High Temperature Properties of the $MoSi_2$ and $MoSi_2$-SiC Nonocomposites

Beáta Ballóková*, Michal Besterci and Pavol Hvizdoš

Institute of Materials Research SAS, Watsonova 47, 040 01 Košice, SR

(Received June 2, 2009; final form June 11, 2009)

ABSTRACT

High temperature properties of the monolithic $MoSi_2$ and $MoSi_2$ composite reinforced by nano-SiC particles were studied. The materials were prepared via powder metallurgy using high temperature controlled reaction sintering (CRS).

Creep testing in four-point bending and in compression was performed in order to determine high temperature properties of the experimental materials. Comparison of the materials showed that incorporating of nano SiC particles into the $MoSi_2$ matrix resulted in improvement of creep resistance for temperatures up to 1473 K for applied stress from 50 to 100 MPa. Creep stress exponent (n) of the composite, measured after compressive creep testing, was 1.27 (1273 K) and 3 (1473 K), respectively. Microstructure and its response to high temperature loading were investigated by TEM using the thin foil technique.

Based on the presented parameters of creep kinetics and transmission electron microscope analyses probable mechanism of creep deformation was determined.

Keywords: molybdenum disilicide, composite materials, four point bending creep, compressive creep, TEM

1. INTRODUCTION

$MoSi_2$ based materials have become in recent years an attractive option for high temperature applications in oxidizing or other aggressive environments. Molybdenum disilicide is a case of a borderline material between ceramic and intermetallic compound, with combination of covalent and metallic bonds. At room temperature it is brittle as ceramics and at high temperatures it behaves plastically as metall /1-3/. Polycrystalline $MoSi_2$ has a brittle-to-tough transition at about 1273 K. It has high melting point, 2303 K, and very good oxidation resistance at temperatures up to 1973 K. One of main aims of research in this field is to improve its low temperature fracture toughness at temperatures below 1273 K and creep properties above 1273 K /2/.

$MoSi_2$ is a thermodynamically stable in presence of various secondary phases, such as Si_3N_4, SiC, nano SiC, Al_2O_3 and ZrO_2, which allows to develop a wide variety of composites. Due to present metallic bonds it is possible to machine these materials by electric discharge erosion, i.e. much more simply and cheaply than typical ceramics. By incorporating secondary particles into the matrix it is possible to optimize its high temperature mechanical and physical properties /4-6/.

---

*e-mail:bballokova@imr.saske.sk

2. EXPERIMENTAL MATERIAL AND METHODS

The starting material was prepared according to patent /7/ in the Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung, in Dresden, Germany. The method is based on high-energy milling (HEM) of high purity coarse-grained powders of Mo and Si with mean grain size 100 to 500 µm. After several hours long milling in a planetary mill Pulverisette 5 (made by Fritsch) in argon atmosphere highly dispersed powder mixtures were obtained. In order to prepare the composites, during milling also nano-sized SiC dispersoid ceramic particles were introduced into the matrix. Milled mixtures were compacted by cold pressing to high densities (above 95% of theoretical density) and subsequently by pressureless reaction sintering at 1773 K in vacuum.

Experimental materials were delivered in shape of discs with 100 mm diameter and 5 mm thickness. From those the bars with dimensions of 3 x 4 x 45 mm^3 for creep in bending as well as small prisms (2 x 2 x 4 mm^3) for compressive creep tests were cut by electric discharge technique. The four-point bending and compressive creep testing were carried out using high temperature testing furnace HTTF 2, by SFL Ltd./Instron, Inc., UK.

The specimens were loaded in four-point flexure in air at temperatures of 1273, 1473, 1573, and 1673 K ± 273 K and loaded by 100 MPa at a loading rate of 0.5 $mm.min^{-1}$. The outer and inner rollers spans were 40 and 20 mm, respectively. Deformation was measured in terms of deflection between the centre of the bar and the inner rollers by two LVDTs (linear variable differential transducer) with accuracy ±1 µm. Data acquisition and processing was carried out digitally. The relationship between tensile surface strain rate and applied stress is characterized by semi-empirical formula (1).

$$\dot{\varepsilon} = const.\exp\left(-\frac{Q_A}{RT}\right)\left(\frac{\sigma}{E}\right)^n\left(\frac{b}{d}\right)^p \qquad (1)$$

where R is gas constant, (R = 8,314472 $J.K^{-1}.mol^{-1}$), T is absolute temperature in K, Q_A is creep activation energy, $kJ.mol^{-1}$, σ – stress, b – Burgers vector, E – elastic module, d – grain size, p, n – materials constants, n is creep stress exponent.

