PREPARATION AND CHARACTERIZATION OF CERAMICS LASER ALLOYED WITH WO_3 AND CUO NANOPOWDERS

S. Schreck, S. Sachse, M. Rohde

Forschungszentrum Karlsruhe GmbH, Institute for Materials Research I,
Hermann von Helmholtzplatz 1, 76344 Eggenstein-Leopoldshafen, Germany

ABSTRACT

A surface layer of a ceramic substrate can be modified by introducing a second phase into a melt pool generated locally by a laser beam. CuO, WO_3 powders with nano-sized particles were used to alloy alumina and a glass ceramic LTCC (Low Temperature Co-fired Ceramic). Depending on the process parameters the nano-particles were melted during the laser process and solidified during cooling in the ceramic matrix. As a result a composite with complex multiphase micro-structure was developed with particle agglomerates, small crystals as well as grains covered with reaction phase, in parts with typical length scales down to the submicron range. Also the geometry of the modified area could be controlled by the process parameters.
A significant change of properties could be established for the laser alloyed tracks. Especially the thermal and elec-trical properties were changed in comparison to that of the ceramic substrate. The developed composites showed a measurable electrical conductivity with a negative temperature coefficient for the resistivity. Therefore, the resistivity decreases with increasing temperature, which is typical for a thermally activated conduction mechanism as in semiconductors. The thermal conductivity could be increased to about 20% for CuO- and up to 70% for WO_3-powder compared to the unmodified LTCC-substrate.

1. INTRODUCTION

The use of commercial ceramics is restricted because of their thermophysical and mechanical properties. These material properties can be changed by introducing a second phase into the ceramic matrix. For this, different thermal processing techniques can be used. The laser supported technique has the advantage that the modification of the properties can be restricted to a defined area. The embedding of the second phase can lead to a reinforcement of the mechanical strength, to an improvement of the tribological properties of the ceramic surfaces or a local increasing of the thermal and electrical conductivity, while the properties of the bulk of the ceramic are in their original state [1,2]. Compared to thin- and thick film technology which are used for ceramic metallization, no lithographic process steps are necessary.

The laser supported modification of ceramics is based on a heating of the ceramic up to the melting temperature and the powdered additive is introduced into the melt pool. After solidification a composite material is developed. If the additives are melted during the process , it is called laser-alloying. Otherwise if the particles persist, the process is called laser-dispersing.

The absorption of the laser wavelength and the focus diameter as well as the laser power and the scanning velocity determine the width and the depth of the melt pool which can range from several microns up to 1000 µm. The laser process is characterized by a rapid heating, a short-time melting and a rapid solidification. The commingling of the additive and the ceramic melt is governed by capillary forces and the Marangoni convection which is excited by the temperature gradients and by the surface tension and the viscosity [3]. In addition wettability of the ceramic plays an important role in case of melted additives.

Several investigations were made using metal additives like W and Cu to produce thermal and electrical conducting lines in Al_2O_3, LTCC or Cordierite ($2MgO.2Al_2O_3.5SiO_2$) [4,5]. A significant increase of thermal conductivity could be established using microscaled powders and the electrical resistance of the fabricated line could be adjusted from semi-conducting to metallic behaviour depending on the thermal treatment.

Within this paper we report on our studies on the effect of nanosized powders alloyed into the surface of alumina and LTCC. Because of the strong oxidation reac-tion for metal nano-particles, we used only metal-oxid additives of WO_3 and CuO. It can be expected from published data of the properties of nano-scaled composite materials [6-9] that laser surface modifying with nano-particles leads to completely different characteristics for the microstructure and the properties compared to the use of powders with particles sizes in the range of some µm.

 ISBN :978-2-35500-003-4

2. EXPERIMENTALS

A CO_2 -laser (wavelength λ=10,6 µm) was used to modify the ceramic substrates. The laser was operated in its cw-mode and the laser power could be varied between 10-400 W. The laser beam was moved across the substrate with a defined scanning velocity and could be focussed in a circular diameter of about 300µm for producing small tracks or a 6 mm-wide line for producing extended areas.

