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Ceramics International 28 (2002) 93–97

CERAMICS
INTERNATIONAL

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Thermal properties of the plasma-sprayed $MgTiO_3$–$CaTiO_3$ and $CaTiO_3$

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Received 25 January 2001; received in revised form 7 April 2001; accepted 20 May 2001

Abstract

The thermal diffusivity and thermal conductivity of plasma-sprayed materials $MgTiO_3$–$CaTiO_3$ and $CaTiO_3$ were investigated over the range of 20–500 °C using the flash method. The thermal diffusivity of both materials decreases with increasing temperature. The thermal conductivity of both materials is nearly the same; with increasing temperature it first decreases and then it increases. The thermal diffusivity was measured at room temperature after annealing up to 800 °C. This value increased after annealing above 600 °C. © 2002 Published by Elsevier Science Ltd and Techna S.r.l.

Keywords: C. Thermal properties; Coatings; $CaTiO_3$; $MgTiO_3$–$CaTiO_3$; Plasma spraying

1. Introduction

Coating by plasma spraying is one of fastest growing industrial technologies in the last 20 years. Most coatings consist of oxide ceramics, such as Al_2O_3 or ZrO_2. Such coatings often exhibit unique and unusual properties related to their complex phase composition and microstructure.

Plasma sprayed coatings exhibit highly anisotropic microstructure with a large content of amorphous phase and small content of recrystalled phase. Generally the deposits are composed of crystallographic phases different from the original feedstock materials [1–3].

Beside the silicate group there are many other materials e.g. titanates which are not routinely used yet for plasma spraying. Titanates in general, represent a wide and important group of technical ceramics. Interesting members of this group are perovskites $M^{II}TiO3$, which are face-centered cubic (M = Ca, Ba, Sr) or trigonal (M = Fe, Co, Ni, Mn, Mg) depending on chemical composition. From these were chosen two materials for plasma spraying. $CaTiO_3$, is relatively chemically simple and inexpensive material, and more complex mixture of geikeilite–perovskite $MgTiO_3$–$CaTiO_3$. This material with Mg:Ca ratio equal to 94:6 exhibits permitivity independent of temperature [4]. The basic structure of $CaTiO_3$ is cubic but in most cases the structure is deformed to orthorhombic or monoclinic. Geikeilite $MgTiO_3$ has rhombohedral structure.

Plasma sprayed ceramic coatings are often used in technical applications at higher temperatures. Therefore, the knowledge of thermal properties, especially the thermal conductivity, is very important.

The aim of this work was to determine the temperature dependence of the thermal diffusivity and thermal conductivity for plasma sprayed $MgTiO_3$–$CaTiO_3$ and $CaTiO_3$ materials.

2. Experimental details

Samples were manufactured using a high-throughput water-stabilised plasma spray system WSP PAL 160 (Institute of Plasma Physics, Prague, Czech Republic). The water in this system is used for stabilizing the electric arc and as the medium from which the plasma is created. This system operates at about 160 kW arc power and can process large amounts of material per hour.

The materials for this study were pre-processed by milling and sieving to suitable grain size. Plasma spraying

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PII: S0272-8842(01)00062-1

was done on two different steel substrates. Steel plates of size 60×70×8 mm (determination of density, porosity and coefficient of thermal expansion-CTE) and steel pads of diameter 16×2.5 mm thick (determination of thermal diffusivity) were used. The coatings on the steel plates 60× 70×8 mm were about 2.5 mm thick and were stripped after spraying from the plates by a patented process. The resulting free-standing coatings were cut with a diamond saw into smaller pieces as necessary for measuring (density, porosity and CTE). The deposits on the 16×2.5 mm steel pads were about 0.7 mm thick. To obtain the optimum thickness of the coatings, the surface of the sample was ground and polished to the thickness about 0.4 mm. Surfaces of the coatings on steel pads were blackened by carbon black.

The thermal diffusivity was measured by the flash method for two layers [5]. Measurements were made with the apparatus described earlier [6,7]. For heating a Xe pulse lamp with a pulse length of 1 ms was used. Thermal diffusivity was measured up to 500 °C in argon. Coating volume density and open porosity were measured by the Archimedean (water immersion) method and density measurement using a He pycnometer (Accupyc 1330, Micromeritics, USA). The linear thermal expansion was measured using the Netzsch 402E dilatometer. The characteristics of these powders and coatings are listed in Table 1. The dependence of the density on temperature was calculated from density at room temperature and the thermal expansion. Specific heat was measured by a differential calorimeter (Perkin Elmer 7, Perkin Elmer, USA) at the Department of Dielectrics, Institute of Physics AVCR, Prague, Czech Republic. Thermal conductivity was calculated as product of thermal diffusivity, density and specific heat.

