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Screen printed electro-conductive ceramics

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Abstract

Screen printed, electro-conductive ceramic thick-films were developed for the use as resistance heating elements. Two particulate composites, Al_2O_3/TiN and Si_3N_4/TiN, as well as a single phase material, indium-tin-oxide, were selected for this purpose and were characterized with respect to their microstructures and their electrical properties. For the use as thick-film heating elements it was necessary to develop microstructures with high densities. In case of the composite materials the variation of the electrical conductivity in dependence of the ratio of conducting to insulating phase could be described by the percolation theory. The percolation threshold of these thick-films is influenced by the film thickness which is an effect of the transition region between the three dimensional and the two dimensional case. An application for the electro-conductive ceramic films is their use as high temperature heating elements. Different devices were realized and operated up to temperatures of 1000 °C.

Keywords: Composites; Electrical conductivity; Films; Heating elements

1. Introduction

Conventional thick-film materials for heating elements are resistor or noble metal conductor paste compositions.[1] In case of the resistors the applications are limited to temperatures below 400 °C due to the inherent glass matrix of these systems. For temperatures up to 800 °C noble metal heating elements can be used (e.g. platinum). For higher temperatures no satisfying materials are available. Ceramic materials show a pronounced high temperature strength and a good corrosion resistance. Therefore screen printed, electro-conductive ceramic layers were developed for the use as high temperature heating elements.

Electro-conductive ceramics with metallic conduction behavior are the nitrides, borides and carbides of the transition metals from the IV to the VI group of the periodic table. From this group titanium nitride (TiN) was selected as an appropriate material. As the densification of commercial TiN powders is not possible under reasonable conditions a second phase of better sinterability was added. Alumina (Al_2O_3) is a common ceramic material which can be pressureless densified and has a similar thermal expansion coefficient as TiN and was therefore selected as the matrix material. As Al_2O_3 is already used in the matrix, Al_2O_3 was also selected as the substrate material.

Silicon nitride (Si_3N_4) was also considered as a substrate material because of its higher strength but initial experiments have shown that Al_2O_3/TiN layers do not adhere to the substrate. To overcome this problem Si_3N_4/TiN pastes were developed and used in combination with Si_3N_4 substrates. A disadvantage of this combination is the different thermal expansion coefficients of Si_3N_4 and TiN.

There are only a few oxide ceramics showing a reasonable electrical conductivity. One of them is indium-tin-oxide (ITO) which is a semiconducting material and is usually processed by thin film technologies. ITO powders can be pressureless sintered by either using sintering aids or very fine powders. As the thermal expansion coefficients of ITO and Al_2O_3 are similar, Al_2O_3 was selected as the substrate material.

In order to achieve reproducible resistivities of the ceramic layers it was necessary to yield a microstructure as dense as possible. The densification of screen printed films is hindered due to the constrained sintering conditions. So far dense films could be obtained only by

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liquid phase sintering and by applying an external pressure. However, ceramic films with a high density could be obtained by pressureless sintering, after improving the screen printing paste composition.

2. Experimental procedure

2.1. Preparation of screen printed electo-conductive layers

Commercial grades of Al_2O_3 (Alcoa A16SG), Si_3N_4 (UBE SN-E10) and TiN (H.C.Starck Grade C) were selected. The Si_3N_4 powder was modified by adding the sintering aids Y_2O_3 and Al_2O_3 using organic precursors. A submicron ITO powder was prepared by a spray calcination route using indium and tin salts.[2] The preparation of the conducting mixtures of Al_2O_3/TiN (16–70 vol.% TiN) and Si_3N_4/TiN (25 and 50 vol.% TiN) was achieved by ball milling the appropriate powder fractions for 15 h in ethanol.

Screen printing pastes with a high solid loading (up to 40 vol.%) were developed which was necessary to yield a dense microstructure after sintering. For the paste preparation an organic vehicle, based on terpineol as the solvent, ethyl cellulose as the binder and rheological modifier, and a commercial dispersant (Hypermer KD-1, ICI) were selected.

The screen printing was done with a semi-automatic screen printer (EKRA M2). The films were leveled at room temperature for 10 min and then dried at 80 °C. The Al_2O_3/TiN and Si_3N_4/TiN layers were sintered in a nitrogen atmosphere at 1850 °C (10 min, 0.7 MPa) and 1900 °C (30 min, 1 MPa), respectively. In case of the Si_3N_4 layers a BN/Si_3N_4 sinter bed was used to avoid evaporation losses of Si_3N_4. The ITO layers were sintered at 1350 °C (300 min) in air.

