

MICROSTRUCTURAL STUDY ON LOW TEMPERATURE CO-FIRED CERAMIC MATERIALS FOR FUEL CELL COMPONENT USING NUCLEAR TECHNIQUES

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ABSTRACT

The realization fuel cell component based on low temperature co-fired ceramic (LTCC) technology requires the investigations of fired LTCC microstructures. Nuclear techniques, x-ray diffraction, scanning electron microscope, neutron imaging and neutron scattering, were used to characterize the LTCC samples. The majority of the works involved using small angle neutron scattering (SANS) studies on the microstructural of LTCC ceramic tape and development of neutron tomography for future tool to visualize channels inside the fired tape. Most SANS characterization were carried out at SANS instrument at BATAN, Indonesia. Standard sample for resolving tens of micron of object size were measured using simple neutron tomography setup utilizing monochromatic SANS beam at Malaysian Nuclear Agency. The initial microstructural findings indicates that organic additives shape the final microstructural of LTCC after firing with the glassy material possibly fill the space left by the burned organic additives. The tomography results showed that 40 micron size object can be differentiated. The conductor deposited on LTCC is preliminary investigated which will later be used as support for catalyst.

ABSTRAK

Komponen sel bahanapi yang direalisasikan berdasarkan teknologi seramik pembakaran bersuhu rendah (LTCC) memerlukan penyelidikan struktur mikro LTCC yang dibakar. Teknik nuklear, difraksi sinar-x, mikroskop elektron imbasan, pencitraan neutron dan hamburan neutron, digunakan untuk mencirikan sampel LTCC. Sebilangan besar kerja yang terlibat menggunakan kajian hamburan neutron sudut kecil (SANS) menentukan mikro struktur pita seramik LTCC dan pengembangan tomografi neutron untuk alat masa depan untuk memvisualisasikan saluran di dalam pita yang dibakar. Sebilangan besar pencirian SANS dilakukan pada instrumen SANS di BATAN, Indonesia. Sampel standard untuk menyelesaikan puluhan mikron ukuran objek diukur menggunakan penyediaan tomografi neutron sederhana dengan menggunakan sinar SANS monokromatik di Agensi Nuklear Malaysia. Penemuan mikrostruktur awal menunjukkan bahawa aditif organik membentuk struktur mikro akhir LTCC setelah menembak dengan bahan berkaca mungkin memenuhi ruang yang ditinggalkan oleh bahan tambahan organik yang dibakar. Hasil tomografi menunjukkan bahawa objek

berukuran 40 mikron dapat dibezakan. Konduktor yang disimpan di LTCC disiasat awal yang kemudiannya akan digunakan sebagai sokongan untuk pemangkin.

Keywords: LTCC, XRD, SEM, SANS, fuel cell

INTRODUCTION

Low temperature co-fired ceramics (LTCC) technology is a ceramic based electronics packaging technology. The technology allow circuits to be constructed within a ceramic block substrate that enables three-dimensional integration of passive elements such as resistors, inductors and capacitors for a complete electronic circuit [1]. The materials for LTCC microelectronic packaging need to meet stringent requirements in term of electrical, thermal and mechanical properties. Commercial available LTCC systems are glass+ceramic and glass-ceramic.

In the glass-ceramic system, crystallizable glasses were used. The degree of crystallization is crucial to be controlled because it will affect the final properties of tape (mechanical and electrical). Most crystallizable glass type LTCC systems are based on cordierite glass-ceramics. On the other hence, glass+ceramic is a mixture of high melting ceramic fillers and low softening glass and fired at elevated temperature. The properties of this type LTCC were controlled by the ration of glass to the ceramics and the individual properties of the mixtures. Typical systems are borosilicate + alumina and lead borosilicate + alumina. Apart from electronics, because of the modular structure of LTCC, it is possible that LTCC can be used as a fuel cell unit. Figure 1 shows a schematic diagram of a ceramic based fuel cell. The ceramic fuel cell components can be prepared a solid-state. It is simple and an extremely versatile process, best suited for bulk production. In their applications, ceramic oxides are required to have definite shape and microstructure. These characteristics of the sintered body are highly dependent on the starting powder characteristics. It is advantageous to have the material in nano-crystalline form so that its powder characteristics can be precisely tuned. The first part of the investigation is to look onto the microstructural of LTCC using small angle neutron scattering (SANS) technique and developing Nuclear Malaysia own tomography system for fuel imaging.

