

MoSi₂ - Al₂O₃ DOUBLE-MATRIX COMPOSITES PREPARED BY IN SITU REACTIONS

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Composites consisting of MoSi₂ and Al₂O₃ interlocked matrices with porosity below 1% were prepared by the reactive hot-pressing of Mo, Si and Al₂O₃ powder mixtures at 1500 °C for 2h. The electrical resistivity of the as-prepared materials decreases from 3.1 × 10⁻⁵ Ω m to 1.4 × 10⁻⁶ Ω m as MoSi₂ content increases from 30 vol % to 50 vol %. Insufficient chemical stability and creep resistance of double-matrix MoSi₂-Al₂O₃ materials were observed in air above 1100 °C, probably due to oxygen transport into the interior of material along the MoSi₂ - Al₂O₃ interface.

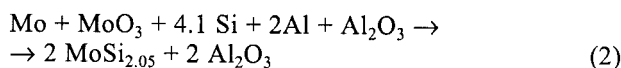
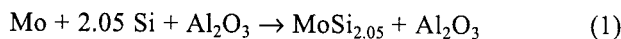
INTRODUCTION

Molybdenum disilicide (MoSi₂) has a high melting temperature (2030 °C) and excellent oxidation resistance at high temperature. The appropriate electrical properties of MoSi₂ led in the past to utilizing of this compound in manufacture of heating elements. The attributes listed above together with high Young's modulus (379 GPa at room temperature for polycrystalline MoSi₂), relatively low density (6.27 g cm⁻³), high thermal conductivity (145 W m⁻¹ K⁻¹ at 1000 - 2000 °C) and suitability for the electrical discharge machining make MoSi₂ based materials also serious candidates for structural applications. However, the low fracture toughness at room temperature ($K_{IC} < 4$ MPa m^{1/2}) and low tensile strength and creep resistance at high temperatures of pure MoSi₂ (brittle to ductile transition above 950 °C) must be improved. In order to alleviate these deficiencies in mechanical behaviour, a number of investigations have been carried out, based mostly on the incorporation of a second material with a good mechanical properties at room as well as at high temperature. Particularly MoSi₂-SiC composites have been studied intensively [1 - 4].

The electrical resistivity of MoSi₂ is relatively low, about 3 × 10⁻⁷ Ω m at room temperature, and despite its increase with temperature a high current level is necessary to achieve high working temperature of the heating element. Therefore, an increase of electrical resistivity is needed to decrease the electrical current necessary at the heating element working temperature and also an improvement of mechanical properties at high temperature will be advantageous.

Alumina (α-Al₂O₃) was chosen in this work for the partial replacement of MoSi₂ because of its appropriate physical properties (coefficient of thermal expansion, thermal conductivity, Young's modulus, melting temperature [5]) and thermochemical stability in contact with MoSi₂. The high thermochemical stability of pure MoSi₂ in air depends exclusively on formation of gas-tight SiO₂ surface layer. It must be emphasized,

that thermochemical stability of MoSi₂-Al₂O₃ composites depends on the contiguity of Al₂O₃. Two different situations exist, either individual Al₂O₃ particles are present in a continuous MoSi₂ matrix or both materials form two interlocked matrices. In the former case only the surface Al₂O₃ can react with SiO₂, contrary to the two continuous phases supposing the oxygen transport along the interface. Hence, in air it must be expected that mullite will be formed in the presence of alumina. The volume increase during mullite formation may damage the protective layer. Moreover, the first liquid appears in the Al₂O₃ - SiO₂ system at 1590 °C. At this temperature in presence of oxygen, the partial pressure of MoO₃ gas considerably exceeds the atmospheric pressure and consequently severe bloating could occur. If the protective layer is not able to hinder oxygen transport into the interior of the material at high temperature, a successive transformation from a conductive to a nonconductive material and degradation of mechanical properties can be expected. The principal aim of the present work was to prepare double-matrix composites with different electrical resistivity according to the reaction schemes



and to estimate the thermochemical stability of the prepared composites in air. The dilution of MoO₃ in reaction (2) allows a better control of the aluminothermic reaction and the slightly increased Si content against the stoichiometric ratio depresses the Mo₅Si₃ formation [6].

