Impression creep of $MoSi_2$

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Abstract

The creep behaviour of a monolithic molybdenum disilicide has been investigated within a temperature range from 1100 °C to 1250 °C at applied stresses from 20 MPa to 100 MPa in air using the impression test method. The strain-time relationships have been recorded, and the creep exponents as well as the activation energies of creep have been calculated. The results are compared to the creep results of the same material tested in four-point bending mode. The stress exponent in impression was found to be approximately 1, and the apparent activation energy approximately 250 kJ mol^{-1}. In lower stress-temperature range the creep behaviour of $MoSi_2$ in impression and bending mode is very similar, however at higher stress-temperature range the creep rate, stress exponent and activation energy are significantly lower in impression.

Key words: impression creep, molybdenum disilicide, stress exponent, activation energy

1. Introduction

There is an increasing need for structural materials that can withstand oxidizing environments at high 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 the carbon dioxide exhaust level. Similarly, advanced aircraft engine designs require new materials that can operate at temperatures higher than those, which are tolerable for superalloys. Materials based on $MoSi_2$ are promising candidates for a wide variety of elevated temperature structural applications above 1000 °C 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 their low fracture toughness at lower temperatures (< 1000 °C) and low strength and creep resistance at high temperatures. In order to improve the fracture toughness, various approaches based on the incorporation of SiC, Nb, ZrO_2 particles, or SiC whiskers into the matrix have been used [5–10].

Different approaches have been used to improve the creep resistance of $MoSi_2$-based materials and different testing methods have been used for their characterization [11–13]. Petrovic et al. and Sadananda et al. [11, 14, 15] summarized the effect of the applied stress, grain boundary, Al-addition and carbon addition as well as the effect of the SiC and Si_3N_4 addition on the creep behaviour of $MoSi_2$. According to the results the creep mechanisms in $MoSi_2$-based materials appear to be a combination of dislocation glide/climb process, as well as grain boundary sliding. The extent of grain boundary sliding depends on the amount of silica present in the material, as well as on the grain size of the MoS_2 matrix. Stress exponents for the creep of $MoSi_2$ and $MoSi_2$-based composites tested in compression are in the vicinity of 1–5, while creep activation energies are in the range of 200–600 kJ mol^{-1}. The majority of the creep tests have been realized in compression, but tensile creep tests have been performed [13, 16], too. Yoon et al. [16] have shown that creep rates in tension are higher than creep rates in compression, due to the intensive grain boundary sliding and cavitation processes.

One very useful method for creep testing of less creep-resistant materials, especially for newly developed systems, is the impression method. This method has been originally applied for measuring the viscosity of glasses; later the method was introduced

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for other materials, too [17, 18]. During this test a probe in the form of cylinder, cone or sphere is pressed into the surface of the tested sample at a constant load and temperature and the impression depth as a function of the time is recorded. The creep curves resulting from the impression test have usually a short primary transient stage, and a long secondary stage with constant impression velocity. Comparing to conventional (tensile, flexural or compression) creep tests, the impression creep test is simpler and requires smaller samples, which is a significant advantage at testing newly developed materials.

There are only a limited number of papers in the literature dealing with impression creep testing of ceramics using flat ended cylindrical indenter and only a few papers reporting impression creep of $MoSi_2$ based materials [19, 20]. These results show that the creep rates and stress exponents obtained in impression and compression tests are in agreement, but the activation energies are significantly different.

The aim of the present investigation is to study the impression creep of $MoSi_2$ in the range of 1100–1250 ℃ at relatively low applied stresses from 20 MPa to 100 MPa in air.

2. Experimental

The material used in this investigation was monolithic $MoSi_2$, prepared by Cesiwid, Erlangen, Germany. Specimens for impression and bending creep test were cut to the dimension $3 \times 4 \times 13$ mm^3 and $3 \times 4 \times 45$ mm^3, respectively.

During the impression creep test flat cylindrical probe (hot pressed SiC) with a diameter of 2 mm was used (Fig. 1). The specimens were heated to the test temperatures in a range of 1100–1250 ℃ in air, at a rate of 5 ℃ min^{-1} and after a short dwelling time (10 min) have been loaded with selected loads of 20, 60 and 100 MPa. The load remained unchanged during the whole test. The impression depth was measured as a difference between two LVDT elements, which were attached to the lower and upper SiC supports via thin alumina rods, and recorded as a function of time. Deformation accumulated during the experiment was intentionally limited only to approximately 0.5 % strain to prevent systematic errors due to sample deformation. After the experiment no chemical changes were observed at the contact area test probe material-tested material at the applied test conditions.

