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High-temperature fracture toughness of SiC–$Mo_5(Si,Al)_3C$ composites

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Abstract

The fracture toughness (K_{1C}) of melt-infiltrated SiC–$Mo_5(Si,Al)_3C$ composites was measured from room temperature to 1400°C using the indentation strength method at 1 atm argon atmosphere. The fracture toughness was found to increase from 3.6 MPa·$m^{1/2}$ at room temperature to 7.7 MPa·$m^{1/2}$ at 1400°C. This increase was mainly attributed to the plastic deformation of the infiltrated $Mo_5(Si,Al)_3C$ phases at high temperatures, which act as ductile toughening inclusions. The influence of annealing temperatures and atmospheres on K_{1C} was studied. The effect of indentation load on K_{1C} was also analyzed.

Keywords: Composites; Melt infiltration; SiC-$Mo_5(Si, Al)_3C$; Toughness

1. Introduction

In the past 20 years, ceramic materials have won increasing importance for structural applications despite their inherent brittleness.[1–3] Efforts have been made in both the range of applications suitable for ceramics and the development of advanced ceramic materials with an improved damage tolerance. In the search for new materials for high temperature applications, molybdenum carbosilicide (Mo_5Si_3C) was targeted not only because it has a high melting point of above 2000°C, but also because it has a relatively complex crystal structure that may lead to better creep resistance than that of $MoSi_2$.[4,5] Moreover, it is the only stable ternary phase in the Mo–Si–C system,[6,7] thus it is chemically compatible with SiC, C and $MoSi_2$ at high temperatures. Mo_5Si_3C was found in hot-pressed (HP) $MoSi_2$ compacts when carbon was used as the deoxidant to remove SiO_2 at the grain boundaries, and the presence of Mo_5Si_3C phases was suggested to improve the mechanical properties of the $MoSi_2$ compact.[8] Monolithic Mo_5Si_3C and $Mo_5Si_3C/MoSi_2$ composites were synthesized by Suzuki et al.[5] through an HP process, and the mechanical properties (strength, toughness, modulus and hardness) were tested at room temperature. Although Mo_5Si_3C has the potential to be a new matrix material or second phase reinforcement,[5] our investigations showed poor oxidation resistance of the monolithic Mo_5Si_3C compacts at elevated temperatures.[9] The addition of Al or B to Mo_5Si_3C or composite with SiC could greatly improve the oxidation resistance of the material. The SiC–$Mo_5(Si,Al)_3C$ composites were thus fabricated and characterized in our lab, and the high temperature fracture toughness is reported here.

The SiC–$Mo_5(Si,Al)_3C$ composite was fabricated by a melt infiltration process. Fracture toughness of the composite was measured at both ambient and elevated temperatures using an indentation strength (IS) method,[10] where pre-cracks were formed by a micro-indenter, followed by strength determination. The influence of temperature, annealing temperature, annealing atmosphere and indentation load on the toughness was investigated.

2. Experimental procedures

The SiC–$Mo_5(Si,Al)_3C$ composite was made by a melt infiltration process. An infiltrant of an $Mo_{10}Si_5AlC_2$ composition was prepared from the raw powders of $MoSi_2$ (circa 2.93 μm Japan New Metals), SiC (α, circa

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3.2 μm, purity 99%, Showa Denko, Japan), Mo (circa 1.3 μm, purity 99.94%, Japan New Metals) and Al (circa 1.3 μm, purity 99.94%, Japan New Metals). The powders were mixed by wet ball milling in alcohol for 3 h, followed by drying in an oven at 100°C. The powder mixture served as the infiltrant, which reacts to form the single phase $Mo_5(Si,Al)_3C$ during heating to the infiltration temperature. Porous SiC preforms with 40×16×6 (mm) dimensions were prepared from the same SiC powder as above by molding in a die followed by cold isostatic pressing (CIP) at 300 MPa. The relative density of the preforms was ~70%, with a remaining porosity of ~30%. The infiltration was performed at 1950°C in an induction furnace in 1 atm argon to reduce the possible evaporation of the infiltrant. Typically, the temperature was ramped to 1950°C in 5 min from 1000°C, held for 20 min, followed by a 5-min cool down to 1000°C, where the power was cut off. The microstructure of the infiltrated samples was characterized using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS). The crystalline phases of the composites were determined using an X-ray diffractometer (XRD).

