High Temperature properties of CaBi₂Ta₂O₉/Bi₄Ti₃O₁₂

CaBi₂Ta₂O₉/Bi₄Ti₃O₁₂の高温特性

Tomoya Yamamoto^{1[‡]}, Syohei Nozawa¹, Minori Furukawa¹, Hajime Nagata², and Makiko Kobayashi¹ (¹Kumamoto Univ., ²Tokyo Univ. of science) 山本智也^{1[‡]}, 野澤勝平¹, 古川美徳¹, 永田肇², 小林牧子¹ (¹熊本大学, 東京理科大学)

1. Introduction

Non-destructive testing (NDT) is widely used in thermal power plants and is important because small defect lead to serious accidents. Therefore, various NDT methods have been developed. Sol-gel composite ultrasonic transducers have been developed to improve high temperature durability, because so-gel composite transducers do not require couplant, nor backing material, and can apply for curved surfaces¹⁻⁵⁾. For carbon dioxide emissions reduction, new-generation thermal power plants has been developed, though NDT method is the issue. In thermal power plants, ultrasound NDT is often used for cooling pipe inspection, though operation temperature of new-generation thermal power plant will be ~700°C in order to increase efficiency. In the previous research, CaBi₂Ta₂O₉(CBTa)/ $Pb(Zr,Ti)O_3(PZT)$ ultrasonic transducers were developed and confirmed that there was high temperature durability up to 840°C in a short time⁵). However, at high temperatures, lead contained in PZT vaporizes and adversely affects environment, so it is necessary to develop lead-free substances. Therefore, it is necessary to develop new lead-free sol-gel composite.

In this research, new sol-gel composite, CBTa/Bi₄Ti₃O₁₂(BiT) was developed. CBTa was chosen as ferroelectric powder phase material because Curie temperature is sufficiently high such as 923°C. BiT was adopted because it is lead-free and the Curie temperature is relatively high such as 675°C. The bulk property was used because it is difficult to measure BiT sol-gel solution property. In this research, high temperature durability of CBTa/BiT transducers were examined. Ultrasonic performance of CBTa/BiT samples were investigated at various temperatures.

2. Sample fabrication

Samples were manufactured by sol-gel spray technique^{1, 3-5)}. First, BiT sol-gel solution was manufactured. CBTa/BiT sol-gel composite was prepared by mixing CBTa piezoelectric powders and BiT sol-gel solution by a ball mill machine for about 1 day. Next, the dimensions of titanium substrates were $30 \times 30 \times 30 \times 3$ mm was covered with an

80-µm-thick paper mask with a 20×20 mm, then CBTa/BiT sol-gel composite was sprayed onto the titanium substrate. Titanium was chosen as substrate material because of high temperature durability and low thermal capacitance. Thermal process, drying at 150°C and firing at 650°C were carried out for 5min each other, was processed after spray coating. These processes repeat until the target films thickness became about 50µm. When CBTa/BiT thin film reached the target film thickness, a platinum upper electrode was formed by drying at 150°C and firing at 700°C for 2 h each other. The upper platinum electrode was formed in the center of the film with 10mm diameter. Next, poling process was performed. For poling, corona discharge was used. Poling was carried out by heating at 950°C for 10 min. There were two reasons for the temperature set for polling. First, since the titanium substrate was thin, it is rapidly cooled down and it reached the target temperature which was slightly higher than Curie temperature of BiT sol-gel phase. Second, it was high enough to promote molecular movement to assist poling. The output voltage was about 31 kV and the output current was about 0.13 mA. The electrical filed was supplied until the sample was cooled down to room temperature. CBTa/BiT fabricated on a titanium substrate is shown in Fig. 1.



Fig. 1. Optical image of CBTa/BiT on $30 \times 30 \times 3mm$ titanium substrate.

3. Experimental results

The maximum temperature test was carried out to confirm the operable limit temperature of CBTa/BiT ultrasonic transducer. The sample was put into the furnace and platinum electrical cables were connected to a platinum top electrode and titanium substrate through holes of the furnace. Platinum electrical cables were the digital oscilloscope connected to and pulser/receiver (P/R). A digital oscilloscope was used for data recording. The furnace temperature was changed from room temperature by 100°C increments, and from the 800°C, which is around the Curie temperature of CBTa, the data was recorded every 10°C. Every temperature, holding time was 5 min. Ultrasonic measurement results in pulse-echo mode at room temperature and 800°C are shown in Figs. 2 and 3, respectively. Multiple reflected echoes are clearly observed with reasonable signal-to-noise ratio (SNR).



Fig. 2. Ultrasonic response of CBTa/BiT sample fabricated on 3-mm-thick titanium substrate at room temperature.



Fig. 3. Ultrasonic response of CBTa/BiT sample fabricated on 3-mm-thick titanium substrate at 800°C.

Fig. 4 shows the sensitivity calculation results of the acceleration deterioration test. The sensitivity was calculated by following equation:

Sensitivity = -
$$(20\log_{10}V_1/V_2 + \text{gain of P/R})$$
 (dB) (1)

Where V_1 is the ideal amplitude, 0.1 (V_{p-p}) in this experiment, V_2 is the amplitude (V_{p-p}) of the second reflected echo from the bottom surface of the substrate. From Fig. 4, the sensitivity was suddenly decreased above 700°C. It is caused by depoling of CBTa piezoelectric powder phase.



Fig. 4. Temperature dependence of CBTa/BiT sensitivity of CBTa/BiT

5. Conclusions

sol-gel CBTa/BiT composite was temperature developed for high ultrasonic applications at 700°C. CBTa/BiT films were fabricated at on titanium substrates by sol-gel spray technique. The maximum operation temperature test was carried out and the ultrasonic performance of the CBTa/BiT was confirmed with reasonable SNR at 800°C. The result of the maximum temperature test was comparable with that of CBTa/PZT. Therefore, CBTa/BiT demonstrated the potential for NDT of the new-generation thermal power plants. Long term operation test is required and will be operated soon.

References

- T. Yamamoto, M. Kobayashi: Jpn. J. Appl. Phys. 57 (2018) 07LB16.
- 2. M, Yugawa, T, Yamamoto, M, Kobayashi: Proc. USE. (2017) 3P1-7.
- T. Yamamoto, M. Yugawa, M. Kobayashi, H. Nagata: Proc. IEEE Int. Ultrason. Symp. (2017) 875.
- 4. T. Kibe, K. Kimoto, M, Kobayashi: Proc. IEEE Int. Ultrason. Symp. (2016) 980.
- F. B. Cegla, P. Cawley, J. M. Allin, and J. O. Davies: IEEE Trans. Ultrason. Ferroelectr. Freq. Control, vol. 58. (2011) 156.