The second phase was added using the so called precoating process. In a first step a powder suspension was applied to the substrate surface and after drying a defined precoating thickness was adjusted. Afterwards the laserbeam was scanned across the precoated substrate whereby the precoating and the surface of the substrate were melted locally. The principle of the process is shown in Fig.1

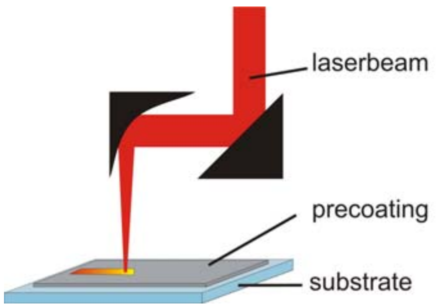

Fig.1.: Principal sketch of the laser supported precoating process.

Following this fabrication route a commercial alumina (Al_2O_3, Al24 from Friatec) and a commercial LTCC (low temperature co-fired ceramics, Du-Pont 951 based on Al_2O_3-SiO_2-PbO) [10] were modified. The applied nanoscaled powders were made of Tungsten(VI)oxide (WO_3, Sigma Aldrich) with a particle size <150 nm and Copper(II)oxide (CuO, Sigma Aldrich) with an average particle size of 30 nm. The precoating thickness was set to 200 µm. To reduce thermal stress during the laser process, the alumina substrates with a thickness of 8mm were preheated up to 1100 °C. Because of the good thermal shock resistance of the LTCC substrates (thickness 1mm) the preheating temperature was set in this case to only 800 °C. The laser power was varied in the range of 10-30 W for the focus with the circular diameter and between 100-150 W for the rectangular focus. In some experiments the laser beam was slightly defocussed. Laser scanning speed was set to 250, 500 or 1000 mm/min.

After laser processing, i.e. after solidification and cooling different characterization methods were applied to the modified ceramic substrates. Microstructure was studied using light and scanning electron microscopy (SEM) accompanied by energy dispersive x-ray analysis (EDX) for a qualitatively examination of the chemical composition.

The temperature dependent electrical conductivity was determined on selected samples by a standard two-point measurement using a digital multimeter (Keithley multimeter 195A) with a measurement range up to 20 MΩ. The temperature was varied from room temperature (RT) up to 400 °C.

Thermophysical properties were characterized using standard measurement techniques: the thermal diffusivity was measured by a laser flash method [lit] and the specific heat by differential scanning calorimetry (DSC) and for were carried out for temperatures between RT and 500 °C. Thermal conductivity λ was calculated from the measured data [11] by the following equation:

$\lambda=\alpha*c_p*\rho$ (1),

where α is the thermal diffusivity, c_p the specific heat and ρ the density.

3. RESULTS

3.1 Microstructure

The cross-sections of the modified laser tracks showed different geometries depending on the process parameters. Fig,2 shows schematic pictures and exemplary light microscopy pictures of LTCC-substrates alloyed with nanoscaled-WO_3.

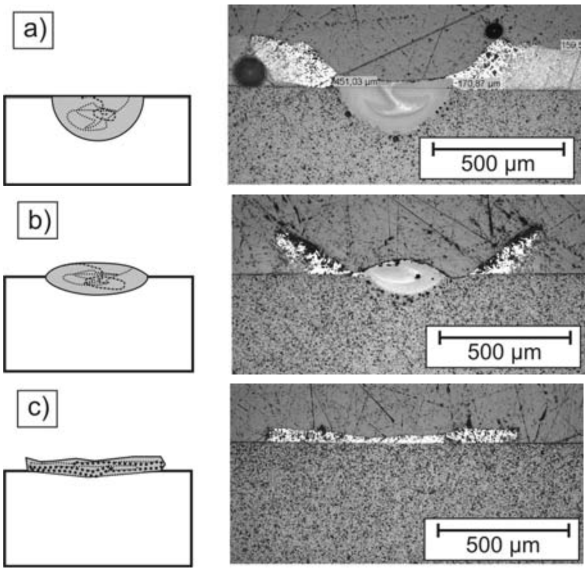

Fig.2: Schematic pictures and light microscopy pictures of different cross-sections of WO_3-laser alloyed LTCC. From a) to c) decreasing laser power density.