Samples for microstructure analysis of as-received and crept materials were prepared using standard procedures and investigated using optical microscopy, as well as scanning and transmission electron microscopy (SEM and TEM). X-ray microanalysis (EDX) was used for identification of individual phases present in the microstructure.

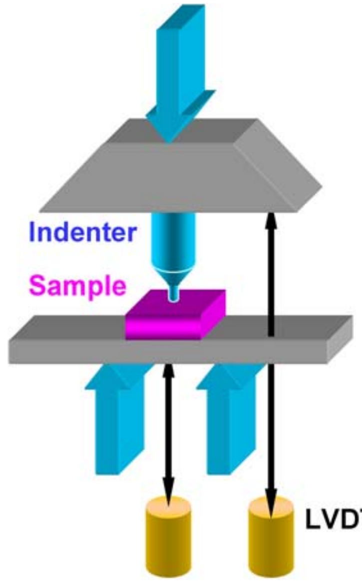

Fig. 1. Schematic illustration of the impression creep test.

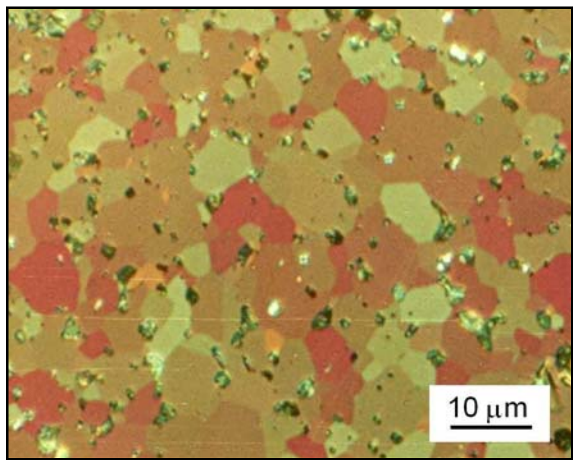

Fig. 2. Microstructure of the investigated material in cross-polarized illumination.

Thin foils were prepared by grinding, dimpling and ion-beam thinning.

For comparison, creep tests have been carried out in four-point bending mode with inner/outer roller spans 20/40 mm at temperatures from 1100 ℃ to 1200 ℃ under the same applied stresses from 20 MPa to 100 MPa.

3. Results and discussion

3.1. Microstructure characteristics

Characteristic microstructure of the investigated material is illustrated in Fig. 2. Three different phases

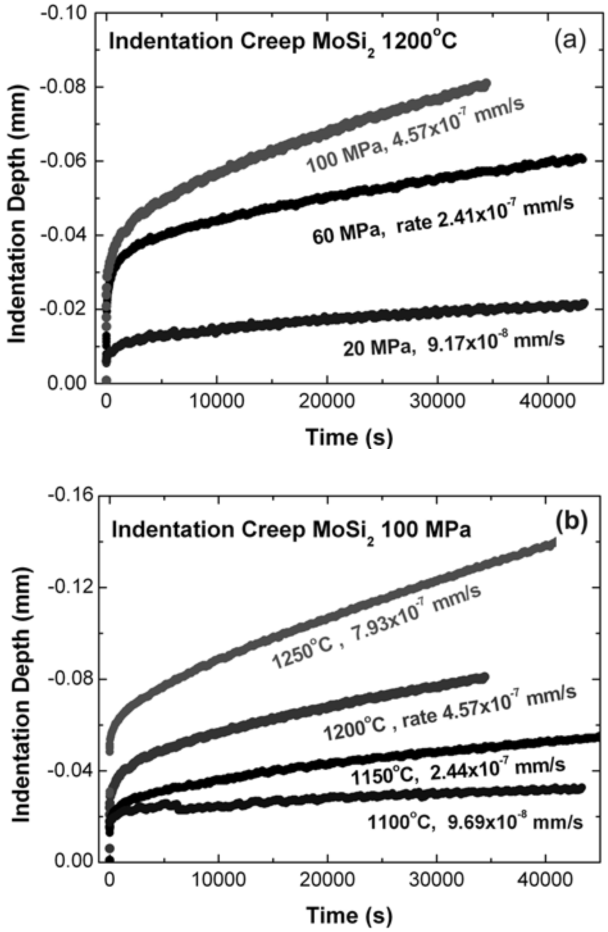

Fig. 3. Creep curves at the temperature of 1200 ℃ (a) and applied stress of 100 MPa (b).