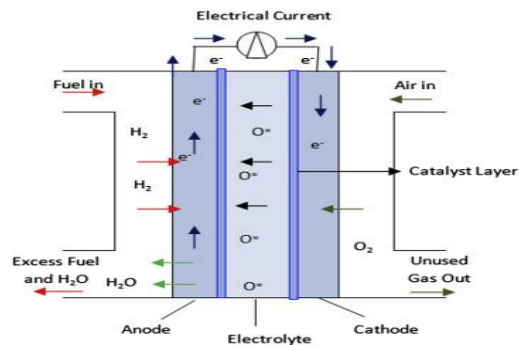


Figure 1. Diagrammatic representation of solid oxide (ceramic) fuel cell [2]. Note: Anode and cathode are made from a ceramic material

EXPERIMENT

Sample preparations

LTCC tape sample was prepared by combination alumina, Al₂O₃ as filler and commercial borosilicate glass. The physical characteristics of the glass and alumina are shown in Table 1 as supplied by the manufacturer. The weight percentage of filler and the addition of titanium isopropoxide were varies in order to studied their effect to the physical properties of the develop tape. Table 2 shows the composition of each sample.

Oil was used as dispersant and an organic acid was used stabilizer in the mixture of ceramic particles and organic additives. Slurries of ceramic particles with organic solvents were prepared and casted on a tape casting

machine. The thickness of the tape was set to 0.5 mm. The green body of tape was then dried at 30 °C before it was cut for 5 to 8 layers and laminated at 21 MPa and 70 °C respectively. The laminated samples were then fired at temperature in the range of 850 to 1000°C for 10 minutes in a temperature-controlled tube furnace. This prepared tape was coded as batch S-45.

Characterizations

All samples were characterized in terms of their physical properties such as density, crystalline phase, surface morphology, dielectric and thermal properties. The thickness of the tape was measured using a Vernier caliper. The laminated and fired density was determined using the standard relation of mass & volume. The crystalline phase of the tape was identified using a Bragg-Brantano XRD technique with Cu anode. The instrument was operated at a power rating of 40 kV and 40 mA, scanning parameters of 2 θ ranging from 20 to 80° with typical step size of 0.02° and at a measuring time of 25 s per step. The microstructure and surface morphology was analyzed from field enhanced scanning electron microscope (FE-SEM) image. Commercial silver paste was printed on surface of and it was fired at temperature in the range of 850 to 1000°C. The compatibility of paste is evaluated through observation and conductivity test.

Measurements were carried out using the 36 m SANS instrument at Neutron Scattering Lab (NSL) at BATAN (Serpong, Indonesia). A small circular sample area of 10 mm diameter was exposed to the neutron beam for 0.5 or 1 hour. The scattered elastic part, due to inhomogeneities in the sample microstructures, was registered on a two-dimensional (2D) position sensitive detector (128 x 128 pixels). The efficiency of the detector was calibrated using water as scattering standard. The scattering data were corrected for empty beam, background counts and detector efficiency, and then radially summed. No neutron tomography measurement was carried out on the samples but a neutron tomography simple system was evaluated to see whether such system can differentiate micron size structures for later use on the samples.

RESULTS AND DISCUSSION

Table 1 shows the physical properties of the sintered tape at 900°C. The tape shrank in the z-direction (thickness) up to 29% giving a final thickness of about 70 micron. The shrinkage in x- and y-direction is quite significant but did not cause the tape to bend. The fired tape remained flat. The material is mostly crystalline as concluded from the XRD pattern obtained [3].

Figure 2 a) shows the SEM image on the surface of the tape. Most pores seemed to be covered by glass material that melted during sintering process. SANS scattering profile indicates that the existence of oriented structure shown by the non-isotropic scattering [4]. The intensity versus scattering vector (Figure 3) shows small bump at 0.03 Å⁻¹. The formation of this structure was believed to be caused by melting glass that replaced the space left behind when organic additives with oriented structure burned during sintering.

