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Synthesis of Y_2O_3 Films by Spray Coating with Milled EDTA·Y·H Complexes

Keiji Komatsu, Tetsuo Sekiya, Ayumu Toyama, Atsushi Nakamura, Ikumi Toda, Shigeo Ohshio, Hiroyuki Muramatsu, Hidetoshi Saitoh, Atsushi Nakamura, Ariyuki Kato

***Abstract*—**Yttrium oxide (Y_2O_3) films have been successfully deposited with yttrium-ethylenediamine tetraacetic acid (EDTA•Y•H) complexes prepared by various milling techniques. The effects of the properties of the EDTA•Y•H complex on the properties of the deposited Y_2O_3 films have been analyzed. Seven different types of the raw EDTA•Y•H complexes were prepared by various commercial milling techniques such as ball milling, hammer milling, commercial milling, and mortar milling. The milled EDTA•Y•H complexes exhibited various particle sizes and distributions, depending on the milling method. Furthermore, we analyzed the crystal structure, morphology and elemental distribution profile of the metal oxide films deposited on stainless steel substrate with the milled EDTA•Y•H complexes. Depending on the milling technique, the flow properties of the raw powders differed. The X-ray diffraction pattern of all the samples revealed the formation of Y_2O_3 crystalline phase, irrespective of the milling technique. Of all the different milling techniques, the hammer milling technique is considered suitable for fabricating dense Y_2O_3 films.

***Keywords*—**Powder sizes and distributions, Flame spray coating techniques, Yttrium oxide.

I. Introduction

THERMAL spray refers to a class of processes in which fully or partially melted form of a powder feedstock is sprayed onto a substrate. Some of the commonly practiced thermal spray processes, include plasma spraying, arc spraying, flame/combustion spraying, high velocity oxygen fuel (HVOF) spraying and so on. In all these processes, powder feedstock or raw material is considered to be a fundamental experimental parameter [1], [2]. Based on systematic studies, several researchers have reported that the powder diameter [3], powder distribution [4], powder feeding weight [5], and powder morphology [6], [7] give significant influences on the characteristics of the final coating. For instance, Chivavibul et al. have demonstrated the variations in the crystalline phase, morphology, porosity, mechanical, and electrical properties of WC films fabricated by the HVOF process, based on the characteristics of the raw material [8]. Thus, characteristics of the raw powder are one of fundamental parameters in the thermal spraying techniques.

Recently, metal oxide coatings have been successfully deposited by spraying metal-ethylenediamine tetraacetic acid (EDTA) complexes using a commercial flame spray apparatus [9]. In this method, metal oxide films are fabricated from a metal-EDTA crystal with approximately 50 μm along major axis and 20 μm along minor axis [9]. The resulting metal oxide coating exhibited uniform stoichiometry based on the composition of the initial metal-EDTA complex [10]-[15]. The morphology of a metal-EDTA complex depends on the metal ion species in the metal-EDTA complex. The morphology control of the metal-EDTA complex was accomplished by controlling the processing parameters, such as stirring and pH during the synthesis procedure [16]. However, the controlling morphology of the metal-EDTA complex is an intricate process. Morphology depends on the nature of metal species and desired concentration. Therefore, identifying a simple and reliable technique would be much appreciated, especially during commercial-scale production.

Fig. 1 shows the schematic illustration of the process adopted for the deposition of the metal oxide coating. The metal oxide films were deposited on SUS substrates with the metal-EDTA complexes. For an example, we focused on the metal-EDTA complex, which is the raw material in the synthesis. More specifically, the diameter of the raw material influences the properties of the resulting film. Smaller diameter of raw materials facilitates the formation of high dense film with low porosity and micro crack [17]. These improvements in the quality of the raw material could be realized by adopting pre-treatment techniques, such as milling. For example, Fang et al. have demonstrated improvement in the mechanical properties of the WC film by preparing WC raw materials in nanocrystalline form [18]. In addition, use of frozen-milled WC raw materials could decrease the crystallite size in the final WC film [19]. In general, these results imply that the properties of the film were tuned by pre-treatment of the raw materials.

