

# Partially stabilized ZrO<sub>2</sub> particle–MoSi<sub>2</sub> matrix composites

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A 30 vol % partially stabilized ZrO<sub>2</sub> particle–MoSi<sub>2</sub> matrix composite was synthesized by hot pressing to 96% theoretical density at 1700° C. No chemical reactions between the PSZ and MoSi<sub>2</sub> were observed after hot pressing, indicating thermodynamic stability of these species. The composite formed an adherent and coherent glassy-appearing oxidation layer after oxidation at 1500° C. The room temperature indentation fracture toughness of the composite was 2.5 times that of pure MoSi<sub>2</sub>. These results demonstrate the feasibility of PSZ particle–MoSi<sub>2</sub> matrix composites.

## 1. Introduction

Molybdenum disilicide (MoSi<sub>2</sub>) is a potential matrix material for high temperature structural composites, for use at temperatures in the range of 1400 to 1600° C under oxidizing conditions. This material has a melting point of 2030° C, exhibits excellent high temperature oxidation resistance, and possesses a brittle-to-ductile transition in the range of 900 to 1000° C.

MoSi<sub>2</sub> cannot, however, be employed by itself as a structural material due to its low room temperature fracture toughness, and low yield strength levels at elevated temperatures. It must be reinforced in order to significantly improve both its room temperature and elevated temperature mechanical properties. Previous work has dealt with the SiC reinforcement of MoSi<sub>2</sub> materials [1–5].

A very attractive alternative reinforcing species for MoSi<sub>2</sub> is partially stabilized ZrO<sub>2</sub> (PSZ), due to its potential for both low temperature transformation toughening and elevated temperature dispersion strengthening, and the fact that its thermal expansion coefficient is a reasonably good match to the thermal expansion coefficient of MoSi<sub>2</sub>. PSZ has proven very successful as a high toughness monolithic material [6–10]. Additionally, PSZ particles have been employed to significantly toughen Al<sub>2</sub>O<sub>3</sub> matrix composites [10–12].

The purpose of the present investigation was to establish the feasibility of the PSZ particle–MoSi<sub>2</sub> matrix composite system. Such feasibility hinges upon three major factors. First, PSZ and MoSi<sub>2</sub> must be thermodynamically stable chemical species. Second, presence of the PSZ particles should not degrade the elevated temperature oxidation resistance of the composite significantly. Third, an improvement in room temperature fracture toughness should occur as a result of the presence of the PSZ particles in the MoSi<sub>2</sub> matrix. These three issues have been initially examined in the present investigation.

## 2. Experimental procedure

Partially stabilized ZrO<sub>2</sub> powder containing 2.3 wt % (4.92 mol %) CaO was employed in this investigation. A SEM micrograph of the starting PSZ powder is shown in Fig. 1. A relatively large distribution of PSZ particle sizes was present in the powder, with particles ranging from approximately 5 μm down to submicrometer size. X-ray analysis of the PSZ powder showed a major monoclinic phase and minor cubic phase, with no prominent evidence of retained metastable tetragonal phase.

Appropriate amounts of PSZ powder and MoSi<sub>2</sub> powder (–400 mesh) were mechanically blended to yield a composite containing 30 vol % PSZ reinforcement. The powder blend was then dispersed in an aqueous media at a pH of 9.5. The solids loading was approximately 50 wt %, and the aqueous dispersion was mechanically stirred and ultrasonicated to keep constituents from settling prior to slip casting. The dispersion was then slip cast into a plaster-of-paris mould. Upon drying, the green slip cast body was comminuted to –10 mesh shards, for use in hot pressing.

Composites were hot pressed in graphite dies with grafoil liners, in an argon atmosphere. Hot pressing conditions for the 30 vol % PSZ particle–MoSi<sub>2</sub> matrix composites were 1700° C and 30 MPa.