Table 1. The physical properties of the sintered tape fired at 900°C.

Specification	S-45 (2011)
Thickness (green), mm	0.1
Shrinkage x, y (%) $\pm 0.3^*$	17
Shrinkage z (%) $\pm 0.5^*$	29
Dielectric constant	5.47
Dissipation Factor @ 1MHz (Max)	2.6×10^{-3}
Density (g/cm ³)	2.2

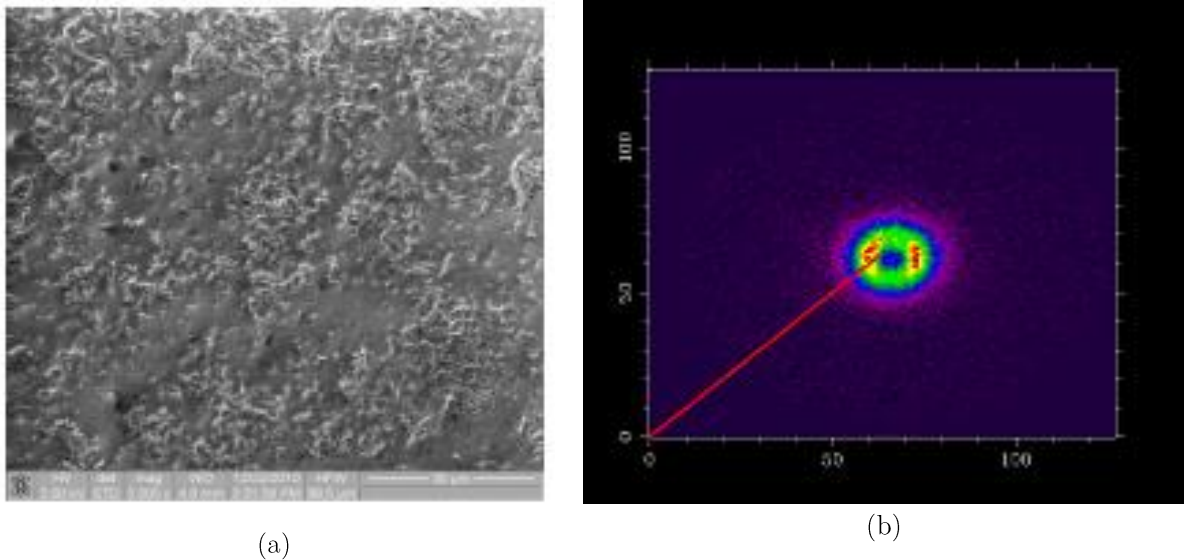


Figure 2. (a) SEM image of tape sintered at 900°C and (b) scattering profile at 400cm sample to detector position (wavelength = 3.9Å)

It is not believed that this non-isotropic scattering was caused by artifacts of Smarter instrument. This oriented structure findings needs to be compared with other SANS instrument for confirmation and the Malaysian Nuclear Agency's SANS instrument (mySANS) can be used. The mySANS is now almost fully operational after a lot of repaired and refurbished done. It is now has a new data acquisition system based on IgorPro [5] and direct beam shows homogenous distribution (Figure 4). Initial investigation on the sample are hampered by reactor operation time as the sample need to be irradiated for a long time to match the experiment at Smarter which has a much higher flux.

In the case of the electrode material, the silver paste when applied on the surface of the tape did not evaporate after firing. The paste was found to be well deposited on the surface and silver conductivity not affected.

Neutron tomography was not used to study the sample yet. Most works involved on imaging standard sample to evaluate the performance of the tomography setup. CCD camera was used for the imaging. This involved resolving object with size in micron. Standard samples were provided by Paul Scherrer Institute (PSI).

