1P1-2

High Temperature Properties of $CaBi_4Ti_4O_{15}$ /$Bi_4Ti_3O_{12}$

$CaBi_4Ti_4O_{15}$ / $Bi_4Ti_3O_{12}$ の高温特性

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1. Introduction

In recent years, ultrasonic non-destructive testing (NDT) in industrial field has been growing demand.[1),2)] Ultrasonic transducers made by sol-gel composite has been developed for industrial NDT applications.[3-7)] The sol-gel composite is prepared by mixing a piezoelectric powder and a sol-gel solution and it has mainly three advantages. The first one is high temperature durability. This enables ultrasonic NDT at high temperature during operation. The second one is no need of couplant or backing material. These benefits are important especially at high temperatures. The third one is fabrication facility on curved surfaces. Considering ultrasonic NDT in various situations in industrial applications, there is a demand for fabrication on curved surfaces.

In previous study, sol-gel composite ultrasonic transducers $CaBi_4Ti_4O_{15}$(CBT)/Pb(Zr,Ti)O_9(PZT) were manufactured and demonstrated possibility for long term monitoring at 600 °C.[5-7)] However, at high temperatures, Pb in PZT sol-gel phase would vaporize and may affect environment, so it is desired to develop lead-free piezoelectric material. Therefore, in this research, CBT/$Bi_4Ti_3O_{12}$(BiT) which is a new material, was developed. CBT was chosen since it is lead-free, high Curie temperature material, and it can be used at high temperature up to 600 °C continuously from the previous research. BiT was used because it is lead-free, relatively high Curie temperature, and relatively high dielectric constant material. In this research, high temperature durability of CBT/BiT at 600 °C was investigated.

2. Fabrication process

Fabrication process is similar to previous studies.[3-7)] After mixing self-manufactured BiT sol-gel solution and commercial CBT powder, the mixture was ball milled until an appropriate viscosity for spray coating was achieved. Thereafter, the prepared mixture was coated on a titanium substrate by a manual spray coating method. The dimension of titanium substrate was ~3cm, ~3cm, and ~3mm. This dimension titanium was used as a substrate because of low thermal capacitance and high temperature resistance. After spray coating, drying process and firing process was carried out at 150 and 650 °C for 5 minutes each, respectively. These processes, spray coating, drying, and firing, were repeated until the film thickness was reached to the target thickness and the film thickness was measured by a micrometer after each firing process. The target film thickness in this study was 50 µm and those processes were repeated 5 times. By sol-gel spray method, the maximum coating thickness by one process was ~ 50 µm to avoid cracks or peeling. Platinum paste was coated on the manufactured film as top electrode. For curing of platinum paste, thermal processes at 150 °C and 700 °C were executed for 2 hours each. After top electrode fabrication, poling process was carried out at high temperature. After heating the substrate at 700 °C for 10 minutes, the samples were poled by corona discharge. The output voltage of power supply was about 29kV. In this study, the distance between the needle tip and the film was adjusted at a distance between 25 and 30 mm to prevent dielectric breakdown of the film due to arc discharge.

3. Experimental results

CBT/BiT high temperature durability was investigated. Platinum wires were connected to the top electrode and titanium substrate for electrical connection and a ceramic weight was placed onto them as shown in **Fig. 1.** Platinum wires were used because of high temperature durability. A ceramic weight was used because of high temperature durability and no peeling by thermal expansion mismatch caused by adhesive material. The whole sample shown in Fig. 1 was placed inside a furnace and ultrasonic measurements were carried out pulse-echo mode and recorded by a digital oscilloscope at various temperatures.

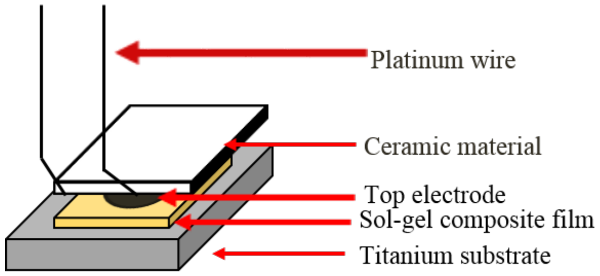

Fig. 1 Schematic of sample fixture.

In the pulse echo mode, reflected echoes from the bottom of 3 mm thick titanium substrate were measured from RT to 600 °C. During the measurement, the temperature was increased by 100 °C increment and the temperature was maintained for 5 minutes before data recording. **Figs. 2-3** shows ultrasonic response in time domain at RT and 600 °C, respectively. Clear multiple echoes with comparatively high signal to noise ratio (SNR) were obtained even at high temperature such as 600 °C. Indeed, signal at 600 °C seems better than that at room temperature, and further curing of platinum top electrode was suspected reason. These results were comparable with that of CBT/PZT. The SNR was stable from room temperature to 600 °C. From this result, CBT/BiT film demonstrated the potential as lead-free high temperature ultrasonic transducer up to 600 °C.

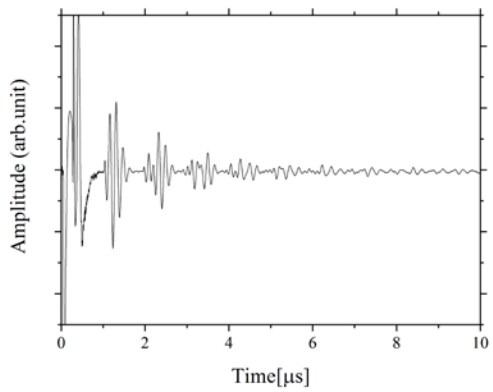

Fig. 2 Ultrasonic response from 3 mm thick titanium substrate at room temperature.

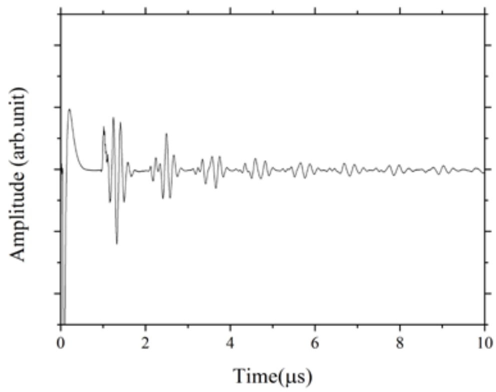

Fig. 3 Ultrasonic response from 3 mm thick titanium substrate at 600℃.

4. Conclusions

In this research, lead-free sol-gel composite CBT/BiT was developed and high temperature durability was investigated. CBT/BiT sol-gel composite films were fabricated on a 3 mm thick titanium substrate by spray coating method. In order to deternine the high temperature durability of CBT/BiT ultrasonic transducers, ultrasonic measurement at various temperatures, i.e. from RT to 600 °C was carried out in an electrical furnace. As a result, ultrasonic response was comparable with that of CBTPZT and CBT/BiT ultrasonic transducer showed the possibility of high temperature NDT applications up to 600 °C. It is necessary to conduct thermal cycle test and long-term duration test to determine real application possibility.

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