## 3. Results

### 3.1. Composite microstructure

The hot pressed 30 vol % PSZ particle–MoSi<sub>2</sub> matrix composite microstructure is shown in Figs 2 and 3. Hot pressing at 1700° C produced densities in the range of 96% theoretical. As may be seen in Figs 2 and 3, the average phase size of the PSZ phase was of the order of 20 μm while the average grain size of the MoSi<sub>2</sub> was approximately 15 μm.

Importantly, X-ray diffraction analysis of the hot pressed composite material showed that there was no

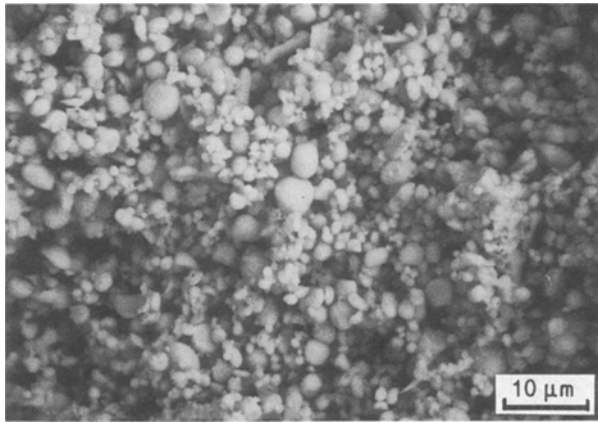


Figure 1 SEM micrograph of starting 2.3wt% CaO partially stabilized  $ZrO_2$  powder.

reaction between the PSZ and  $MoSi_2$  as a result of hot pressing at  $1700^\circ C$ . This indicates that  $ZrO_2$  and  $MoSi_2$  are thermodynamically stable species, at least up to the hot pressing temperature. It also shows that the presence of the zirconia stabilizing CaO did not induce any reactions. The X-ray diffraction pattern of the PSZ after hot pressing was similar to the powder PSZ pattern.

### 3.2. Oxidation behaviour

In order to provide a preliminary assessment of the oxidation behaviour of the 30 vol % PSZ particle- $MoSi_2$  matrix composite, a composite specimen was subjected to an oxidation exposure of 2 h at  $1500^\circ C$  in air, furnace heating and cooling to and from the  $1500^\circ C$  hold temperature. The resultant oxide layer formed is shown in Fig. 4. This layer was macroscopically glassy-appearing and both coherent and adherent to the composite surface. Its thickness was approximately  $50 \mu m$  for the 2 h at  $1500^\circ C$  exposure. The glassy oxide layer contained a whitish-appearing particulate phase, presumably rich in  $ZrO_2$ .

For comparison purposes, a pure  $MoSi_2$  specimen was oxidized along with the composite. The pure  $MoSi_2$  material exhibited a thinner oxide layer, estimated to be on the order of  $5 \mu m$  in thickness.

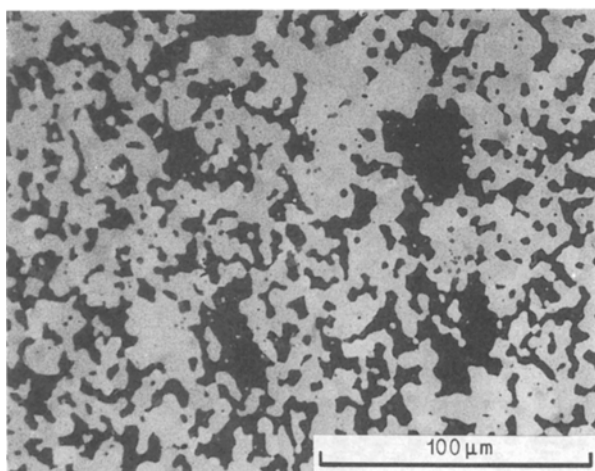


Figure 2 Bright field micrograph of 30 vol % PSZ- $MoSi_2$  matrix composite. PSZ is the dark phase.