2.2. Characterization

The sintered films were characterized by scanning electron microscopy with respect to their microstructure. The sheet resistances were measured at room temperature and the temperature coefficients of resistance were determined within the range from room temperature to 1000 °C.

2.3. Modeling of the percolation threshold

The percolation threshold was calculated for simple cubic and hexagonal close packing using a model consisting of mixtures of insulating and conducting spheres of equal radii. A Monte Carlo method was applied to determine the percolation threshold for the transition region between the two dimensional and the three dimensional case.

2.4. Heating elements

Different heating elements were realized and operated at temperatures up to 1000 °C.

3. Results and discussion

3.1. Properties of the sintered films

3.1.1. Al_2O_3/TiN

The Al_2O_3/TiN pastes were printed, sintered and characterized with respect to their sheet resistances. A TiN content of 18 vol.% was necessary to achieve an electrical conducting material. In Fig. 1 the sheet resistance for the different layers with a layer thickness of about 30 μm are plotted versus the TiN content in the powder mixture. With increasing TiN content the sheet resistance decreases by three orders of magnitude down to a value of 0,2 Ω/sqr at 70 vol.% TiN. The resistivity of pure TiN cannot be reached due to the increasing porosity at the TiN rich side which can be explained by the lower sinter activities of those composites. The densification of the particulate composites depends only on the good sinterability of Al_2O_3. TiN does not sinter without external pressure.

The cross-section of a screen printed, sintered Al_2O_3/TiN layer containing 25 vol.% TiN in the composite material is shown in Fig. 2. The white grains correspond to TiN, whereas Al_2O_3 appears grey. Despite of the constraint conditions due to the rigid substrate the Al_2O_3/TiN layer could be sintered to full density. This was accomplished by the development of an improved paste with a high solid loading.

Layers with a thickness of about 5 μm were also prepared using a screen with a higher mesh number. The printed layers could also be sintered to full density at low titanium nitride contents. To maintain electrical conduction in these layers a TiN content of 25 vol.%

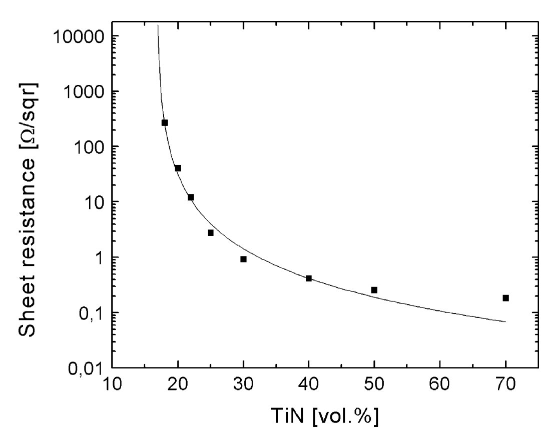

Fig. 1. Sheet resistance of sintered Al_2O_3/TiN thick-films with different TiN contents.

was necessary. This shift of the percolation threshold can be explained by looking at the change of the percolation threshold from three to two dimensions. The percolation threshold for conducting and insulating mixtures of spheres with equal radii depends on the coordination number of the spheres.[3] For a monolayer of spheres with highest packing factor (hexagonal close packing) the percolation threshold is 50% (58% in the simple cubic case). In three dimensions the threshold is decreased to 19.8% (32% in the simple cubic case) due to the higher coordination number. The change of the percolation threshold was modeled for the transition region between the two dimensional and the three dimensional case. The calculation shows a decrease of the percolation threshold with increasing layers of spheres (Fig. 3).

For five monolayers of hexagonal close packed spheres a percolation threshold of 25 vol.% is obtained. This value is close to the percolation threshold measured for the 5 μm thick Al_2O_3/TiN films. These films contain about five grains in the vertical direction.

In addition to the electrical properties at room temperature the temperature coefficient of resistance is important with respect to the use as heating elements. Due to the metallic conduction behavior of TiN a positive temperature coefficient with a value of 1600 ppm/K was measured for the Al_2O_3/TiN material.