EXPERIMENTAL PART

The used powder materials were Mo (Chempur Cat.No. 009261, Germany), Si (Chempur Cat.No. 009383, Germany), MoO₃ p.a. (Schering-Kahlbaum,

Table 1. Calculated compositions and densities of the samples prepared.

sample No.	MoSi _{2,05} (vol.%)	starting composition (mass %)						density (g cm ⁻³)
		Mo	Si	Al ₂ O ₃	Al	MoO ₃	Nb	
2	20	17.43	10.49	72.08				4.45
3	30	24.94	14.97	60.09				4.67
4	40	31.76	19.06	49.18				4.90
5	50	37.98	22.80	39.22				5.12
55	50	24.66	22.20	24.77	6.94	18.49	2.94	5.12

Germany) and Al₂O₃ (Martoxide, CS-400/M, Germany). The appropriate amount of reagents was attrition milled in heptane for 4h and subsequently dried in air. The theoretical composition of the composites and their densities are summarized in table 1. The powder was uniaxially pressed in a steel die into disc-shaped compacts with a diameter of 50 mm and a thickness of about 13 mm using a pressure of 70 MPa. The pellets were hot-pressed at a pressure of 30 MPa in a graphite die in vacuum. The same heating rate 25 °C min⁻¹ up to 1500 °C with 2 hours hold and cooling rate 40 °C min⁻¹ were used for all samples except for sample 55 for which the maximum temperature was increased up to 1700 °C. The 25 × 5 × 1.5 mm bars prepared from sintered composites were used for four point measurement of electrical resistivity at room temperature. The chemical stability in air was estimated using direct (AC current) and indirect heating of 45 × 5 × 1.5 mm bars and also by the thermogravimetric measurement (TG) at 1100 °C for 5 hours. The 2.5 mm deep notch was cut in the middle of each bar used for direct heating to create a small space of maximum temperature. Two water-cooled terminals have been used to connect an AC current to the opposite ends of tested bar. The maximum surface temperature measured by wire optical pyrometer was 1600 °C. The indirect heating of composites was performed in a chamber furnace at 1700 °C for 60 hours.

The microstructural and composition changes of composites were followed by optical and electron microscopy (SEM, HREM) and by X-ray diffraction (XRD). The density of the samples was measured using the Archimedes method.

The Vickers indentation method was used to determine the hardness and to assess the fracture toughness. The creep resistance was measured by means of an Instron 1362 tester.

RESULTS AND DISCUSSION

Two solid phases, tetragonal MoSi₂ and α-Al₂O₃ were detected in all as-prepared samples by XRD. The physical properties of the prepared materials are summarized in table 2. Niobium was added to improve the room temperature fracture toughness of the composite. Its positive effect on this property is evident from the K_{IC} data in table 2, sample 55. Similarly as in the case of many cermets, the minor phase being continuous between 20 and 30 vol% as is evident from the resistivity difference between sample 2 (nonconductive) and sample 3 (conductive) in table 2. Thus a MoSi₂-Al₂O₃ electroconductive material with a resistivity ranging approximately from 10⁻⁴ to 10⁻⁷ W m can be prepared.

The microstructures of samples 5 and 55 are shown in figures 1, 2. The higher porosity of sample 55 despite the higher hot-pressing temperature is evident from these micrographs as well as from the measured densities (table 2). It can be explained by the higher total volume decrease during the reaction according to equation (2) compared to reaction (1).

Probably the higher total porosity due to the higher volume decrease cannot be eliminated with the hot-pressing parameters used in this work. The parameters of synthesis according to reaction (2) have not been optimized to decrease the final porosity and

Table 2. Physical properties of the materials prepared.

Sample No.	Density (g cm ⁻³)	Porosity (%)	H_V (50 N) (Gpa)	K_{IC} (MPa m ^{1/2})	ρ (Ω m)
2	4.30	3.4	14.1	4.4	3.5 · 10 ³
3	4.55	2.6	13.8	4.5	3.1 · 10 ⁻⁵
4	4.82	1.6	13.7	4.8	4.3 · 10 ⁻⁶
5	5.08	0.8	13.5	4.8	1.4 · 10 ⁻⁶
55	4.96	3.1	10.6	6.2	1.5 · 10 ⁻⁶

H_V - Vickers hardness at a load of 50 N; K_{IC} - fracture toughness calculated according Shetty et al. [9]; ρ - electrical resistivity.