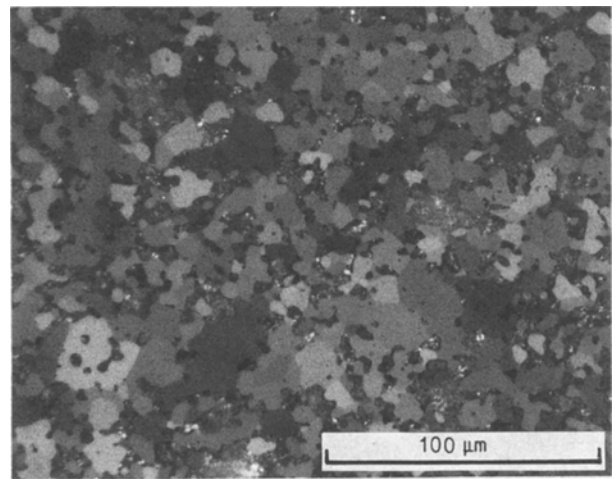


Figure 3 Polarized light micrograph of 30 vol % PSZ- $MoSi_2$  matrix composite. PSZ is the non-optically active phase.

### 3.3. Indentation fracture toughness

Microhardness indentation fracture toughness measurements were made on polished sections of the 30 vol % PSZ particle- $MoSi_2$  matrix composite, and also on pure  $MoSi_2$  for comparison purposes. A 10 kg Vickers indentation was employed. Typical indentations are shown in Fig. 5. It is evident that, at constant indentation load, the radial crack pattern is significantly larger for pure  $MoSi_2$  than for the composite.

Indentation fracture toughness values were calculated using the formulations of Anstis *et al.* [13]. Fracture toughness and hardness values obtained are given in Table I. One may see that the 30 vol % PSZ particle- $MoSi_2$  matrix composite exhibited an indentation fracture toughness value 2.5 times greater than that of pure  $MoSi_2$ . Table I also shows that the composite was lower in hardness than pure  $MoSi_2$ .

A higher magnification view of one of the indentation radial cracks in the composite is shown in Fig. 6. Crack segments run both along the PSZ- $MoSi_2$  phase boundaries and through the PSZ phase itself. Crack bridging of the PSZ phase is also evident in Fig. 6.

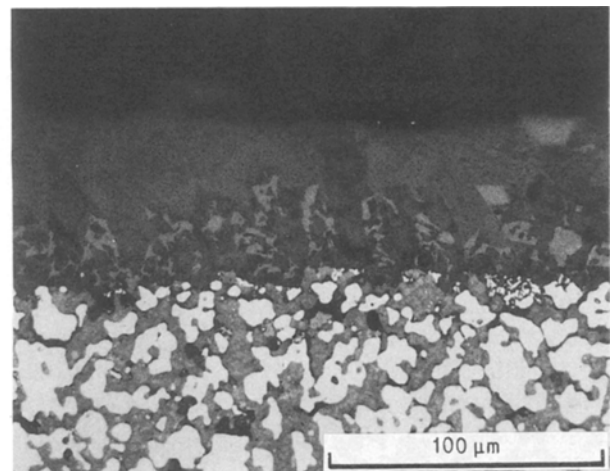


Figure 4 Oxidation layer on 30 vol % PSZ particle- $MoSi_2$  matrix composite after an oxidation treatment of 2 h at  $1500^\circ C$  in air.