have been identified: matrix $MoSi_2$ grains, SiO_2, and a small amount of Mo_5Si_3 (hexagonal Nowotny phase). TEM observations of the as-received materials proved that silica (SiO_2) particles were frequently present in the triple grain junctions of $MoSi_2$ grains and occasionally they were placed intra-granularly, inside the $MoSi_2$ grains. The mean grain size of $MoSi_2$ was approximately 7 μm. The silica particles were usually spherical, with the diameter of the inter-granular particles in a range from 1 to 5 μm and the intra-granular ones with a diameter from 0.2 to 2 μm. Using HRTEM it was found that the grain boundaries were clear without the presence of SiO_2.

3.2. Creep behaviour

No significant deformation has been detected during the impression creep at the temperature of 1100 ℃. Characteristic creep curves are illustrated at the temperature of 1200 ℃ and applied stress of 100 MPa in Fig. 3. The creep curves show a short primary stage with a prolonged secondary stage from which the minimum creep rate was calculated.

Table 1. The values of the stress exponents of the impression and bending creep of $MoSi_2$

Temperature (℃)	$n_{\text{impress.}}$	n_{bending}
1100	0.8	1.3
1150	1.0	1.6
1200	1.0	2.4
1250	1.0	–

Table 2. Apparent activation energies of the impression and bending creep of $MoSi_2$

Stress (MPa)	$Q_{\text{impress.}}$ (kJ mol^{-1})	Q_{bending} (kJ mol^{-1})
20	211	206
60	260	301
100	240	535

The calculated values of the creep exponent for the temperatures above 1150 ℃ are very similar and have a value approximately 1 (Table 1). The values of the apparent activation energy of the impression creep change from 211 kJ mol^{-1} to 260 kJ mol^{-1} (Table 2).

According to Feng et al. [21] at low stresses creep rates of $MoSi_2$ vary linearly with stress indicative of Newtonian viscous flow behaviour with stress exponent $n = 1$ similarly as it was found in this investigation using impression method. Sadananda et al. [14] investigated the effect of the grain size (from 4 to 20 μm) on the creep rate of $MoSi_2$ in low-load regime tested in compression mode and found that the creep rate was changing by 3 to 4 order of magnitude by the changing grain size. The material investigated in the present study with the grain size of 7 μm exhibits lower but comparable creep rate compared to the material with similar grain size in their study. Tanaka et al. [22] determined the activation energy as a function of grain size of $MoSi_2$ in the Newtonian viscous range ($n = 1$). According to the results the activation energy increases linearly from small grain sizes (4 μm) and reaches a plateau for grain sizes approximately 20 μm. The average activation energy (250 kJ mol^{-1}) of the material (grain size 7 μm) tested in the present investigation is in an excellent agreement with these results.

According to the value of the stress exponent $n = 1$ and activation energy $Q = 250$ kJ mol^{-1} it seems that during the impression test in the temperature range from 1100 ℃ to 1250 ℃ the creep is controlled by grain boundary diffusion.

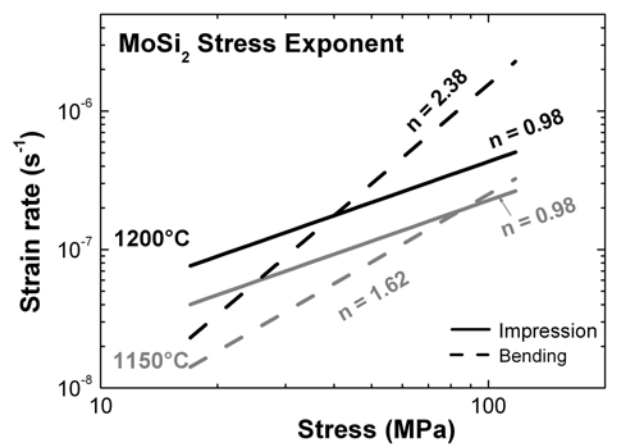

Fig. 4. Comparison of the stress exponents of the studied material in bending and impression creep.