In this study, we demonstrated the above mentioned fact by synthesizing Y_2O_3 films from EDTA·Y·H complexes prepared by various milling techniques, such as commercial milling, mortar milling, ball milling, and hammer milling. Surface morphology and powder distribution of the EDTA·Y·H complex prepared by the milling techniques were systematically analyzed. Correspondingly, the crystal structure, surface/cross-sectional morphology, and elemental distribution

K Komatsu, I. Toda, S. Ohshio and H. Saitoh are with the Nagaoka Univeristy of Technology, 1603-1 Kamitomioka-Machi, Nagaoka, Niigata, Japan (phone: +81-258-47-9342; fax: +81-258-47-9300, e-mail: Keiji_Komatsu@ mst.nagaokaut,ac,jp).
T. Sekiya. A. Toyama and H. Muramatsu were with the Nagaoka Univeristy of Technology, 1603-1 Kamitomioka-Machi, Nagaoka, Niigata, Japan (e-mails:tatzelwurm129obm@gmail.com,Ayumu_Toyama@mst.nagaokaut.ac.jp, muramatsu@mst.nagaokaut.ac.jp).
A. Nakamura is with the Chubu Chelest Co., Ltd., 3-3-3 Hinagahigashi, Yokkaichi, Mie 510-0886, Japan is also with the Nagaoka Univeristy of Technology, 1603-1 Kamitomioka-Machi, Nagaoka, Niigata, Japan as visiting associate professor (phone:+81-59-346-2840, e-mail: nakamura_a@ chubuchelest.co.jp)

of the Y_2O_3 films synthesized from the different EDTA·Y·H complexes, were also studied.

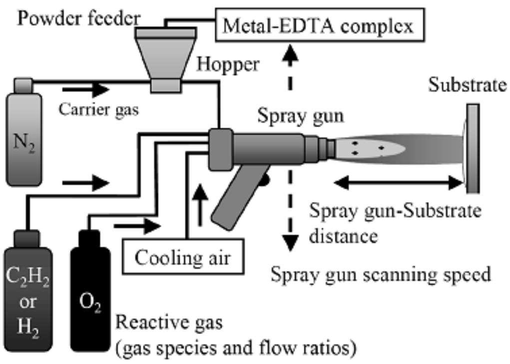

Fig. 1 Schematic illustration of the steps involved in the deposition of oxide films from metal-EDTA complex

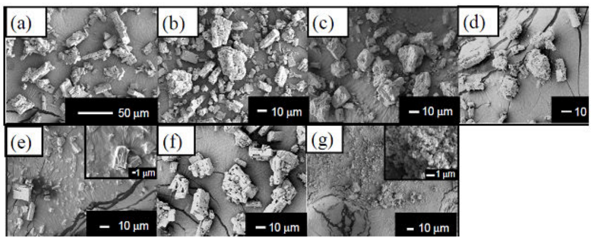

Fig. 2 Surface SEM images of the different EDTA·Y·H complexes prepared by various milling techniques: (a) as-prepared (no milling), (b) commercial milling (30 s), (c) commercial milling (60 s), (d) mortar milling (dry), (e) mortar milling (wet), (f) hammer milling, and (g) ball milling. Insets in (e) and (d) represent the high-magnification image of the area shown in the square

II. Experimental Method

A. Materials

For the synthesis of Y_2O_3 films, EDTA·Y·H (Chubu Chelest Co., Ltd.) complex was initially prepared. Furthermore, to investigate effect of characteristics of the raw EDTA·Y·H crystal on the properties of the Y_2O_3 film, we prepared seven types of EDTA·Y·H crystals by various milling techniques. (1) Commercial milling: Milling time was varied between 30 s and 60 s. (2) Mortar milling: Milling was performed in dry and wet alumina mortar. Here, ethanol was used in wet milling, which was then dried in a conventional oven at 65°C for 24 h. (3) Ball milling technique: The EDTA·Y·H powders were added in plastic bottle with alumina balls of diameter 5 mm and ethanol solution. This mixture was then stirred at 90 rpm for 24 h. The obtained white slurry was dispersed in hot water and the crystals were extracted. (4) Hammer milling crasher (NH-34, Sansho Industry Co., Ltd.) was also used for the preparation. Finally, seven different EDTA·Y·H complexes were prepared by various milling techniques.