The fracture toughness was characterized by an indentation strength (IS) method. Beams for toughness testing were cut from the infiltrated samples by a diamond saw, and ground to the nominal dimensions of 3×2×12× (mm). The tensile surface was polished with 1 μm diamond paste to remove residual stress due to machining and to produce a finish for optical microscopic observations. The edges of the prospective tensile face were also slightly chamfered. The indentation was made by a Vickers indenter with a dwell time of 30 s under loads from 98 to 294 N. Special care was taken to orient one set of the radial cracks to be parallel to the cross-section of the specimen where the prospective rupture would occur. IS beams were fractured using a three point bending test with an outer span of 8 mm and a crosshead speed of 70 μm/min under 1 atm argon atmosphere. The temperature during the high-temperature bending tests could be controlled within ±10°C. The testing system was equilibrated for 10 min at the selected temperatures prior to testing. Every specimen was checked to confirm that the fracture was initiated from the indent. The fracture specimens that did not fail from the indention were not included in the data pool. At least five effective specimens were tested for each condition. The fracture toughness was then calculated according to the following equation.[10]

$$K_{IC} = \eta \cdot \left(\frac{E}{H}\right)^{1/8} \left(\sigma \cdot P^{1/3}\right)^{3/4} \quad (1)$$

where η is an empirically derived constant equal to 0.59, E/H is the modulus-to-hardness ratio, σ is the fracture strength and P is the indentation load. As the determination of H at high temperatures was not attainable in the present study, the term of $\eta \cdot (E/H)^{1/8}$ in Eq. (1) was assumed to be 0.88, which will not cause a large error in the K_{1C} evaluation due to the insensitivity of the K_{1C} on the E/H values.[10]

3. Results and discussion

3.1. Infiltration process

The infiltrant was found to melt at ~1850°C, and spontaneous infiltration was observed above 1950°C. The contact angle between the molten infiltrant and the SiC plate was roughly measured to be ~30° at 1950°C at 1 atm argon. Several minutes were sufficient for a complete infiltration of the preform, but the relative density could only reach ~90% in this case. Non-infiltrated areas up to 50 μm were frequently observed in the microstructure. The infiltration speed in the surface region was much higher than that of the interior region. Namely, the surface could be fully infiltrated in less than 1 min, whereas the interior region remained non-infiltrated. The non-infiltration was identified to be mainly caused by small amounts of inherent impurities of SiO_2 and free carbon in the SiC raw powder. For example, a large uninfiltrated area (up to several millimeters) was often observed in the interior region if a few per cent of free carbon was intentionally put into the preform. The non-infiltration associated with free carbon would be attributed to the gas evolution of SiO and CO inside the body due to the reactions between the SiO_2 and free carbon. A big resistance to the infiltration would arise when these gases were encased in the preform. Infiltration at slow speed was found to be one of the most effective ways to eliminate the large non-nfiltration areas in the products because uniform infiltration was attainable during slow speed infiltration. These gases could come out through the porosity in the non-nfiltrated parts of the preform, therefore, the accumulation of gases inside the preform would not occur. The relative density of the products could reach 95% in this case. As shown in Fig. 1, the composite is very dense, and pores larger than 10 μm are very rare in the microstructure. The composite is only composed of two phases as indicated by the typical XRD pattern in Fig. 2, consistent with the SEM/EDS analyses. Aluminum was only found in the Mo_5Si_3C phase. The composition of the bright phases in Fig. 1 was determined by EDS to be $Mo_{0.628}Si_{0.330}Al_{0.042}$, though the carbon amount could not be accurately determined.

