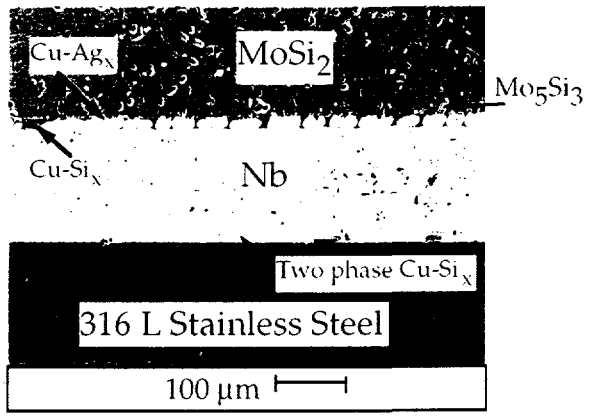

Figure 2. SEM micrograph of a $MoSi_2$/Cusil/Nb/ Cusil/316L joint.

4.1.2 Cusil/Ni/Cusil interlayer; Cusil/Ni-10Fe/Cusil interlayer: Pure Ni was examined owing to its ductility and enhanced oxidation resistance with respect to Nb. Its CTE is somewhat higher and would be expected to lead to increased stresses, as has been observed by other investigators [9]. Because of these potential CTE mismatch effects, Ni-10Fe was also investigated because its CTE, for the temperature range of interest, is below that of the silicide and would be expected to lead to diminished joint stresses. Successful joints were produced using both the PVD Ni (500 mm) and Ni-Fe (90-10, 500 mm thick) alloy as the interlayer. The chemistry of the interfaces were very similar in the two interlayer systems, and is summarized as follows. Copper and silver diffusion from the Cusil foil occurred into the bulk $MoSi_2$. These elements presumably entered into solid solution. An Ag-rich zone was observed adjacent to the $MoSi_2$. This region was devoid of significant amounts of Cu. A solid solution of Cu and Ni (approximately 70-30) was detected next to the Ag rich phase. Similar elemental separation was observed on the SS 316L side, namely the region in the vicinity of the Ni or Ni-Fe interlayer consisted of a Cu-Ni alloy (approximately 70-30) while the region in the vicinity of the SS 316L consisted of a Ag rich zone. These features were identical for both the interlayers, and can be seen in Figure 3.

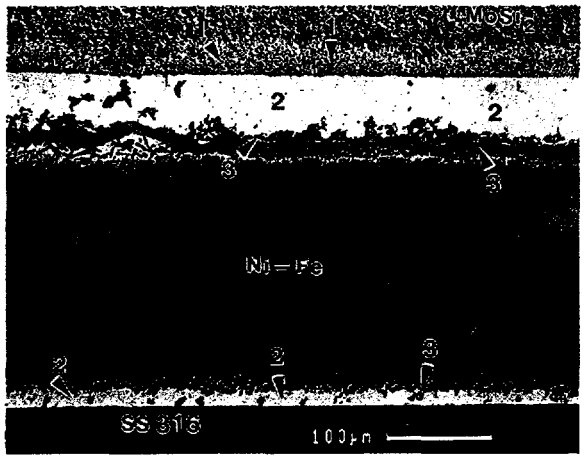

Figure 3. SEM micrograph of a $MoSi_2$/Cusil/Ni-Fe/ Cusil/316L joint. (1: Diffusion zone, 2: Ag rich phase 3: Cu-Ni solid solution)

4.1.3 Al/Ta/Al interlayer: Tantalum was investigated because its CTE falls below that of the silicide, and so would be expected to reduce residual thermal stresses in any joints produced. It is highly refractory, but exhibits poor oxidation resistance; however, because Ta-Ti alloys have been shown to have good oxidation and corrosion resistance [10], the chemistry of Ta interlayers was of interest. Aluminum is a low melting point braze that wets $MoSi_2$ [6] and reacts with Ta, allowing for a possible transient phase effect.

Figure 4 shows the interface after bonding at 1h. at 710°C. Energy dispersive spectroscopy identified several Ta-Al phases. Reference to the Ta-Al phase diagram suggests these to be Ta_2Al and TaAl, whose melting temperatures are 2100°C and 1770°C, respectively. The near complete reaction and disappearance of the Al after only 1 h. of bonding time suggests that this is a potential high temperature joining system, particularly if Ta-Ti alloys were used as interlayers.

