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Creep behaviour of $MoSi_2$–HfO_2 composites

M. BESTERCI*, B. BALLÓKOVÁ, P. HVIZDOŠ
Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 043 53 Košice, Slovakia

R. SCHOLL, A. BÖHM
Fraunhofer Institut für Fertigungstechnik und Angewandte Materialforschung, Dresden, Germany

Several ways of improving the performance of $MoSi_2$-based composites have been developed by incorporating SiC and ZrO_2 particles or SiC whiskers into the matrix [1–4]. During the last decade, a number of papers have been dedicated to the study of creep behaviour of $MoSi_2$-based materials, mainly in compression and tensile loading mode [5–8]. The aim of this work was to investigate the creep resistance of the $MoSi_2$–HfO_2 materials in air at temperatures above 1100 °C. After preliminary bending strength tests the samples were tested in bending in the temperature range 1100–1400 °C under a load of 100 MPa.

The materials were prepared by powder technology using a high-energy milling process. The mechanical treatment was started from coarse-grained elemental powders with a diameter of 100–500 μm. This powder mixture was crushed for some hours in a high-energy ball mill using argon. Calorimeter measurements were carried out to explain the influence of milling time on the heat flux during heating from room temperature to high temperature. The milled powders were densified by hot pressing at 1550 °C in vacuum. Experimental materials were supplied in form of bending bars with dimensions of 3 mm × 3.5 mm × 35 mm. The strength tests were carried out using samples with tensile surface polished down to 1 μm finish in order to avoid fracture initiation from machining flaws.

The creep tests were carried out in four-point bending in air using the same 11/22 mm fixture. The samples, loaded statically by a dead-weight system to a constant stress of 100 MPa, were tested at (1100–1400) ± 1 °C. From measured deflection of the middle of the sample the outer fibre strain was calculated and the strain-time ($\varepsilon - t$) profiles were recorded. The experimental setting allows deflections up to 1 mm to be measured which limited the bending strain that could be properly detected to 1%. Assuming Arrhenian temperature dependence of the stationary creep rate:

$$\dot{\varepsilon} = \mathrm{const} \cdot \sigma^{\mathrm{n}} \exp\left(-\frac{Q_{\mathrm{A}}}{RT}\right),$$

where R is the gas constant, T the temperature in Kelvin, σ the applied stress, n the stress exponent, the apparent activation energy (Q_{A}) was calculated from the strain rate vs. $1/T$ plot.

The results of the strength test are given in Table I. At temperatures above 1200 °C, the material exhibited a dramatic reduction of the elastic properties which resulted in large sample deflection. Consequently, at these temperatures the information about strengths has only a comparative value. At 1400 °C, the deflection exceeded measurable range and the samples were not broken. The results of the creep tests are illustrated in Figs 1–2. Fig. 1 shows the creep curves as a function of temperature.

Fig. 2 summarizes the temperature dependence of the creep rates. In no experiment was tertiary creep reached, and in the given experimental setting it was not always possible to determine the stationary creep exactly. In such cases the minimum values of the strain rate, calculated from the final (usually nearly straight) part of the creep curve, were taken as the "steady-state" strain rates. Nevertheless, the obtained results were consistent and they are mutually comparable. The apparent activation energy lay around 500 kJ/mol. Again, it is in a very good agreement with earlier findings [9], where for 100 MPa at 1100–1200 °C the values of Q_{A} were found to be between 440 and 634 kJ/mol for $MoSi_2$ and $MoSi_2$–SiC.

The microstructure and its response to high temperature load were investigated by TEM using thin foil technique. Thin foils were prepared from as-received and crept specimens by ion beam thinning technique. The microstructure studies were performed using a JEOL 2010 TEM (200 kV) with EDX analysis facilities for identification of individual phases. TEM studies showed that the matrix consisted of $MoSi_2$ grains with size of about 5 μm (Fig. 3). These grains were well developed. Unlike [10], where the crept $MoSi_2$ materials contained many dislocations, subgrains, and dislocation grids, our material was virtually free of dislocations, even after the creep test. These facts, together with findings in [7, 9], according to which the value of creep stress exponent n was between 1 and 2 for $MoSi_2$-based materials, suggest that the creep in $MoSi_2$ is dominated by diffusion of atoms (Cobble model). The similarity of apparent activation energies for various $MoSi_2$-based materials suggests that this diffusion takes place inside $MoSi_2$ grains. According to [11], the activation energy for diffusion of Si in $MoSi_2$ is equal to 250 kJ/mol, which corresponds to the results for low stresses (<20 MPa). Higher Q_{A} values at 100 MPa

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*Author to whom all correspondence should be addressed.

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TABLE I Results of the bending strength tests at high temperatures

	Experimental materials ($MoSi_2$-HfO_2)	
Temperature (°C)	Strength (MPa)	Deflection (mm)
1100	600	0.1
1200	490	0.1
1300	350	>0.9
1400	340 (not broken)	>1.0

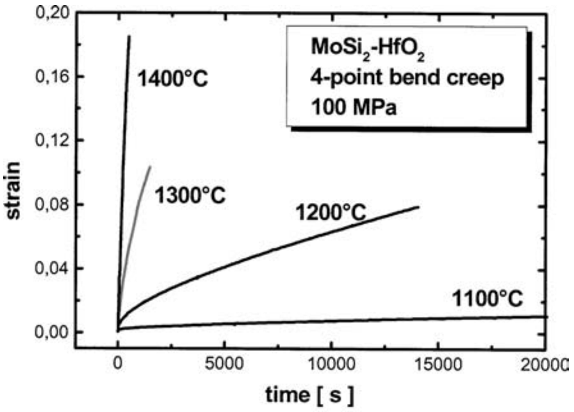


Figure 1 Creep curves for $MoSi_2$–HfO_2.