The creep activation energy for the experimental materials loaded by constant stress was determined from dependence of creep rate $\dot{\varepsilon}$ on 1/T.

The flexure loading set-up was modified in order to measure creep in compression. Specimens were placed between two flat blocks made from Al_2O_3 and loaded by a dead-weight system. These tests were performed in air at 1073, 1273, 1473 K under series of static loading of 50, 80, and 100 MPa, with aim to determine values of the stress exponent. Barrel-like deformation was observed only in monolithic $MoSi_2$ under 100 MPa at very high temperatures (above 1273 K), which is in agreement with results in literature /12/. In order to identify the most probable creep mechanisms transmission electron microscopy analysis was applied.

The creep strain was continuously monitored and all experiments (flexural and compressive) were finished after the steady-state strain rate had been reached. Maximum relative deformation was not to be higher than 1%.

In the present work high temperature properties of monolithic $MoSi_2$ and $MoSi_2$ - nano SiC composite are studied and compared, and probable creep mechanisms are determined.

3. RESULTS AND DISCUSSION

3.1 Measurement of creep characteristics in four-point bending

Figure 1 shows the creep curves of monolithic $MoSi_2$ and $MoSi_2$ – 10% nano SiC composite obtained at 1273 K and 1473 K under load of 100 MPa. Since under the applied conditions the creep curves did not exhibit typical, clearly distinguishable, three stages of creep (strain rate decreases practically during the whole test), the minimum values of strain rate were taken as the steady-state creep rate. These values were calculated from the final (usually very nearly linear) part of the creep curve. Even though, strictly speaking, these might not be the exact secondary creep rates, the results were consistent and mutually comparable. Comparing the creep resistance of both materials at 1273 K it can be seen, that the material with nano-SiC particles had higher resistance (i.e. lower deformation rate) than the monolithic material. With increasing temperature the creep resistance decreases. Here, surprisingly, it was found that the resistance of the composite decreased more than that of the monolith.

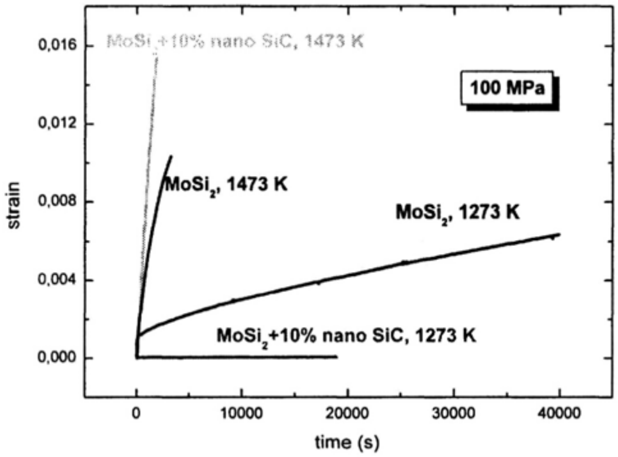

Fig. 1: Creep curves for studied materials (stress 100 MPa, temperatures 1273 and 1473 K), four point bending creep

Under 100 MPa the composite was more creep resistant up to 1473 K, as it is shown in Figure 2 in terms of temperature dependence of the creep strain rate.

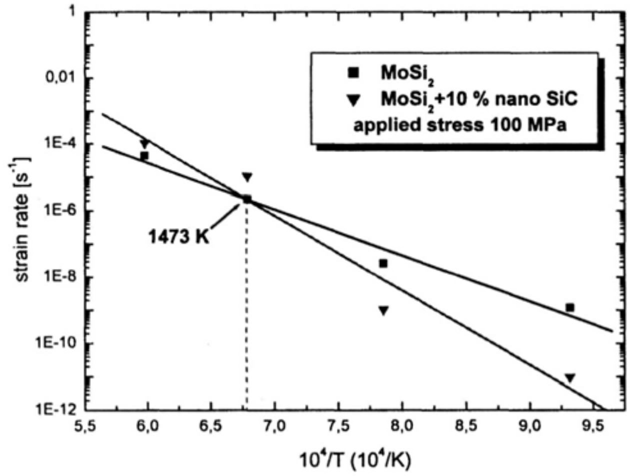

Fig. 2: Temperature dependence of the steady-state creep rates, four point bend creep