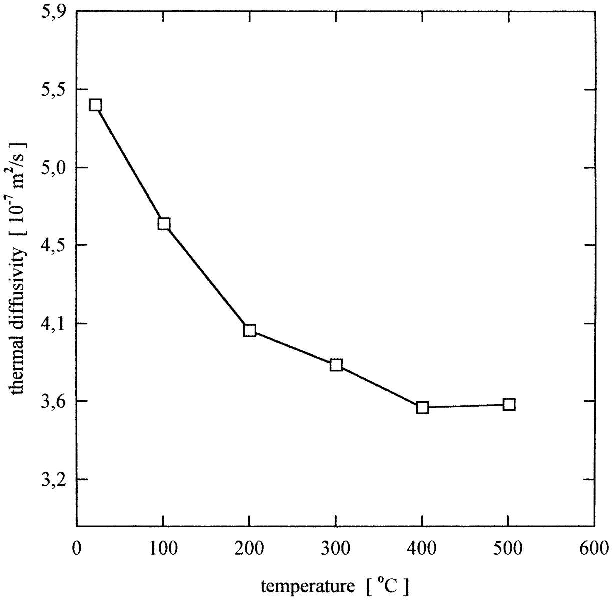

Fig. 1. The temperature dependence of the thermal diffusivity of $MgTiO_3$–$CaTiO_3$ deposits.

3. Results and discussion

3.1. $MgTiO_3$– $CaTiO_3$

Fig. 1 shows the temperature dependence of the thermal diffusivity $MgTiO_3$–$CaTiO_3$ deposits. The dependence of the specific heat on temperature is described in Fig. 2a. It shows that the specific heat increases with the increasing temperature. The density decreases with the

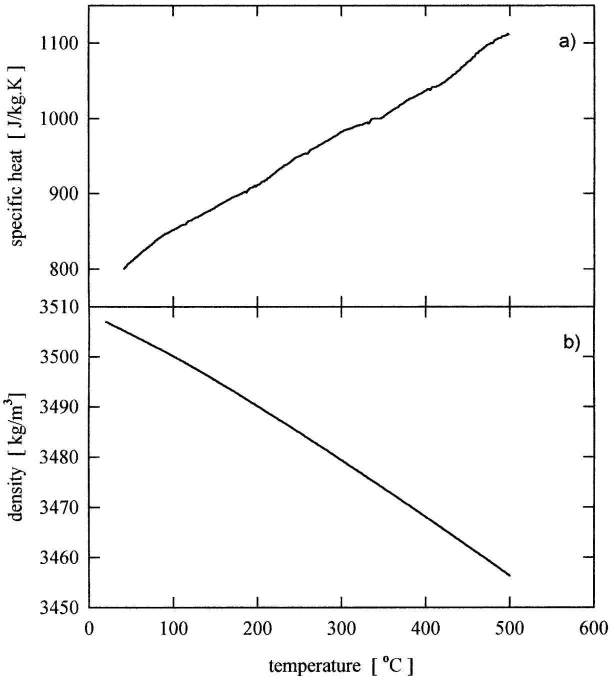

Fig. 2. The temperatue dependence of (a) the specific heat and (b) the density of $MgTiO_3$–$CaTiO_3$ deposits.

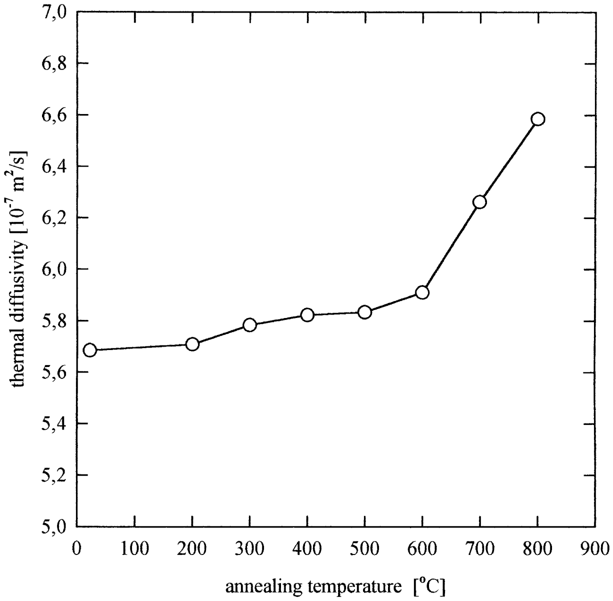

Fig. 3. The temperature dependence of the thermal conductivity of $MgTiO_3$–$CaTiO_3$ deposits.