3.2. Fracture toughness

The fracture toughness values are plotted as a function of temperature in Fig. 3. The room-temperature

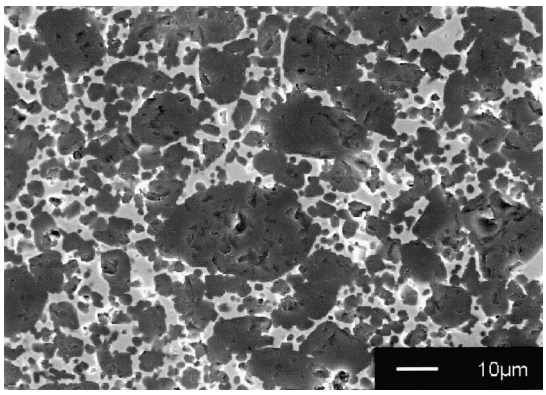

Fig. 1. Microstructure of SiC–$Mo_5(Si,Al)_3C$ composite infiltrated at 1950°C for 20 min under 1 atm argon atmosphere. Dark phases are SiC and bright phases are $Mo_5(Si,Al)_3C$.

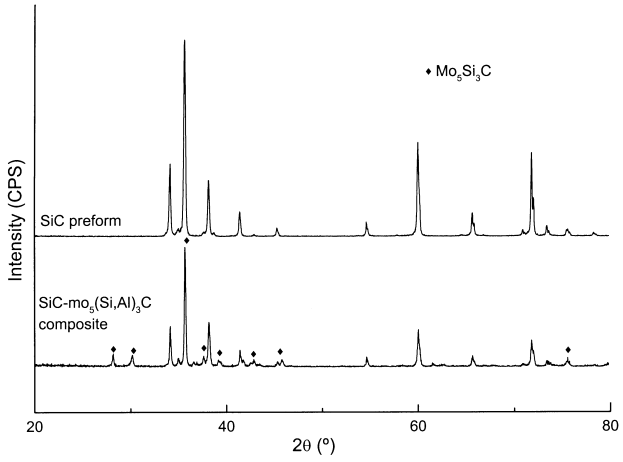

Fig. 2. Typical XRD pattern of the infiltrated SiC–$Mo_5(Si,Al)_3C$ composite. The XRD pattern of the as-CIPed SiC preform is also plotted for comparison.

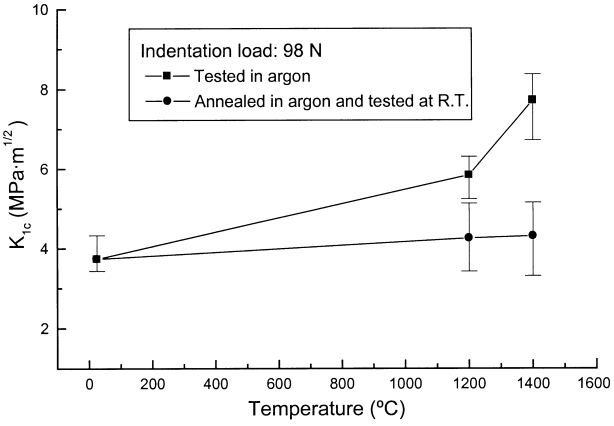

Fig. 3. Fracture toughness of the SiC–$Mo_5(Si,Al)_3C$ composite as a function of testing temperature. The toughness values of specimens annealed in argon were also included for comparison.

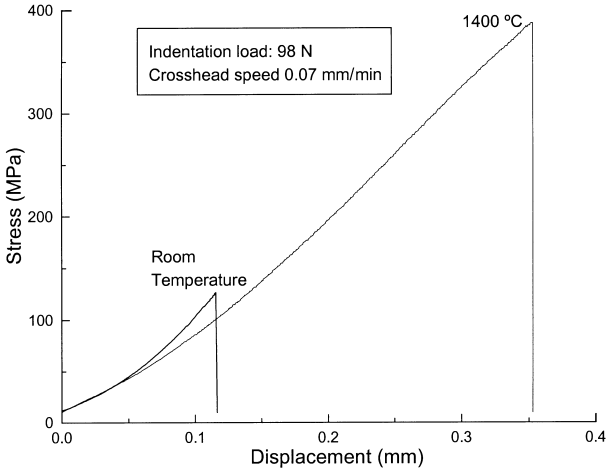

Fig. 4. Stress-displacement curves of SiC–$Mo_5(Si,Al)_3C$ composites at room temperature and 1400°C.