Relatively high value of activation energy in the case of composite (429 kJ/mol) when compared to that of the monolith (264 kJ/mol) suggests that with increasing temperature its strain rate increases more. Then, when determining the mechanism of creep, one has to keep in mind important role of nanoparticles, regularly dispersed within the whole matrix which has very low mean grain size. This fact, due to higher volume fraction of grain boundaries, facilitates sliding along their boundaries. Such mechanism of grain boundary sliding and grain rotation was studied in /8/.

Creep characteristics of the experimental materials during testing were studied only at 100 MPa stress (because of limited supply of experimental materials). That is why in this case it was not possible to calculate the stress exponent and to fully identify the micromechanism of creep. However, based on our knowledge of microstructure we infer that diffusion and dislocation mechanisms would be present. Moreover, it is clear that the grain size plays an important role, which means that also grain boundary sliding and grain rotation takes place, namely the so-called Rachinger sliding /9,10/, i.e. redistribution of grains without their elongation. Since no significant cavitation was observed, this sliding will be accompanied by intense diffusion within the volume of matrix grains.

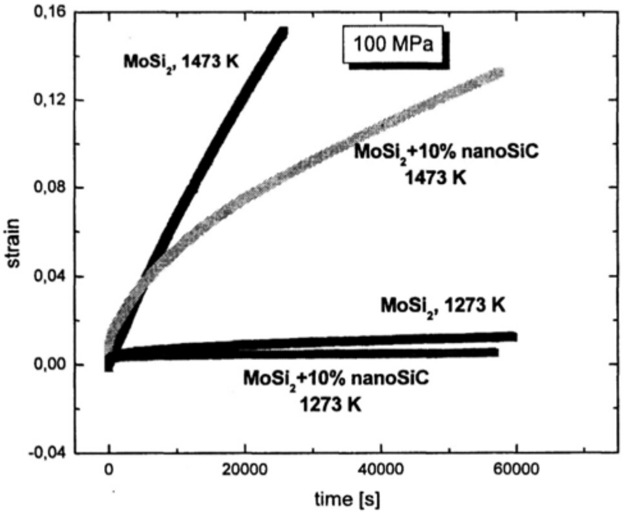

Fig. 3: Creep curves for studied materials (stress 100 MPa, temperatures 1273 and 1473 K), compressive creep

3.2 Measurement of creep characteristics in compression

Figure 3 shows typical creep curves in terms of deformation vs. time plots, measured in compression at 1273 and 1473 K and constant stress 100 MPa.

The highest creep rate, increasing with temperature, had the monolithic material. Similarly as in flexural testing, also the creep resistance of the composite with 10% nano SiC drops with increasing temperature.

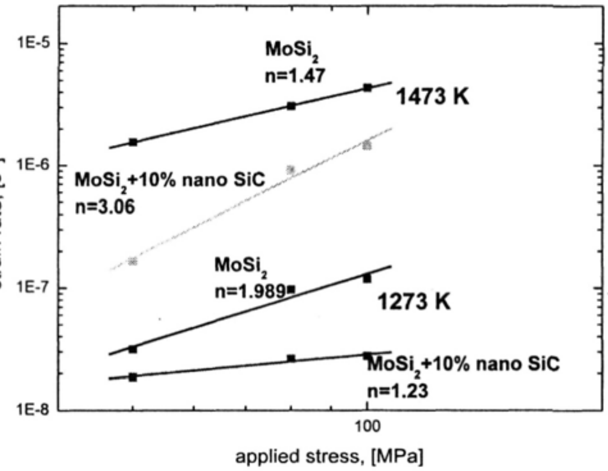

Fig. 4: Creep rate as a function of applied stress, temperatures 1273 K and 1473 K, compressive creep

Figure 4 shows the creep strain rate as function of the applied stress (50, 80, 100 MPa) at temperatures 1273 K and 1473 K. In the case of the composite, the stress exponent has at 1273 K value 1.23 but at 1473 K it increases up to 3.06. These values indicate that the dislocation movement, which controls the mechanism of creep diffusion, determines the final creep rate. For cases when "n" is lower than 3 it is usually assumed, that the creep rate is connected to the transitional mechanisms, which include both dislocation climb and dislocation sliding.