B. Experiment

Y_2O_3 films were coated from the EDTA·Y·H complexes using the method described as follows. A conventional flame spray apparatus consisting of a feed unit (5MPE, Sulzer Metco) and a spray gun (6P-II, Sulzer Metco) was used for reactive spraying. These commercial flame spraying equipment are usually used to deposit metal films with an acetylene flame. The raw material was placed into a feed unit and transported by a N_2 gas flow to the spray gun, when the vibrator in the feed unit was turned on. The carrier gas flow rate was 7.1 L/min. A mixture of H_2 and O_2 at flow rates of 32.6 and 43.0 L/min, respectively, was used as the flame gas. During this process, the EDTA·Y·H powder mixes with the flame and reacts with oxygen, resulting in thermal decomposition of EDTA. The reacted particles were then sprayed onto a stainless-steel substrate (SUS304, 30 × 50 × 1 mm^3) that was previously polished by #60 alumina particles (99.7% pure, 212–250 µm particle size, Fuji Manufacturing Co., Ltd.). The stand-off distance (a distance between the spray gun and the substrate) was 130 mm. The deposition duration was approximately 6 s. Gun traverse rate was 50 mm/s. Subsequently, the spray nozzle was moved in the longitudinal direction and the deposition duration was continued approximately for 6 s in each area without pre-heating the substrate.

The crystallinity and phase of the deposited films was analyzed by using X-ray diffraction (M03XHF22, MAC Science Co., Ltd.) with Cu Kα radiation. The particle size distribution in the raw metal-EDTA complexes was determined using a particle size analyzer (MT-3300, Nikkiso). The surface and cross-sectional morphologies of the films were observed by using field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL). The elemental distribution in the samples was estimated by performing energy-dispersive X-ray (EDX) analysis combined with FE-SEM. A cross-sectional polisher (CP; JEOL SM-09010) was used to prepare the samples for observing the cross-sectional morphology and elemental distribution. Then, the samples were embedded in resin (JEOL G2) and polished using abrasive waterproof paper (Noritake Coated Abrasive Co., Ltd. C947 H #400, #1000, #1500). Cross-sectional porosity of the prepared samples was estimated by using the software, image j [20].

III. Results and Discussion

Fig. 2 shows the SEM images of the raw EDTA·Y·H powders prepared by various milling techniques. It could be realized that morphology and diameter of the raw EDTA·Y·H powders changed for the samples prepared by various milling techniques. In general, milling process is not only a miniaturization phenomenon but also a granulation phenomenon [21], [22]. In this study, we observed both size reduction as well as granulation of the EDTA·Y·H complexes. In case of mortar milling and ball milling, we could mainly observe reduction in the particle size. More quantitatively, EDTA·Y·H powders prepared by mortar milling technique had particles of size approximately 5 µm (Fig. 2 (e) and inset: high-magnification SEM image). In case of ball milling (Fig. 2 (g)), the resulting EDTA·Y·H powders were of size approximately 1 µm. On the other hand, granulation effect was observed in EDTA·Y·H powders prepared by commercial milling technique (Figs. 2 (b) and (c)). The granulation effect is characterized by the formation of secondary particles of diameter bigger than the as-prepared powders. Intriguingly, both milling and granulation effects were observed in EDTA·Y·H powders prepared by Hammer milling technique (Fig. 2 (f)). Here, some of the primary particles granulated to form secondary particles of diameter several ten microns.

