Fabrication and properties of thermoelectric oxide thick films deposited with aerosol deposition method

Y. Nakamura *, Y. Matsufuji, and M. Inoue
Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku-cho, Toyohashi, Aichi, 441-8580, Japan
E-mail: nakamura@ee.tut.ac.jp

Abstract. Thermoelectric materials can directly convert thermal energy to electric energy via Seebeck effect and have attracted attention for clean energy harvesting material. Ca$_3$Co$_4$O$_{9+δ}$ (Co349) oxide shows a high thermoelectric performance. Since the Co349 is a misfit-layered oxide, the c-axis oriented structure should be required to achieve high thermoelectric performance. In this study, the Co349 thick film was deposited with aerosol deposition (AD) method. The effect of process parameters on the microstructure and thermoelectric properties were investigated. The thermal strain caused by the difference in thermal expansion coefficient should be less than 0.2%. The deposition rate of 2 µm/min could be attained by controlling particle size distribution. The c-axis oriented Co349 film was obtained after the annealing at the temperature higher than 700°C. Seebeck coefficient of 170 (µV/°C) and electrical conductivity of 110 (S/cm) were achieved at 700 °C in the film annealed at 900 °C for 1 hour. The thermoelectric performance could be kept up to the thick film of 55 µm. These values were as high as those of the usual bulk samples. This suggests that the AD process is effective to fabricate thick film type thermoelectric module.

1. Introduction

Large amount of thermal energy is not effectively used and thrown away as a waste heat. Since this heat is usually dispersed widely and relatively small scale, it is difficult to harvest effectively. Power generation by thermoelectric (TE) energy conversion is promising method to improve efficiency of energy resources because TE power generation system can directly convert waste heat into electricity without driving parts. In particular, TE oxides, which generally show high chemical stability even at high temperatures in air, are promising materials for power generation systems using high-temperature waste heat.

Among the thermoelectric materials, Ca$_3$Co$_4$O$_{9+δ}$ (Co349) oxides were found to show high thermoelectric performance, e.g. ZT~1 in single crystal [1], while this dimension less figure of merit, ZT of polycrystalline sample decreased to about 1/3. This p-type cobaltite, Co349, is a misfit-layered oxide, which consists of alternating layers of a Ca$_2$CoO$_3$ rock-salt-type layer and a CdI$_2$-type CoO$_2$ layer stacked in the c-direction. Due to this layered structure, electrical properties of Co349 such as Seebeck coefficient (S) and electrical conductivity (σ) could be enhanced by forming c-axis aligned textured structure using hot pressing (HP) [2,3] and spark plasma sintering (SPS) [4,5].

Published under licence by IOP Publishing Ltd
For practical usage of TE power generation system, downsized and highly integrated TE modules are required as well as lower production costs. In the case of bulk application, the assembly processes using small pieces are not easy. On the other hand, thin films produced by vapor growth methods has relatively slow growth rates and is not easy to form well grain-aligned structure without using single crystalline substrates. Hence, the development of a novel production method, which can achieve higher deposition rates and high degrees of grain orientation, is expected for production of highly integrated TE modules with low production cost.

The aerosol deposition (AD) is a technique to prepare high-density ceramic thick film by ejecting aerosol consisting of a mixture of fine ceramic particles and gas from the nozzle to the substrate [6-9]. In this method, the ejecting ceramic powder was synthesized by conventional solid-state reaction method. The dense thick film of PZT and $\alpha$-Al$_2$O$_3$ could be obtained with high deposition rate of several $\mu$m/min by proper control of particle size and ejecting condition. In addition, the patterned film could be also formed using a mask deposition. Using the AD method, planer thick film type and multi-layered thick film type TE modules [10] could be achieved.

In this work, the Co349 thick films were fabricated with AD method at room temperature. The effect of process parameters on microstructure and properties was investigated.