Table 1
Comparison of the density of the feedstock powder with the resulting coating density, coating volume density, open porosity and coefficient of the thermal expansion (CTE) over the range 250–600

Material	Feedstock density (kg/m^3)	Coating density (kg/m^3)	Coating volume density (kg/m^3)	Average open porosity (%)	CTE (10^{-6} K^{-1})
$MgTiO_3$–$CaTiO_3$	3807	3735	3549	3.502	$9.68_{(250–600)}$
$CaTiO_3$	4016	3996	3684	6.95	$13.4_{(250–600)}$

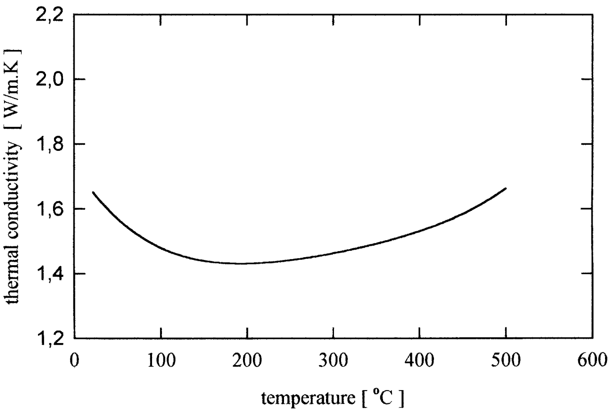

Fig. 4. The effect of annealing on thermal diffusivity at room temperature of $MgTiO_3$–$CaTiO_3$.

increasing temperature as in Fig. 2b. The temperature dependence of the thermal conductivity of $MgTiO_3$–$CaTiO_3$ is shown in Fig. 3. In the mathematical model of Larson and Koyama [5] the interface between two layers is characterised by perfect thermal contact therefore the resulting thermal conductivity values include the value for the magnitude of the interfacial thermal barrier.

To measure the effect of annealing on the thermal diffusivity of the plasma sprayed coatings, samples were annealed at various temperatures. Samples were annealed for 2 h in a furnace in air with identical rates of heating and cooling (5 K/min). After annealing the surface of the sample was blackened and measurement was made at room temperature. These results are in Fig. 4. For annealing below 600 °C a little increase of the thermal diffusivity was observed, above this temperature a large increase occurred. After annealing to about 800 °C the thermal diffusivity increased about 17%. This result suggests that annealing above 600 °C causes irreversible changes. X-ray diffraction of this plasma sprayed material [8] shows that, after spraying, $MgTiO_3$, Mg_2TiO_4 and $MgTi_2O_5$ are found. After annealing of this material up to 1250 °C/2 h only $MgTiO_3$ and $CaTiO_3$ are found. At the same time relatively small porosity change are observed (as sprayed 5.8%, after annealing 680 °C/2 h~6.2%, 1250 °C/2 h~5.4%). These results suggests that annealing of the plasma sprayed $MgTiO_3$–$CaTiO_3$ materials causes complex changes and that it is impossible from these results to decide the unambiguous cause of the thermal difussivity increase. Taylor [9] studied influence of heat treatment of plasma-sprayed YSZ on the thermal diffusivity and found an increase of the thermal diffusivity with both the increasing temperature and annealing time.

