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Selection of Materials for Use at Temperatures Above 1500°C in Oxidizing Atmospheres

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Abstract

The purpose of this work was to select materials for applications in oxidizing atmospheres at temperatures of a minimum of 1500°C. Several requirements had to be fulfilled, e.g. long-term oxidation resistance, low vapour pressure, high creep resistance and low gas permeability. Another important point was to avoid reactions and sintering in material combinations with silica forming materials. The investigation was based on a detailed literature screening, followed by compatibility tests at 1600°C in air with potential materials (Al_2O_3, ZrO_2, CeO_2, La_2O_3, Y_2O_3, HfO_2, $MgO{\cdot}Al_2O_3$) and $Mosi_2$ as an example of a silica-forming material. The result of these experiments was, that only Y_2O_3 and HfO_2 did not show severe reactions in contact with $MoSi_2$. Since most of the materials available did not fulfill all the requirements, some new materials were investigated: CIPed $MoSi_2$ with different additives (SiC, ZrB_2) and recrystallized SiC (RSiC) with a polymer (polysiloxane) derived $MoSi_2$-filled coating. The oxidation behaviour of these materials was evaluated by continuous thermogravimetric measurements at 1500°C over a period of 100 h in air and by detailed postexperimental investigations. © 1999 Elsevier Science Limited. All rights reserved

1 Background and Objectives

The present investigation was based on the development of a thermogravimetric equipment for measurements in oxidizing atmospheres at temperatures above 1500°C. For that, a novel weighing principle is used in this method, which is able to distinguish between the mass change of the specimen and that of the specimen carrying parts. The specimen is detached from the weighing bar for a short time and the balance is tared just before the weight is determined. Thus, it is possible to discriminate the influence of the mass change by oxidation of the weighing bar on the weighing results. After defined periods of time, the weighing cycle is repeated again and again, until the end of the exposure time is reached. The result is a quasi-continuos measurement of the weight as a function of time. Details are given elsewhere.[1]

Another very important point for the design of this equipment is the proper selection of the construction material. Some special requirements have to be fulfilled: First of all a sufficient high temperature ($T > 1500$°C) oxidation resistance is necessary. In order to avoid any influence on the measurements by reactions with the specimen, e.g. by evaporation of the material used for the reaction chamber and condensation on the specimen, the materials should have a sufficiently low vapour pressure ($< 10^{-4}$ bar at 1500°C). The parts which are in direct contact with the specimen should not show contact reactions leading to sticking effects or the formation of a liquid phase. It is obvious that there cannot be a single material, that can falfill all these requirements. For each material tested, a suitable partner for the specimen carrying parts has to be found. Another demand on some parts of the apparatus is a sufficient creep resistance at very high temperatures. Last but not least the availability of the material as a semi-product (rods, plates,...) or its fabrication at a reasonable price is an important point to be considered.

2 Results

2.1 Literature screening

In order to get an information about potential materials, a detailed literature screening was carried out on the criteria mentioned in Table 1 and on oxidation resistance. The main criterion was a suf-

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Table 1. Properties of various high-temperature materials[2]

	Evaporation	*Mechanical properties*	*Thermal shock resistance*	*Availability, price*
ZrO_2	+	○	–	+
MgO	–	+	○	+
$A1_2O_3$	○	○	○	+
SiC	○	+	+	+
$Mosi_2$	○	–	+	○
HfO_2	?	+	?	–
Y_2O_3	?	+	?	–
CeO_2	?	?	?	–
La_2O_3	?	?	?	–
Mullite ($3A1_2O_3{\cdot}2SiO2$)	?	–	○	○
Spinel ($MgO{\cdot}A1_2O_3$)	?	○	○	○

+ good, ○ sufficient,– poor, ? not known.

ficient oxidation resistance for temperatures of at least 1500°C. In the group of the non-oxide ceramics, only the silica forming materials are showing a sufficiently low parabolic rate-constant (<10 $\mu m^2 h^{-1}$). Therefore materials like HfB_2 or HfC are not present in Table 1, as well as materials with a melting point under or only slightly above 1500°C. Moreover materials are not listed, which are sensitive to moisture (e.g. CaO) or which are toxic either during their fabrication or in service (e.g. BeO and ThO_2).