fracture toughness of the composites is 3.6 MPa·$m^{1/2}$, which is fairly consistent with the toughness values of SiC based composites in the literature.[11,12] The room temperature K_{1C} of Mo_5Si_3C was reported to be 3.7 MPa·$m^{1/2}$ by Suzuki et al.[5] and 2.7 MPa·$m^{1/2}$ (indentation fracture method) by Ross et al.[4] As no toughening mechanism was employed in the present composites, a high K_{1C} value is not expected. As seen from the figure, the fracture toughness increases significantly at elevated temperatures, reaching a mean value of 7.7 MPa·$m^{1/2}$ at 1400°C. To verify whether this increase was caused by crack healing during exposure at high temperatures, a set of precracked specimens was annealed at 1200°C and 1400°C in argon for 20 min (typical testing duration), then tested at room temperature. The fracture toughness of the heat-treated specimens only slightly increased to a mean value of 4.2 MPa·$m^{1/2}$ in the samples annealed at 1400°C. This small increase in toughness could be due to slight changes in the crack fronts,[13] or due to annealing-out of the residual stress produced by the indentation.[14] However, it is clear that crack healing at elevated temperatures was not significant, and cannot be addressed to the high toughness value (7.7 MPa·$m^{1/2}$) measured at 1400°C. The high toughness values at elevated temperatures would be mainly attributed to the plastic deformation of the infiltrated intermetallic phases. As seen from the typical stress-displacement curves in Fig. 4, the behavior was linear elastic at room temperature, but revealed definite plastic deformation at 1400°C. Fractographic analyses also showed the same trends. The room temperature fracture mode in Fig. 5(a) shows a typical brittle mode, but plastic deformation of the infiltrated phases is evident at 1400°C [Fig. 5(b)]. The composite could be toughened by infiltrated phases through crack bridge mechanism.[15,16] Additional energy is needed for a crack to pass through the toughening inclusions, which then appears in macroscopic terms as increased toughness.[1] The high-temperature K_{1C} values of the present composites are

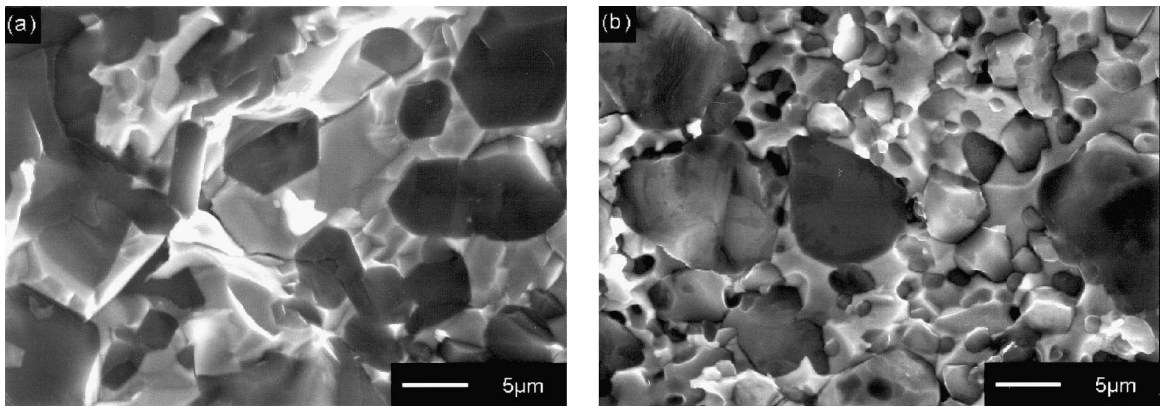

Fig. 5. Fracture surfaces of SiC–$Mo_5(Si,Al)_3C$ composites after fracture at (a) room temperature and (b) 1400°C in argon.

impressive in some senses. Although SiC fiber-reinforced SiC (SiC/SiC) composites were reported to show almost constant K_{1C} values from room temperature up to more than 1000°C in inert environments,[17,18] a significant reduction in the K_{1C} values was actually found in air above 1000°C.[19,20] The decrease in the K_{1C} value was attributed to the interfacial oxidation and fiber degradation at elevated temperatures.[21,22] As such a failure mechanism does not occur in the present composites, a significant reduction in the K_{1C} value is not expected at elevated temperatures even in air.