 ISBN :978-2-35500-003-4

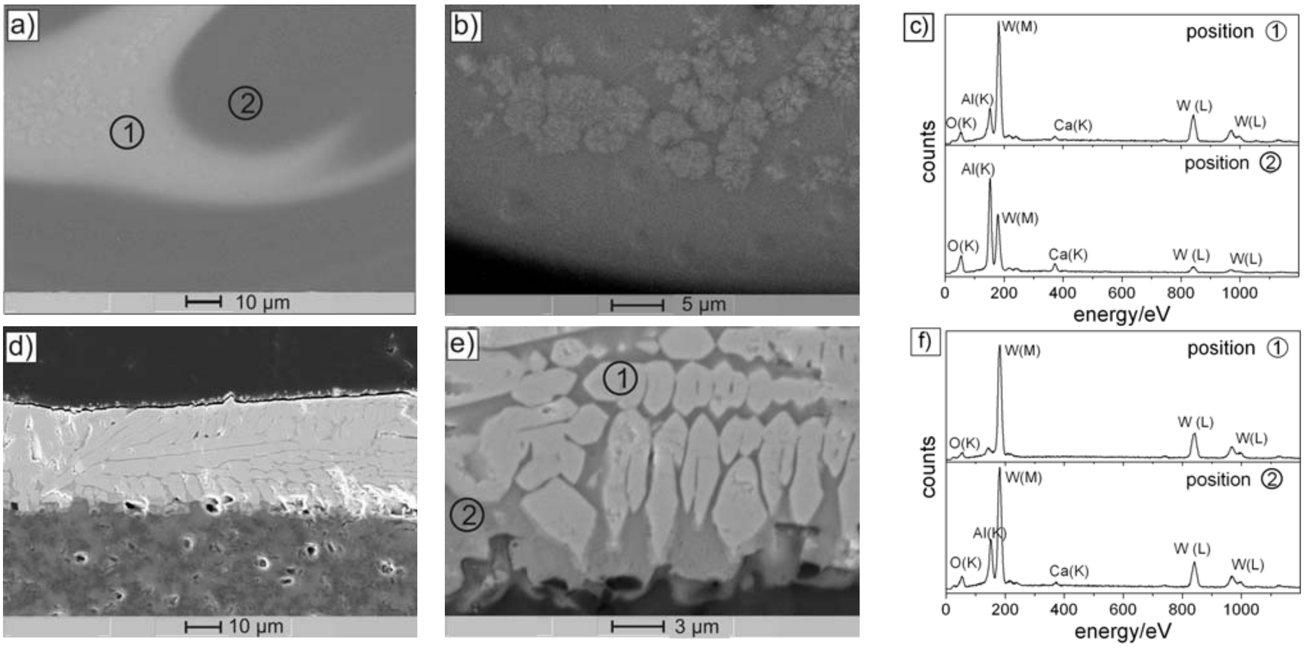

Fig.3: SEM-images of laser alloyed LTCC with nano-WO_3 and EDX-analysis of different elements of the micro-structure; a),b),c) in case of a developed melt pool and d),e),f) for a layer located at the top of the ceramic surface.

High laser density resulted in a large melt pool, localized at the surface of the substrate with a thickness up to 300 µm (Fig.2a). As a consequence of a reduction of laser density a smaller melt pool was developed, especially the thickness was reduced (Fig.2b). In both cases the added material could be observed inside the solidified melt and a convex bow of the modified area could appear. A further reduction of laser density resulted in a laser track which was characterized by only a very small amount of melted substrate but a compacted layer on the substrate surface (Fig.2c).