2. Experimental
Calcined powder was prepared by conventional solid-state reaction method from the raw materials of CaCO$_3$, Bi$_2$O$_3$, and Co$_2$O$_3$. These powders were weighted in the molar ratio of Ca:Bi:Co = 2.7:0.3:4.0, and were mixed. The mixed powder was calcined at 900°C for totally 60h with intermediate grindings. The calcined powder was finally crashed by ball milling for 24 and 48 h to obtain an appropriate particle size. The Co349 powders were mixed with a N$_2$ carrier gas to form an aerosol flow, and the gas flow rate of 1 L/min was used. This aerosol flow was transported through the nozzle of 10mm x 0.5 mm into an evacuated deposition chamber and deposited on substrates of Si, quartz, sapphire, SUS410, and (GdCa)$_3$(GaMgZr)$_5$O$_{12}$ (SGGG) that were located 10 mm from the nozzle. The film areas were limited in 3mm x 20mm using metal mask. The deposited films were annealed for crystallization at temperatures up to 900 °C for 1 h in air. The crystallinity of the films was analyzed by X-ray diffraction (XRD), and the microstructure was observed with scanning electron microscopy (SEM). Electrical conductivity was evaluated by conventional four-probe method, and Seebeck coefficient was obtained in the temperature range from 400 °C to 700°C in a direction parallel to the surface of the substrate.

3. Results and discussion
3.1. Effect of substrate
The effect of the difference in thermal expansion coefficient between substrate and Co349 was examined by heating the deposited film to 750 °C for 1h. After this heat treatment, the films deposited on quartz and Si substrates showed cracks and were detached from the substrates. The results were summarized in Table 1 with the thermal expansion coefficients of the substrates and the thermal strain caused by cooling from 750°C to room temperature (R.T.) where the thermal expansion coefficient of $\alpha_{Co349} = 9 \times 10^{-6}$/K was used for Co349 to calculate the thermal strain during cooling. As shown in Table 1, the films with the thermal strain larger than 0.47% were detached from the substrate, while the films with thermal strain less than 0.14% did not show any cracks and detachment. In addition, the Co349 films deposited on sapphire substrate showed neither detachment nor cracks after heating up to 900°C. This suggests that the deposited Co349 films show neither cracks nor detachment from the substrate in the case of the thermal strain less than 0.2%, which is the destruction strain commonly used. In the following experiments, we used the SGGG substrate whose thermal expansion coefficient is almost equal to Co349.
Table 1 Thermal expansion coefficient of substrate and the existence of detachment of film from substrate after heat treatment at 750°C for 1h.

| Substrate | Thermal expansion coefficient, $\alpha_{\text{sub}}$ (1/K) | Thermal strain (750°C to R.T.) | Detachment |
|-----------|--------------------------------------------------------|--------------------------------|-------------|
| quartz    | 0.5x10^{-6}                                           | 0.61%                          | Yes         |
| Si        | 2.41x10^{-6}                                          | 0.47%                          | Yes         |
| sapphire  | 7.0x10^{-6}                                           | 0.14%                          | No          |
| SGGG      | 9.0x10^{-6}                                           | 0%                             | No          |
| SUS       | 10.4x10^{-6}                                          | -0.10%                         | No          |

3.2. Effect of particle size distribution

Figure 1 shows the SEM image of the Co349 powder used for AD deposition. Before ball milling, the particle size was in the range between 3 µm and 15 µm. After ball milling for 24 h, the minimum particle size decreased to about 1 µm however large particles of larger than 10 µm still existed. After ball milling for 48 h, most of the particle had a diameter from 0.1 to several µm and some of them showed the particle size about 7 µm. As shown in this image, the number of small particle with the size of a few microns increased as increasing ball milling time, while the relatively large particles about 5-7 µm were still existed after ball milling for 48 h.

Using these powders, Co349 films were deposited with AD process, and the deposition rate was evaluated. In the case of using the powder ball milled for 48 h, a pressed powder structure that was weak and easily falling to pieces was obtained, and a dense adhered film was not attained. In the AD processing, since the dense film is formed by the reduction of crystallite particle size by fracture or plastic deformation at room temperature, the particle speed, which depends on the gas flow rate, should be higher than a critical particle speed [7]. The small particles in the powder ball milled for 48 h may not have enough particle speed to form dense film. To overcome this issue, the increase in gas flow rate would be required. However, the large particles with high speed damaged the substrate and the formed film. Hence, the selection of gas flow rate and the simultaneous control of the particle size distribution are required for the formation of dense film.