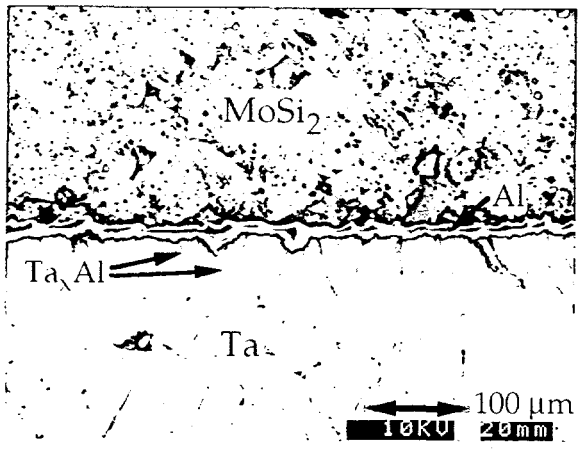

Figure 4. SEM micrograph of an Al/Ta/Al interlayer.

For this system, the Ta thickness used was 125 μm. Despite its low CTE, the extent of stress relief is still limited by thickness. In this case, cracking occurred in the $MoSi_2$, initiating at the free surface and eventually propagating parallel to the interface at a distance of about 500 μm, Figure 5. This type of residual stress cracking is common in dissimilar material joints [11], and could likely be alleviated by thicker interlayers. Despite this cracking, the interface away from the crack appeared to be strong, dense, and continuous, suggesting that further investigations into Ta and Ta alloys as interlayers are warranted, in particular using thicker interlayers.

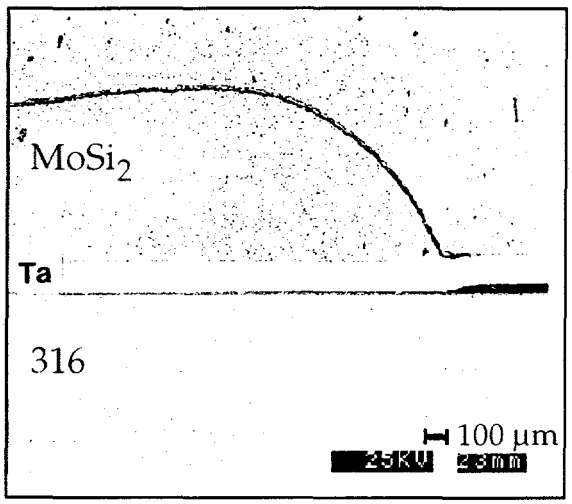

Figure 5. SEM micrograph of a $MoSi_2$/316L joint using an Al/Ta/Al interlayer. Note the crack path.

4.1.4 $MoSi_2$/Al/$MoSi_2$ Joints: Applications exist in which it is necessary to join $MoSi_2$ to itself. Normally, high temperature (> 1500 °C) methods are used to promote sintering between the pieces to be joined. A thermodynamic analysis, discussed later in this paper, suggested low temperature routes for joining using Al as a transient braze. Joining was accomplished both in the controlled environment, and also in air. The braze consisted primarily of Si saturated Al. After 60 minutes at 730 °C, approximately half of the Al was replaced by a Mo-Si-Al ternary phase. The remaining interface consisted of Si saturated Al, and a SiO_2 based phase.

$MoSi_2$/Al/$MoSi_2$ joints were also bonded in a controlled atmosphere at 730°C. After 15 minutes the Al foil remained intact with no noticeable diffusion observed. However, at 60 minutes of exposure, Si enriched Al regions were detected in the sample. The extent of Al diffusion was fairly large. Additionally, a ternary phase of Mo-Al-Si was also detected at the interface. The phases observed were identical to those observed in joints produced in air excepting for the absence of the SiO_2-based phase. A micrograph of the joint produced in the controlled atmosphere can be seen in Figure 6. Further work will investigate the thermodynamics of bonding and phase development, as well as performing mechanical testing of the joints.

One problem that will be studied is the impact of Al on the pesting behavior of $MoSi_2$. Previous studies have indicated that under certain conditions the presence of Al can accelerate the pesting reaction [12].