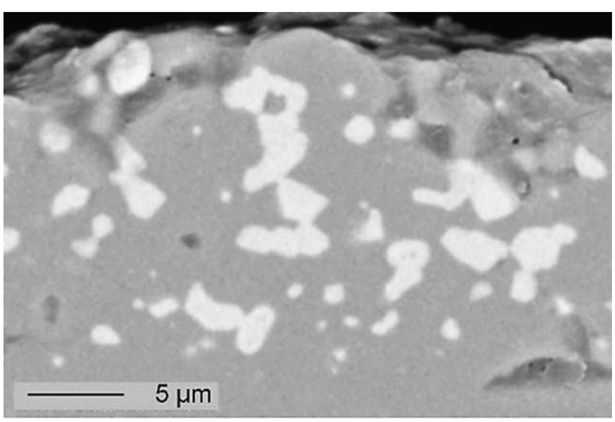

Fig 2. SEM image of a cross-section of an Al_2O_3/TiN film containing 25 vol.% TiN (grey: Al_2O_3, white: TiN).

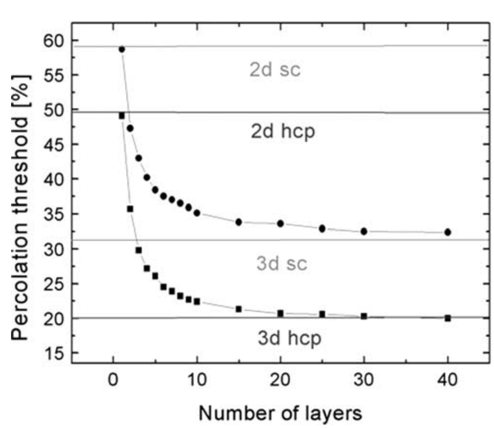

Fig. 3. Percolation thresholds for mixtures of conducting and insulating spheres with equal radii for simple cubic and hexagonal dense packing going from two to three dimensions.

3.1.2. Si_3N_4/TiN

The Si_3N_4/TiN mixtures were sintered onto Si_3N_4 substrates. The sheet resistances of the composites are higher compared to the equivalent Al_2O_3/TiN composites which is due to some remaining porosity, as it is shown in Fig. 4.

Like the Al_2O_3/TiN composite the Si_3N_4/TiN material shows a positive temperature coefficient of resistance, but in this case no reproducible value could be obtained. With multiple cycling steps the electrical resistance increased to higher values. The reason for this behavior could be the very different thermal expansion coefficients between TiN and Si_3N_4 leading to thermal stresses between the Si_3N_4 substrate and the Si_3N_4/TiN layer. Therefore this material is not suitable as a heater material.

3.1.3. Indium-tin-oxide (ITO)

The ITO films were sintered onto alumina substrates. After sintering there is still some porosity present in the microstructure (Fig. 5). The films show a sheet resistance of about 30 Ω/sqr. The ITO layers have a negative temperature coefficient of resistance of about 700 ppm/K which is due to the semiconducting behavior the material.

3.2. Heating elements

Different heating devices were developed using either Al_2O_3/TiN or ITO as the heater material which was screen printed and sintered onto alumina substrates. After optimization of the heater pattern these devices could be operated up to a temperature of 1000 °C (Fig. 6). In case of the Al_2O_3/TiN material the hot regions were coated with Al_2O_3 to protect the TiN

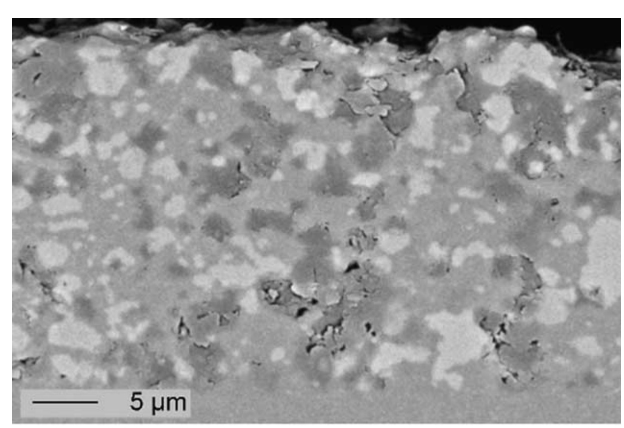

Fig. 4. SEM image of a cross-section of a Si_3N_4/TiN film containing 25 vol.% TiN (grey: Si_3N_4, white: TiN, black: pores).