SEM-images of WO3/LTCC samples are shown in Fig.3. EDX-analysis showed that in case of a developing melt pool (see Fig.2a), a tungsten rich phase could be found finely dipersed inside the ceramic matrix. In Fig.3 a typical cross-section can be seen with a bright phase in the middle of the melt pool and a magnification if it is shown in Fig.3b. EDX-analysis of this bright phase (position 1 in Fig.3a) showed an increased amount of tungsten compared to the surrounding grey phase (pos.2). The distribution of the additive indicates the appearance of a convection inside the melt pool.

Fig.3c shows a SEM-image of a WO_3-layer located at the top of the ceramic surface like in the principle sketch in Fig.2c. The magnification in Fig.3d shows a granular microstructure and Fig.3f the EDX-analysis. Grains of tungsten oxide (pos. 1) were developed with sizes in the range of some microns. They were embedded in a matrix (pos. 2) which exhibit a significant amount of aluminum, which is an indication for the infiltration of substrate melt.

A similar behaviour could be recognized for laser tracks alloyed with CuO. Depending on laser power a compacted CuO-layer on the top of the ceramic surface or a melt pool with a fine dispersed CuO-phase could be fabricated. Fig.4 a,b,c show SEM-images of a laser track produced with a reduced laser density because of a defocused laser beam. The CuO-particles with an initial average particle size of 30 nm were melted by the laser beam and crystallise. In parts a dendritical solidification could be observed. Solidified substrate material could be found inside the CuO-layer. Whereas the light-grey phase (1) in Fig.4b consisted mainly of copper and oxygen, a significant amount of aluminium, silicon and calcium (principal constituents of the LTCC) could be detected by EDX-analysis in the dark-grey phase (2) at the top of the layer in Fig.4c.

In case of laser power densities above 15 kW/cm^2 and a scanning speed of 500 mm/min or lower a distinct melt pool was developed and the copper-oxide phase was finely dispersed inside the solidified substrate matrix. Fig.4d shows a SEM-image of a section with a relatively high amount of the additive phase. In the magnifications in Fig.4e,f fine structures of CuO can be observed with sizes down to the nm-range. Particles or agglomerates can be observed as well as fine crystallites, like in the section displayed in Fig.4f, which is located at the border of the melt pool to the substrate.