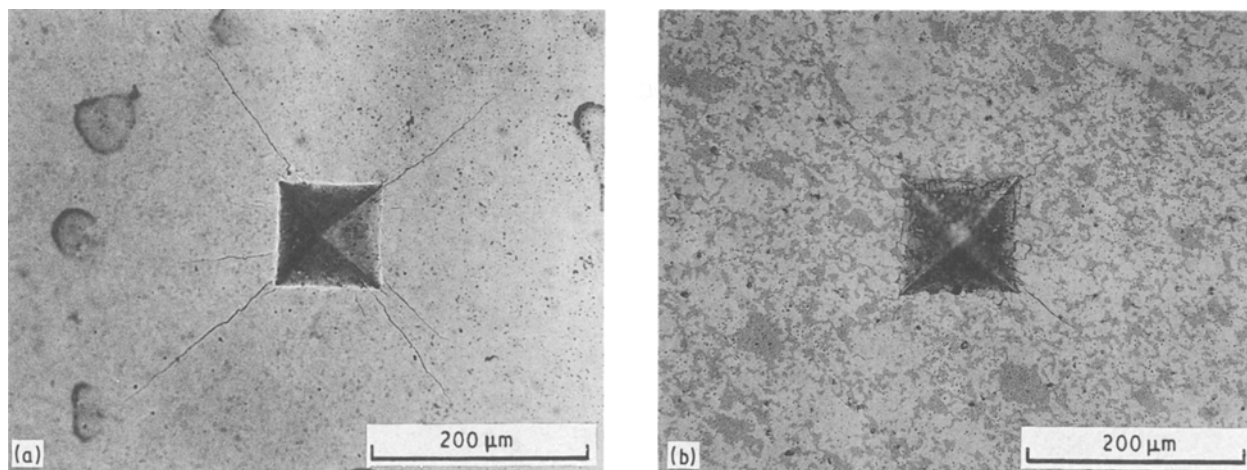


Figure 5 10 kg Vickers microhardness indentations in (a) pure MoSi<sub>2</sub> and (b) 30 vol % PSZ particle-MoSi<sub>2</sub> matrix composite.

#### 4. Discussion

Results of this investigation have determined that ZrO<sub>2</sub> partially stabilized with CaO additions is thermodynamically stable with MoSi<sub>2</sub> to a temperature of 1700°C, thus, a major element of the feasibility of the PSZ particle-MoSi<sub>2</sub> matrix composite concept has been established. The absence of chemical reactions means that the tetragonal-to-monoclinic martensitic transformation which produces the transformation toughening effect will not be negatively influenced by any potential changes in composition due to chemical reactions. This indicates that it should be possible to optimize the transformation toughening mechanism to significantly toughen the composite material at low temperatures.

The oxidation behaviour of the 30 vol % PSZ particle-MoSi<sub>2</sub> matrix composite was encouraging, in that a coherent and adherent glassy-appearing oxide layer was formed after air exposure at 1500°C. Phase species present in the composite oxide layer are expected to be ZrO<sub>2</sub>, ZrSiO<sub>4</sub>, and SiO<sub>2</sub>, since pure MoSi<sub>2</sub> forms a glassy SiO<sub>2</sub> oxide layer at this temperature. The ZrO<sub>2</sub>-SiO<sub>2</sub> phase diagram indicates that the solid phases ZrO<sub>2</sub>-ZrSiO<sub>4</sub> and ZrSiO<sub>4</sub>-SiO<sub>2</sub> are thermodynamically stable until a temperature of approximately 1700°C, where a ZrO<sub>2</sub>-liquid two-phase field forms.

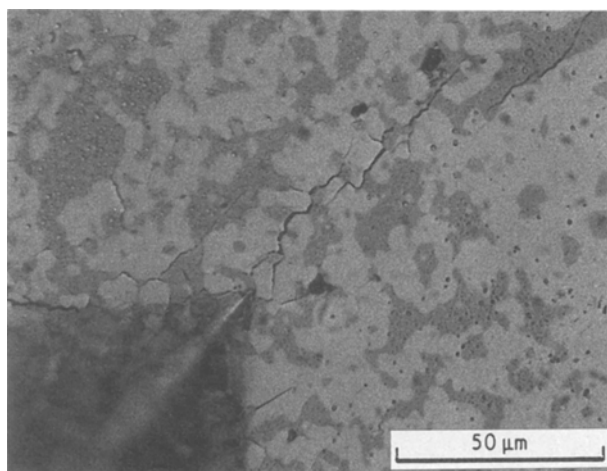


Figure 6 Indentation radial crack in the 30 vol % PSZ particle-MoSi<sub>2</sub> matrix composite.