Based on the data from Table 1 and the criteria mentioned above, SiC and $MoSi_2$ were selected as structural materials for the use at 1500°C and above. $MoSi_2$ shows a very good oxdation resistance up to 1700°C but only a limited creep resistance, because of the drop of strength above 1100°C. In order to improve the mechanical properties, the $MoSi_2$-matrix was reinforced with suitable particles. Recrystallized SiC (RSiC) shows an outstanding creep resistance, because of the absence of an intergranular glass-phase, which would behave in a viscous manner at longer times at such high temperatures. However, this material has only a reduced oxidation resistance. The large amount of open porosity (up to 15%) leads to an enhanced internal oxidation and, thus, to a destruction of the structure. Therefore a coating based on $MoSi_2$ was applied to increase the oxidation resistance.

2.2 Experimental investigations

The oxidation behaviour of $MoSi_2$-coated RSiC and particle reinforced $MoSi_2$ was evaluated by continuous thermogravimetric measurements at 1500°C over a period of 100 h in air, followed by detailed postexperimental investigations.

2.2.1 RSiC with $MoSi_2$/polysiloxane-derived coating

RSiC with a raw density of 2·75 $g\,cm^{-3}$, corresponding to a porosity of 15%, was coated with a polymer derived $MoSi_2$-filled coating. The reaction-pyrolysis of $MoSi_2$-filled polysiloxane, carried out by the University of Erlangen-Nürnberg, is a novel route to produce high temperature stable, oxidation resistant composites.[3] This principle has been applied for the coating of RSiC. After the material has been dip-coated in a polysiloxane/$MoSi_2$-slurry, the material is subjected to a pyrolysis process. The Si-organic precursor is converted into an oxycarbide glass (SiO_xC_y) in which $MoSi_2$ is embedded. Figure 1 shows the oxidation kinetics of such a material.

The slope of the curve of the coated material decreases after approx. 30 h. This is a hint to the formation of a closed silica-layer on the top of the coating, which was detected in the postexperimental investigations. The formation of this protective layer slows down further oxidation inside the pores of the RSiC. The uncoated material however shows an increasing mass gain, because of the high surface area exposed to further oxidation. Microprobe (EPMA) and transmission electron microscopic (TEM) investigations have shown that in the coating, besides the formation of Mo_5Si_3, nanocrystalline SiC-precipitations inside the oxycarbide glass matrix have formed.

2.2.2 Particle reinforced $MoSi_2$

Pre-investigations revealed that SiC and ZrB_2 are suitable particles for the reinforcement of $Mosi_2$.

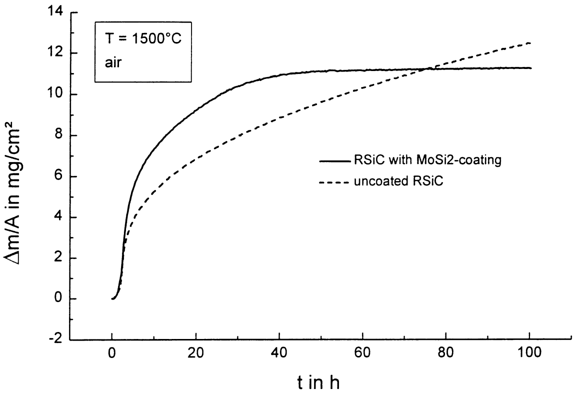

Fig. 1. Oxidation kinetics of uncoated and $MoSi_2$-polysiloxane coated RSiC.

