Thermophysical properties of ceramic substrates with modified surfaces

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Abstract

Within this study we have studied the laser induced changes of the thermophysical properties using a laser supported modification process. Metal-ceramic composites have been produced by a laser dispersing process. Two types of substrates have been included, namely pure Al₂O₃ and Al₂O₃ reinforced with 10-wt% ZrO₂. As a modifying material during the laser process hard metal powders like TiN, WC and W have been applied in order to produce a metal-ceramic composite with metal concentration between 30 to 50 %. Standard measurement techniques like the Laser-Flash method and differential scanning calorimetry (DSC) have been used to measure the thermal diffusivity and the heat capacity of the ceramics before and after the laser processing. These properties have been evaluated within a temperature range from room temperature up to 1400 °C. The experimental results show that the effective thermal conductivity will be enhanced within the laser modified region. The increase of this heat transport property due particle dispersion into the ceramic matrix depends on the thermal conductivity of the second phase material.
Introduction

Single phase commercial ceramics suffer regarding their poor thermophysical and mechanical properties which restricts their technical application. Introduction of a second phase, which can be selected in order to optimize these properties, can lead to a reinforcement of the mechanical strength and also to an enhancement of the thermal conductivity. Different thermal processing techniques can be applied to achieve this property modification by producing ceramic-metal composites with metal particles embedded in a continuous ceramic matrix. Among these methods laser supported modification techniques have the advantage that mechanical and tribological properties [1,2] can be improved, thermal and electrical conductance can be adjusted [3,4] while the property modifications are restricted to a localized surface area leaving the bulk of the ceramic in its original state.

Within this paper we report about our studies on the effect of a metal particle phase dispersed into the surface of a ceramic on the effective thermal conductivity of the composite using a laser modification process. The thermophysical properties of the original ceramic substrates were measured as a function of the temperature from room temperature up to 1400 °C. Namely, the thermal expansion, the specific heat and the thermal diffusivity were determined using standard measurement techniques.

Experimental

Two different ceramic substrate materials were included within this study (see Table I). An alumina substrate with a small porosity of 5% and an zirconia reinforced alumina consisting of 10 wt.-% ZrO₂ and 90 % Al₂O₃. The thermal conductivity of the as-received materials were determined by measuring the thermal diffusivity with the laser-flash method (LFA 427, Netzsch) and the heat capacity by the DSC-technique (DSC404, Netzsch). For the correction of the temperature dependent density values due to thermal expansion, the relative length change was measured with a double push-rod dilatometer (ED402, Netzsch). All measurements were performed within a temperature range from room temperature (RT) up to 1400 °C.

The surface of the ceramic substrate were modified using a laser process [1,4]. The beam of a high power CO₂-laser were scanned across the surface of the sample with a laser power adjusted in order
to melt the substrate locally. Hard metal particles were introduced into the melt pool using an injection technique or a pre-placed powder coating. After the solidification a ceramic-metal composite has been developed with properties depending on the hard metal powder used within the process. Two different hard metal powders were included in this study, namely WC and TiN. For the laser processing a rectangular beam profile of 6x1 mm² were used with a typical laser power of 240 W and a scanning velocity of 250 mm/min. During the process the substrate was heated to a temperature of 1500 °C to avoid a thermal induced development of cracks within the ceramic matrix. The substrate were modified down to a dispersing depth of about 400 – 500 μm with a hard metal volume fraction of 30 % for WC and 50 % for TiN.

The cross-sectional microstructures of the laser modified substrates show that the TiN, particles which appear as white in the microscope image, are embedded in the grey ceramic matrix.

Table I: Ceramic substrate materials

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃ (AL24; Friatec)</th>
<th>90Al₂O₃-10ZrO₂ (SN80; Ceramtec)</th>
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</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>3.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>&lt; 5</td>
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</table>

Fig. 1: Microstructures of the laser modified ceramics: Al₂O₃ substrate (left) and 90Al₂O₃-10ZrO₂ (right) substrate laser modified with TiN
Results and discussion

The thermal expansion data for the ceramic substrates used within this study are shown in Fig. 2. The Al24 ceramics show typical values for polycrystalline alumina [5] starting from $6.0 \cdot 10^{-6} \text{ K}^{-1}$ at room temperature up to $10 \cdot 10^{-6} \text{ K}^{-1}$ at 1500 °C. The CTE of the zirconia reinforced sample behaves very similar up to a temperature of about 750 °C. Above this temperature the CTE values start to deviate from the Al24 values, running through a local minimum at 950 °C and increases again for temperatures higher than 1100 °C. This specific behaviour is due to a volume change within the unit cell which is associated with the monoclinic to tetragonal transformation in ZrO$_2$ [6].