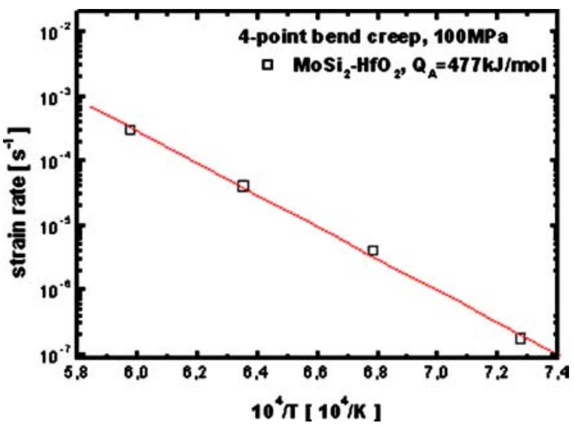


Figure 2 Temperature dependence of the steady-state creep rates. Calculation of the activation energies.

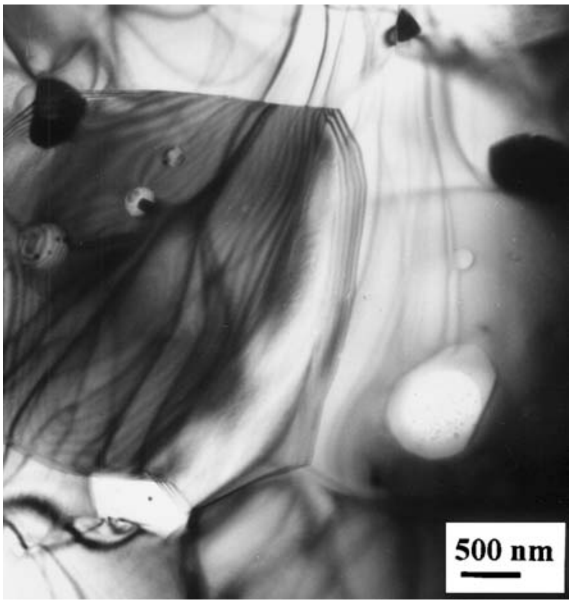
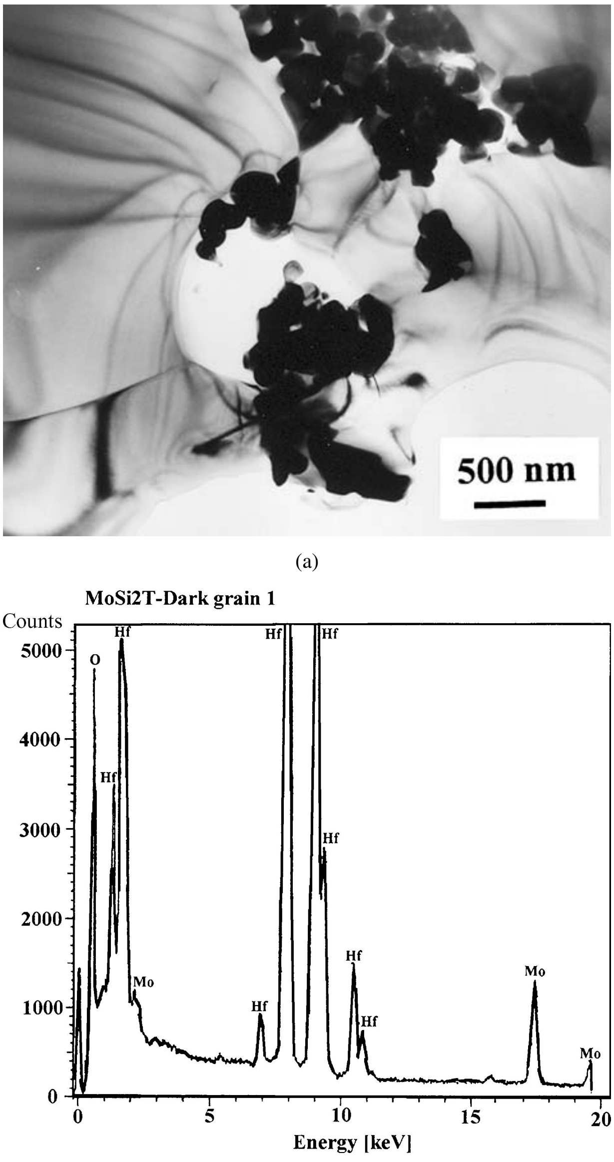


Figure 3 Microstructure of $MoSi_2$–HfO_2. Inter- and intragranular silica pockets.



(a)

(b)

Figure 4 TEM micrograph showing the location of silica glass (white) and HfO_2 particles (black)—(a). EDX spectrum of dark particles showing its composition—HfO_2—(b).

indicate that probably some additional mechanisms are present. Amorphous SiO_2 glass was identified by TEM and EDX analysis, and was concentrated mainly intergranularly, in triple grain junctions, in regions with size of about 1 μm. Smaller amounts were found as intragranural globulitic particles with size <0.5 μm. As was found for other $MoSi_2$ materials [10], silica glass does not wet the grain boundaries. A hafnium-rich phase formed mainly as small particles of size of about 200 nm. These particles frequently formed clusters positioned intergranularly or along the boundaries of the matrix grains, as is shown in Fig. 4a. EDX analysis confirmed that this phase was HfO_2 (Fig. 4b). HfO_2 did not form secondary, grain boundary binding phase.

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