The temperature dependence of the steady-state creep rates is illustrated in Fig.5. In the measured stress interval (50-100 MPa) the apparent values of activation energies are basically independent of load.

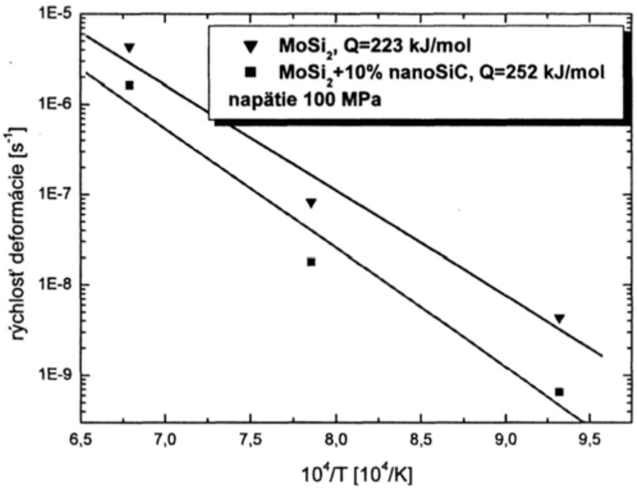

Fig. 5: Temperature dependence of the steady-state creep rates, compressive creep

Sadananda et al. /11/ showed that creep resistance of polycrystalline $MoSi_2$ is very sensitive to grain size and is controlled mainly by dislocation slide and climb as well as by grain boundary sliding. In their work they report the stress exponent to be from 5 to 8, which is a value that is higher than for both Nabarro-Herring ($n = 2$) and Coble ($n = 3$) creep mechanisms. For composite materials they had found that for 5% to 20% of SiC particles the creep rates were higher than for monolithic $MoSi_2$. This is because with higher volume fraction of SiC particles the mean matrix grain size diminishes which facilitates grain boundary sliding. With respect to results published in /12/, according to which the stress exponent in $MoSi_2$ based materials is between 1 and 2, it is suggested that the dominant mechanism of creep deformation is diffusion of atoms (probably Coble or Nabarro-Herring model). From the agreement between apparent activation energy values for different types of $MoSi_2$ based materials it can be assumed that diffusion takes place mostly inside the $MoSi_2$ grain, i.e. Nabarro-Herring mechanism. According to Kofstad /13/ the activation energy of diffusion of silicon atoms within $MoSi_2$ crystals is 250 $kJ.mol^{-1}$, which corresponds to the results obtained at low stresses (<20 MPa). In literature there are no reliable accurate values of diffusion of Mo within $MoSi_2$ but according to Sadananda they fall within interval 350-450 $kJ.mol^{-1}$.

TEM studies of the deformation micromechanisms in crept materials (1473 K, 100 MPa) show the presence of dislocations inside the matrix grains, Figure 6a. These results are in agreement with the work /11/ where edge-dislocations and dislocation networks were observed. These can became the origins of internal stresses which subsequently prevent further creep deformation. In TEM neither fracturing on matrix/particle interphase boundaries, nor between adjacent matrix grains was found. Also no cavitation on grain and/or particle boundaries was identified, Figure 6b.