Fig. 3 shows the powder diameter distribution in EDTA·Y·H powders prepared by various milling techniques. Table I summarizes the estimated median diameters (average powder diameter) and powder distribution range. In case of EDTA·Y·H powders prepared by commercial milling technique, the diameter and powder distribution range were found to change with increase in milling time. With increase in milling time, the median diameter decreased from 36.20 μm to 24.92 μm and 18.95 μm, while the powder distribution range expanded from 10-100 μm to 2.1–105 μm and 2.5–88 μm. On the other hand, in case of EDTA·Y·H powders prepared by hammer milling technique, the median diameter decreased to 27.89 μm. Then, the powder distribution range also decreased to 7.1–88 μm. In contrast, the median diameter and powder distribution range of EDTA·Y·H powders prepared by ball milling technique significantly increased to 73.77 μm and 2.5–1184 μm, respectively. In previous report, the ball milling technique tends to narrow down the powder distribution range [23]. In that report, UO_2 powders with the narrower powder distribution were obtained by increasing the milling time. The report also suggested a minimum powder diameter of approximately 1 μm by performing general milling techniques, such as commercial milling, hammer milling, and ball milling. Based on these previous results and that obtained from the present study, it suggested that the median diameter and the powder distribution range depends on the type of milling technique.

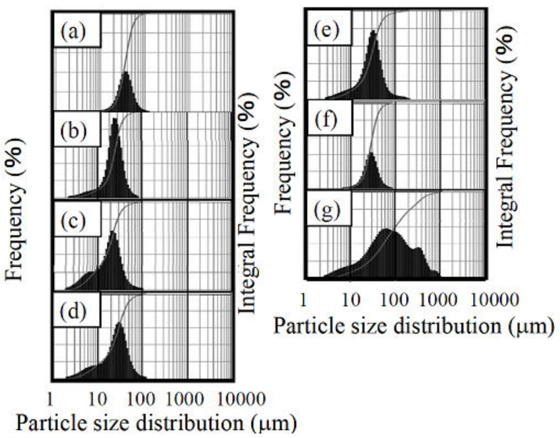

Fig. 3 Particle distributions in the EDTA·Y·H complexes prepared by various milling techniques: (a) as-prepared (no milling), (b) commercial milling (30 s), (c) commercial milling (60 s), (d) mortar milling (dry), (e) mortar milling (wet), (f) hammer milling, and (g) ball milling

TABLE I
ESTIMATED MEDIAN DIAMETERS AND POWDER DISTRIBUTION RANGE VALUES FOR EDTA·Y·H COMPLEXES PREPARED BY VARIOUS MILLING TECHNIQUES

Milling technique	Median diameter, D50 (μm)	⊿D(D90-D10) (μM)
As-prepared (no milling)	36.20	35.64
Commercial milling (30s)	24.92	23.28
Commercial milling (60s)	18.95	29.90
Mortar milling (dry)	25.80	41.37
Mortar milling (wet)	29.38	41.91
Hammer milling	27.89	25.65
Ball milling	73.77	343.92

TABLE II
ESTIMATED FEED WEIGHT VALUES AND STATEMENT IN EXPERIMENTAL FOR EDTA·Y·H COMPLEXES PREPARED BY VARIOUS MILLING TECHNIQUES

Milling technique	Feed weight (g/min)	Flowed or Flowed with pulsing or Not flowed
As-prepared (no milling)	9.8	Flowed
Commercial milling (30s)	9.5	Flowed
Commercial milling (60s)	10.1	Flowed
Mortar milling (dry)	8.5	Flowed with pulsing
Mortar milling (wet)	—	Not flowed
Hammer milling	7.6	Flowed
Ball milling	—	Not flowed

Table II lists the powder flow rate of EDTA·Y·H powders prepared by various milling techniques. The EDTA·Y·H powders flow in the powder feeder, react with H_2-O_2 flame, and form films on SUS substrate. It should be noted that the EDTA·Y·H prepared by wet mortar milling and ball milling remained in the powder feeder, and did not form on SUS substrate. In addition, the EDTA·Y·H powder pulse flowed in case of dry mortar milling. These results imply that the existence of powder with diameter less than 10 μm tends to decrease the powder flow rate. Notably, the existence of powder with diameter less than 5 μm decreased the rate, which in turn hindered the formation of films. This could be attributed to the following three steps. (1) Existence of the smaller powders increases the surface activity for the powders [24]. (2) Consequently, the activated powders would have attached to tube between the powder feeder and spray gun. (3) The aggregation of the attached powders would have resulted in close-packed tube. Therefore, differences in the morphology and surface activity of the powders contribute to its flow properties. In general, straric acid is used to suppress the degradation in powder flow property, and also used to fabricate films by using smaller quantity of raw powder [25]. Therefore, straric acid is added as a granulating agent during the synthesis, in order to improve the powder flow property. Unfortunately, the resulting films contained organic components, as determined from the infrared spectroscopy (IR). Thus, straric acid was not used in this study.