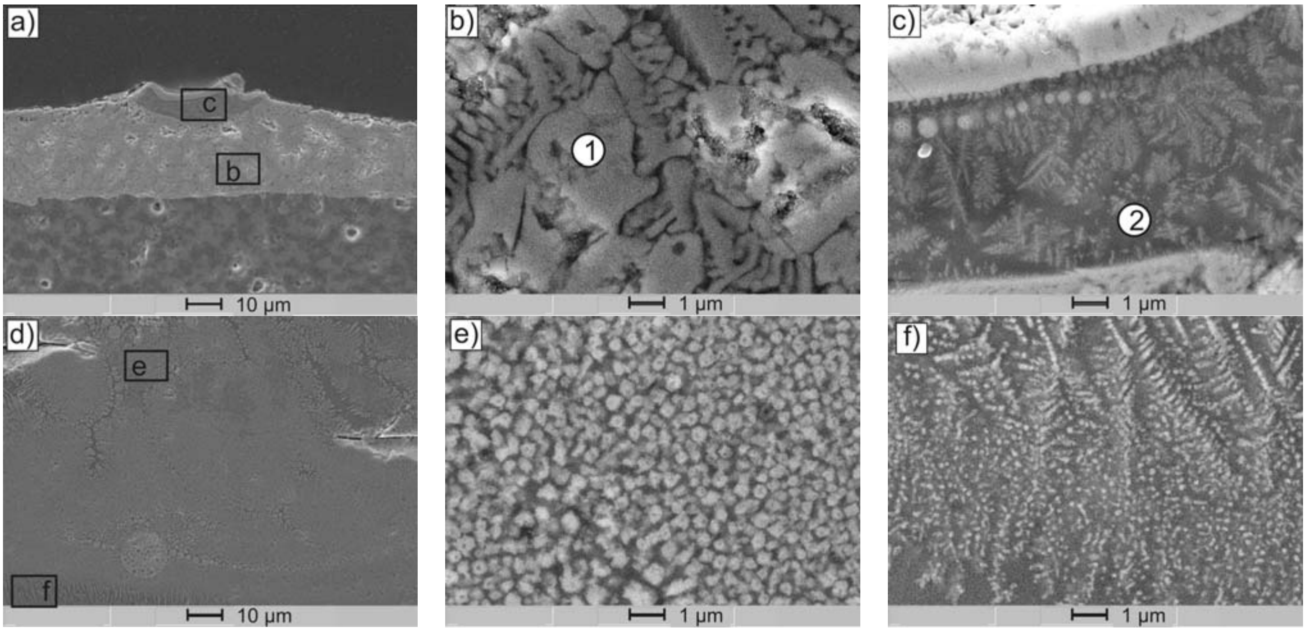

Fig.4.: SEM-images of laser alloyed LTCC with nano-CuO; a),b),c) of a layer located at the top of the ceramic surface and d),e),f) of a developed melt pool.

The alloying of alumina with CuO resulted in a modified area which was characterized by a grain refinement. Whereas the starting alumina substrate exhibit a bimodal distribution of the grain size with grains between 5-10 µm and 50 -100µm, the modified CuO/alumina had a grain size in the range of 10-15 µm.

The alloying of alumina with WO_3-nanopowder even resulted in a medium grain size below 3 µm. In both cases a reaction phase could be detected at the grain boundaries with a significant amount of copper-oxide and tungsten-oxide respectively. The lateral size of the grain boundary phase varied between 100 to 500 nm. Sporadic also small particles or agglomerates of the additive with a diameter smaller than 1 µm could be observed inside the alumina grains.

3.2 Electrical properties

The electrical resistance was measured on selected samples within a temperature range from room temperature up to 400 °C. Typical track length was set to 1cm and the contact was made by conductive paste of platinum. Because of the different geometries of the examined tracks the absolute values of the resistance could vary and the attention was focused on the temperature behavior.

The electrical resistance measurements of laser alloyed tracks on LTCC with nano-WO_3-powder were carried out on wide tracks, because of the larger cross-section. In Fig.5a the measured values are displayed with a logarithmic scale (to the basis 10) for the resistance. Values lower than 20 MΩ could be measured above 150 °C. A further increasing of the temperature resulted in an exponential reduction of the resistance within the next 100 °C. Accordingly the graph in Fig.5a shows a steep linear decrease, which is followed by a section with a small negative slope for temperatures above 250 °C. Repeated measurements showed slightly changed absolute values of the resistance but the same temperature behavior. The negative temperature coefficient of the resistance for the WO_3/LTCC-composite is typical for the conduction mechanism in semiconductors [12].

For the copper-oxide tracks a resistance lower than 20 MΩ could be established already for room temperature (Fig.5b). Track 2 was a small track with a cross-section characterized by a CuO-layer on the top of the ceramic surface like in Fig.2c. and track 3 was a wide one, with a significant part of the CuO located in a top layer. For both an identical behavior could be established with a exponentially decreased resistance for increasing temperature, which can be seen by the nearly linear behavior for the logarithmic resistance, especially above 150°C. Track 1, which was characterized by a fine dispersed CuO-oxid phase inside a solidified LTCC-matrix like in Fig.2a) showed a higher absolute value for the resistance. It could be measured first above 175 °C and showed an intense decrease with increasing temperature, which could be described by a linear reduction of the logarithmic resistance with temperature but with a larger slope compared to track 2 and 3. The measured values of the CuO/LTCC tracks offer a good reproducibility.