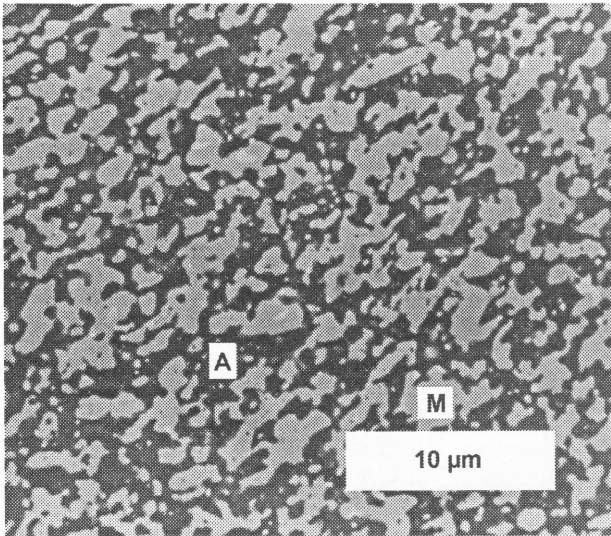


Figure 1. SEM micrograph of sample 5 (polished surface; A - Al₂O₃, M - MoSi₂).

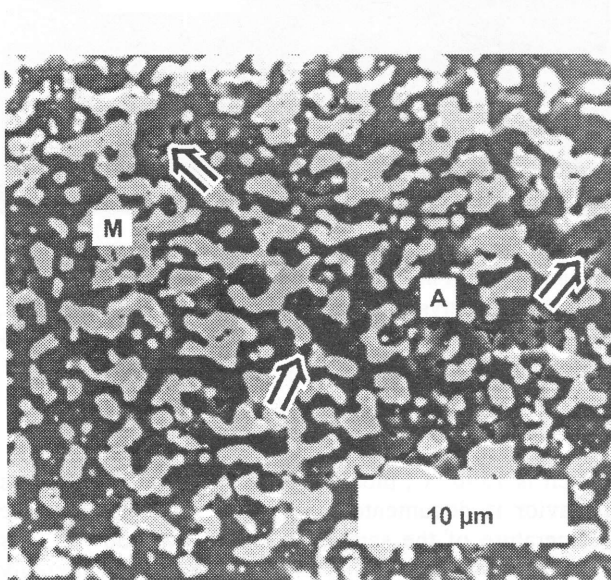


Figure 2. SEM micrograph of sample 55 (polished surface; A - Al₂O₃, M - MoSi₂; arrows mark pores).

materials were prepared according to the reaction scheme (1).

The oxidation test of sample 4 prepared by reaction (1) and measured by TG shows a total weight loss of 0.13 % during the temperature increase up to the maximum temperature 1100 °C followed by a slow weight gain of 0.15 % after 5 hours. Such behavior can be explained by the MoO₃ and SiO₂ formation supposing the presence of a sufficient amount of oxygen. Such a situation probably occurs on the surface.

The next reaction steps at higher temperature are the evaporation of MoO₃ and the formation of a protective Al₂O₃-SiO₂ based layer, which contains mullite (Al₆Si₂O₁₃) and SiO₂. The partial pressure of

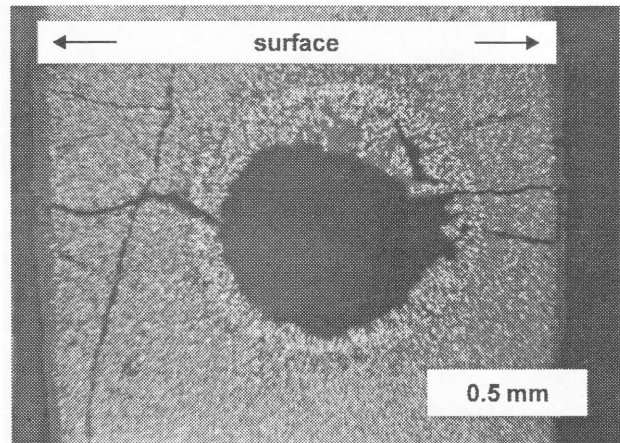


Figure 3. Optical micrograph of cross section of sample 3 in the maximum temperature zone after 2h of direct heating (maximum surface temperature 1600 °C).