The thermal conductivity of the as-received ceramics are shown in fig. 3 as a function of temperature. The thermal conductivity values decrease with increasing temperature and follow approximately a $1/T$ behaviour which is typical for the most pure dielectric materials [7,8] in the temperature range above room temperature. In the Al24 sample the thermal conductivity value is reduced compared to the corresponding value of pure dense alumina [8,9] which is about 33 W/mK at ambient temperatures. This reduction is due to the porosity which is approximately 5 % in Al24. The thermal conductivity of the zirconia reinforced alumina SN80 is significantly higher than the Al24 values over the whole temperature range, although the SN80 ceramic contains 10 wt.-% of the poorly conducting ZrO$_2$-
An explanation of this effect may be that a pore volume of 5 % in Al24 reduces the thermal conductivity more than 10 wt.-.% of a second phase with low heat conduction incorporated in an overall dense alumina matrix.

The thermal conductivity of the laser modified ceramics is shown in fig. 4 as a function of the temperature. The data were obtained from laser flash measurements of the effective thermal diffusivity on laser modified sample of a total thickness of about 1.5 mm. The thickness of the laser dispersed region was between 0.4 to 0.5 mm. The thermal conductivity values of the laser modified zone were extracted using a two-layer model [10]. For the calculation procedure based on the two-layer model the thermal conductivity values of the non-modified ceramics were considered along with the measured thickness ratio of the non-modified to modified region. All modified ceramics exhibit a higher thermal conductivity compared to the as-received materials. The enhancement in the thermal conductivity values is highest at low temperature decreases with rising temperatures. But even at the highest temperature significantly increased values can be observed.

Among the laser modified ceramics those substrates, which were modified with WC particles, show higher thermal conductivity values than the ceramics dispersed with TiN particles for all measured temperatures despite the fact that the volume fraction of WC is about 30 % whereas it is approximately
50 % for TiN particles. Qualitatively, this can be explained by the higher thermal conductivity of WC, which is at room temperature between 80 – 129 W/mK [11] for bulk tungsten carbide, compared to 22-28 W/mK for bulk titanium nitride [12].

Fig. 4: Thermal conductivity of the laser modified ceramics

However, using the established models for the effective thermal conductivity in heterogeneous materials [13,14] the increasing thermal conductivity due to dispersion of TiN particles in SN80 and Al24 can not be explained if one assumes that the thermal conductivity of TiN is within the range given in the literature [12]. Since the corresponding room temperature values of Al24, SN80 and TiN are very close, it would be expected that the thermal conductivity of the ceramic-metal composite would not change significantly. This is in contradiction to the experimental results which showed an increasing effective thermal conductivity over the whole temperature range. It seems to be that the thermal conductivity of bulk TiN, which were mostly performed on sintered samples with finite porosity [12] and with a small amount of a TiOx, are representative for the thermal conductivity of a single particle.

Similar considerations can be made for WC as dispersing phase. Calculations based on the model of Hasselmann et. al. [13] lead to the result that the effective thermal conductivity at room temperature is about 41 W/mK in the WC dispersed Al24 ceramic and about 50 W/mK in WC modified SN80 using
the measured values of the as-received ceramics and a thermal conductivity value of 125 W/mK for the WC thermal conductivity. These estimated values are also significantly below the measured ones and the explanation for this difference may be the same as in the case of the TiN modified samples.

**Conclusion**

Within our study on the effect of laser induced dispersing of different hard metal powders on the effective thermal conductivity of ceramic substrates the experimental results show the modification process leads to a significant enhancement of the thermal conductivity within the dispersed region. However, the measured effective thermal conductivity values are much higher than the model predictions based on thermal conductivity of the non-modified sample and the corresponding bulk values of the dispersed phase materials TiN and WC. As a probable explanation for the observed differences can be considered that bulk values of these hard metals are not reflecting the inherent thermal conductivity of the material but a reduced effective thermal conductivity which may be due to internal thermal barriers.

**Acknowledgements**

The author wish to thank K. Poser and S. Schreck for the preparation of the laser modified ceramic samples. These studies were supported by the Deutsche Forschungsgemeinschaft (DFG) in context with the Sonderforschungsbereich 483 “High performance sliding and friction systems based on advanced ceramics”.

**Literature**


