Synthesis of (Y,Er)₂O₃ Films from Multiple-Nuclei EDTA·(Y,Er)·H Complexes by Flame Spray Method

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In this investigation, rare earth metal oxide films were synthesized from metal complexes of ethylenediaminetetraacetic acid (metal-EDTA) by utilizing a flame spray technique. Two raw metal-EDTA powders were prepared as starting materials in order to synthesize (Y,Er)₂O₃ films on stainless steel (SUS) substrates by a reaction that is promoted by the combustion of gaseous H₂-O₂. Molecularly mixed EDTA·(Y,Er)·H and mechanically mixed EDTA·Y·H + EDTA·Er·H complexes were subsequently prepared. The existence of Y₂O₃ and Er₂O₃ crystalline phases was confirmed for the EDTA·Y·H + EDTA·Er·H mixtures. Lamellar structures were formed on the film with a porosity of 9.5%. Alternatively, a homogenous, (Y,Er)₂O₃ film was obtained from the EDTA·(Y,Er)·H complex, with a film porosity of 31.8%. These results indicate that uniform (Y,Er)₂O₃ films were synthesized on SUS substrates from molecularly mixed EDTA·(Y,Er)·H powders. [doi:10.2320/matertrans.T-M2015832]

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1. Introduction

Metal-ethylenediaminetetraacetic acid (metal-EDTA) complexes are key intermediates in the synthesis of metal oxides. Some characteristics of metal-EDTA complexes include low decomposition temperatures,^{1,2)} and a uniform stoichiometry that can be utilized in the design of metal-EDTA solutions.³⁾ The metal-EDTA complexes are converted to metal oxides through firing in an atmosphere containing an oxidative conditions. Additionally, multiple-nuclei metal oxides are synthesized from multiple-nuclei EDTA complexes.^{4,5)} For example, hollow metal oxide particles were obtained through spray drying and oxidation processes in air.^{6,7)} The obtained metal oxide particles possessed a uniform stoichiometry, which was confirmed by a particle analyzing system.⁸⁾ Another example was reported by Nakamura *et al.*, in which strontium titanium oxide (SrTiO₃) films were fabricated with a Sr/Ti elemental ratio of approximately 1.00.⁹⁾ The EDTA·Sr·NH₄ and EDTA·Ti·NH₄ pellets were then applied as a target in the production of the SrTiO₃ films using the laser deposition method. Therefore, the synthesis of metal oxides using a metal-EDTA complex is advantageous for easily obtaining well-organized ceramic powders with a complicated metallic composition.

Various metal oxide films were synthesized from metal-EDTA powders in a commercial flame spray apparatus.^{10,11)} For example, a thick yttria (Y₂O₃) film was fabricated on a stainless steel (SUS) substrate with the EDTA·Y complex in the presence of the combustion gases C₂H₂-O₂ and H₂-O₂. The formation of thick metal oxides, Y₂O₃, europia (Eu₂O₃), and erubia (Er₂O₃) films with high deposition rate was accomplished with metal-EDTA powders in an H₂-O₂ flame.¹²⁾ The decomposition and oxidation of the metal-EDTA subsequently occurred, and the porosity of the films was in the range of 6–15%. The properties of the films varied with the species of metal ion in the metal-EDTA complex. The degree of collision of the particles at the impact to

substrate is also thought to be a function of the volume and mass of the particles. Therefore, the true density of the metal oxide particles is quite significant in this process.

In this study, the molecularly mixed EDTA·(Y,Er)·H and mechanically mixed EDTA·Y·H + EDTA·Er·H complexes were utilized as the starting materials, and the formation of (Y,Er)₂O₃ films on SUS substrates is expected from this work. There exist three potential candidates for the reactions involving metal-EDTA complexes. One expected process is the independent decomposition/oxidation for EDTA·Y·H and EDTA·Er·H complexes. The second potential process involves the preferential decomposition/oxidation of either the EDTA·Y·H or EDTA·Er·H complex. The third potential process is the simultaneous decomposition/oxidation of both the EDTA·Y·H and EDTA·Er·H. We investigated the obtained films using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX). The thicknesses and cross-sectional porosities of the films were also estimated from the obtained SEM and EDX images. The reaction processes for the molecularly mixed EDTA·(Y,Er)·H and the mechanically mixed EDTA·Y·H + EDTA·Er·H complexes are subsequently discussed.