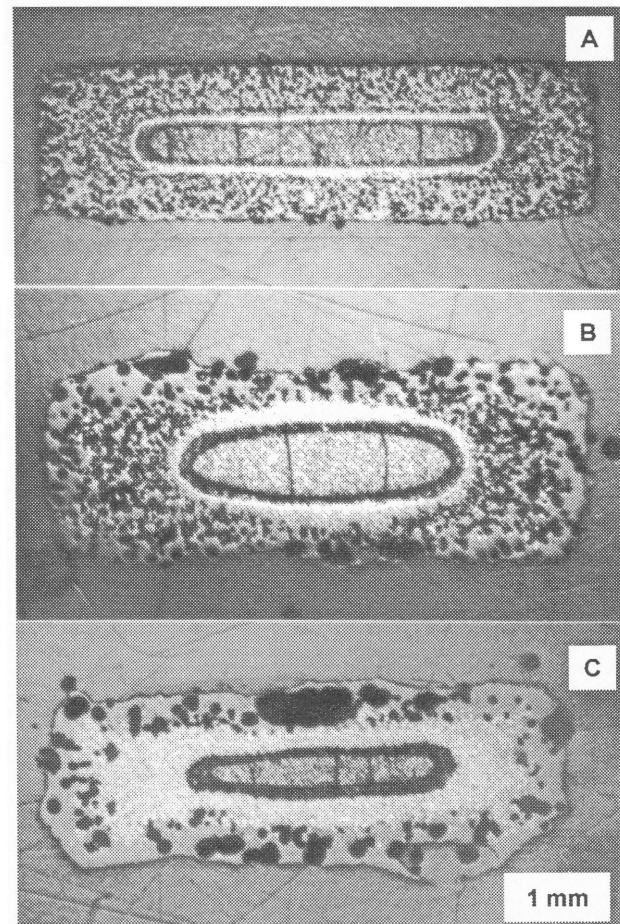


Figure 4. Optical micrographs of samples 3 - A, 4 - B and 5 - C after annealing at 1700 °C in air for 60 hours. Cracks present due to tensile stress are visible in the centers of samples.

MoO₃ exceeds atmospheric pressure at 1155 °C [7] and above the solidus temperature in the Al₂O₃-SiO₂ system