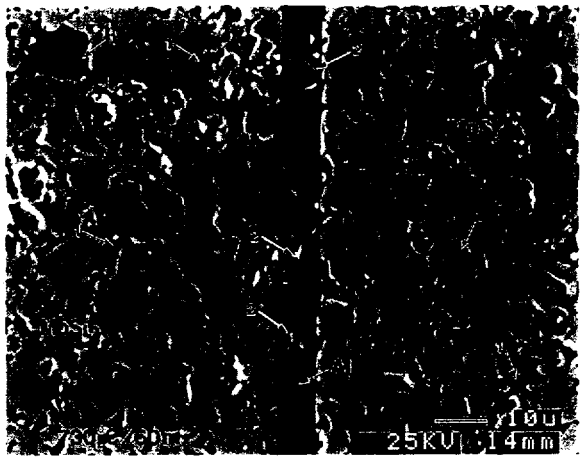

Figure 6. SEM micrograph of a $MoSi_2$/Al/$MoSi_2$ joint produced in a controlled atmosphere at 730°C for 60 minutes. (1: Si saturated Al, 2: Mo-Si-Al ternary)

4.1.5 Al/$MoSi_2$ and Cu/$MoSi_2$ Chemistry: Wetting experiments of both Al and Cu on $MoSi_2$ have been carried out in previous studies [6]. Wetting and subsequent joining of both of these metals to the silicide can be understood by examining the reduction of $MoSi_2$ to Mo_5Si_3 and the solution of Si into molten copper. The reactions at 1127 °C can be written and summed as follows [13].

$MoSi_2 \longrightarrow Mo + 2\ Si$ $\qquad \Delta G° = 116{,}732$ J/mole

$Mo + 3/5\ Si \longrightarrow 1/5\ Mo_5Si_3$ $\qquad \Delta G° = -67{,}592$ J/mole

$7/5\ Si \longrightarrow [7/5\ Si]_{Cu}$ $\qquad \Delta\bar{G}_{Si} = RT \ln (\mathbf{a}_{Si})$

$MoSi_2 \longrightarrow 1/5\ Mo_5Si_3 + [7/5\ Si]_{Cu}$ $\qquad \Delta G° = 49139 + RT \ln (\mathbf{a}_{Si})$

where $\Delta G°$ is the standard state free energy change at 1400K, $[Si]_{Cu}$ indicates Si in solution in molten Cu, and $\Delta\bar{G}_{Si}$ is the partial molar free energy of mixing for Si in Cu, and is a function of the activity of Si, $\mathbf{a}_{Si}$, in the melt. The solubility of Mo in molten Cu is minimal at the temperature of interest and therefore was not considered. Assuming Raoultian behavior of Si in Cu, this simplified analysis rationalizes the ready reaction of $MoSi_2$ with Cu. These calculations illustrates the reactivity of $MoSi_2$ with braze materials, and also the ease with which $MoSi_2$ is wet by a variety of metals. This is due to the significant solubility of Si in many braze materials of interest. Similar calculations hold for Al as well.

4.2 Mechanical Testing

Four-point bend tests for both the Cusil/Nb/Cusil and Cusil/Ni/Cusil joints showed linear strains to failure. Average failure strength of the Cusil/Nb/Cusil joints was 85 MPa. Failure appeared to initiate in the silicide and propagated along a path parallel to and approximately 10 μm from the interface, Figure 7. For the Cusil/Ni/Cusil samples, four-point bend strengths also had an average value of 85 MPa. Fracture again occurred in the $MoSi_2$, and remnants of the $MoSi_2$ were observed to remain adhering to the fracture surface. Cracking parallel to the interface is often seen in joints of dissimilar materials [14]. Plasticity of the interlayer [15] and relative toughness of the interface and the silicide [16] all favor cracking in the $MoSi_2$, though details such as the distance from the interface at which the crack propagates, and the above contributions to fracture energies, cannot be predicted.

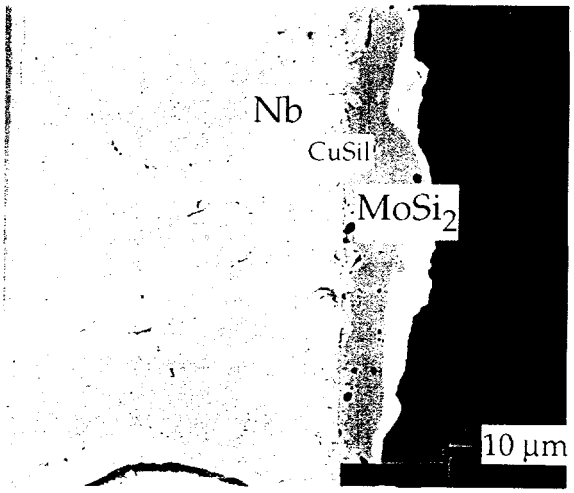

Figure 7. Crack path in a $MoSi_2$/Nb/316L joint after four-point bending.

