Evaluation of screen-printable type S (Pt-PtRh) thermocouples on different ceramic substrates

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Abstract

The application of thermocouples as temperature sensors has been well known and has already been established for many years. However, for classical thick-film technology using screen-printing and firing, no standardized solutions exist. The here-presented newly developed PtRh thick-film compositions (90% Pt,10% Rh) allows to construct thick-film type S thermocouples (Pt/PtRh), following the IEC temperature characteristics. They can be fired in air, and therefore can be easily integrated into existing thick-film components and devices. In an earlier study, the new Pt-Rh composition was successfully tested on alumina substrates. Their electrical characteristics is equal with classical wire type S thermocouples. This study continues the investigations of thick-film thermocouples. We tested the newly developed pastes for high temperature applications on alumina substrates and evaluated the application of the new screen-printable type S thermocouples on LTCC ceramics. Three possible configurations were investigated: deposited on already fired LTCC substrates (post-fired), screen-printed and co-fired with LTCC tapes on the top surface as well as as buried structures. The paper presents the results of our evaluation and discusses further possible applications.

Keywords: tape technology, LTCC, thick-film type S thermocouple

Introduction

The application of thermocouples as temperature sensors is well known and has already been established for many years. Typical thermocouples consist of two connected wires with different Seebeck coefficients. For classical thick-film technology using screen-printing and firing, no standardized solutions exist. Scattered attempts apply non-standardized Au and Pt inks [1-4], but on a formulation that leads to reliable long-term stable devices with a characteristics according to IEC or ANSI has not been reported so far. The newly developed Pt-Rh thick-film composition (90% Pt,10% Rh) allows to construct thick-film type S thermocouples (Pt/Pt-Rh), following the IEC characteristics. They can be fired in air atmosphere, and therefore can be easily integrated into existing thick-film components and devices. First promising results were presented in [5]. The experimental Pt-Rh paste DuPont 9151 was used in combination with platinum ink DuPont 9141R (this combination is later marked in text as LT thermocouple) on 96 % alumina substrates. Both materials were separately fired at 950 °C. The output voltages of thick-film thermocouple temperature sensors made of Pt- and Pt-10%Rh-pastes obey the German and European standard DIN EN 60584. This paper presents further investigations of thick-film type S thermocouples. Our goals were, on the one hand, to increase the operation temperature beyond 850 °C, and on the other hand, to test the applicability of the newly developed compositions on Low Temperature Co-fired Ceramics (LTCC), which has been studied in the last years for different kind of sensors and meso-scale devices [6, 7].

High-temperature thick-film thermocouples

Typical type S wire thermocouple can measure the temperature up to 1600 °C. Since the initial newly developed pastes for LT thermocouples had a low firing temperature of 950 °C, they have been tested only up to 850 °C. To extend the operation temperature of thick-film structures two new pastes were developed: The Pt paste DuPont 9142 and the Pt-10%Rh paste DuPont 9152 (HT thermocouple). They can be fired at 1200 °C und thus can be used at temperatures above 1000 °C.

The test structures were prepared and evaluated in the same way as described in [5]. Both materials were screen-printed on 96% alumina substrate and fired separately at 1200 °C (4h heating, 20 min. peak, 4 h cooling). The functionality tests were conducted in a tubular furnace. The furnace was heated stepwise up to 1200 °C. The measured thermovoltages of two HT thermocouples were converted into a temperature reading, using the built-in conversion function of the used Keithley 2700 Multimeter operated with Multiplexer Module 7700. As a reference, the signal from a wired type K thermocouple, which was placed very close to the HT thermocouple, was recorded. Fig. 1 presents an exemplary measurement.

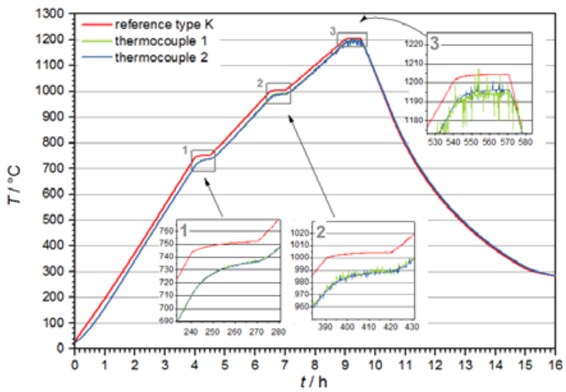

Fig. 1 Response of two HT thermocouples to step-like temperature changes.