Based upon the thickness of oxide layers formed, the oxidation rate of the PSZ particle-MoSi<sub>2</sub> matrix composite is estimated to be about ten times greater than that of pure MoSi<sub>2</sub> at 1500°C. The composite, however, contained 30 vol % of the ZrO<sub>2</sub> phase, a large amount. Decreasing the volume fraction of PSZ particulate phase and/or decreasing the size of the PSZ particles may be expected to lower the oxidation rate of future composites. The oxidation rate of the present composite in relation to pure MoSi<sub>2</sub> is approximately equivalent to that of hot pressed Si<sub>3</sub>N<sub>4</sub> [14].

The 30 vol % PSZ particle-MoSi<sub>2</sub> matrix composite was 2.5 times tougher than pure MoSi<sub>2</sub> at room temperature. This is a very significant toughening effect. The measured indentation fracture toughness of the composite, 6.56 MPa m<sup>1/2</sup>, is in the range of advanced monolithic Si<sub>3</sub>N<sub>4</sub> materials. This result establishes that a PSZ particulate phase will significantly improve the fracture toughness of MoSi<sub>2</sub>.

The exact mechanisms responsible for this improved fracture toughness were not established in the present study, and await further, more detailed investigations. Heating the 4.92 mol % CaO stabilized-ZrO<sub>2</sub> to the hot pressing temperature of 1700°C would result in predominantly tetragonal phase at this temperature, with a minor amount of cubic phase [10]. Since no tetragonal phase was observed by X-ray diffraction after the composite was cooled from the hot pressing temperature, this would indicate that the tetragonal-to-monoclinic phase transformation occurred during cooling, due to the relatively large size of the PSZ dispersed phase in the composite (Fig. 2). The presence of the internal microstructural stresses produced by the tetragonal-to-monoclinic phase transformation may be the major factor contributing to the improved fracture toughness of the present composites.

The current investigation has established the feasibility of PSZ particle-MoSi<sub>2</sub> matrix composites, in

TABLE I Indentation fracture toughness results

Material	Hardness (GPa)	Fracture toughness (MPa m <sup>1/2</sup> )
Pure MoSi <sub>2</sub>	10.00	2.58
30 vol % PSZ-MoSi <sub>2</sub>	8.49	6.56

terms of thermodynamic stability, oxidation behaviour, and fracture toughness. This composite system is particularly interesting for the following reasons. First, the thermal expansion coefficients of MoSi<sub>2</sub> and ZrO<sub>2</sub> are similar (MoSi<sub>2</sub> = 7.2° C<sup>-1</sup>, stabilized ZrO<sub>2</sub> = 7.5° C<sup>-1</sup>, at room temperature). This means that any thermal expansion mismatch stresses in the composite system will be minimal. Secondly, the possibility exists that a PSZ particulate morphology may be employed to achieve *both* room temperature toughening and elevated temperature dispersion strengthening, using the same reinforcement phase.

## 5. Conclusions

Partially stabilized ZrO<sub>2</sub> is a very attractive reinforcement material for MoSi<sub>2</sub>, due to its potential for both low temperature transformation toughening and high temperature dispersion strengthening. The feasibility of partially stabilized ZrO<sub>2</sub> particle–MoSi<sub>2</sub> matrix composites has been demonstrated. A 30 vol % PSZ particle (2.3 wt % CaO)–MoSi<sub>2</sub> matrix composite was hot pressed at 1700° C, achieving 96% theoretical density. No chemical reactions between the PSZ and MoSi<sub>2</sub> phases were observed after hot pressing, indicating thermodynamic stability of these phases. Oxidation of the composite for 2 h at 1500° C in air lead to the formation of an adherent and coherent glassy-appearing oxide layer. The room temperature indentation fracture toughness of the 30 vol % PSZ particle–MoSi<sub>2</sub> matrix composite was 6.56 MPa m<sup>1/2</sup>, a value 2.5 times that of pure MoSi<sub>2</sub>.

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