2. Experimental Procedure

2.1 Process and materials

We prepared raw materials via metal-EDTA route.^{6–12)} For example, the reagent used was obtained from Y₂(CO₃)₃ for the preparation of crystalline EDTA·Y·H complexes. A mixture of Y₂(CO₃)₃ and EDTA·4H₂O solution was stirred. Then, the solution with EDTA·Y·H was concentrated using an evaporator to form a slurry. The slurry was cooled to room temperature and stirred. Finally, the crystalline EDTA·Y·H was separated from the slurry using a centrifuge. Based on the protocol mentioned above, the EDTA·Y·H, the EDTA·Er·H and EDTA·(Y,Er)·H complexes (Chubu Chelest Co., Ltd.) were prepared for the synthesis of the films in this study. The molar ratio for the EDTA·(Y,Er)·H complex was Y : Er =

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1 : 1. The obtained EDTA·Y·H + EDTA·Er·H materials were weighed as a 1 : 1 molar ratio, and were subsequently mixed with a commercial milling machine for 30 s. The mixed complex was then prepared through mechanical mixing. Hence, the “molecularly mixed” EDTA·(Y,Er)·H and the “mechanically mixed” EDTA·Y·H + EDTA·Er·H were prepared.

A conventional flame spray apparatus consisting of a feed unit (5MPE, Sulzer Metco) and a spray gun (6P-II, Sulzer Metco) was used to carry out the reactive spraying. This equipment is used commercially for flame spraying, and typically deposits metal films with an acetylene flame. The mixture was then placed into the feed unit and transported by a N₂ gas flow to the spray gun, and the vibrator in the feed unit was then turned on. The carrier gas flow rate was 7.1 L/min. A mixture of H₂ and O₂ at flow rates of 32.6 and 43.0 L/min, respectively, was used as the flame gas. The EDTA·(Y,Er)·H and the EDTA·Y·H + EDTA·Er·H powders were mixed with the flame and reacted with O₂ after the thermal decomposition of EDTA. The reacted particles were then sprayed onto a SUS substrate (SUS304, 30 mm × 50 mm × 1 mm) that was previously sand-blasted by #60 alumina particles (99.7% pure, 212–250 μm particle size, Fuji Manufacturing Co., Ltd.), resulting in the deposition of a metal oxide film. The stand-off distance (a distance between the spray gun and the substrate) was 150 mm. Gun traverse rate was 50 mm/s. The spray nozzle was moved in a longitudinal direction, and the duration of the deposition to go through whole substrate was approximately 6 s/scan without pre-heating the substrate. The total duration of the deposition was 24 s for total spraying time. An interval duration of approximately 30 s was set for each spray scan.

2.2 Evaluation method

XRD (M03XHF22, MAC Science Co., Ltd.) was conducted with Cu K α radiation in order to observe the crystal structure. The surface and cross-sectional morphologies of the films were observed by performing field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL). The elements contained in the sample, and their distributions, were estimated by performing energy-dispersive X-ray (EDX) spectroscopy, combined with FE-SEM. Film thicknesses and cross-sectional porosities for the obtained samples were estimated by using ImageJ software (available for free at <http://rsbweb.nih.gov/ij/>).

3. Results and Discussion

We prepared EDTA·(Y,Er)·H and EDTA·Y·H + EDTA·Er·H complexes as starting materials. From surface SEM observation, the morphologies of the two complexes are quite different, as shown in Fig. 1. The mechanically mixed EDTA·Y·H + EDTA·Er·H complex consists of an aggregation of rectangular parallelepipeds (Fig. 1(a)). The powder was simple mixture of the particle containing Y or Er based complex (Fig. 1(b)). Alternatively, the aspect ratio of the molecularly mixed EDTA·(Y,Er)·H complex was higher than the aspect ratio of the mechanically mixed EDTA·Y·H + EDTA·Er·H complex (Fig. 1(c)). Each particle contains both of Y and Er based complexes (Fig. 1(d)).

Fig. 1 SEM and elemental mapping images of raw metal-EDTA complexes: (a), (b) EDTA·Y·H + EDTA·Er·H, and (c), (d) EDTA·(Y,Er)·H. Black points indicate Er atom, and gray points indicate Y atom.

Fig. 2 Photographs of films synthesized on SUS304 substrates using the flame spray apparatus from (a) EDTA·Y·H + EDTA·Er·H, (b) EDTA·(Y,Er)·H crystals.

Therefore, the elemental distributions in the raw metal-EDTA complexes were quite different.

