

## Creep behavior of $\text{MoSi}_2$ and $\text{MoSi}_2 + \text{SiC}$ composite

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Recently, there has been an increasing need for structural materials that can withstand oxidizing environments at elevated temperatures up to 1500 °C. Such materials are important for modifications in energy production technologies with the aim to improve their efficiency and to reduce carbon dioxide exhaust level. Similarly, advanced aircraft engine designs require new materials that can operate at temperatures higher than those tolerable for superalloys. Materials based on  $\text{MoSi}_2$  are promising candidates for such applications thanks to their high melting point (2030 °C), excellent oxidation and corrosion resistance, and high temperature ductility above the brittle–ductile transition temperature in the vicinity of 1000 °C [1–4]. However, the main disadvantage, limiting their use, is the low fracture toughness at lower temperatures (<1000 °C) and the low strength and creep resistance at high temperatures. In order to improve the mentioned properties, various approaches based on incorporating of SiC, Nb, and  $\text{ZrO}_2$  particles or SiC whiskers into the matrix have been used [5–10].  $\text{MoSi}_2 + \text{SiC}$  composites were generally developed to increase the fracture toughness compared to  $\text{MoSi}_2$ . However, the fracture toughness has not been improved by the addition of SiC particles because the SiC particles themselves or their clusters are the strength-degrading fracture origins.

The aim of the present work was to study and compare the creep behavior of monolithic  $\text{MoSi}_2$  and  $\text{MoSi}_2 + \text{SiC}$  composite and to investigate the influence of the SiC particles on the creep mechanisms in the temperature range 1100–1200 °C in air.

The materials used in this investigation were monolithic  $\text{MoSi}_2$  and  $\text{MoSi}_2 + 20 \text{ vol}\% \text{ SiC}$ , prepared by Cesiwid, Erlangen, Germany. Specimens for bending creep tests were cut to the dimensions 3 mm × 4 mm × 45 mm and polished with 15 μm finish on their tensile surface.

The creep tests were carried out in the four-point bending mode with inner/outer roller spans of 20/40 mm. The bending bars were tested at temperatures from 1100 to 1200 °C under loads from 20 to 100 MPa. The tests were realized in a creep furnace with a dead weight loading system in air. From specimen deflection data, measured by two inductive transducers between the center and the inner roller and collected by a computer data acquisition system, the outer fiber strain was calculated and recorded. The accuracy of

the deflection measurement was approximately  $\pm 1 \mu\text{m}$ . The creep experiments at all stress/temperature combinations were carried out up to 1% bending strain.

Samples for microstructure analysis were prepared using standard procedure and investigated using optical microscopy, as well as scanning and transmission electron microscopy (SEM and TEM). The volume fraction of individual phases (pores) was measured using an image analyzer and statistical methods. X-ray microanalysis (EDX) was used for the identification of individual phases present in the microstructure.

Thin foils of the as-received materials and the tensile surfaces of the crept specimens were prepared for the microstructure and substructure observations, which were carried out using high resolution TEM (HRTEM) techniques in order to identify the high temperature deformation mechanisms.

Microstructures of the studied materials are shown in Fig. 1a and b. Using SEM and EDX it was found that there were three different phases present in the microstructure of the monolithic  $\text{MoSi}_2$ : matrix  $\text{MoSi}_2$  grains,  $\text{SiO}_2$ , and a little of  $\text{Mo}_5\text{Si}_3$  (hexagonal Nowotny phase). TEM observations of the as-received materials proved that silica ( $\text{SiO}_2$ ) particles were frequently present in the triple grain junctions of  $\text{MoSi}_2$  grains and occasionally were placed intragranularly, inside the  $\text{MoSi}_2$  grains. The mean grain size of  $\text{MoSi}_2$  was approximately 7 μm. The silica particles were usually spherical with diameter of the intergranular particles in the range from 1 to 5 μm and the intragranular ones with diameter from 0.2 to 2 μm. HRTEM was used to determine whether there was any amorphous phase present at the grain boundaries. It was found that the grain boundaries were clear and the  $\text{SiO}_2$  did not wet the matrix boundaries, Fig. 2. The composite material, besides the features common to monolithic material, contained SiC grains with an average size of 5 μm, clusters of grains, and a porosity of 3.2 vol%. The  $\text{MoSi}_2$  matrix grains were larger than those in the monolithic material and typically had dimensions from 10 to 15 μm. Comparison of their room-temperature mechanical properties was presented elsewhere [11].