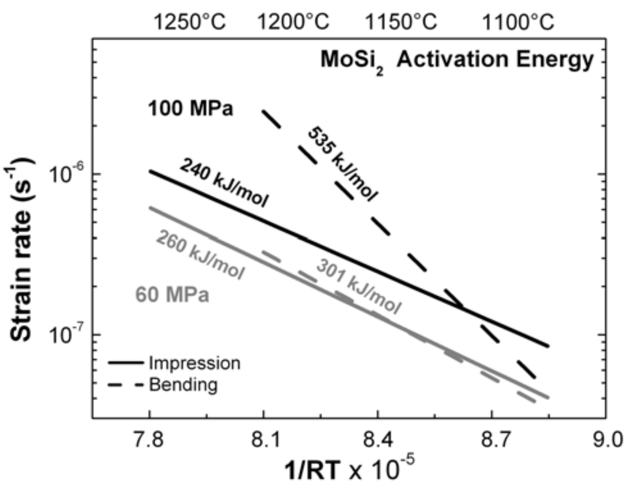

Fig. 5. Comparison of the apparent activation energy of the studied material in bending and impression creep.

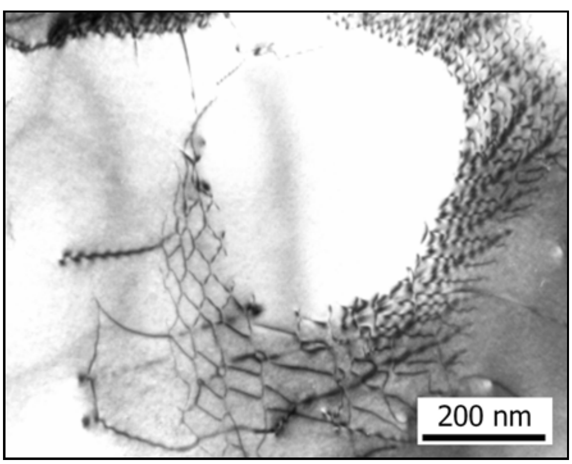

Fig. 6. Dislocation networks in $MoSi_2$ grains found after creep in bending at 1200 ℃.

Comparing the influence of the applied stress on the strain rate in impression and in bending (Fig. 4), it is visible that at the low stresses the impression method results in a higher creep rate compared to the bending method. By increasing the applied load, the strain rate is increasing in the case of the bending mode faster compared to the strain rate in impression, especially at the temperature of 1200 ℃. At the temperatures of 1100 ℃ and 1150 ℃ and applied stress of 100 MPa the both methods result approximately in the same strain rate, but at 1200 ℃ the strain rate in bending is significantly higher than in impression.

The stress exponents in bending change from 1.3 (measured at the temperature of 1100 ℃) to 2.4 (measured at the temperature of 1200 ℃), while in impression they are constant at the whole temperature range. Similarly as the stress exponents, the apparent activation energies in the impression creep test stay practically constant in the entire stress interval (Fig. 5) but the apparent activation energy in the bending mode increases with the applied stresses from 206 to 535 kJ mol^{-1}. This value, in combination with the stress exponent value of about 2.4, suggests a change in the creep controlling mechanisms, in this case it is probably dislocation climb [23]. This fact is also supported by the TEM observations of the specimens after bending creep testing, where a large number of dislocations in the $MoSi_2$ grains have been found (Fig. 6).

Butt et al. [20] studied the impression creep behaviour of SiC particle – $MoSi_2$ composite with 0–40 vol.% of SiC in the temperature range from 1000 to 1200 ℃. They found direct comparison between impression and compression creep, however it is not possible to predict compression creep behaviour based on the impression creep data because of different rate controlling mechanisms in different methods. They used very high punch pressure from 258 to 362 MPa, therefore it is not possible to compare their results with the results of the present investigation.

The differences in the creep behaviour of the $MoSi_2$ tested in compression, tension and impression mode can be explained by the different stress fields which can lead to the mobilization of different creep controlling mechanisms. Experiments will be carried out in the future to fully understand the creep mechanisms of $MoSi_2$ at impression, compressive and tensile tests.

4. Conclusions

– Creep behaviour of a monolithic molybdenum disilicide has been investigated within a temperature range from 1100 ℃ to 1250 ℃ at applied stresses from 20 MPa to 100 MPa in air using impression testing method.

– The stress exponent in impression was found to be approximately 1, and the apparent activation energy approximately 250 kJ mol^{-1}.

– In lower stress – temperature range the creep behaviour of $MoSi_2$ in bending and impression mode is very similar, however at higher temperature/stress the creep rate, stress exponent and activation energy are significantly lower in impression.

– The impression method was found useful for the characterization of creep behaviour of $MoSi_2$ and can be useful for design of less creep resistant materials in complex stress fields.

Acknowledgements

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