Similar to the measurement of LT thermocouples as shown in [5], both screen-printed HT thermocouples react fast on temperature changes. There are small differences between reference and measured samples during the heating period (see insets 1 and 2), but there is no difference during the cooling phase. Some spikes in case of one tested thermocouple at temperatures above 1000 °C are probably caused by inductive coupling due to the on-off switching of the high heating currents of the furnace. Therefore, no spikes appear during cooling.

Application of Pt/Pt-Rh thermocouples on LTCC ceramics

Whereas platinum-based pastes for alumina have been known and available for many years, the dedicated platinum paste for Low Temperature Co-fired Ceramics (LTCC) does not exist, mostly due to the relatively low firing temperature of LTCC and the possible unwanted interactions that may occur during the co-firing process. Thus neither LTCC platinum thick-film pastes for heating elements or resistive temperature sensors exist, nor are reliable standardized temperature sensors like type S thermocouples mentioned.

Since our previous investigations had proved that some kind of platinum pastes can be used on LTCC ceramics as resistive temperature sensors [8-10], we evaluated the new screen-printable type S thermocouples deposited on LTCC ceramics and compared it with the results obtained on alumina substrates. We tested both compositions (for low und high temperature applications) in three possible configurations: deposited on already fired LTCC substrates (post-fired), screen-printed and co-fired with LTCC tapes on the top surface as well as as buried structures.

Preparation and optical evaluation of thick-film thermocouples on LTCC ceramics.

Depending on configuration, the thermocouples on LTCC were prepared as follows:

- on already fired LTCC substrates (DP951, thickness 550 µm) LT thermocouples were screen-printed.
- On unfired 951PX (254 µm thickness before firing) LT and HT types were screen-printed and dried at 120 °C. The additional two layers of 951PX tape were added for mechanical stability and laminated at 21 MPa, 70 °C for 10 minutes.
- The substrates with buried thermocouples were made by covering green laminates as described above with a 114 µm thin DP951PT tape with cut-outs in the contact area.

All samples were fired at 850 °C using the typical profiles for DuPont tapes. The substrate thickness after firing was about 600 µm for surface thermocouples and 680 µm for buried ones, respectively. At first, the samples were optically evaluated.

Fig. 2 shows a part of an LT thermocouple made on already fired LTCC substrates. The quality of Pt and Pt-Rh lines is very good without visible deformation. The line width is close to the designed 200 µm.

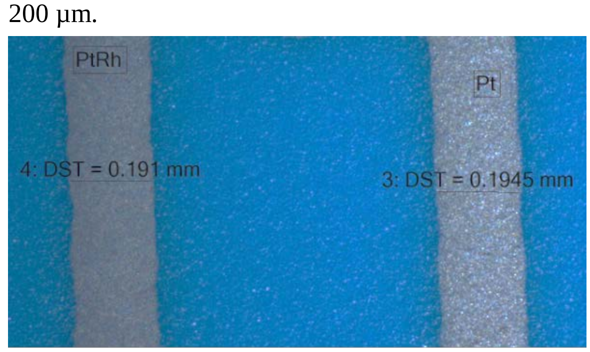

Fig. 2 LT thermocouple screen-printed on an already fired LTCC substrate

Co-firing of the developed pastes gave mixed results (Fig. 3). Whereas the quality of thick-film layers for both variants of Pt-Rh composition is good and the lines shrink generally together with the LTCC tapes during firing, LT and HT versions of platinum behave differently.