A photograph of the two metal oxide films fabricated on the SUS304 substrates is shown in Fig. 2. For the deposition of the Y₂O₃ and Er₂O₃ films on SUS substrates, the colors of these films were white and pink, respectively.¹²⁾ This result implies that the color of obtained films would be a blend of the colors of these films, which is referred to as magnolia. The color of obtained metal oxide films is in fact magnolia, which is thought to be derived from the color of the raw metal-EDTA powders.

Figure 3 displays the SEM of the film surfaces, and the elemental mapping images of the obtained films for the EDTA·Y·H + EDTA·Er·H and EDTA·(Y,Er)·H complexes. For the mechanically mixed EDTA·Y·H + EDTA·Er·H complex (Fig. 3(a) and Fig. 3(b)), the powder was simple mixture of the particle containing Y or Er based complex. Mixture of the metal oxide particles was observed. The mixture was synthesized from Y or Er based complex. Particularly, the flat morphology of the obtained particles with the Er count was confirmed in the film. Alternatively, each particle was contained both of Y and Er atoms counts for molecularly mixed EDTA·(Y,Er)·H complex (Fig. 3(c) and Fig. 3(d)). The existence area of elemental amounts was equal for both Y and Er. The elemental distributions of the obtained metal oxide films varied according to the mixing procedure for the raw metal-EDTA complex. In a previous study, the metal species in the raw metal-EDTA complex changed the particle

Fig. 3 Surface SEM and elemental mapping images of films synthesized on SUS304 substrates using the flame spray apparatus from (a), (b) EDTA·Y·H + EDTA·Er·H, (c), (d) EDTA·(Y,Er)·H crystals. Black points indicate Er atom, and gray points indicate Y atom.

Fig. 4 Cross-sectional SEM and elemental mapping images of films synthesized on SUS304 substrates using the flame spray apparatus from (a), (b) EDTA·Y·H + EDTA·Er·H, (c), (d) EDTA·(Y,Er)·H crystals. Black points indicate Er atom, and gray points indicate Y atom.

behavior during the reaction process.¹²⁾ Therefore, these results implied that the formation of the obtained metal oxide films would be different between the mechanically mixed EDTA·Y·H + EDTA·Er·H complex and the molecularly mixed EDTA·(Y,Er)·H complex.

The cross-sectional morphology and elemental distribution were observed by conducting SEM and EDX analyses. Figure 4 displays the cross-sectional SEM and elemental mapping images for the obtained films of the EDTA·Y·H + EDTA·Er·H and EDTA·(Y,Er)·H complexes. An average thickness of 12.6 μm was reported for the film synthesized on the SUS substrate with mechanically mixed EDTA·Y·H + EDTA·Er·H complex. The estimated cross-sectional porosity was 9.5%. The sample was contained Y or Er atom from cross-sectional observation, and the lamellar elemental distributions of Y and Er atoms were confirmed. Alternatively, the sample was contained both of Y and Er

Fig. 5 XRD profiles at $2\theta = 10\text{--}80^\circ$ for films synthesized on SUS304 substrates using the flame spray apparatus from (a) EDTA·Y·H + EDTA·Er·H, (b) EDTA·(Y,Er)·H crystals compared to ICDD cards of cubic Y_2O_3 , cubic/monoclinic Er_2O_3 and $(\text{Er}_{0.333}, \text{Y}_{0.667})_2\text{O}_3$ crystals.

atoms in the film obtained from the molecularly mixed EDTA·(Y,Er)·H complex, and an average thickness of 21.6 μm was reported for the film synthesized on SUS substrate. The estimated cross-sectional porosity was 31.8%. The estimated film thickness and porosity varied according to the mixing procedure of the raw metal-EDTA complex. From observed microstructures in obtained films, the decomposition/oxidation processes for these complexes would be depended on their preparation method. These phenomena were different from established thermal spray techniques. In established techniques, collision energy of flying particles to the substrate during deposition is one of key factors for determining film's microstructure.^{13,14)}