The creep tests showed a remarkable difference between the creep behavior of both materials, as can be seen from Fig. 3. At the test condition of 1100 °C/100 MPa the monolithic  $\text{MoSi}_2$  exhibited a strain of 0.15% after a loading time of 2 hr, while the

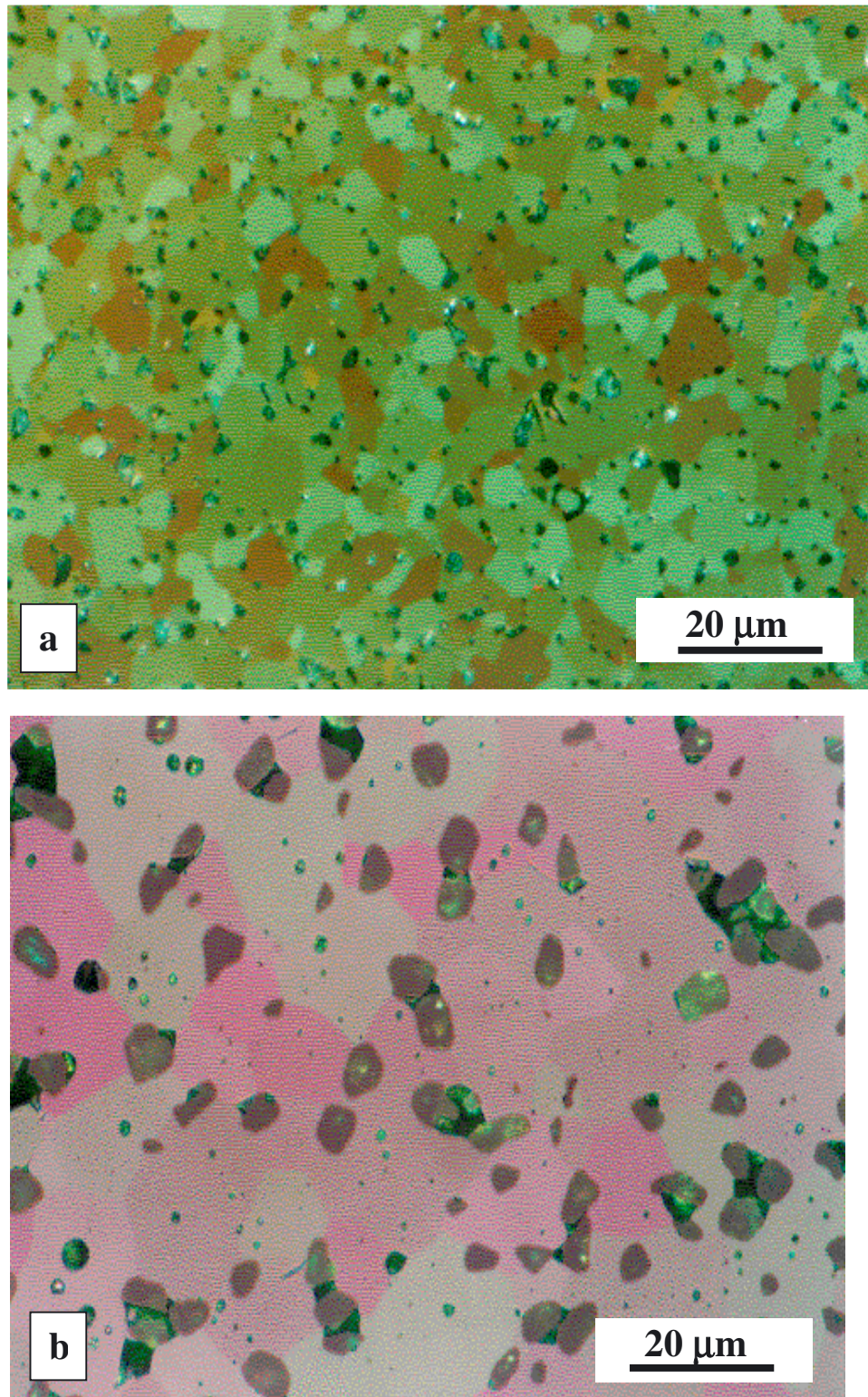


Figure 1 Microstructure of the investigated materials in cross-polarized illumination: (a) monolithic MoSi<sub>2</sub> and (b) MoSi<sub>2</sub> + SiC.