In both classes of samples, fracture was apparently limited by the strength of the $MoSi_2$. However, typical strength values for hot pressed $MoSi_2$ of this quality are in the range of 400 MPa, significantly higher than the measured bond strengths. It is likely that residual stresses significantly reduced the strength of the bond below the intrinsic strength of the $MoSi_2$. For instance, using the formulation of Kimura, *et al.*[17] for joined cylinders, residual tensile stresses of approximately 900 MPa could be expected at the $MoSi_2$ free surface. To estimate residual stresses, indentation cracks were placed in the $MoSi_2$ at a variety of distances from the interface. Figure 8 plots indentation crack length in the $MoSi_2$ for cracks, both parallel and perpendicular to the interface, as a function of distance from the interface. The increase in crack lengths parallel to the interface indicates residual axial tension in the test beams, which would reduce their apparent strength.

An estimate of the residual stress can be obtained by modeling the indentation as a centrally loaded crack using the formulation [18]

$$K = (\sigma_{\text{applied}} + \sigma_{residual})\sqrt{\pi a}\,\frac{2}{\pi}\sin^{-1}(b/a)$$

where, K = stress intensity factor
σ_{applied} = indenter-applied stress
$\sigma_{residual}$ = residual stress contribution
a = crack length
b = length of crack on which opening stresses are applied.

By assuming that cracks perpendicular to the interface are stress free, the value of residual stress contributing to the increased crack length parallel to the interface can be estimated. Using b/a = 0.2 and K_{MoSi_2} = 3.5 MPam$^{1/2}$ gives a value of $\sigma_{residual}$ = 450 MPa. This stress value is in agreement with the reduced value one would expect in the stressed joint *vis a vis* the stress free $MoSi_2$.

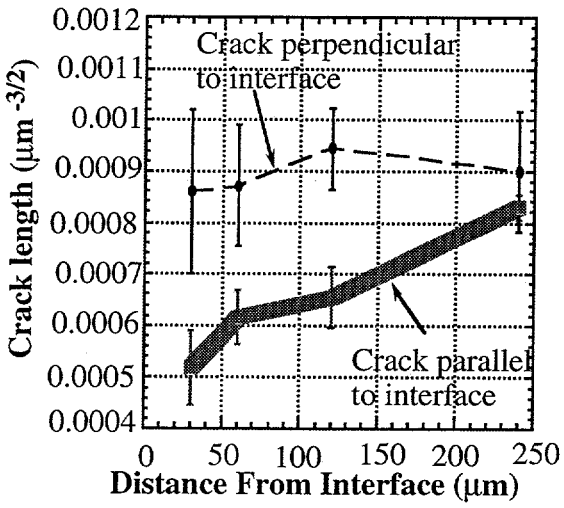

Figure 8. Indentation crack lengths in $MoSi_2$ parallel and perpendicular to the interface.

5. Concluding Remarks

This study focused on the chemistry and viability of joints using a variety of interlayer materials. Cusil is a common braze material that was successful in these experiments because of its ability to readily wet $MoSi_2$. Aluminum also worked well as a braze because of its good wetting behavior but had an additional advantage of acting as a transient bonding phase, thereby allowing for potentially higher service temperatures of the joints. Actual joint design, however, depends on many other factors including the geometry of the joint. It is well known that larger joints lead to larger values of residual stress, for the same interlayer thickness. Other work [8] has shown that under certain geometries, Ni interlayers lead to catastrophic cracking in the silicide, through a combination of geometry and CTE mismatch effects. The optimum combination of interlayer thickness, CTE, and yield strength has not yet been determined, but will sensitively depend on final application temperatures and joint geometries.

Other ongoing work includes joining $MoSi_2$ to other commercially important materials, in particular Inconel 600 and 60-40 brass. However, when using interlayers, this investigation has already proven several viable braze/interlayer combinations that will work with $MoSi_2$. In the case of difficult to braze materials, such as Ni superalloys, it will only be necessary to identify brazes compatible for joining to them. Because joints with brass will necessarily experience lower service temperatures, work is progressing to investigate direct bonding of $MoSi_2$ to the brass, using only an intermediate braze. Some success has been had using In-based alloys, and other low temperature brazes including Pb- and Sn-based materials are being tested.

Acknowledgments

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