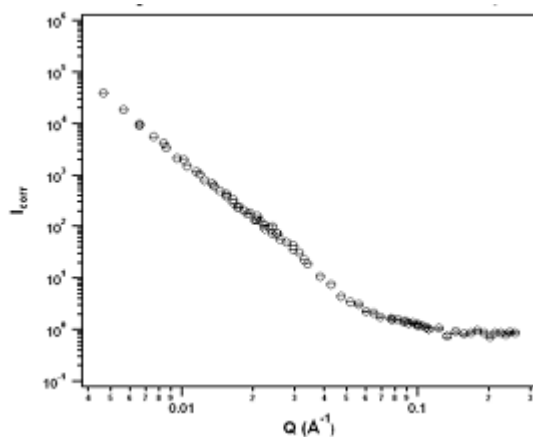


Figure 3. Intensity vs. scattering vector profile for dimensional tape sample sintered at 900°C. Oriented structure possibly at 0.03 Å⁻¹.

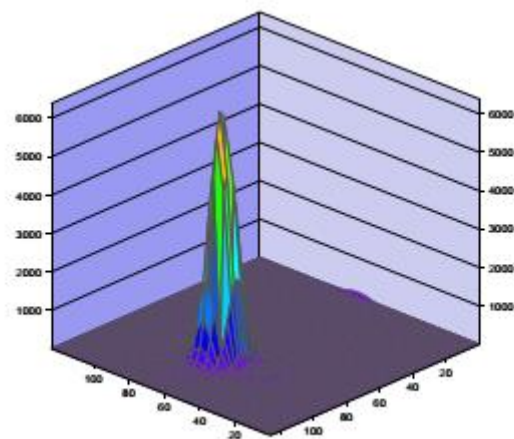


Figure 4. Direct beam profile at 2-position sensitive detector of mySANS.

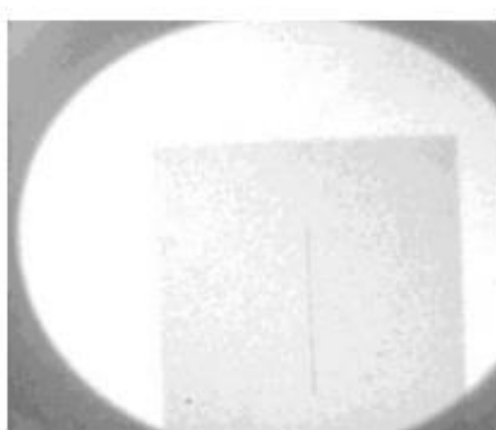


Figure 5. Radiographic image of thin iron solid layer (40 micron) sandwiched between aluminium blocks.

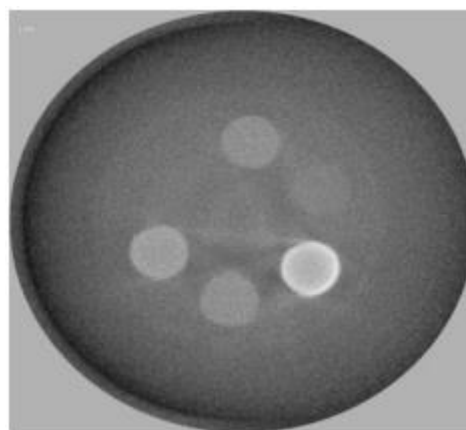


Figure 6. Tomographic image of aluminum cylinder with smaller cylinder of different materials inside.

Figure 5 shows the radiographic image of thin iron solid layer (40 micron) sandwiched between aluminum blocks. The layer is the fine vertical dark line in the middle of the block. Figure 6 shows tomographic image of aluminum cylinder with smaller cylinder of different materials inside it. This tomography utilizes the monochromatic neutron beam of wavelength about 5Å.

CONCLUSION

The LTCC material was believed to contain oriented structures that originated from organic additives used. This structure was formed by glassy material that replaced the organic additives after firing. This can be utilized to generate lines for fuel movement if porosity structure can be controlled. The possible setup of fuel cell LTCC may utilize beta-aluminate as solid electrolyte and silver catalyst electrode. Oriented structure and porosity analysis will be carried based on the scattering data obtained and the oriented structure will be confirmed with mySANS. Tomography characterization will be carried out on the tape sample when the system is established.

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