MoSi<sub>2</sub> + 20% SiC composite showed the same level of strain after more than 20 hr.

At the testing conditions of 1200 °C/20 MPa the strain in the monolithic MoSi<sub>2</sub> had a value of approx. 0.6% after 20 hr, while the composite had less than 0.1% at the same conditions, Fig. 3b.

Fig. 4 shows the creep rates as a function of applied stresses for both monolithic and composite materials at three different testing temperatures together with the calculated creep exponents. The values of the creep exponents are similar for both materials, about

1.75. However, they are lower in comparison with MoSi<sub>2</sub> composites reinforced with 20% SiC whiskers [12].

The apparent activation energies calculated from the Arrhenius plots are given in Fig. 5. The apparent activation energy of the monolithic MoSi<sub>2</sub> at the low applied stress had a value of approximately 250 kJ/mol, which is in good accordance with the activation energy for diffusion of silicon in MoSi<sub>2</sub> [13]. The apparent activation energy at the highest applied stress (100 MPa) was 634 kJ/mol, which, in combination

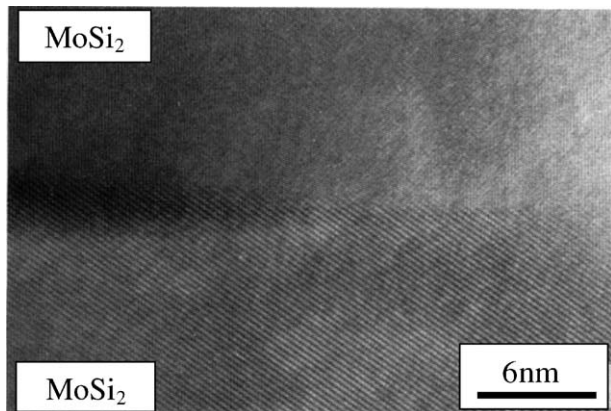


Figure 2 HRTEM of the MoSi<sub>2</sub>/MoSi<sub>2</sub> boundary in monolithic MoSi<sub>2</sub>.

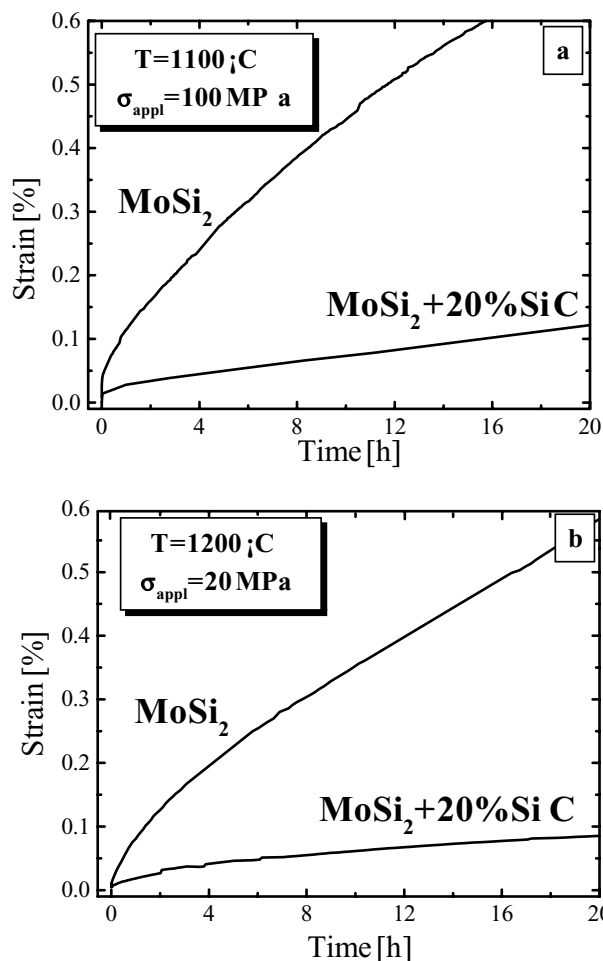


Figure 3 Comparison of the creep behavior of the studied materials at 1100 °C (a) and 1200 °C (b).

with the stress exponent value of about 2.4, suggests a change in the creep controlling mechanism, which in this case was probably a dislocation climb [14]. This fact is also supported by TEM observations of the samples after creep testing, where a large number of dislocations in the MoSi<sub>2</sub> grains was found, Fig. 6a and b. The lower creep rate in the case of MoSi<sub>2</sub> + SiC composite can be explained by the different SiO<sub>2</sub> content in the monolithic and composite MoSi<sub>2</sub>, and by the presence of the SiC grains in the microstructure of the composite.

