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X-RAY CHARACTERIZATION OF RESISTOR/DIELECTRIC MATERIAL FOR LOW TEMPERATURE CO-FIRED CERAMIC PACKAGES

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ABSTRACT

High temperature XRD has been employed to monitor the devitrification of Dupont 951 low temperature co-fired ceramic (LTCC) and Dupont E84005 resistor ink. The LTCC underwent devitrification to an anorthite phase in the range of 835-875 °C with activation energy of 180 kJ/mol as calculated from kinetic data. The resistor paste underwent devitrification in the 835-875 °C range forming monoclinic and hexagonal celcian phases plus a phase believed to be a zinc-silicate. RuO_2 appeared to be stable within this devitrified resistor matrix. X-ray radiography of a co-fired circuit indicated good structural/chemical compatibility between the resistor and LTCC.

INTRODUCTION

Hybrid microcircuits represent a $14 billion market, globally [1]. Microcircuits that employ thick film resistors play an important role in this market as sensors and electronic components for automotive applications and in consumer electronics [2]. There has been increasing motivation to move passive components, such as thick film resistors, from the surface configuration to that of a buried component within the multi-layered circuit structures. The benefits for this modification include increased miniaturization and circuit density, and enhanced reliability of these devices.

However, there are also significant challenges to overcome in this transition. In previous circuit printing configurations, resistors printed on the surface of a dielectric (such as alumina) could be trimmed if the resistance value was not correct after the processing conditions [2]. In the case of a buried resistor, the component can not be trimmed, and therefore requires a better understanding of the materials behavior so that consistent resistance values can be obtained during processing without corrective action on the circuit after fabrication. In addition, there are issues concerning the physical/chemical compatibility of the resistor and dielectric materials

DISCLAIMER

used in the fabrication of these circuits. In this paper we investigate a Dupont low-temperature co-fired ceramic (LTCC) and a new Dupont experimental resistor ink designed to be used specifically for buried resistor components. High-temperature x-ray diffraction (HTXRD) was employed to investigate these two component materials to better understand the phase formation which occurs within the materials during processing, and hence, obtain an improved understanding of processing/property relationships for fabricated devices containing buried resistor circuits.

EXPERIMENTAL

Samples of Dupont 951 LTCC were prepared by heating a piece of the green-tape to 450 °C for 2 hours for binder burnout. Next, the LTCC was ground in a mortar and pestle (under methanol) to form a slurry. Finally, the slurry was added dropwise onto 1 cm square, 10 mil thick, alumina substrates to achieve a ~50 μm thick layer of LTCC powder for use in HTXRD measurements. Because the Dupont E84005 resistor material was already prepared as a paste, it was simply painted onto alumina substrates to form a ~50 μm layer for HTXRD analysis. High temperature XRD was performed on a Scintag X_1 powder diffractometer. This system was equipped with Cu Kα radiation, an incident-beam focusing-mirror, and a peltier-cooled solid-state detector. This diffraction system was also equipped with a Buehler HDK 1.6 furnace for *insitu* heat treatment of samples. Temperature calibration was performed using known melting point standards. The calibration procedure has been outlined in detail elsewhere [3]. Both LTCC and resistor samples were heated in air to peak firing temperatures ranging from 835 – 875 °C. The samples were held at the peak firing temperatures for soak times in the range of 40 - 120 min (depending on temperature). Diffraction scans for standard analysis were typically 20 – 38 °2θ at a scan rate of 3 °2θ/min. For kinetic studies of the LTCC, scan ranges we from 26.5 – 29.5 °2θ at a scan rate of 1 °2θ/min.

X-ray radiography was performed on a test circuit composed of resistors and silver conductor paths sandwiched between two layers of Dupont LTCC tape. The circuit was printed onto the LTCC tape using an Ohmcraft Micropen. This system has been described in detail elsewhere [4]. After printing, the circuit was laminated and fired using the following schedule: 5 °C/min to 450 °C, hold 2hrs, 5 °C/min 850 °C, hold 20 min, furnace cool. Radiography was performed using a 12kW rotating anode source (Cu Kα radiation) running at 30 kV and 10 mA. The source was equipped with a 165 mm long collimator with a 4 mm diameter aperture. The sample was placed in front of the aperture and Kodak SO-163 film was placed directly behind the sample to collect a contact image. The exposure time was 2 seconds. The processed negative image was enlarged 20X.