Identification of the crystalline structure of the obtained films was conducted by XRD measurements. Figure 5 displays the XRD profiles at $10\text{--}80^\circ$ of the two films deposited on SUS substrates. Diffraction peak splitting was observed in the deposited film containing the EDTA·Y·H + EDTA·Er·H complex. Alternatively, splitting was not observed in the deposited film containing the EDTA·(Y,Er)·H complex. Next, the peak assignments for the films were performed using ICDD cards. The XRD profiles at $30\text{--}35^\circ$ of the two films deposited on the SUS are shown in Fig. 6. The existence of three crystalline structures— Er_2O_3 with monoclinic (ICDD card No: 01-077-6226), Er_2O_3 with cubic (ICDD card No.: 00-008-0050), and Y_2O_3 with cubic systems (ICDD card: 00-041-1105)—were confirmed for the film obtained from EDTA·Y·H + EDTA·Er·H. In a previous study, cubic Er_2O_3 films were synthesized using the atomic

Fig. 6 XRD profiles at $2\theta = 30\text{--}35^\circ$ for films synthesized on SUS304 substrates using the flame spray apparatus from (a) EDTA·Y·H + EDTA·Er·H, (b) EDTA·(Y,Er)·H crystals compared to ICDD cards of cubic Y₂O₃, cubic/monoclinic Er₂O₃ and (Er_{0.333}, Y_{0.667})₂O₃ crystals.

layer deposition method.¹⁵⁾ The Er₂O₃ films are a candidate material for optical communications¹⁶⁾ and prototype reactors.¹⁷⁾ Alternatively, the crystal species of the (Y,Er)₂O₃ were confirmed in the films containing the EDTA·(Y,Er)·H complex. Six ICDD cards of the (Y,Er)₂O₃ crystal exist, which are (Er_{0.9}, Y_{0.1})₂O₃ (ICDD card No: 00-058-0482), (Er_{0.8}, Y_{0.2})₂O₃ (ICDD card No: 00-058-0589), (Er_{0.667}, Y_{0.333})₂O₃ (ICDD card No: 00-0587-1094), (Er_{0.333}, Y_{0.667})₂O₃ (ICDD card No: 00-057-1095), (Er_{0.2}, Y_{0.8})₂O₃ (ICDD card No: 00-057-1093), and (Er_{0.1}, Y_{0.9})₂O₃ (ICDD card No: 00-057-1092). An ICDD card for the (Er_{0.333}, Y_{0.667})₂O₃ crystal is shown in Figs. 5 and 6. Small differences were observed in the ICDD cards for the Y₂O₃, Er₂O₃, and (Y,Er)₂O₃ crystals. The coating would be composed of the solid solution of Y₂O₃ and Er₂O₃ in various compositions. Therefore, we conducted quantitative elemental analysis for the obtained metal oxide particles under the same conditions as the EDTA·(Y,Er)·H complex by ICP-AES, which was conducted in order to investigate the stoichiometric values of Y and Er atoms in the sample. The quantitative analysis results are shown below. The obtained molar ratio was Y : Er = 1.052 : 1.000 for these particles. Alternatively, the obtained ratio for the EDTA·(Y,Er)·H complex was 1.007 : 1. These ratio values indicate that no deviation of the Y and Er compositions from the raw materials occurred. A uniform (Y,Er)₂O₃ layer was then synthesized on the SUS substrate with multiple-nuclei EDTA·(Y,Er)·H complexes using a commercial flame spray apparatus.

Here, we discussed the reaction processes of the mechanically mixed EDTA·Y·H + EDTA·Er·H and molecularly mixed EDTA·(Y,Er)·H complexes. For the mechanically mixed Y-EDTA + Er-EDTA complex, Y₂O₃ and Er₂O₃ particles were formed individually during the reaction process. Alternatively, the existence of (Y,Er)₂O₃ crystals were confirmed in the films prepared from EDTA·(Y,Er)·H. In thermodynamic terms, no solid solubility limits were observed in Y₂O₃-Er₂O₃ system,¹⁸⁾ which defines as the congruent melting phenomenon. Lamellar structures of Y₂O₃ and Er₂O₃ were obtained from the mechanically mixed EDTA·Y·H + EDTA·Er·H complex, and the flying particles of Y₂O₃ and Er₂O₃ each possess a different mass and velocity, based on the characteristics of the raw material (particle sizes, shapes, densities and so on). The attainment duration to the SUS substrate for these flying particles depended on the oxide species. Therefore, a lamellar structure layer of Y₂O₃ and Er₂O₃ was formed from the mechanically mixed EDTA·Y·H + EDTA·Er·H complex. Alternatively, the formation of a uniform (Y,Er)₂O₃ layer was obtained from the EDTA·(Y,Er)·H complex in an H₂-O₂ flame. After the decomposition and oxidation processes of the EDTA·(Y,Er)·H complex, the flying particles of (Y,Er)₂O₃ produced a porous metal oxide layer with the EDTA·(Y,Er)·H complex. These results indicate that a uniform multi-metal oxide layer was synthesized from the multiple-nuclei EDTA·(Y,Er)·H complex. Additionally, these results suggest that the metal oxide layer structures are controlled by the combination methods of the metal ions and the metal complex.