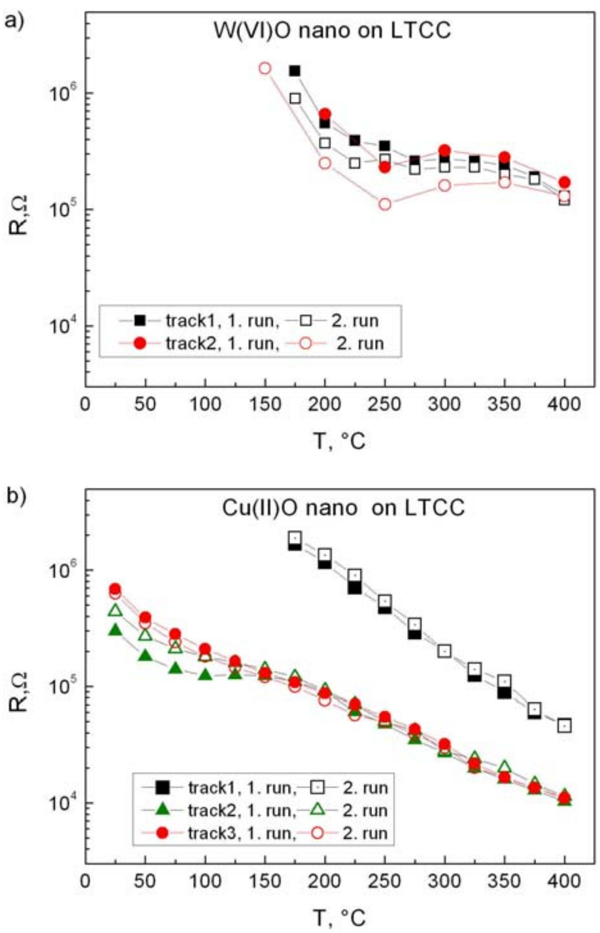

Fig.6: Electrical resistance for laser alloyed tracks with nano powders of a) WO_3 and b) CuO.

3.2 Thermal properties

Using the laser flash method the thermal diffusivity was determined for the unmodified LTCC-substrates as well as for the modified LTCC for a temperature range from room temperature up to 500 °C. The highest values were observed at room temperature. The as received ceramic offer a value of 0,012 cm^2/s and the laser modified samples offer a 0,001 cm^2/s higher value for CuO/LTCC and a 0,005 cm^2/s higher value for WO_3/LTCC. With increasing temperature thermal diffusivity was reduced for all samples with a similar behavior.

Whereas the unmodified LTCC showed 0,008 cm^2/s at 500 °C, CuO-samples showed 0,0095cm^2/s and WO_3-samples 0,0125 cm^2/s. The effective thermal conductivity was calculated by equation (1) based on the measured data for thermal diffusivity, specific heat and density. Because of the very small value of thermal expansion the density of LTCC was set to a constant value of 3,3 g/cm^3 for all temperatures.

In Fig.7 the thermal conductivity is plotted as function of temperature for the modified ceramic compared to the as-received LTCC. Within the observed temperature range the modified ceramics show a higher thermal conductivity compared to the original ceramic. At room temperature the thermal conductivity of the CuO/LTCC is about 20 % higher than that of the unmodified LTCC and the WO_3/LTCC composite even exhibits a value of 0,042 W/cmK which is a bout 70 % higher than the value 0,025 W/cmK for the as-received ceramic. In addition the non-modified LTCC shows a slowly decreasing thermal conductivity with increasing temperature whereas for the WO_3/LTCC and the CuO/LTCC -composites no significant change of thermal conductivity with temperature could be observed. Consequently the difference between the modified and the unmodified LTCC is more pronounced at higher temperatures.

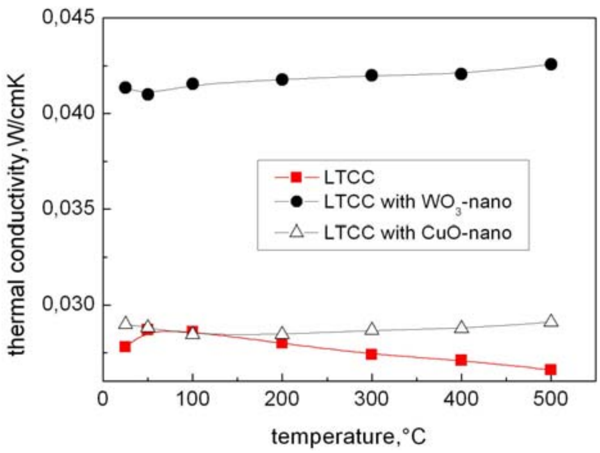

Fig.7: Thermal conductivity of the laser modified LTCC with WO_3-nano powder and CuO-nano powder in comparison to the as received substrate material.

