International Journal of Thermophysics, Vol. 28, No. 5, October 2007 (© 2007)
DOI: 10.1007/s10765-006-0142-2

Thermophysical Properties of Ceramic Substrates with Modified Surfaces[1]

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Laser induced changes of thermophysical properties using a laser supported modification process have been studied. Metal–ceramic composites have been produced by a laser dispersing process. Two types of substrates have been included, namely, pure Al_2O_3 and Al_2O_3 reinforced with 10 mass% ZrO_2. As a modifying material during the laser process, hard metal powders like TiN and WC have been applied in order to produce a metal–ceramic composite with a metal concentration between 30 and 50%. Standard measurement techniques such as 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 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 to particle dispersion into the ceramic matrix depends on the thermal conductivity of the second-phase material.

KEY WORDS: composites; effective thermal conductivity; heterogeneous materials; laser processing

1. INTRODUCTION

As a result of their poor thermophysical and mechanical properties, the use of single-phase commercial ceramics in technical applications is restricted. The introduction of a second-phase, which can be selected in order to optimize these properties, can lead to a reinforcement of

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[1] Paper presented at the Seventeenth European Conference on Thermophysical Properties, September 5–8, 2005, Bratislava, Slovak Republic.

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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 and the thermal and electrical conductances 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.

In this article, we report 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 temperature from room temperature to 1400°C. Namely, the thermal expansion, the specific heat, and the thermal diffusivity were determined using standard measurement techniques.

2. 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 mass% ZrO_2 and 90 mass% Al_2O_3 were studied. 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 with the DSC technique (DSC404, Netzsch). For correction of the temperature-dependent density values due to thermal expansion, the relative length change was measured with a double push-rod dilatometer

Table I. Properties of the Ceramic Substrate Materials and Additives

	Substrates		*Additives*	
	Al24 Al_2O_3 (Friatec GmbH)	SN80 $90Al_2O_3$–$10ZrO_2$ (CeramTec GmbH)	TiN	WC
Density ($g{\cdot}cm^{-3}$)	3.5	4.1	5.43	15.8
Melting point (°C)	2040	–	2950	2800
Liquidus (°C)	–	2040	–	–
Solidus (°C)	–	1870	–	–
Porosity (%)	5	0	–	–
Grain/Particle size (μm)	10	1.5	13	6

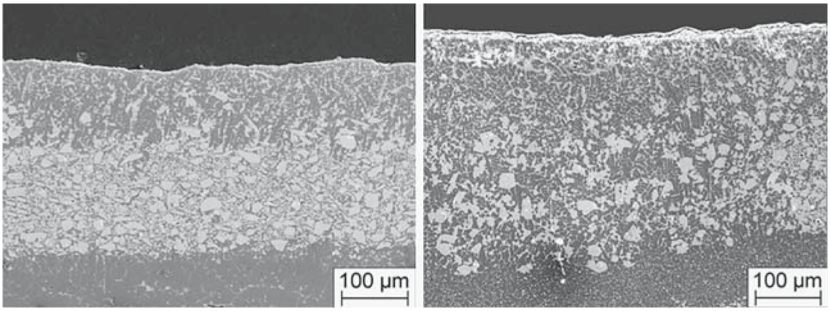

Fig. 1. Microstructures of the laser modified ceramics: Al_2O_3 substrate (left) and $90Al_2O_3$–$10ZrO_2$ (right) substrate laser modified with TiN and WC, respectively.

(ED402, Netzsch). All measurements were performed within a temperature range from room temperature (RT) to 1400°C.

The surface of the ceramic substrate was modified using a laser process [1,4]. The beam of a high power CO_2-laser was 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 in 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 $6 \times 1\,\text{mm}^2$ was used with a typical laser power of 240 W and a scanning velocity of $250\,\text{mm}\cdot\text{min}^{-1}$. During the process, the substrate was heated to a temperature of 1500°C to avoid thermal-induced development of cracks within the ceramic matrix. The substrate was 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 (Fig. 1) show that the hard metal particles, which appear as white in the microscope image, are embedded in the grey ceramic matrix.

3. RESULTS AND DISCUSSION

The thermal expansion data for the ceramic substrates used in this study are shown in Fig. 2. The Al24 ceramics show typical coefficient of thermal expansion (CTE) values for polycrystalline alumina [5] starting from $6.0 \times 10^{-6}\,\text{K}^{-1}$ at room temperature up to $10 \times 10^{-6}\,\text{K}^{-1}$ 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

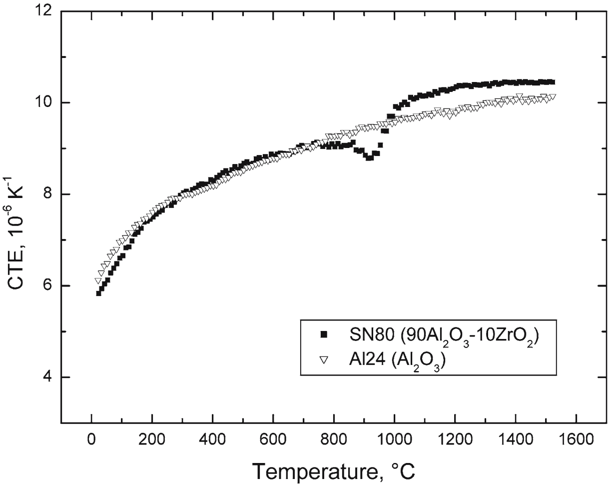

Fig. 2. Coefficient of thermal expansion for Al24 and SN80.