The influence of annealing in air on the fracture toughness was also studied. The pre-cracked specimens were first heated at 1200°C or 1400°C for 20 min in air, then they were fractured at room temperature. Fig. 6 is a plot of the apparent toughness vs annealing temperature. The apparent toughness dramatically increases, and reaches a mean value of 7.1 $MPa{\cdot}m^{1/2}$ in the specimens annealed at 1400°C. This significant increase can be attributed to crack healing caused by oxidation. The overall oxidation reaction of the composite can be expressed as:

$$SiC + O_2 \rightarrow SiO_2 + CO_2 \quad (2)$$

$$Mo_5(Si, Al)_3C + O_2 \rightarrow MoO_3 + SiO_2 + Al_2O_3 + CO_2 \quad (3)$$

The newly formed oxides of SiO_2 and Al_2O_3 fill or heal the crack tips, which could cause effective crack healing. Therefore, the high toughness values given in Fig. 6 are unrealistic, since the values were calculated assuming that the precrack sizes were the same as those of the unoxidized samples.

The influence of indentation load on the toughness was also studied. Fig. 7 shows that the average K_{1C} increases with indentation load. Increasing the indentation load should have no effect on the fracture toughness, since this parameter is incorporated into the equation.[10] This behavior has been previously correlated to the rising "R-curve" behavior or to deviations from the ideal constant (η) of 0.59 in the equation.[23] The derivation of the equation assumes that the far field stress (σ) acts uniformly on the region containing the indentation-generated surface crack and that the constant (η) is uniform and constant as the crack extends

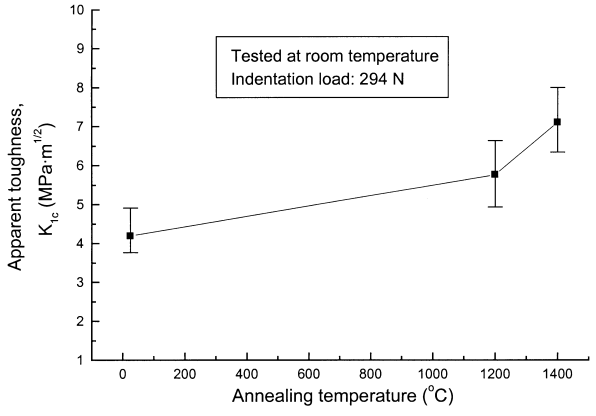

Fig. 6. Room temperature apparent fracture toughness as a function of annealing temperature for the precracked specimens annealed in air for 20 min.

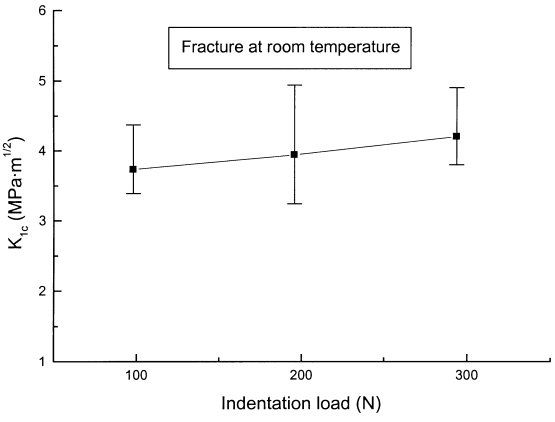

Fig. 7. Fracture toughness as a function of indentation load.

during flexural loading. These assumptions are generally valid only when the indentation crack is much smaller than the specimen dimensions. Therefore, the equation becomes inaccurate as the indentation load and the crack length increase.[24]

4. Conclusions

SiC–$Mo_5(Si,Al)_3C$ composites were fabricated by the melt-infiltration process. Investigations revealed that the non-infiltration was mainly attributed to the gas evolution caused by the reactions between the inherent impurities of SiO_2 and free carbon. Fracture toughness was measured from room temperature to 1400°C using the indentation strength method in 1 atm argon atmosphere. Significant increases in K_{1C} were found at elevated temperatures, which were attributed to plastic deformation of the infiltrated $Mo_5(Si,Al)_3C$ phases. Crack healing was insignificant on samples annealed in argon, whereas severe crack healing occurred in samples annealed in air. The effect of indentation load on K_{1C} was also analyzed.

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