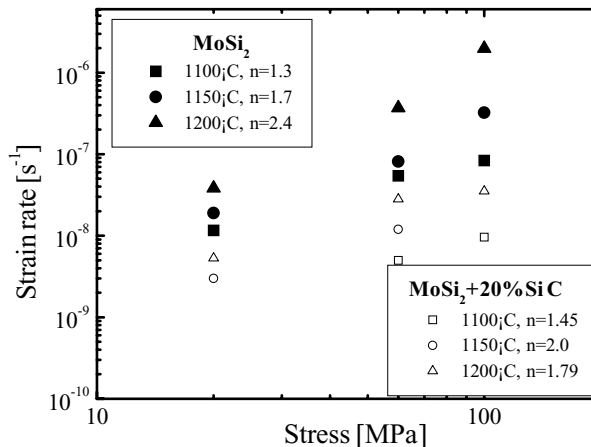


Figure 4 Minimum creep rates as functions of applied stresses. Determination of the stress exponents.

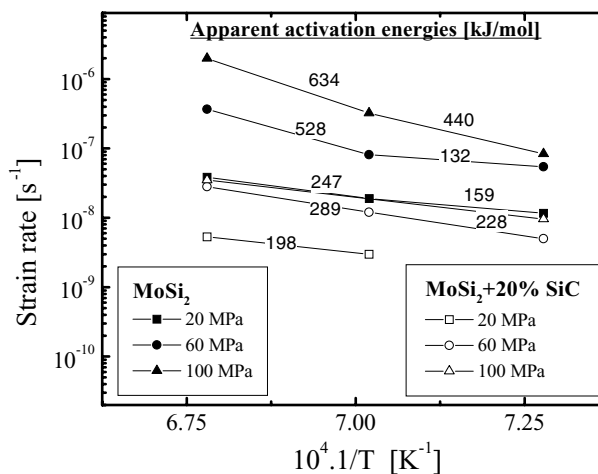


Figure 5 Arrhenius plot for the studied materials. Calculation of the apparent activation energies for creep.

Sadananda *et al.* [12] have shown that the creep behavior (creep rate) of polycrystalline MoSi<sub>2</sub> is very sensitive to grain size and is controlled primarily by dislocation glide/climb, as well as by grain boundary sliding accommodated by dislocation plasticity. The grain size exponent for MoSi<sub>2</sub> was found to be in the range of 5–8, which is higher than expected for Nabarro–Herring creep (grain size exponent of 2) and Coble creep (grain size exponent of 3). For MoSi<sub>2</sub> + SiC composites it was found that in the case of volume fraction of SiC particles from 5 to 20% the creep rate was higher than that of unreinforced MoSi<sub>2</sub>, while creep rates of the composite reinforced with 40% SiC particles were substantially lower. This behavior was found to be related to the fact that on increasing the SiC addition, the grain size of the MoSi<sub>2</sub> matrix reduces, promoting grain boundary sliding.

In the materials studied in the present investigation the grain size of MoSi<sub>2</sub> in the MoSi<sub>2</sub> + SiC composite was found to be significantly higher in comparison with the grain size of monolithic MoSi<sub>2</sub>. This finding itself explains the improved creep resistance. Furthermore, the presence of SiC particles on the grain boundaries of MoSi<sub>2</sub> probably modifies the geometry and chemical composition of the silica phase in the composite,

