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Poling of $Bi_4Ti_3O_{12}/Pb(Zr,Ti)O_3$ by negative corona discharge

負のコロナ放電による $Bi_4Ti_3O_{12}/Pb(Zr,Ti)O_3$ の分極

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1. Introduction

High temperature ultrasonic transducers using have been investigated in the field of non-destructive testing (NDT) for safety assuarance. It is difficult to apply commercial ultrasonic transducer in this application, mainly due to lack of high temperature durability caused by backing material and couplant. Sol-gel composite ultrasonic transducers have been developed to elminate backing material and couplant problems.[1-5] Sol-gel composite made by $Bi_4Ti_3O_{12}$ (BiT) powders and $Pb(Zr,Ti)O_3$ (PZT) sol-gel solution, BiT/PZT, showed good waveforms until around 550℃. However, the characteristics drastically deteriorated above 500℃. The operation temperature of cooling pipes in thermal power plants could reache 600℃. Therefore, it is required to maintain the characteristics up to 600℃.

In this study, poling was performed by BiT/ PZT negative corona discharge. Poling of BiT/PZT with negative corona discharge is considered to be affected by the polarity of the pulsar receiver. Therefore, it is considered that the depolring in the high temperature region changes. As a result, it is considered that the deterioration of characteristics in the high temperature region can be suppressed by the poling due to the negative corona discharge. For that reason, in this experiment, samples polarized by positive corona discharge and samples polarized by negative corona discharge were prepared. The sensitivity of both samples was then compared and examined.

2. Sample fabrication

BiT/PZT sol-gel composite was made by sol-gel spray technique. First, BiT powders and PZT sol-gel solution were prepared. PZT sol-gel solutions was self-manufactured. BiT powders are commercially available. The mixtures of BiT powders and PZT sol-gel solution were ball milled. Then, the mixtures were sprayed onto titanium substrate by automatic spray machine. The dimensions of titanium substrate were 30mm×30mm×3mm. This substrate was chosen due to low thermal capacitance and high temperature durability. After spray coating, the sample was dried at 150°C for 5 min. After drying, the sample was fired at 650°C for 5 min as well. Those spray coating process and thermal process were repeated until film thickness reached 50μm. After film fabrication, poling was operated by positive corona discharge and negative corona discharge at room temperature. The output voltage of the positive power supply was 35.0 kV. And, the output voltage of the negative power supply was 34.0 kV. Optical image of BiT/PZT film onto titanium substrate is shown in **Fig. 1**. Film thickness of positively polarized BiT/PZT was measured by a micrometer and the value were 48μm. Film thickness of negatively polarized BiT/PZT was 51μm. Piezoelectric constant d_{33} was measured by ZJ-3B piezo d33 meter and the value was 22.4pC/N and -21.3pC/N. After these processes, high temperature silver paste was fabricated on the film as a top electrode. The top electrode diameter was about 1cm. For drying silver paste, thermal process at around 100°C were carried out for 2 h.

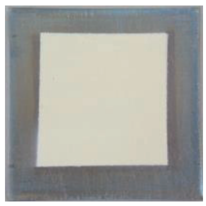

Fig. 1 Optical image of BiT/PZT film

3. Experimental results

Ultrasonic responses of the BiT/PZT samples in pulse-echo mode were recorded from room temperature to 720°C. It is noted that the temperatures are not sample temperatures but temperatures of furnace indicator so that real temperatures must be lower. Platinum wires were used as electrical cables and electrical connection between electrodes and wires were established by a ceramic weight. Samples were set inside an electrical furnace and measurement data was recorded by a digital oscilloscope. First, the ultrasonic response was measured at room temperature in order to confirm the piezoelectricity. Results are shown in **Fig. 2** and **Fig. 3**. Clear multiple echoes from the bottom surface of the titanium substrate were obtained and it was confirmed that poling was successful.

Thereafter, BiT/PZT samples were heated to 720°C. Up to 500°C, the ultrasonic response was measured every 100°C. The ultrasonic response was then measured every 20°C. The electric furnace was held for 5 minutes to keep the temperature. Clear multiple echoes were still observed in both samples at 720°C. However, as mentioned before, the actual temperature of the substrate cannot be accurately determined because substrate temperature measurement was not operated in this time.