Fig. 4 shows surface SEM images of the films on SUS substrate, coated using the different EDTA·Y·H powders prepared by various milling techniques. The SEM image of the film deposited from EDTA・Y・H powders without any milling treatment (Fig. 4(a)) shows the mixed formation of spherical, non-spherical and flattened (splattered) particles. On the other hand, in case of commercial milled and mortar milled

EDTA·Y·H powders, the resulting film exhibited a relatively rough surface compared to film prepared without milling technique. Moreover, the surface of the films obtained by the milling technique consisted of smaller particles of diameter less than 1-3 μm. In contrast, the films obtained by depositing hammer milled EDTA·Y·H powder had flattened particles (Fig. 4 (e)).

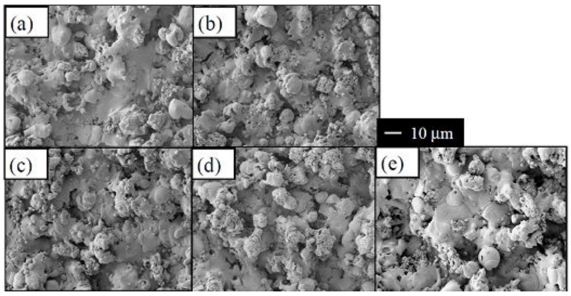

Fig. 4 Surface SEM images of the different films deposited from EDTA·Y·H complexes prepared by various milling techniques: (a) as-prepared (no milling), (b) commercial milling (30 s), (c) commercial milling (60 s), (d) mortar milling (dry), and (e) hammer milling

Fig. 5 shows the XRD profiles of the films on SUS substrate obtained by depositing EDTA·Y·H powder prepared by various milling techniques. The XRD diffraction peaks in all the samples could be assigned to Y_2O_3 (ICDD card No. 01-089-5592) crystal phase with cubic lattice [26]. No differences could be observed in the obtained XRD profiles. All the diffraction peaks and intensities matched almost correctly. This indicates that the formation of crystalline phase does not depend on the milling technique.

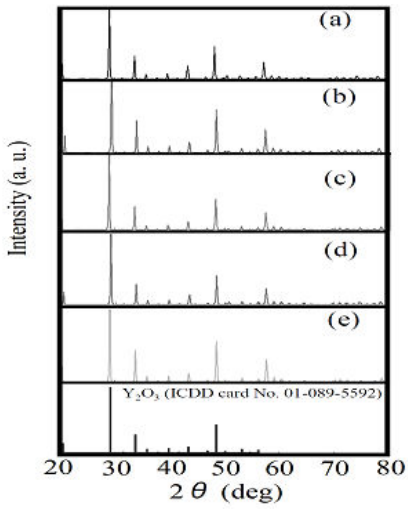

Fig. 5 XRD profiles of the films deposited on SUS304 substrates using flame spraying, obtained from EDTA·Y·H complexes prepared by various milling techniques: (a) as-prepared (no milling), (b) commercial milling (30 s), (c) commercial milling (60 s), (d) mortar milling (dry), and (e) hammer milling, compared with ICDD cards of Y_2O_3 crystal with cubic lattice

Fig. 6 shows the cross-sectional SEM images and 2D elemental mapping images of the different Y_2O_3 films deposited on SUS substrate obtained from EDTA·Y·H powders prepared by various milling techniques. Thickness and cross-sectional porosity of the films were estimated from each image. These estimated values were summarized in Table III. Experimental results indicated that the thickness and the porosity of Y_2O_3 films changed with the milling method. The cross-sectional image of film deposited from hammer-milled EDTA·Y·H showed a dense and flatten morphology with a thickness of 9.7 μm and a cross-sectional porosity of 21.70%. In contrast, an almost sponge-like film was obtained in the case of the Y_2O_3 film deposited from dry mortar-milled EDTA·Y·H powders. The thickness of this film was found to be 11.5 μm, while its cross-sectional porosity was 36.98%. In addition, the film showed formation of large pores. In general, the diameter of the spraying particles influences the degree of flatness, and then contact area between the layer and layer determines the cross-sectional porosity [27]. Therefore, in this study, the thickness and porosity of the Y_2O_3 films deposited on SUS substrate was influenced by the diameter of the particles and the degree of flatness.