RESULTS AND DISCUSSION

Figure 1 shows the devitrification behavior for the LTCC at 875 °C. At room temperature, the diffraction data shows only peaks from alumina and a broad background due to the amorphous content. Upon heating to 875 °C the presence alumina persists, along with new peaks matching an anorthite (Ca-Al-Silicate) structure. The anorthite was observed only after a soak time of 15-20 minutes; the alumina appeared essentially inert to the devitrification reaction. The kinetics for the anorthite devitrification were quite slow and since only one phase was observed to crystallize during processing, modeling of the reaction kinetics was straightforward. A quantitative analysis of the reaction kinetics was performed on a small region of 2θ to obtain reaction rate data. Data were collected at 835, 850 and 875 °C and integrated peak areas of the anothite were used to calculate the rate of devitrification. Figure 2 shows an example of the kinetic data obtained at 850 °C. Table 1 shows the reaction rates (k) for the different temperatures analyzed. From this data, an activation energy (E_a) of 180 kJ/mol was calculated based on a first order reaction behavior [5].

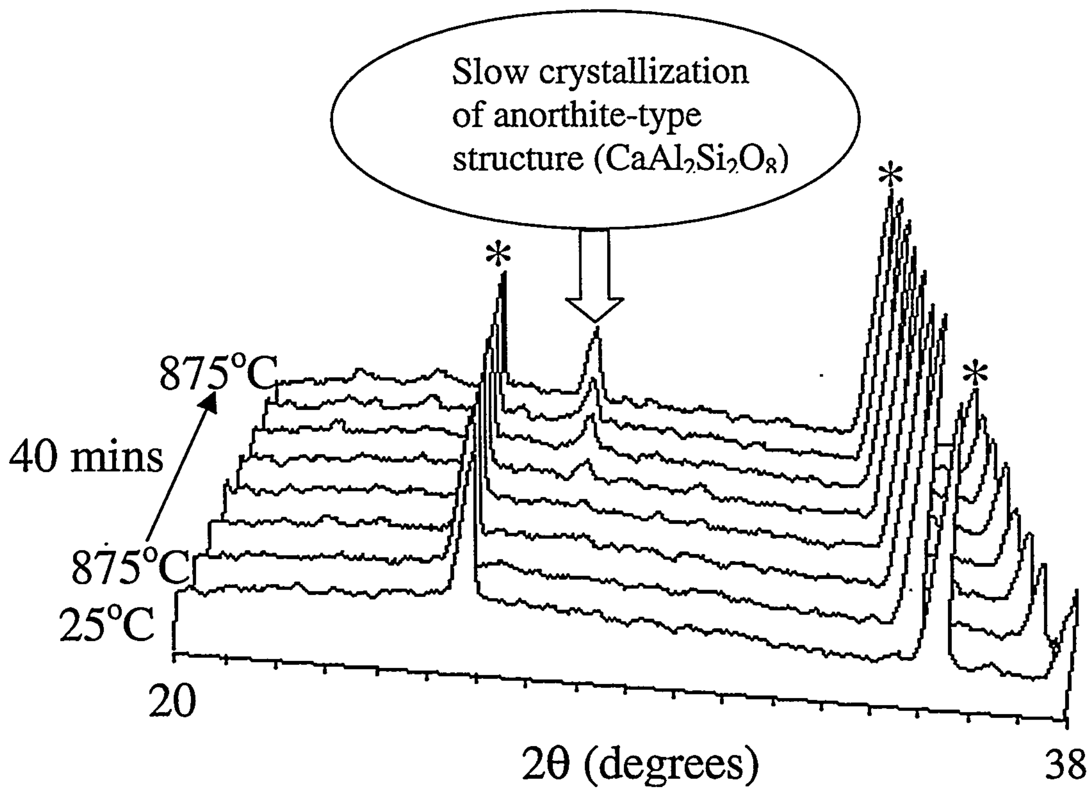

Figure 1. Devitrification of Dupont 951 LTCC at 875 °C. *'s indicate alumina peaks.

