Splat morphology and microstructure of chelate flame sprayed Er$_2$O$_3$ films

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The chelate flame spray (CFS) method is an inexpensive flame spray technique with low energy consumption used to deposit metal oxide (M$_2$O$_3$) films using M-ethylenediaminetetraacetic acid (EDTA·M·H) complexes. In this study, EDTA·Er·H was used as the raw material to investigate the cross-sectional structures of the Er$_2$O$_3$ films, and substrates with different common materials, i.e., quartz glass, stainless steel (304), and aluminum-magnesium alloy (A5052), were selected. We found that in the CFS deposition process, EDTA·Er·H was decomposed, oxidized and melted in the flame to form molten Er$_2$O$_3$ particles, and Er$_2$O$_3$ films with an average thickness of 9.7–13.5 $\mu$m, cross-sectional porosity of 1.6–4.9 $\%$, and crack numbers of 29–51 were deposited on quartz glass. Oxide films with 7.6–14.3 $\mu$m thickness were synthesized on an aluminum-magnesium alloy (A5052) substrate. The cross-sectional porosity and microcrack numbers of these films were 5.2–6.9 $\%$ and 10–20, respectively. In addition, to observe the Er$_2$O$_3$ film stacking structure more clearly, we screened the powder raw materials to make them uniform. The results of this study enable the design of a ceramic film microstructure that reduces cracks in the ceramic film, thereby increasing the application potential.

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1. Introduction

The microstructures and properties of thermally sprayed ceramic coatings have been extensively investigated due to their potential benefits in broad thermal barrier coating applications and sliding wear applications.\textsuperscript{1–4} Atmospheric plasma spraying and high-velocity oxy-fuel spraying are common thermal spray methods due to their high temperature (15,000–20,000 K) and high speed of spray particles.\textsuperscript{5} However, the high energy consumption and large-scale installation requirements limit the further application of these methods.\textsuperscript{5–7} Thus, there is a pressing need to develop spraying techniques with low energy consumption. Recently, metal-ethylene-diaminetetraacetic acid (EDTA) complexes have been used to synthesize metal oxide coatings using a new flame spray method\textsuperscript{9–10} called the chelate flame spray (CFS) technique. In the CFS process, the raw materials of metal-EDTA complexes are placed in a feed unit and transported by flowing carrier gas (N$_2$ or O$_2$) to the spray gun. The gas–solid mixture is introduced into a C$_3$H$_2$O$_2$ or H$_2$O$_2$ flame and reacted with oxygen after the thermal decomposition of EDTA. Thereafter, the melting particles are sprayed onto a substrate at a high speed to deposit ceramic oxide films.\textsuperscript{9} In a previous study, we examined the effect of the starting material state (molecularly or mechanically mixed) and carrier gases (N$_2$, air, and O$_2$) on oxide films by the CFS process.\textsuperscript{10,11} After the porosity of the metal oxide coating was effectively controlled, a preliminary investigation of thermal shock properties was performed.\textsuperscript{9} In the follow-up study, we successfully synthesized Y$_2$O$_3$ films on an aluminum alloy (A5052), and the joining showed strong adhesion without delaminations.\textsuperscript{9}

Cracks in microstructures are key to determining the mechanical behavior and thermal shock resistance of coatings.\textsuperscript{8,12,13} In thermal spray processing, after the raw materials are melted using a high-temperature flame, they are deposited onto the substrate and instantaneously transformed from the molten state to the solid state. During this process, stress is generated on the other side (backside of the splat), which causes cracks in the solidified particles.\textsuperscript{14} Coatings, such as thermal barrier coatings (1273–3273 K), which are one of the most important coating types, are applied in extreme environments such as gas turbine engines.\textsuperscript{15,16} Under these conditions, it is important to...
examine the ceramic films deposited on different materials using the CFS method and analyze the microstructure.

In this work, two series of experiments were performed to study the cross-sectional structure of Er<sub>2</sub>O<sub>3</sub> films deposited by a CFS method. Scanning electron microscopy (SEM) and image analysis software (ImageJ, SmileView) were used to analyze the crack formation mechanism of the Er<sub>2</sub>O<sub>3</sub> films. First, Er<sub>2</sub>O<sub>3</sub> films were sprayed on substrates of different materials—i.e., quartz glass, stainless steel (304), and aluminum alloy (A5052). We examined the effects of the substrate types on the microstructures of the deposited films. Next, Er<sub>2</sub>O<sub>3</sub> films were prepared with various particle sizes of the EDTA·Er·H raw material, and the effect of the raw material size on the cross-sectional structure of these coatings was investigated.