4. CONCLUSIONS

Within this paper we have presented our actual work on the effect of a laser alloying process on the microstructure and the electrical and thermal properties of commercial ceramics using metaloxid-nano-powders.

The surfaces of LTCC and Al_2O_3 ceramics were modified while different microstructures could be adjusted by varying the process parameters. Compacted layers made of CuO or WO_3 could be fabricated which were located at the top of the ceramic surface as well as modified areas with a fine dispersed amount of the second phase inside the ceramic matrix. The microstructure of the composite is characterized by a typical length scale ranging from several microns down to 100-200nm.

The modified laser tracks exhibited a decreasing electrical resistance with temperature. This negative temperature coefficient is characteristic for semi-conducting materials. Especially for the LTCC/CuO-composite an exponentially decreasing behavior with temperature could be established for a temperature range between 25°C to 400°C. The resistance level tended to be in the range of 10^6 down to $10^4\,\Omega$ depending on the developed microstructure and the existent amount of the additive phase.

A significant change of thermophysical properties could be observed as well. It could be shown that the thermal conductivity is significantly enhanced for the laser alloyed areas. In case of nano particles made of WO_3 the modified area showed a 70% higher value for the thermal conductivity compared to the as received ceramic substrate in a temperature range from RT up to 500 °C.

5. REFERENCES

[1] K.-H. Zum Gahr, J. Schneider, "Surface modification of ceramics for improved tribological properties", Ceram. Int. 26 (2000),pp. 363-370.

[2] K. Poser, M. Rohde, J. Schneider, K.-H. Zum Gahr, "TiN-particle reinforced alumina for unlubricated application mated to metallic counter bodies", Materialwissenschaft & Werkstofftechnik 3-4 (2005) pp. 122-128.

[3] U. Duitsch, S. Schreck, M. Rohde, "Experimental and numerical investigations of heat and mass transfer in laser-induced modification of ceramic", Int. J. Thermophys. 24 (2003), pp. 731-740.

[4] S. Rüdiger, H. Gruhn, M. Rohde, K.-H. Zum Gahr, "Laser induced surface modification of Cordierite", Surface engineering, Euromat99, Vol. 11, pp. 510-515, ed. Dimigen, H., Wiley-VCH.

[5] O. Baldus, S. Schreck, M. Rohde, "Writing conducting lines into alumina ceramics by a laser dispersing process", Journal of the European Ceramic Society, 24 (2004), pp. 3759-3767.
[6] P.M. Ajayan, L.S. Schadler, P.V. Braun, Nano-composite Science and Technology, Wiley VCH Verlag, Weinheim, 2003.

[7] R. Duan, J. Kuntz, J. Garay, A. Mukherjee, "Metal-like electrical conductivity in ceramic nano-composite", Scripta Mat. 50 (2004) pp.1309-1313.

[8] H. Wang, Y. Xu, M. Goto, Y. Tanaka, M. Yamazaki, A. Kasahara, M. Tosa, "Thermal conductivity of tungsten oxide nanoscale films", Mat. Trans. 47 (2006) pp. 1894-1897.

[9] M. Gillet, R. Delamare, E. Gillet, "Growth, structure and optical properties of tungsten oxide nanorods", Eur. Phys. J. D34 (2005) 291-294.

[10] M. Rodriguez, P. Yang, P. Kotula, D. Dimos, "Microstructure and phase development of buried resistors in LTCC", J. Electroceram. 5 (2000) pp.217-223.

[11] M. Rohde, B. Schulz: "The effect of the exposure to different irradiation sources on the thermal conductivity of Al_2O_3", J. Nucl. Mat. 173 (1990) pp.289-293.

[12] M. Hutchins, O. Abu-Alkhair, M. Nahass, K. Abdel-Hady, "Electrical conduction mechanisms in thermally evaporated WO_3 thin films", J. Phys.-Cond. Mat. 18 (2006) pp. 9987-9997.