The relation between deposition time and film thickness is shown in Figure 2. The dense film could be obtained in the case of using the powder without ball milling, while the deposition rate of this film was smaller than that using the smaller powder of ball milled for 24 h. In both cases, the thickness of the films increased linearly as increasing deposition time. The deposition rate of about 2 µm/min was obtained by using smaller particles ball milled for 24 h. These results suggest that the appropriate particle size exists in the range about a few µm, and the larger particles larger than about 10 µm would...
damage the deposited film. This would be a reason for small deposition rate in the case of non-ball milled particle that included larger particle.

Figure 2 The relation between the deposition time and film thickness.

Figure 3 XRD patterns of (a) calcined powder, (b) as-deposited film, and crystallized film sintered at (c) 400 °C, (d) 500 °C, (e) 700 °C, and (f) 900 °C for 1 h, respectively.
3.3. Effect of crystallized temperature

Figure 3 (a) shows the XRD pattern of the calcined powder, and Fig. 3 (b) showed that of as-deposited film, respectively. As shown in Fig. 3 (b), the as-deposited film showed weak and broad peaks. This means the formation of nano-crystalline structure and/or the introduction of large strain into the deposited Co349 crystal during the collision of the powders with the substrate.

To improve the crystallinity of the film, the films were sintered for 1 h at the temperatures from 400 °C to 900 °C. The XRD patterns of the sintered films were shown in Fig. 3 (c)-(f). As shown in Fig. 3 (c), the XRD peaks of the sample sintered at 400 °C for 1 h was almost the same as those of as-deposited film. However, the XRD peaks of the sample sintered at 500 °C became sharp, and the improvement of the intensity was also observed. In the case of the samples sintered at the temperature higher than 500 °C, the peak intensity increased as increasing sintering temperature. This means that the sintering at the temperature higher than 500 °C is required to recover the crystallinity of deposited Co349 film. In addition, it should be mentioned that the almost c-axis oriented Co349 films could be obtained by AD method in the samples sintered at the temperature higher than 700 °C since the intensity of the peaks except for (0 0 l) faces was very weak in those samples.

Figure 4 shows the top view and cross sectional images of the samples sintered at 700-900 °C for 1 h, where the horizontal direction of the cross sectional view is in parallel to the substrate face. The sample sintered at 700 °C showed a dense structure and was consisted of the particles with submicron scale. As increasing the sintering temperature, the Co349 grains were grown as platelets, and the sample sintered at 900 °C consisted of the grains grown to 1 µm or larger. In addition, the sintered film was consisted of the plate like crystals piled up in layers as clearly seen in the sample sintered at 900 °C. This also supports that those samples had the c-axis oriented structure as suggested in XRD analysis.

A reason why the c-axis oriented structure could be obtained by AD process is thought to be the platelet shape of the Co349 crystal. The Co349 crystal easily breaks into plate like shape due to the anisotropic structure when the powder was collided with the substrate. The crashed powder with plate like shape would be piled up as the layered structure since the wide ab-face easily becomes parallel to the substrate surface. Such the grains would become large during sintering and formed the c-axis
aligned layered structure. In the end, the high temperature sintering enhanced the grain growth, and the well textured structure was achieved in the sample sintered at 900 °C.

The thermoelectric properties of Seebeck coefficient and electrical conductivity were evaluated in those sintered samples with the thickness of 7 µm. The results were shown in Figure 5 with the properties of bulk samples fabricated with HP [2] and SPS [5] methods. The sample sintered at high temperature showed the large thermopower (Seebeck coefficient), while the difference among the samples was not so large. The sample sintered at 900 °C showed the highest thermopower of about $S = 170 \mu \text{V/°C}$ at 700 °C. On the other hand, the electrical conductivity of the sample sintered at 700 °C was only about $\sigma = 60 \text{S/cm}$, while that of the sample sintered at 900 °C was higher than 110 S/cm. The thermoelectric properties of the sample sintered at 900 °C were as high as those of bulk samples fabricated with HP and SPS method since the dense and well aligned large grain structure was achieved in the sample. As shown in this figure, the difference in electrical conductivity among the samples sintered at different temperature was larger than those in Seebeck coefficient. This would be explained by the connection between grains. Seebeck voltage is the potential difference generated in Co349 grain and was affected by the crystallinity of the Co349 grains. The crystallinity of the Co349 grains would be recovered during the annealing over 700 °C, and the difference among the samples would be small. On the other hand, the electrical conductivity is the transport property and is affected by the crystallinity of Co349 and the connection between the grains. The results shown in Fig. 5 (b) suggested that the grain connection was not enough in the sample annealed at 700°C and became good as increasing the annealing temperature.