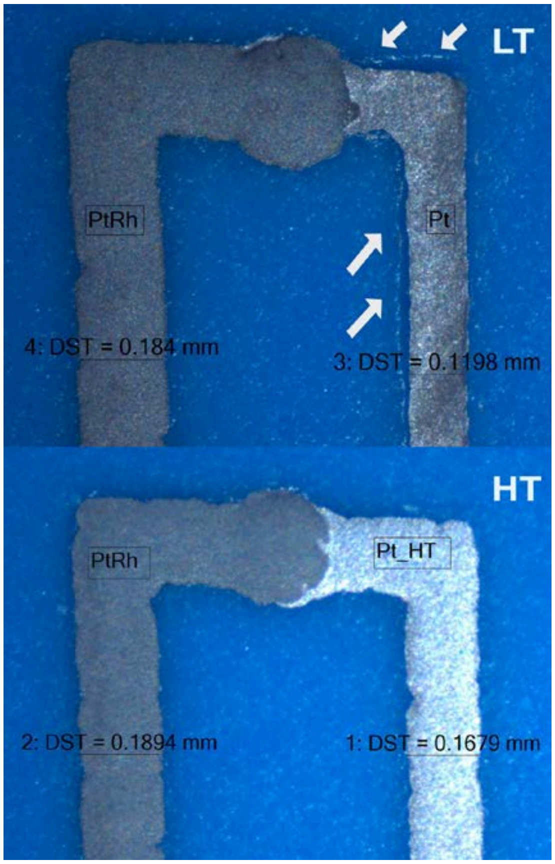

Fig. 3 LT and HT thermocouples co-fired at 850 °C

Platinum paste DuPont 9141R used in LT thermocouple reacts with LTCC tapes during co-firing and shrinks in an uncontrolled manner and much more than LTCC itself. As shown in Fig. 3, the line width of the platinum line for the LT thermocouple is only about 120 µm by screen-printed 200 µm width. Moreover, visible the etched-like border of the original line (marked in the image with white arrows) suggests that the shrinking of the platinum layers occur after the shrinking phase of the LTCC ceramics, which usually occurs at temperatures below 700 °C. The irregularities of the platinum layer surface may indicate poor adhesion or delamination.

In contrast, the experimental platinum composition DuPont 9142 used in the HT thermocouple is much more appropriate for co-firing with LTCC. The shrinkage of the layer is indeed a little higher than the Pt-Rh line (168 µm versus 190 µm after firing), but it seems this does not affect the adhesion of the thick-film.

To evaluate the quality of the buried structures, metallographic specimens were prepared and observed by scanning electron microscope (SEM). The results are given in Fig. 4. They are similar to the surface structures co-fired with LTCC. The Pt-Rh experimental paste DuPont 9151 for the LT thermocouple has a thickness of about 8 µm and no delamination is visible. However, DuPont 9141R platinum paste used in LT thermocouple is not suitable for buried LTCC structures. As shown in Fig. 4, the layer is suspended between LTCC layers (the darker area below platinum layer is an embedding compound). The delamination occurs on the whole length of platinum line.

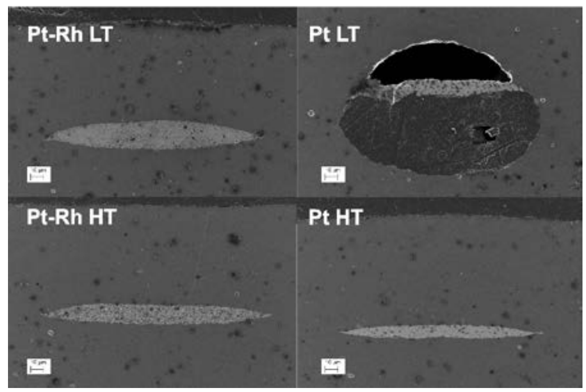

Fig. 4 Cross-section of LT and HT buried thermocouples co-fired at 850 °C

The quality of buried HT thermocouple is very good. The thickness of the layers is a little lower, about 4-7 µm, but the thick-film is perfectly laminated, without visible voids. The reason for the different behavior of platinum inks during co-firing can be the different glass composition used in the LT and the HT variants of the inks.

Based on an optical evaluation of the structures, the thermocouples made as post-fired structures (LT thermocouple) as well as co-fired and buried HT thermocouples were selected for functionality tests.

Functionality test

The functionality test of the thermocouples on LTCC ceramics was similar to the procedure described above and applied in case of thermocouples on alumina. The furnace was heated with a ramp of 10 K/min. Every 200 °C, the temperature was kept constant and stabilized for about 10 min. The maximum test temperature was 800 °C, due to the lower firing temperature of the LTCC structures. For each run, a reference type K wire thermocouple was placed as close as possible to the LTCC thermocouple. The summarized results are presented in Fig. 5. For the sake of clarity, only the behavior during dwell temperatures is shown.