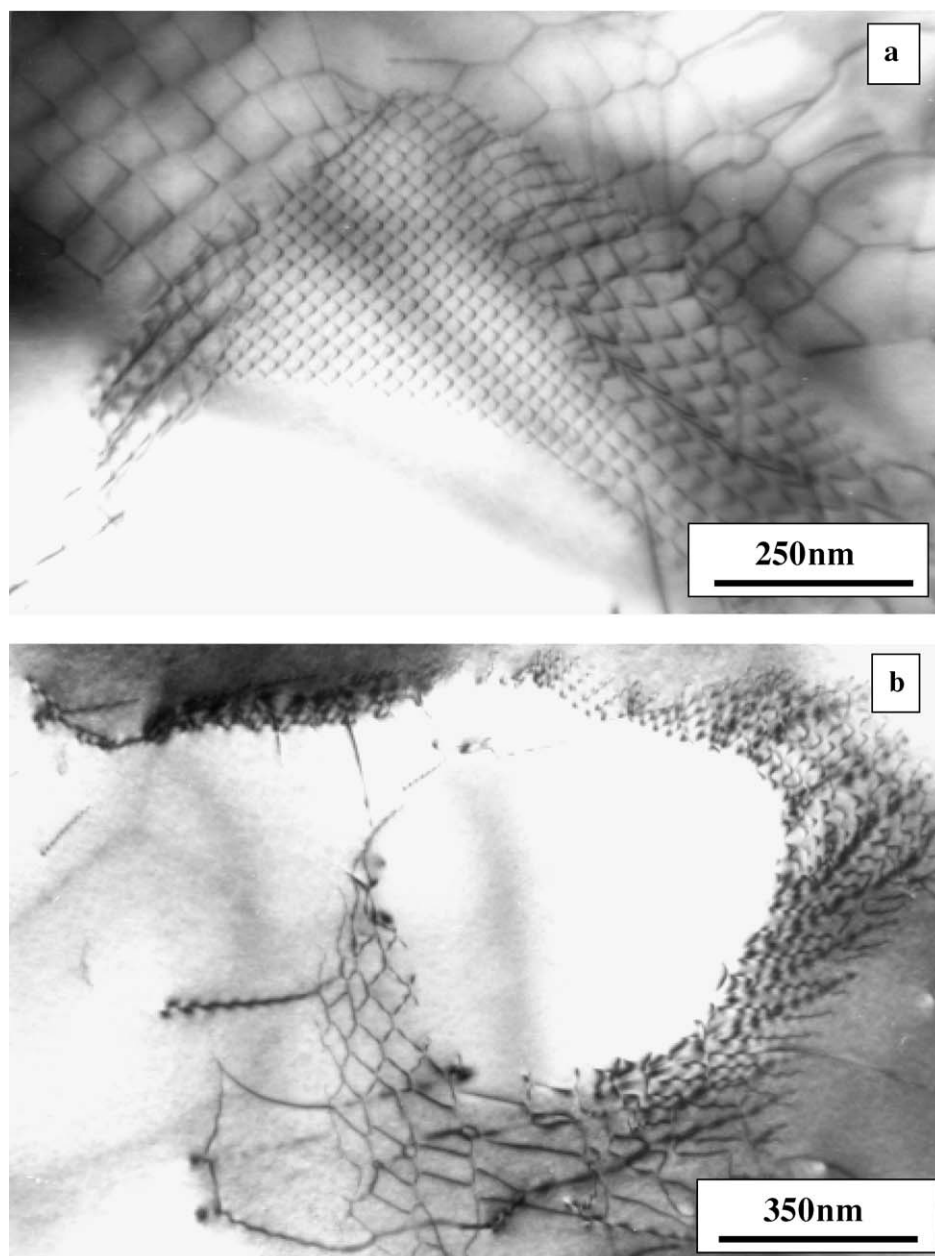


Figure 6 Dislocation networks in MoSi<sub>2</sub> grains in monolithic MoSi<sub>2</sub> (a) and in MoSi<sub>2</sub> + SiC (b).

resulting in a substantially higher creep resistance in comparison with the MoSi<sub>2</sub>.

As a summary one can state that the MoSi<sub>2</sub> + 20% SiC composite exhibited an excellent creep resistance in the temperature range of 1100–1200 °C, with creep deformation rate almost one order lower than that of the monolithic MoSi<sub>2</sub>. The creep of MoSi<sub>2</sub> appears to be controlled primarily by dislocation glide/climb as well as grain boundary sliding accommodated by dislocation plasticity. The grain boundary sliding in the composite is significantly suppressed due to the higher grain size and to the presence of SiC particles on the MoSi<sub>2</sub> grain boundaries.

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