3.4. Effect of film thickness

The effect of film thickness on the thermoelectric properties is shown in Figure 6. The Seebeck coefficient of the samples were almost the same value irrespective of film thickness after sintering at 900 °C for 1h as shown in Fig. 6 (a). On the contrary, The samples with the thickness larger than 5 µm showed almost the same electrical conductivity, however the electrical conductivity of the 1 µm thick sample was only about 40 S/cm which was almost less than half of that of the other samples.

To see the reason for this low electrical conductivity, the cross sectional structure of 7 µm thick sample was observed by SEM and is shown in Figure 7. The Co349 grains in the region about 1 µm thick from the interface between substrate and AD film was small and poor textured compared to upper region in the AD film. The rough interface of the substrate would suppress the grain growth along the surface of the substrate. This rough interface may be caused by the damage due to the

Figure 5 Thermoelectric properties of the samples sintered at 700-900°C for 1h. (a) Seebeck coefficient, (b) electrical conductivity.
collision of large particles in the early stage of AD deposition. As a result, the c-axis textured structure did not be developed in the thin 1 µm thick film, and this poor structure resulted the low electrical conductivity. However, the effect of rough interface was limited near the interface. The well developed textured structure was achieved in the region thicker than 2 µm. Since the effect of poor textured initial layer was not so large in the thick film, the electrical conductivity of those samples showed almost the same value. So the increase in thickness of Co349 film would have less effect to decrease the thermoelectric properties. However, the Seebeck coefficients of the thick films were sharply decreased at 700 °C, while that of the 1µm thick film was not show such the decrease. The reason of this sudden reduction is not clear. Since the electrical conductivity of those samples did not show any change at 700 °C, the microstructure and composition would not be different so much in these samples. Further investigation is needed to clarify this change at 700°C.

4. Summary
The Co349 thick film was fabricated by AD method, and the effect of process parameters on the microstructure and thermoelectric properties were investigated. The Co349 film deposited with AD method showed the dense c-axis oriented structure after sintering at the temperature higher than
700 °C. The film annealed at 900 °C showed the thermoelectric properties as high as those of the usual bulk samples fabricated by HP and SPS method. This high thermoelectric performance could be kept in the thick film of 55µm. This suggests that the AD process is a good candidate to fabricate thick TE films and to realize multi-layered thick film type TE modules.

References

[1] Shikano M and Funahashi R 2003 Appl. Phys. Lett., 82 1851
[2] Xu G, Funahashi R, Shikano M, Matsubara I, and Zhou Y Appl. Phys. Lett. 80 3760
[3] Prevel M, Lemonnier S, Klein Y, Hebert S, and Chateigner D. 2005 J. Appl. Phys. 98 093706
[4] Liu Y, Lin Y, Shi Z, Nan CW, and Shen Z 2005 J. Am. Ceram. Soc. 88 1337
[5] Liu Y, Lin Y, Jiang L, Nan CW, and Shen Z 2008 J. Electroceram. 21 748
[6] Akedo J and Lebedev M 1999 Jpn. J. Appl. Phys. 38 5397
[7] Akedo J 2006 J. Am. Ceram. Soc. 89 1834
[8] Akedo J 2008 J. Therm. Spray Technol. 17 181
[9] Shin KH, Mizoguchi M, and Inoue M 2007 J. Magnetics 12 129
[10] Okamoto T, Horii S, Uchikoshi T, Suzuki TS, Sakka Y, Funahashi R, Ando N, Sakurai M, Shimoyama J, and Kishio K, Appl. Phys. Lett. 89 081912