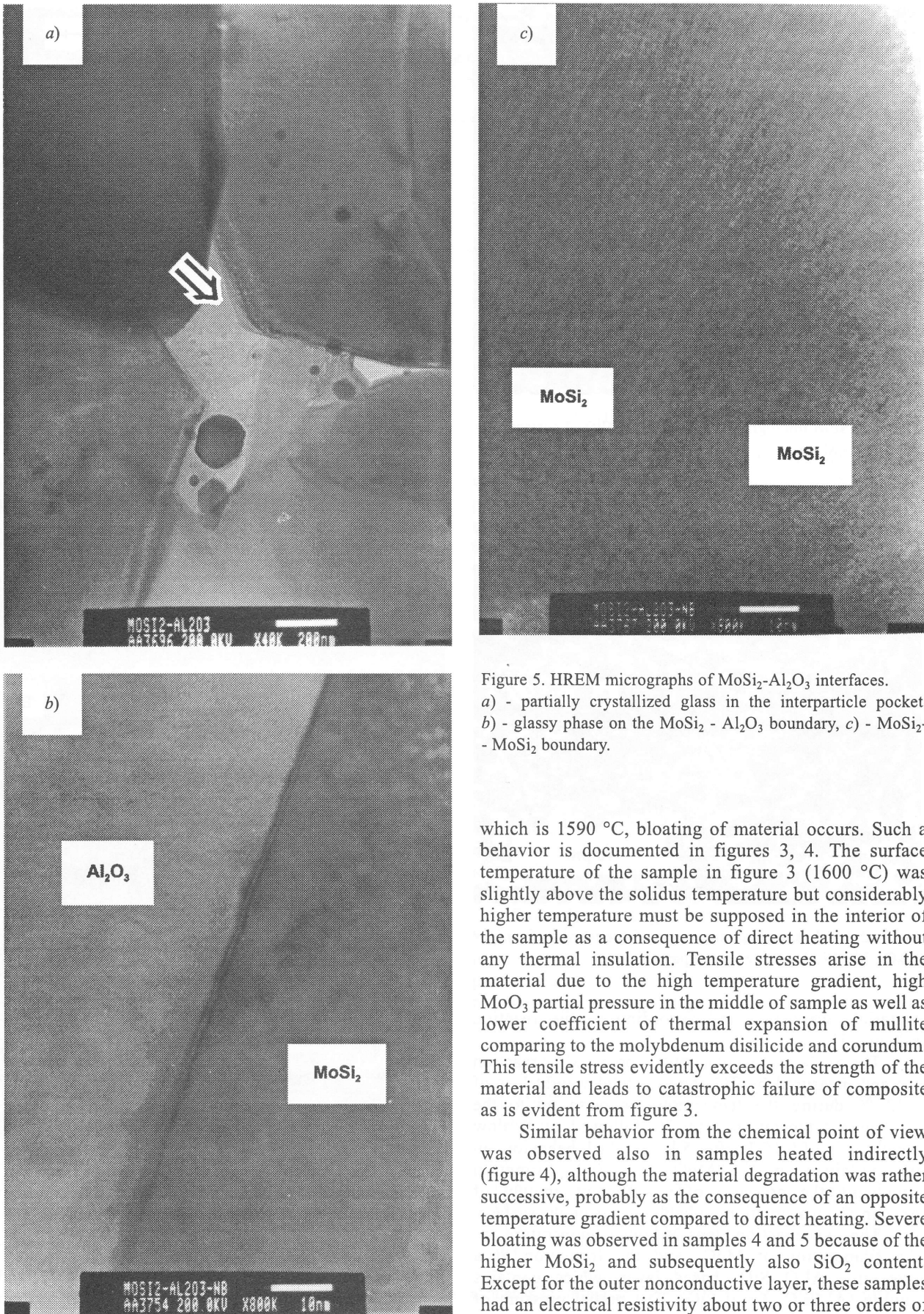


Figure 5. HREM micrographs of MoSi₂-Al₂O₃ interfaces.

a) - partially crystallized glass in the interparticle pocket, b) - glassy phase on the MoSi₂ - Al₂O₃ boundary, c) - MoSi₂-MoSi₂ boundary.

which is 1590 °C, bloating of material occurs. Such a behavior is documented in figures 3, 4. The surface temperature of the sample in figure 3 (1600 °C) was slightly above the solidus temperature but considerably higher temperature must be supposed in the interior of the sample as a consequence of direct heating without any thermal insulation. Tensile stresses arise in the material due to the high temperature gradient, high MoO₃ partial pressure in the middle of sample as well as lower coefficient of thermal expansion of mullite comparing to the molybdenum disilicide and corundum. This tensile stress evidently exceeds the strength of the material and leads to catastrophic failure of composite as is evident from figure 3.

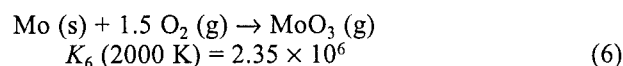
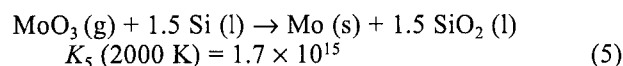
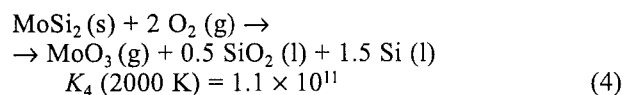
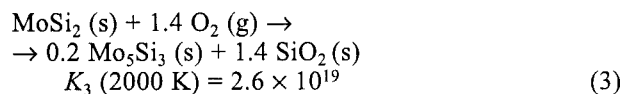
Similar behavior from the chemical point of view was observed also in samples heated indirectly (figure 4), although the material degradation was rather successive, probably as the consequence of an opposite temperature gradient compared to direct heating. Severe bloating was observed in samples 4 and 5 because of the higher MoSi₂ and subsequently also SiO₂ content. Except for the outer nonconductive layer, these samples had an electrical resistivity about two or three orders of