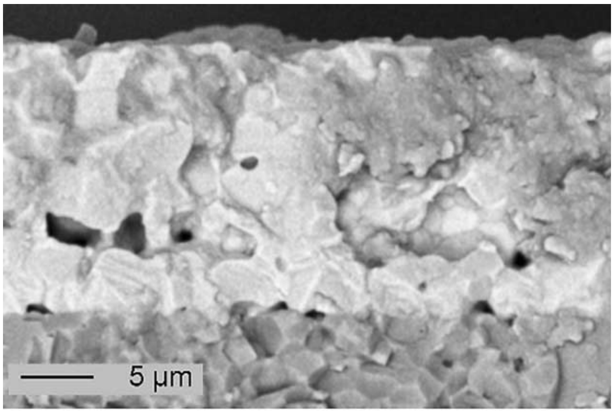

Fig. 5. SEM image of a cross-section of an ITO film (grey: Al_2O_3 substrate, white: ITO film, black: pores).

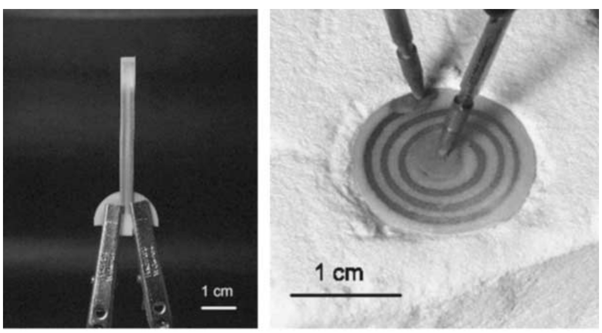

Fig. 6. Two ceramic heating elements during operation (left: needle-like heater, right: disc-shaped heater).

against oxidation. In case of the ITO layers the electrical current has to be limited to avoid the overheating of the material because ITO has a negative temperature coefficient of resistance.

Possible applications for such devices are igniters, heating elements for sensor applications or devices for temperature measurements.

Another application for the screen printed layers lies in the microreaction technology. A heating concept for the operation of a ceramic microreactor was developed.[4] In this case screen printed heating elements were inserted into the reaction chamber and were heated up by induction heating to a temperature of 1000 °C. The integration of the heating elements into the reaction chamber allows the heat to be generated at the reaction zone. (Fig. 7)

4. Conclusion

Screen printed, electro-conductive ceramic films were developed for the use as resistance heating elements. A particulate composite containing Al_2O_3 and TiN and a single phase material ITO have shown to be suitable for the preparation of thick-film heating elements. Films having a dense microstructure which is necessary for the use of such devices could be obtained by using an improved paste preparation.

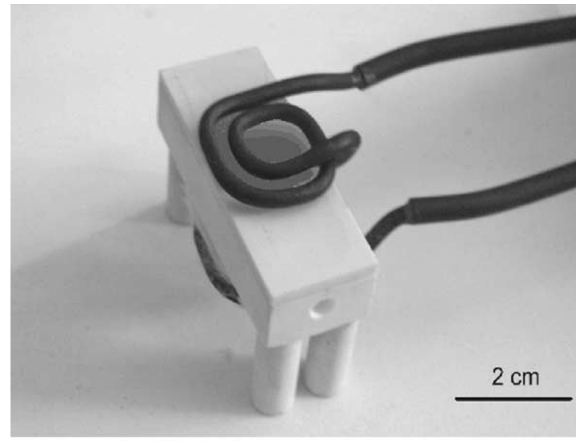

Fig. 7. Ceramic microreactor with integrated screen printed heating elements heated by induction.

The sheet resistances of the Al_2O_3/TiN composites can be varied by changing the ratio of the two components. The percolation threshold of the system is influenced by the thickness of the films.

The temperature coefficient of resistance of Al_2O_3/TiN is positive (1600 ppm/K) whereas the coefficient of ITO is negative (−700 ppm/K).

Both materials can be used for high temperature heating elements. Different structures could be realized onto Al_2O_3 substrates and were heated up to 1000 °C. A ceramic microreactor with inserted screen printed ceramic heating elements could be operated by induction heating up to 1000 °C allowing for a localized heating of the reaction zone.

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