4. Conclusion

Metal oxide films containing multiple nuclei were synthesized on a SUS substrate with two forms of metal-EDTA complexes. Molecularly mixed EDTA·(Y,Er)·H and mechanically mixed EDTA·Y·H + EDTA·Er·H complexes were subsequently prepared. The inhomogeneous, lamellar structures of Y₂O₃ and Er₂O₃ with 9.5% film porosity were synthesized on SUS substrate by the EDTA·Y·H + EDTA·Er·H complexes. Alternatively, the homogenous, (Y,Er)₂O₃ crystalline phase based on Y₂O₃-Er₂O₃ system with a porosity of 31.8% was synthesized on the SUS substrate. Therefore, the formation of a (Y,Er)₂O₃ crystalline phase was carried out by the molecularly mixed EDTA·(Y,Er)·H powder.

REFERENCES

- 1) W. Zhou, Z. Shao and W. Jin: *J. Alloy. Compd.* **426** (2006) 368–374.
- 2) D. Zhang, X. Zhang, X. Ni, J. Song and H. Zheng: *Cryst. Growth Des.* **7** (2007) 2117–2119.
- 3) H.-W. Wang, D. A. Hall and F. R. Sale: *J. Am. Ceram.* **75** (1992) 124–130.
- 4) Y. Narendar and G. L. Messing: *Catal. Today* **35** (1997) 247–268.
- 5) G. Herrera, E. Chavira, J. J.-Mierci, A. Ordonez, E. F.-Israel, L. Banos, E. Bucio, J. Guzman, O. Novelo and C. Flores: *J. Alloy. Compd.* **479** (2009) 511–519.
- 6) H. Saitoh, K. Kawahara, S. Ohshio, A. Nakamura and N. Nambu: *J. J. Ceram. Sci.* **110** (2002) 874–876.
- 7) H. Saitoh, R. Satoh, A. Nakamura, N. Nambu and S. Ohshio: *J. Mater. Sci.* **37** (2002) 4315–4320.

- 8) H. Saitoh, K. Kawahara, S. Ohshio, A. Nakamura and N. Nambu: *Sci. Tech. Adv. Mater.* **6** (2005) 205–209.
- 9) A. Nakamura, R. Satoh, S. Ohshio, N. Nambu and H. Saitoh: *J. J. Appl. Phys.* **41** (2002) 3033–3038.
- 10) H. Akasaka, M. Ohto, Y. Hasebe, A. Nakamura, S. Ohshio and H. Saitoh: *Surf. Coat. Tech.* **205** (2012) 3877–3880.
- 11) K. Komatsu, T. Tsuchiya, Y. Hasebe, T. Sekiya, Y. Hasebe, A. Toyama, A. Nakamura, H. Akasaka and H. Saitoh: *J. Thermal Spray Technol.* **23** (2014) 885–889.
- 12) K. Komatsu, T. Sekiya, A. Toyama, Y. Hasebe, A. Nakamura, M. Noguchi, Y. Li, S. Ohshio, H. Akasaka, H. Muramatsu and H. Saitoh: *J. Thermal Spray Technol.* **23** (2014) 833–838.
- 13) P. Fogarassy, D. Gerday and A. Lodin: *Mech. Res. Comm.* **32** (2005) 221–239.
- 14) S. Sampath, X. Y. Jiang, J. Matejicek, L. Prchlik, A. Kulkarni and A. Vaidya: *Mater. Sci. Eng. A* **364** (2004) 216–231.
- 15) J. Paivasaari, C. L. Dezelah, IV, D. Back, H. M. E. Kaderi, M. J. Heeg, M. Putkonen, L. Niinisto and C. H. Winter: *J. Mater. Chem.* **15** (2005) 4224–4233.
- 16) M. Nolan and S. D. Elliott: *Chem. Mater.* **22** (2010) 117–129.
- 17) A. Suzuki, T. Chikada and T. Tanaka: *J. Plasma Fusion Res.* **89** (2013) 349–358.
- 18) E. R. Andrievskaya: *J. Euro. Ceram. Soc.* **28** (2008) 2363–2388.