magnitude higher in comparison with the as-prepared samples. Sample 3 was nonconductive throughout its cross-section. Such behavior of the MoSi₂-Al₂O₃ composites, that is the bloating and the considerable increase of resistivity during high temperature treatment in air, confirms the chemical instability of MoSi₂ as the only electrical conductive and gas forming component in the as-prepared composites (see equations (4-6)).

A simple calculation of the material phase composition supposing complete oxidation led to the following values in mass %: 90.9 mullite and 9.1 silica for sample 3, 62 mullite and 38 silica for sample 5. These compositions can be expected in the surface layer where no Mo-containing phases were detected.

The thermodynamic calculation for relevant temperatures showed SiO₂ as the only stable solid phase in the molybdenum disilicide - oxygen system. SiO₂ subsequently reacts with Al₂O₃ giving mullite. The presence of mullite and Mo as the major components were determined in samples 3-5 by XRD. t-MoSi₂, t-Mo₅Si₃ and α-Al₂O₃ were determined as the minor phases in samples 4 and 5 in contrast to sample 3, in which only t-Mo₅Si₃ was detected, probably due to the better oxygen transport through the porous outer part of the sample.

In the case of an insufficient oxygen amount, which may be expected in the interior of the sample, the following reactions can be taken into account



where *K* is the equilibrium constant calculated using the data in [7,8]. From a comparison of the equilibrium constant values with XRD results it may be concluded, that the oxidation in the interior of material is governed by the transport of oxygen from the surface. A glassy phase was found in interparticle pockets and on the MoSi₂-Al₂O₃ interfaces, in contrast to MoSi₂-MoSi₂ boundaries (figures 5 a-c). Hence, the interface region between MoSi₂ and Al₂O₃ is probably the main transport path of oxygen. In the composite, in which individual Al₂O₃ particles are embedded in MoSi₂ matrix, no continuous interface between MoSi₂ and Al₂O₃ exists. Therefore, the oxygen transport into the interior of the material is extremely slow. On the contrary, the double matrix MoSi₂-Al₂O₃ composite will be transformed at high temperature in air completely into the mullite-silica material after a sufficiently long heating time. The

attempt to create *in situ* a gas-tight surface layer based on the mullite-silica system was not successful.

Generally, the addition of a ceramic component to the MoSi₂ leads among others to an increase of the high temperature creep resistance, which is low for the pure MoSi₂. The creep resistance of samples 5 and 55 at 1100 °C and 1200 °C in air is documented in figure 6 together with the pure MoSi₂ [10]. The reason for the rapid degradation of creep resistance is the same as in the case of insufficient thermochemical stability of materials. The lower creep resistance of samples 5 and 55 in comparison with pure MoSi₂ is due to the presence of *continuous* Al₂O₃. The thermochemical stability of the described materials in air or oxygen-containing atmosphere can be improved by appropriate coatings.

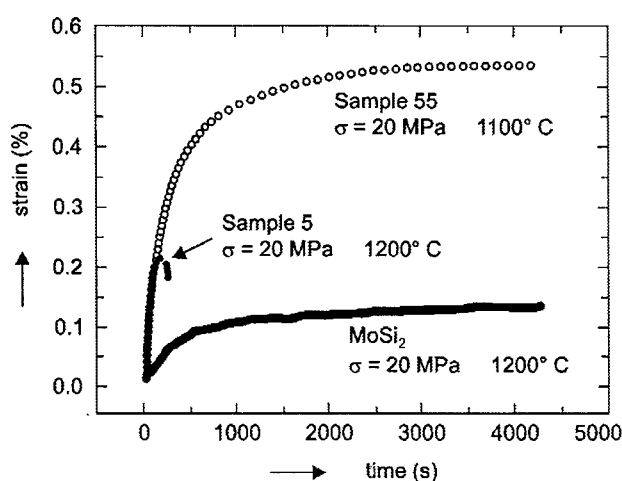


Figure 6. Creep curves of samples 5 and 55 in comparison with pure MoSi₂.