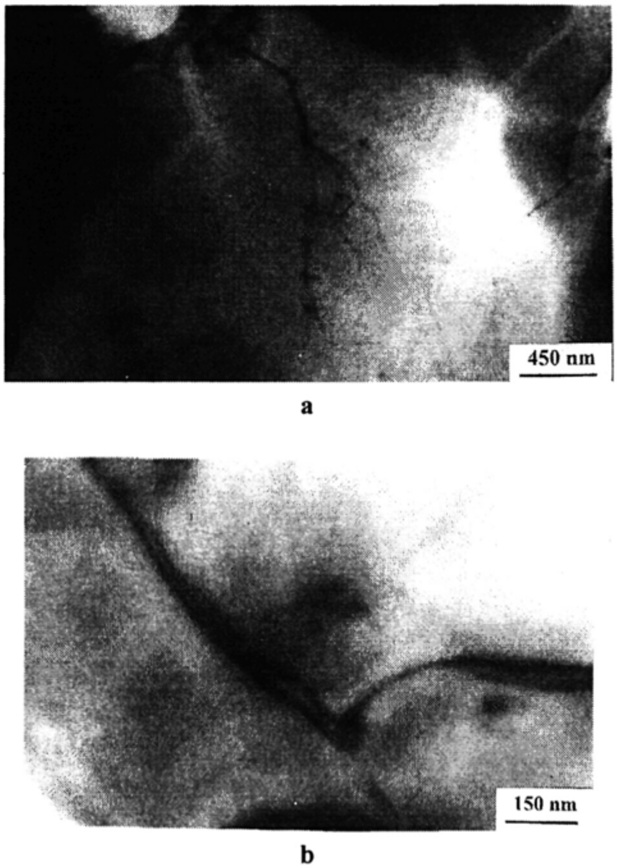

Fig. 6a-b: TEM micrographs of the composite $MoSi_2$ + 10% nano SiC after creep (temperature 1473 K, applied stress 100 MPa, thin foils)

This indicates that creep is controlled by atomic diffusion. Analyses of boundaries between matrix grains observed in thin foils after creep showed presence of amorphous or intercrystalline phase. Similar results were reported in works /14/.

4. CONCLUSIONS

The experiments and obtained results can be summarized as follows:

1. Creep characteristics of experimental materials confirmed improved creep resistance of composite when compared to monolithic $MoSi_2$. However, with increasing temperature the creep resistance of the composite significantly declines, particularly at temperatures above 1473 K.
2. It was impossible identify the deformation mechanisms in flexural creep due to limited number of experiments. Knowledge of microstructure, however, enables to infer that both diffusion and dislocation mechanisms will be present. Important role is played by mean grain size, which means that grain boundary sliding (namely Rachinger type – redistribution of grains without their elongation) and grain rotation will be the most prominent. No significant cavitation was observed which means that the sliding will be accompanied by intense diffusion through the matrix grains.
3. The values of stress exponents and activation energies measured for compressive creep suggest that the dominant mechanism of creep deformation is diffusion of atoms (Coble or Nabarro-Herring model). Based on apparent activation energies it is probable that the diffusion takes place mostly inside the $MoSi_2$ grains, i.e. Nabarro-Herring mechanism is prevalent. The higher Q_A value measured in $MoSi_2$-10% nano SiC (429 kJ/mol) suggests presence of additional mechanisms, most probably grain boundary sliding at higher temperatures, which is enabled by present amorphous phase along boundaries. This means that at higher temperatures the creep resistance of the composites sharply decreases because of their finer grains.

ACKNOWLEDGEMENT

Authors wish to express their thanks to the Agency APVV for the financial support via projects APVV 20-027205 and VEGA 2/0105/08.

REFERENCES

1. J.J. Stephens, *NASA HITEMP Rev.*, (1990).
2. A.K. Vasudevan and J.J. Petrovic, *Mater. Sci. and Eng.*, **A 155**, 1, (1992).
3. C.J. Smith, *NASA HITEMP Rev.*, (1989).
4. R. Gibala, H. Chang, C.M. Czarnik and J.P. Campbell, *Mater. Sci. Eng.*, **A 261**, 122, (1999).
5. Z. Yao, J. Stiglich and T.S. Sudarshan, *Journal of Materials Engineering and Performance*, **8**, 3, 291, (1999).
6. J.J. Petrovic, *MRS Bulletin*, **18**, 7, 35, (1993).
7. R. Scholl and B. Kieback, *Patent DE 44 18 598 A1.*
8. M. Besterci, O. Velgosová and L. Kováč, *High Temp. Mater. and Proc.*, **21**, 1/2, 79, (2002).
9. W.A. Rachinger, *J. Inst. Metals*, **81**, 33, (1952).
10. T.G. Langdon, *Materials Science and Engineering*, **A 283**, 1/2, 266, (2000).
11. K. Sadananda, C.R. Feng, H. Jones and J.J. Petrovic, *Mater. Science and Eng.*, **A 155**, 227, (1992).
12. K. Sadananda, H. Jones, J. Feng, J.J. Petrovic and A.K. Vasudevan, *Ceram. Eng. Sci. Proc.*, **12**, (9-10), 1671, (1991).
13. P. Kofstad, *High Temperature Oxidation of Metals*, New York, Wiley, (1966).
14. P. Hvizdoš, M. Besterci, B. Ballóková, R. Scholl and A. Böhm, *Kov. Mater.*, **39**, 6, 379, (2001).