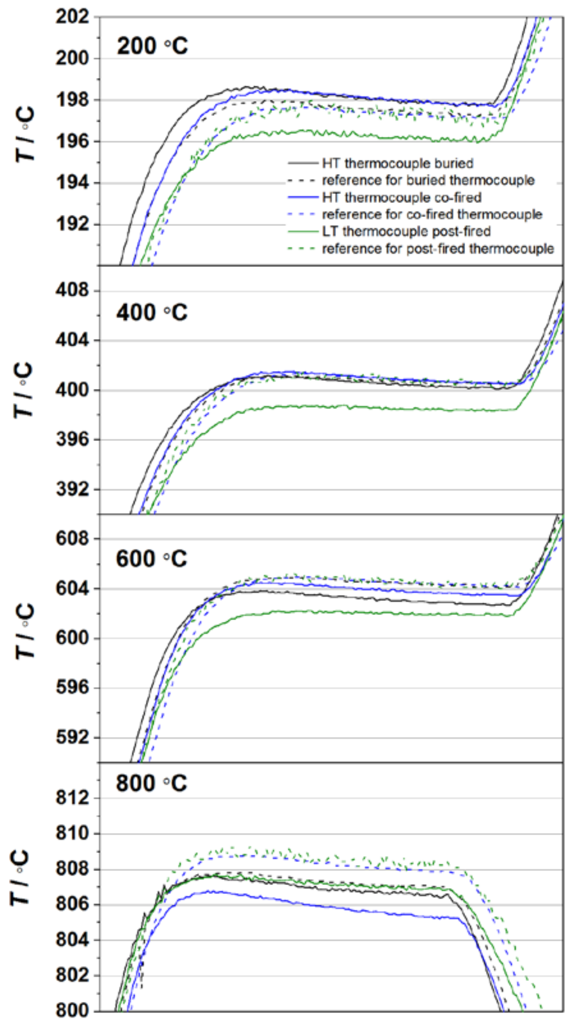

Fig. 7 Response of thermocouples on LTCC ceramics (solid curve) at different dwell temperatures compared with the reference (wire type K thermocouples, dashed)

Generally, thermocouples on LTCC substrates behave similar to structures on alumina as presented in Fig 1 and in [5]. Interestingly, independently of the thermocouple (post-fired, co-fired or buried) the difference between thermocouple signal and reference is much lower than in the case of structures on alumina (see insets in Fig. 1). Whereas the temperature difference by thermocouples on alumina is about 12 °C at 750 °C, for LTCC thermocouples this difference does not exceed 3 °C. One may explain this phenomenon that the time constant during heating of the LTCC sensors is lower than for alumina sensors due to lower thermal conductivity and the lower thermal capacity of LTCC ceramics. Despite there is no significant difference between post-fired LT thermocouple and co-fired HT thermocouples, the HT thermocouple seems to be the better choice for co-fired structures due to the better printing and firing results.

Conclusions

In this study, a newly developed pastes for thick-film type S thermocouples was evaluated. In addition to the already in [5] investigated Pt/Pt-Rh pastes fired at 950 °C (9141R and 9151, respectively), new pastes for high temperature applications (Pt 9142 and Pt-Rh 9152 fired at 1200 °C) were successfully tested up to 1200 °C.

Moreover, both, LT and HT variants, were tested on LTCC ceramics. LT thermocouples can be successfully applied on already fired LTCC substrates. For co-fired and/or buried temperature sensors, the HT thermocouple appears more suitable owing to the better compatibility with the LTCC material. The initial functionality test proved that lower firing temperatures do not affect the thermoelectric properties of the newly developed materials. The characteristics of thick-film thermocouples on LTCC correspond with the German and European standard DIN EN 60584.

Although the main goal of our investigations are thick-film type S thermocouples, it needs to be mentioned that the new platinum paste 9142 developed for HT thermocouple seems to be also an excellent choice for heating elements and resistive temperature sensors for LTCC ceramics due to the good compatibility.

Since the initial tests were very promising, it makes sense to further investigate the new pastes for high-temperature applications on alumina and as temperature sensors on LTCC ceramics, with special respect to important application-relevant properties like long-term stability and resistant to cyclic temperature changes.

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