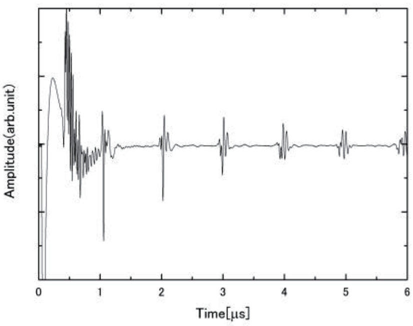

Fig. 2 Ultrasonic response of BiT/PZT film poling by positive corona discharged at room temperature.

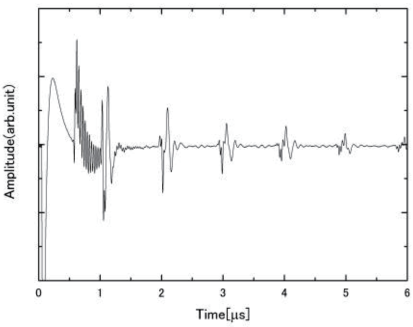

Fig. 3 Ultrasonic response of BiT/PZT film poling by negative corona discharged at room temperature.

As the temperature rises, the piezoelectricity weakens. In order to determine the temperature effect quantitatively, sensitivity was calculated as following equation;

$$\text{Sensitivity} = -\left(20\log_{10}\frac{V_1}{V_2} + \text{Gain of P/R}\right) \quad (1)$$

where V_1 is the reference amplitude, which is 0.8 $V_{p\text{-}p}$ in this experiment, V_2 is the $V_{p\text{-}p}$ of the third reflect echo from the bottom surface of the titanium substrate. P/R means pulser/receiver so that this equation calculates true required gain of pulser/receiver in order to achieve 0.8V. -1 is multiplied to assist intrinsic understanding. The temperature dependence of BiT/PZT sensitivity is shown in **Fig. 4**. It can be seen that negatively polarized BiT/PZT has higher sensitivity in the high temperature region. Depoling of BiT/PZT would affect the result.

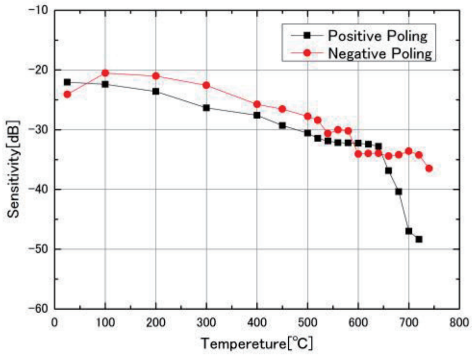

Fig. 4 Sensitivity of BiT/PZT film

4. Conclusion

48μm and 51μm thick BiT/PZT sol-gel composites were fabricated on a 3mm thick titanium substrate to compare negative corona discharge and positive corona discharge. The piezoelectric constant d_{33} was 22.4pC/N and -21.3pC/N. Pulse-echo mode ultrasonic measurement was carried out from room temperature to 720°C. From this study, negatively polarized BiT/PZT has higher sensitivity than positively polarized BiT/PZT in the high temperature region. Further research is required for comparison in thermal cycle test.

References

1. M. Kobayashi, C.-K. Jen, J.-F. Bussiere, and K.-T. Wu: NDT & E Int. **42** (2009) 157.
2. Y. Inada, T. Inoue, M. Kobayashi, H. Nagata, and T. Takenaka: Jpn. J. Appl. Phys. **53** (2013) 07KB10.
3. T. Kibe, K. Kimoto, M, Kobayashi, Proc. IEEE Int. Ultrason. Symp. (2016) 980.
4. K. Kiyofuji, K. Kimoto, M. Kobayashi, Proc. Symp. Ultrasonic Electronics, (2016) 2P1-1.
5. D. Fu, K. Suzuki, and K. Kato, Jpn. J. Appl. Phys. **42** (2003) 5994.
6. T. -C. Wu, M. Kobayashi, M. Tanabe, and C. –H. Yang: sensors. **17** (2017) 1275.
7. M. Kobayashi, T. Inoue and M. Sawada: Proc.Symp. Ultrason Electr(2012)p.209.