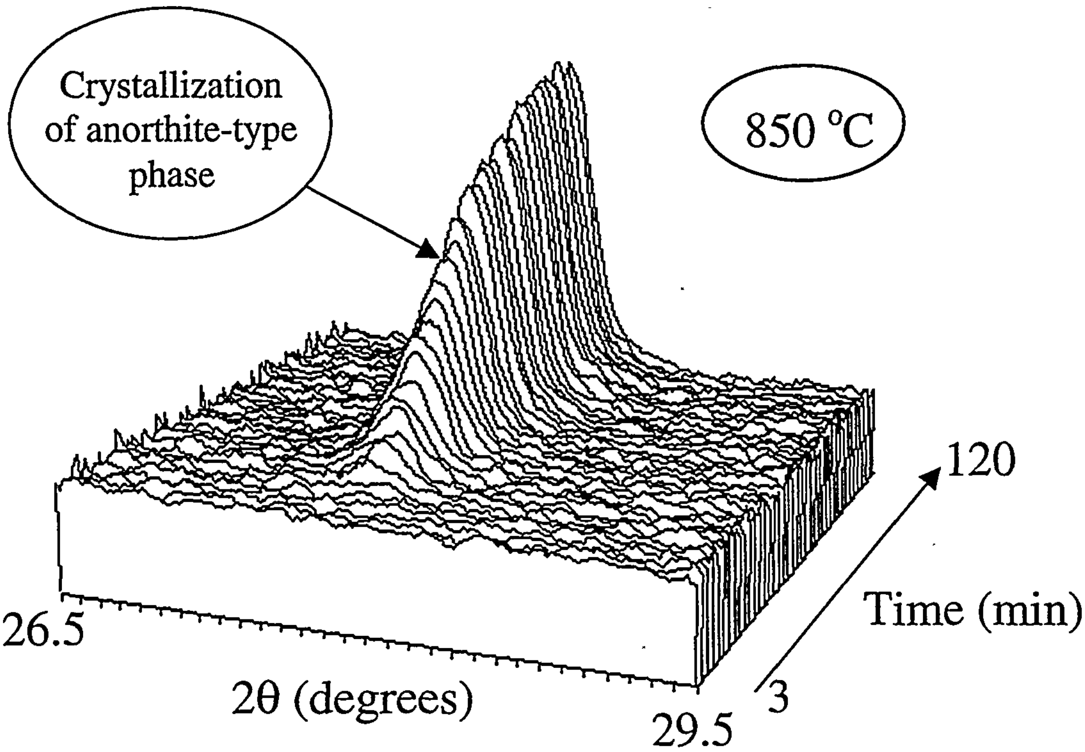

Figure 2. X-ray data showing devitrification behavior for anorthite phase at 850 °C.

Table 1. Anothite Devitrification Kinetics for Dupont 951 LTCC.

Temp. (°C)	Temp. (K)	1/T (K^{-1}) *1000	k (sec^{-1})	Ln k
835	1108	0.9025	5.0e-4	-7.6
850	1123	0.8905	6.6e-4	-7.3
875	1148	0.8711	9.9e-4	-6.9

The HTXRD investigation of the resistor material (see Figure 3) shows some similarities to the LTCC. First, devitrification occurred in the same temperature range. Second, the RuO_2 appeared inert to the devitrification process, similar to the alumina in the LTCC. However, there are some distinct differences in the devitrification process for the resistor material. Figure 3 shows three phases crystallizing from the glass, a monoclinic celcian, a hexagonal celcian, and a 3rd phase that could not be indexed. This phase was tentatively identified as a zinc silicate since further studies via TEM revealed a substantial content of crystalline phase composed of Zn, Si, and O. What is clear from the analysis is that the RuO_2 conductive oxide is stable within this crystallized matrix. Due to the complicated devitrification process of the resistor material, no attempt to model the reaction kinetics was performed.