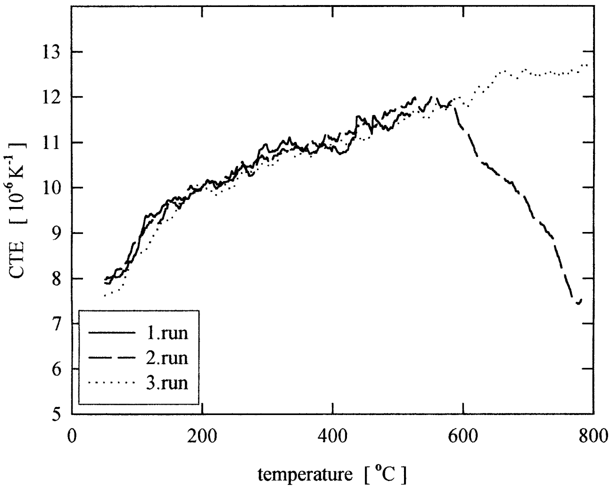

Fig. 5. The temperature dependence of the coefficient of thermal expansion (CTE) of $MgTiO_3$–$CaTiO_3$ deposits.

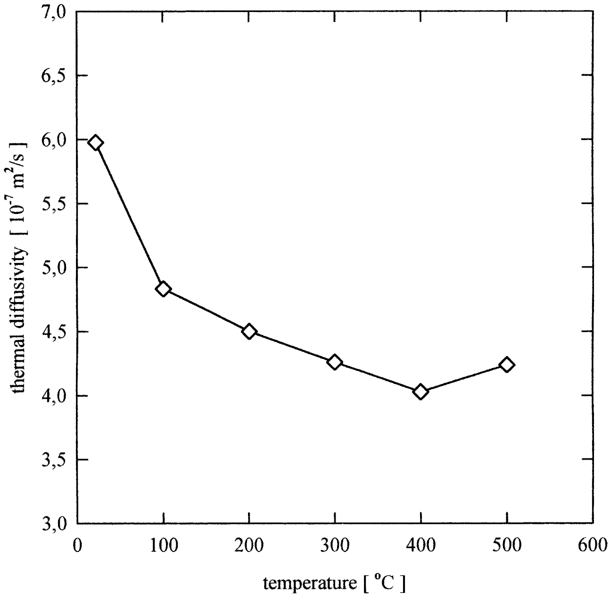

Fig. 6. The temperature dependence of the thermal diffusivity of $CaTiO_3$ deposits.

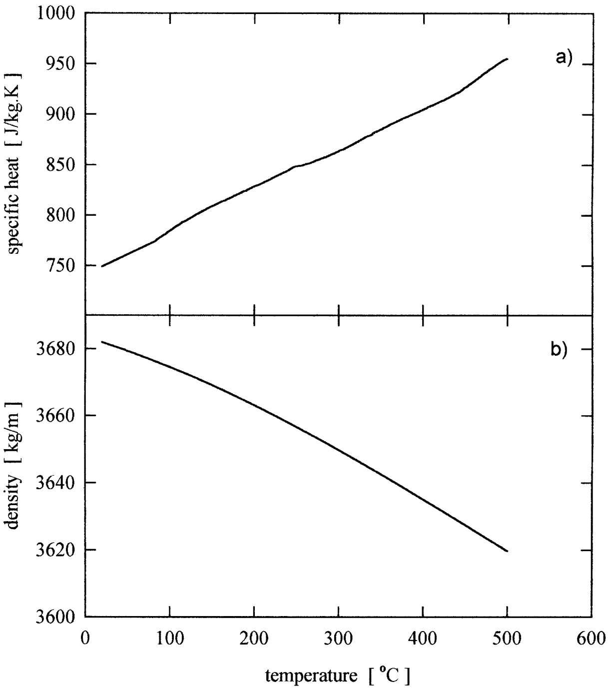

Fig. 7. The temperature dependence of (a) the specific heat and (b) the density for $CaTiO_3$ deposits.

It can be expected that metastable structures exist in the as sprayed material up to 600 °C since plasma sprayed deposits are created by very fast cooling (10^3–10^6 K/s) of particles impacted to substrates [10]. The results indicate that the decomposition of metastable structures occurs during heating above this temperature. This assumption was confirmed by measurement of the temperature dependence of CTE. The results of these measurements are shown in Fig. 5. In this figure there are three curves: the first runs up to 500 °C, the second runs up to 800 °C and the third run repeated a measurement up to 800 °C. All dependencies are practically the same between room temperature and about 500 °C. The first heating of the sample above 500 °C shows a large decrease of CTE, which starts at ~590 °C and continues up to 800 °C. This indicates that irreversible changes occur. Repeated measurement of CTE did not show this effect, suggesting that all changes occurred during the first cycle in which the temperature reached 500–800 °C.