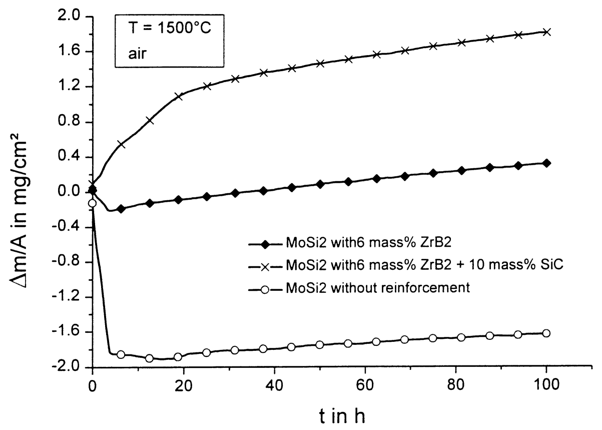

Fig. 2. Oxidation kinetics of particle reinforced Mosi$_2$.

Figure 2 shows the oxidation kinetics of Mosi$_2$ with different reinforcements manufactured by Cesiwid, Erlangen.

The high mass loss in the beginning of oxidation of the Mosi$_2$ without reinforcements can be related to the high amount of Mo_5Si_3 in the raw material. This phase shows a strong tendency toward oxidation with the formation of volatile MoO_3 and in this case the mass loss is higher than that during oxidation of the $MoSi_2$-phase. As soon as a continuous silica layer has formed, slow mass increase starts, with a rate constant typical for a silica former. Addition of ZrB_2 and SiC leads to a faster formation of a closed silica layer. Hence the mass loss in the beginning is very small or even not present. In the case of the ZrB_2-containing material, microanalytical investigations have shown the formation of a significantly thicker layer, probably consisting of a borosilicate glass, with precipitations of ZrO_2. Remarkable in this context is the absence of micro-cracks inside the composite, despite of the CTE-mismatch between the Mosi$_2$-matrix (8×10^{-6}/K) and the SiC-particles ($4{\cdot}5\times10^{-6}$/K).

2.2.3 *Refractories*

As already mentioned, it is of great importance for the operation of the high temperature TGA to avoid any contact reactions (sticking, formation of liquid phases) between specimen and the specimen carrying parts of the equipment. For this reason a suitable inert material has to be found for each specimen. Such a material can then be used either as a bulk material (e.g. disks) or as coating on RSiC-components. In the case of $MoSi_2$ as a specimen, compatibility tests were carried out with potential materials. A thin Mosi$_2$-disk was put upon these materials and exposed to 1600°C over a period of 100 h (see Table 2).

Table 2. Results of the compatibility tests performed with Mosi$_2$ (1600°C, 100 h, air)

Material	*Reaction*	*Ranking*
Al_2O_3	Adhesion	○
ZrO_2 (Ca-stab.)	Sticking, formation of a liquid phase in the contact area	–
Spinel $MgO{\cdot}Al_2O_3$)	Catastrophic reaction	–
CeO_2	Formation of a liquid phase	–
HfO_2 with TiO_2	Formation of a liquid phase	–
Y_2O_3	No severe reaction	+
La_2O_3	Formation of a liquid phase	–
HfO_2	No severe reaction	+

+ good performance, suitable; ○ restricted use only; – unsuitable. serious reactions.

As a result of these tests, only Y_2O_3 and HfO_2 are suitable for the specimen carrying parts in the case of $MoSi_2$ as a testing material.

3 Concluding Remarks

As a result of the investigations it turns out that two materials are suitable for use at temperatures above 1500°C. The first is Mosi$_2$ which exhibits excellent oxidation resistance but must be reinforced by second phase particles to increase the high temperature creep strength. In particular SiC particles are well suited from the viewpoint of oxidation resistance. The second material is RSiC which shows high creep strength but must be protected against oxidation by a Mosi$_2$-based coating. If contact reactions between one of these materials and other materials have to be avoided it would be Y_2O_3 and HO_2 which are virtually inert in contact with silicon surfaces.

References

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