begin to deviate from the Al24 values, reaching a local minimum at 950°C, and again increase for temperatures higher than 1100°C. This specific behavior 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 is shown in Fig. 3 as a function of temperature. The thermal conductivity values decrease with increasing temperature and follow approximately a $1/T$ behavior which is typical for the most pure dielectric materials [7,8] in a temperature range above room temperature. For the Al24 sample, the thermal conductivity value is lower than the corresponding value for pure dense alumina [8,9] which is about $33\,W \cdot m^{-1} \cdot K^{-1}$ at ambient temperature. This difference is due to the porosity which is approximately 5% in Al24. The thermal conductivity of the zirconia reinforced alumina SN80 is significantly higher than Al24 values over the whole temperature range, even though the SN80 ceramic contains 10 mass% of the poorly conducting ZrO_2-phase. An explanation of this effect may be that a pore volume of 5% in Al24 reduces the thermal conductivity more than 10 mass% of a second-phase with low heat conduction incorporated in an overall dense alumina matrix.

The thermal conductivities of the laser modified ceramics are shown in Fig. 4 as a function of temperature. The data were obtained from laser-flash measurements of the effective thermal diffusivity on a laser modified sample with a total thickness of about 1.5 mm. The thickness of the

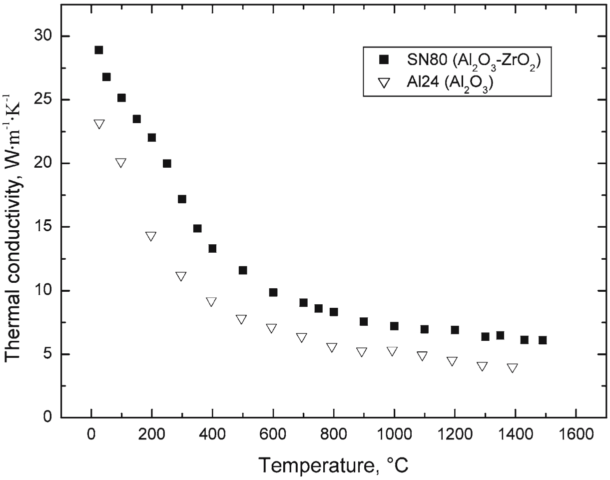

Fig. 3. Thermal conductivity of the as-received ceramic substrates.

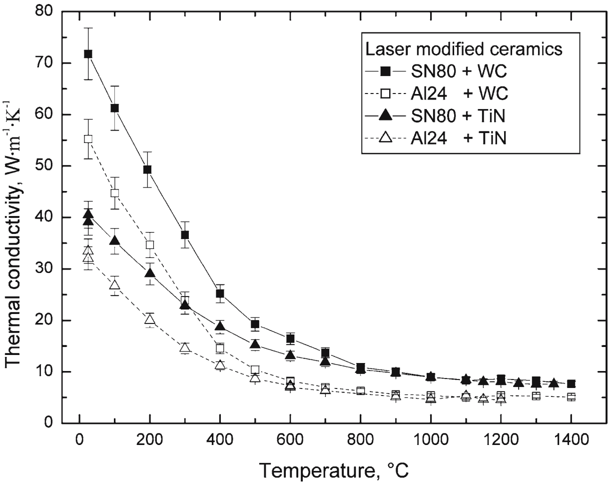

Fig. 4. Thermal conductivity of the laser modified ceramics.

laser dispersed region was between 0.4 and 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 and decreases with increasing temperature. Even at the highest temperature, a significant increase in the values can be observed.

Among the laser modified ceramics, the substrates, which were modified with WC particles, show higher thermal conductivity values than the ceramics dispersed with TiN particles at all measured temperatures although the volume fraction of WC is about 30% compared to approximately 50% for TiN particles. Qualitatively, this can be explained by the higher thermal conductivity of WC, which is between 80 and $129\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ [11] at room temperature for bulk tungsten carbide, compared to 22–28 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ for bulk titanium nitride [12].

However, using the established models for the effective thermal conductivity in heterogeneous materials [13,14], the increase in thermal conductivity due to dispersion of TiN particles in SN80 and Al24 cannot 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 increase in the effective thermal conductivity over the whole temperature range. It seems that the thermal conductivity results for bulk TiN given in Ref. 12, which were performed mostly on sintered samples with finite porosity and with a small amount of a TiO_x , are not representative for the thermal conductivity of a single particle.

Similar considerations can be made for WC as a 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 $41\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ in the WC dispersed Al24 ceramic and about $50\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ in WC modified SN80 using the measured values of the as-received ceramics and a thermal conductivity value of $125\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ for the WC thermal conductivity. These estimated values are also significantly below the measured results and the explanation for this difference may be the same as in the case of TiN modified samples.

4. CONCLUSION

In this study, the effect of laser induced dispersing of different hard metal powders on the effective thermal conductivity of ceramic substrates, the experimental results show that 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 the thermal conductivity of the non-modified sample and the corresponding bulk values of the dispersed phase materials, TiN and WC. A possible explanation for the observed differences can be considered that bulk values of these hard metals do not reflect the inherent thermal conductivity of the material but a reduced effective thermal conductivity which may be due to internal thermal barriers.

ACKNOWLEDGMENTS

The author wishes 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."

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