3.2. $CaTiO_3$

The temperature dependence of the thermal diffusivity of $CaTiO_3$ deposits is shown in Fig. 6. This dependence has a similar character as for $MgTiO_3$–$CaTiO_3$ deposits. The temperature dependence of (a) the specific heat and (b) the density for $CaTiO_3$ deposits is in Fig. 7. The thermal conductivity of this plasma sprayed material (Fig. 8) is the same as for plasma sprayed $MgTiO_3$–$CaTiO_3$ in the whole temperature range. The effect of annealing on thermal diffusivity at room temperature of $CaTiO_3$ is nearly the same as for the $MgTiO_3$–$CaTiO_3$ and is in Fig. 9.

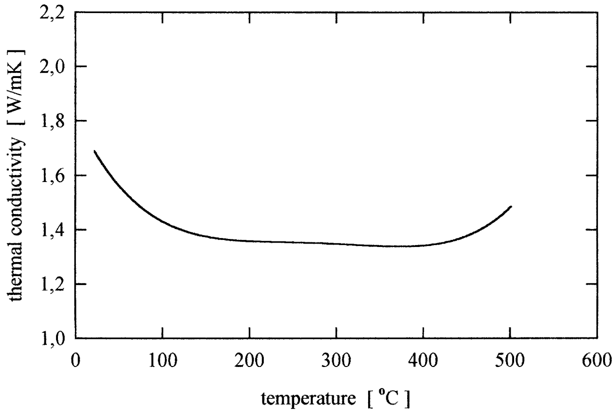

Fig. 8. The temperature dependence of the thermal conductivity of $CaTiO_3$ deposits.

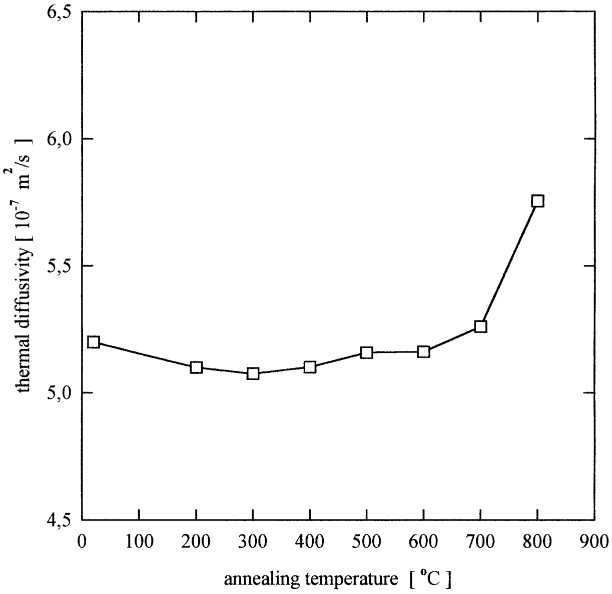

Fig. 9. The effect of annealing on thermal diffusivity at room temperature of $CaTiO_3$.

4. Conclusions

It was found that the thermal diffusivity of the plasma sprayed $MgTiO_3$–$CaTiO_3$ material decreases with increasing temperature. The thermal conductivity decreases up to 200 °C and increases above this temperature. During annealing of the deposits at various temperatures below 600 °C, the thermal diffusivity does not significantly change, above this temperature it increases. Changes occurring in this material above 600 °C were also confirmed by dilatometry. CTE shows sintering/phase change in the temperature range of 590–800 °C. This irreversible change was not found during repeated run. The changes occurring in plasma-sprayed deposit $MgTiO_3$–$CaTiO_3$ during heat treatment are complex and are under further investigation.

The thermal diffusivity of $CaTiO_3$ decreases with increasing temperature. The thermal conductivity decreases up to 250 °C and further increases. The thermal diffusivity and thermal conductivity of $CaTiO_3$ were nearly the same as in $MgTiO_3$–$CaTiO_3$ deposit. The effect of annealing on the thermal diffusivity at room temperature of $CaTiO_3$ is nearly the same as for $MgTiO_3$–$CaTiO_3$.

Acknowledgements

This work was supported by the Czech Grant agency under grant No. 104/99/0304. Further authors would like to acknowledge help with Specific heat measurements by our colleagues from Institute of Physics Department of Dielectric AVCR, Prague, Czech Republic.

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