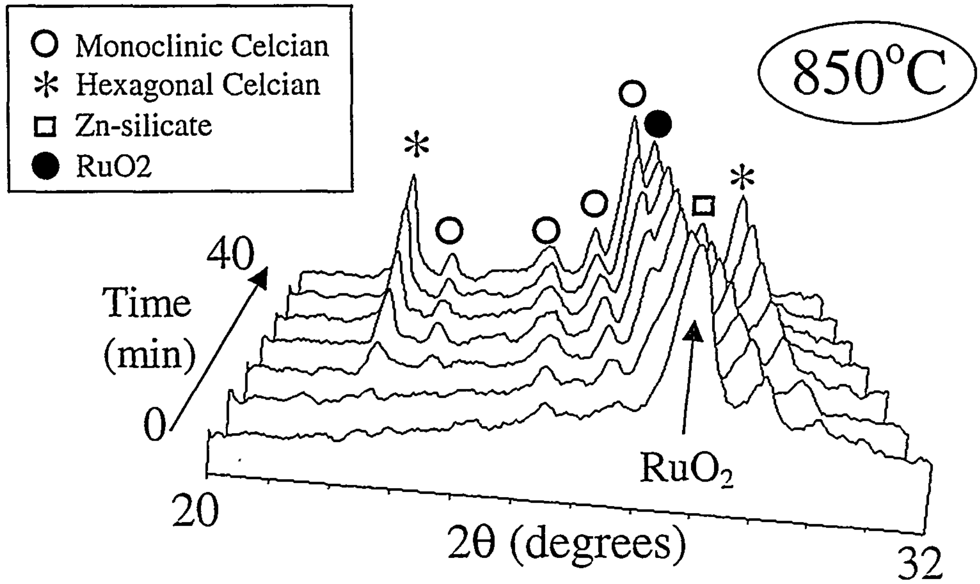

Figure 3. HTXRD data for resistor paste showing devitrification at 850 °C.

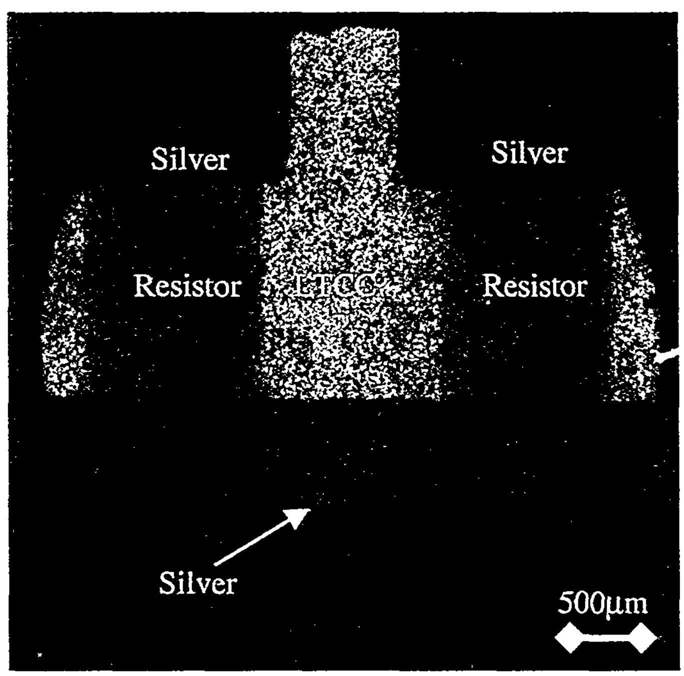

Figure 4. X-ray Radiograph of circuit showing resistors & silver electrodes embedded in LTCC.

An x-ray radiograph for a sample test circuit is shown in Figure 4. This image shows part of an embedded circuit. The circuit is composed of several test resistors in a long row, two of which are viewed in Figure 4. The resistors connect to individual silver electrodes (top) and a common silver electrode (bottom). This X-ray radiograph reveals that the resistors have well defined boundaries with the LTCC as well as with the silver electrodes. All the materials appear to be structurally compatible with one another. There does not appear to be a reaction interface at the boundaries of these materials or a high degree of porosity. Additionally, there is no evidence of cracking due to thermal expansion mismatch or differential sintering. All of these observations are encouraging and indicate that the resistor material is well suited for fabrication of buried components.

CONCLUSION

High temperature XRD is a useful tool to measure the kinetics of glass-ceramic devitrification. The Dupont LTCC showed devitrification of an anorthite phase in the range of 835-875 °C with activation energy of 180 kJ/mol as calculated from kinetic data. The resistor paste showed devitrification of both monoclinic and hexagonal celcian phases as well as a phase believed to be a zinc-silicate. RuO_2 appears to be stable within this devitrified matrix. X-ray radiography results indicate good structural/chemical compatibility between the resistor and LTCC as demonstrated by the distinct interfaces in the observed radiographs.

ACKNOWLEDGMENTS

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