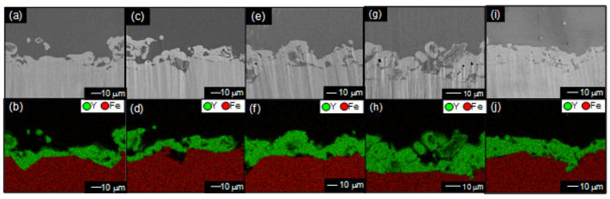

Fig. 6 Cross-sectional SEM images and EDX profile of the films deposited on SUS substrate obtained from EDTA·Y·H complexes prepared by various milling techniques: (a) and (b) as-prepared (no milling), (c) and (d) commercial milling (30 s), (e) and (f) commercial milling (60 s), (g) and (h) mortar milling (dry), (i) and (j) hammer milling

Furthermore, we analyzed the effect of diameter and morphology on the properties of the resulting film. No significant influence could be observed with respect to the crystal structure. For commercial applications, the flow property of the raw metal-EDTA powder depends on milling technique. Therefore, powder diameter and powder distributions were found to be the fundamental factors. In other words, the results obtained from this study clearly demonstrated that the properties of the films could be controlled by changing the properties of the raw metal-EDTA complex powder. Of all the milling techniques, hammer milling technique is ideally suitable for fabricating dense metal oxide films, because of the smaller diameter and narrow size distribution of the raw powders.

IV. Conclusion

In summary, Y_2O_3 metal oxide films were deposited by flame spraying EDTA·Y·H complexes prepared by various milling techniques. In this study, we analyzed systematically the effect of the properties of the raw material EDTA·Y·H on the properties of the deposited Y_2O_3 films. For this, seven different types of EDTA·Y·H powders were prepared by milling the EDTA·Y·H complexes using milling techniques such as commercial milling, mortar milling, hammer milling, and ball milling. Experimental results clearly indicated that the size and distribution of the powders changed depending on the milling method. However, no significant differences in terms of crystal structure and elemental analysis observed in all the seven different Y_2O_3 films. Comparing the different milling techniques, the hammer milling technique was found to be the most appropriate method for synthesizing dense Y_2O_3 films.

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K Komatsu was born in Japan in 1985. He received doctoral degree at Nagaoka University of Technology in 2013. He is a postdoctoral fellow researcher in Nagaoka University of Technology. His major study filed is inorganic materials/physical properties, such as functional oxides phosphor materials.

T. Sekiya was received master degree at Nagaoka University of Technology in 2013. He graduated the Nagaoka University of Technology in 2013.

A. Toyama was received master degree at Nagaoka University of Technology in 2014. He graduated the Nagaoka University of Technology in 2014.

A. Nakamura was received doctoral degree at Nagaoka University of Technology. He is with the Chubu Chelest Co., Ltd. and he is also with the Nagaoka Univeristy of Technology as visiting associate professor. His major study filed is inorganic materials/physical properties.

I. Toda was received doctoral degree at Nagaoka University of Technology in 2011. He is a postdoctoral fellow researcher in Nagaoka University of Technology. His major study filed is inorganic materials/physical properties, such as carbon materials (activated carbons).

S. Ohshio is a technical specialist at Nagaoka University of Technology. His major field studies are science education and inorganic materials/physical properties

H. Muramatsu was with the Nagaoka Univeristy of Technology. He received doctoral degree at Shinshu University in 2007. He transferred to Shinshu University in 2014. His research themes are synthesis of novel carbon nanomaterials, carbon materials, nanoscale materials.

H. Saitoh received doctoral degree at Nagaoka University of Technology in 1990. He is a professor in Nagaoka University of Technology. His research themes are crystal growth of thin films, crystal growth of thin films, material design of superhard compound, material design of superhard compound, and opto ceramic materials, opto ceramic materials.