CONCLUSIONS

Homogeneous composites with a low porosity (< 1 %), consisting of MoSi₂ and Al₂O₃ interlocked matrices were prepared by reactive hot-pressing of Mo, Si and Al₂O₃ mixtures at a pressure of 30 MPa and temperature 1500 °C for 2 hours in vacuum.

The Mo and Al₂O₃ can be partially replaced by MoO₃ and Al, respectively, but it is necessary to optimize the heat treatment schedule to achieve low porosity.

The electrical resistivity of prepared materials decreases from 3.1 × 10⁻⁵ Ω m to 1.4 × 10⁻⁶ Ω m as the MoSi₂ content increases from 30 vol % to 50 vol %.

Insufficient chemical stability and creep resistance of double-matrix MoSi₂-Al₂O₃ materials were observed in air above 1100 °C, regardless of their composition.

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References

1. French J.D., Wiederhorn S.M., Petrovic J.J.: *Mater.Res.Soc.Symp.Proc.* 288, 1099 (1993).
2. Ramamurty U., Kim A.S., Suresh S., Petrovic J.J.: *J.Am.Ceram.Soc.* 76, 1953 (1993).
3. Jayashankar S., Kaufman M.J.: *J.Mater.Res.* 8, 1428 (1993).
4. Gedevisishvili S., Munir Z.A.: *Scripta Metall.Mater.* 31, 741 (1994).
5. Munz D., Fett T.: *Mechanisches Verhalten keramischer Werkstoffe*, p.11-17. Springer -Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong 1989.
6. Vasudevan A.K., Petrovic J.J.: *Mater.Sci.Eng. A155*, 1, (1992).
7. Barin I., Knacke O.: *Thermochemical properties of inorganic substances*. Springer -Verlag, Berlin, Heidelberg, New York 1973.
8. Knacke O., Kubaschewski O., Hesselmann K.: *Thermochemical Properties of Inorganic Substances II*, 2nd ed. Springer - Verlag, Berlin, Heidelberg, New York 1991.
9. Shetty D.K., Wright I.G., Mincer P.N., Clauer A.H.: *J.Mater.Sci.* 20, 1873 (1985).
10. Hvizdoš P.: private communication.

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MoSi₂ - Al₂O₃ DVOJMATRICOVÉ KOMPOZITY
PRIPRAVENÉ REAKCIAMI *IN SITU*

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Reakčným žiarovým lisovaním práškových zmesí Mo, Si a Al₂O₃ vo vákuu pri 1500 °C s výdržou 2 h sa pripravili kompozitné materiály s nízkou pórovitosťou, zložené z dvoch navzájom sa prelínajúcich matric, MoSi₂ a Al₂O₃. Časť Mo možno nahradiť MoO₃ pri súčasnej náhrade ekvivalentnej časti Al₂O₃ hliníkom. Zmena zloženia východiskovej reakčnej zmesi vyžaduje úpravu podmienok eliminácie pórovitosti. Zistilo sa, že elektrický merný odpor klesá s rastúcim obsahom molybdénsilicidu od hodnoty 3.1 · 10⁻⁵ W m pri obsahu MoSi₂ 30 obj.% na hodnotu 1.4 · 10⁻⁶ W m pri 50 obj.% MoSi₂. Chemická stabilita, resp. odolnosť proti oxidácii pripravených materiálov pri teplotách nad 1100 °C vo vzduchu je nedostatočná, pravdepodobne následkom nepretržitého transportu kyslíka pozdĺž fázového rozhrania MoSi₂ - Al₂O₃ za tvorby SiO₂ a mullitu. Z rovnakých príčin dochádza k rýchlej degradácii mechanických vlastností, čo sa demonštrovalo meraním odolnosti voči creepu. Nepodarilo sa vytvoriť *in-situ* ochrannú povrchovú vrstvu na báze mullitu a SiO₂.