2. Experimental details

The EDTA precursor powder was complexed and decomposed at approximately 673 K<sup>10</sup>) and the SEM images of the EDTA metal complex are shown in Fig. 1. The EDTA complex powder EDTA·Er·H (Chubu Chelset Co., Ltd.) was used to synthesize the Er<sub>2</sub>O<sub>3</sub> films in the CFS process. To obtain various particle sizes of the raw material, sieves (Kansai Wire Netting Co., Ltd.) with mesh sizes of 75, 53, and 45 μm were vertically stacked, and the unscreened raw material was passed through from the top, as shown in Fig. 1(a). Including the unscreened cuboid EDTA·Er·H powder, five raw material particle sizes—i.e., unscreened [Fig. 1(b)], 75-μm-on [Fig. 1(c)], 53-μm-on [Fig. 1(d)], 45-μm-on [Fig. 1(e)], and 45-μm-pass [Fig. 1(f)]—were selected for the experiments. For the substrates, quartz glass, stainless steel (304), and aluminum alloy (A5052) were selected because they are commonly used in modern precision optical instruments and in the automotive field<sup>9),17</sup>) Except for quartz glass (DAICO MFG Co., Ltd.), which was directly purchased in a disk shape of π x (25)<sup>2</sup> x 5 mm<sup>3</sup>, the substrates were simply processed into 30 x 50 x 1 mm<sup>3</sup> pieces for the rectangular stainless steel substrate (304 Ni–Cr–Mn–Si–C) and 100 x 100 x 10 mm<sup>3</sup> for the square aluminum alloy substrate (A5052 Al–Mg, Fuji Manufacturing Co., Ltd.). Although the thicknesses of each substrate are different in this study, the effect of the substrate thickness on the microstructure of the film can be ignored because the solidification speed of Er<sub>2</sub>O<sub>3</sub> molten droplets is a key factor, and this may be dependent on the thermal sensitivities in each substrate, as shown in Table 1. All substrates were blasted with #60 alumina grit (purity of 99.7%, particle size of 212–250 μm, Fuji Manufacturing Co., Ltd.) for 1 min at a pressure of 0.6 MPa and then ultrasonically precleaned with acetone for 5 min twice before each deposition process.

A flame-spraying apparatus consisting of a feed unit (5MPE, Sulzer Metco) and a spray gun (6P-II, Sulzer Metco) was used to perform each spraying. EDTA·Er·H was placed in the feed unit and transported to the spray gun by O<sub>2</sub> as a carrier gas with a measured powder feed rate of approximately 5 g/min. The carrier gas flowrate was set to 7.1 L/min. The flowrates of the combustion gases H<sub>2</sub> and O<sub>2</sub> were set to 32.6 and 43.0 L/min, respectively. The distance between the spray gun and the substrate (nozzle-substrate distance) was 150 mm, and the details are shown in Table 2. The gun traverse rate was 50 mm/s. The spray nozzle was moved in a longitudinal direction, and each pass of the flame over the whole substrate occurred within 1–2 s, as shown in Fig. 2. During the spraying process, the temperature of the flame was approximately 2773–3273 K, resulting in a substrate temperature over 493 K<sup>18</sup>). Thus, after two scans, the sample was allowed to cool for 5 min. An infrared camera (Accura Spray-G3: Tecnar) was used to measure the velocities and temperatures of the particles during and after the deposition process. All samples were subjected to 4 scans with a cooling interval of 5 min after two scans.

X-ray diffraction (XRD) analysis was performed to observe the crystal structures of the deposited films. The XRD measurements (M03XHF22, MAC Science) were taken on an instrument with a CuKα X-ray source and

| Table 1. Substrate properties used in thermal spraying |
|---|---|---|---|
| Substrate | Size (mm<sup>2</sup>) | Thickness (mm) | Coefficient of thermal expansion (10<sup>−6</sup>°K<sup>−1</sup> at 273 K) | Thermal conductivity [W/(mK)] |
| Quartz glass | π x (25)<sup>2</sup> | 5 | 0.5 | 1.38 |
| Stainless steel | 30 x 50 | 1 | 17.6 | 16.7 |
| Aluminum alloy (A5052) | 50 x 50 | 10 | 23.8 | 138 |

| Table 2. Deposition parameters for CFS Er<sub>2</sub>O<sub>3</sub> films |
|---|---|
| Carrier gas | O<sub>2</sub>: 7.1 L/min |
| Combustion gases | H<sub>2</sub>: 32.6 L/min |
| | O<sub>2</sub>: 43.0 L/min |
| Spray-distance | 150 mm |
| Powder feed rate | 5 g/min |

Fig. 1. The powder state of raw material EDTA·Er·H. (a) Sieve stacking, SEM images of the raw materials (b) unscreened, (c) residual on the 75-μm sieve, (d) residual on the 53-μm sieve, (e) residual on the 45-μm sieve, and (f) passed through the 45-μm sieve. Their average particle sizes were 67.89, 82.37, 63.37, 54.71, and 42.26 μm, respectively.

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wavelength of 1.54 Å operated at 40 kV × 40 mA in the scan range of 2θ = 10°–80° with a step size of 0.02°. The surface and cross-sectional morphologies of the samples were observed using field-emission SEM (FE-SEM) (JSM-6700F, JEOL) under an acceleration voltage and irradiation current of 5 kV × 8 μA and 12 kV × 20 μA, respectively. Secondary electron and backscattered electron (compositional) images of the deposited films were acquired. The porosity was measured by digitizing the obtained SEM images using commercial software (ImageJ). The average thickness was determined from 20 transverse sections in images using commercial software (ImageJ). The average thickness was determined from 20 transverse sections in the whole image, and measurements were repeated three times. The microstructural characterization of flame spray coatings involves quantitative measurements of geometrical features such as porosity and cracks; thus, the porosity was estimated from the area ratio of the film in the image. The microstructure of the Er2O3 film deposited on different substrates was analyzed as follows. First, each obtained COMPO image was digitized using ImageJ. Image analysis is established as a reliable method for determining pore size and morphology in thermal sprayed coatings, keeping in mind its resolution limits. Therefore, the numbers of cracks, crack lengths, and crack areas were measured from the digitized (black and white) image. In addition, the acquisition parameters were fixed to an image resolution of approximately 7.0 × 10⁻³ μm/pixel, and based on these conditions, a series of 10 images was recorded to obtain an accurate value.

3. Results and discussion

3.1 Characterization of Er2O3 coatings on different substrates

Figure 3 shows the XRD patterns of the Er2O3 films deposited on the three substrates. The peaks in the XRD profiles were assigned using the International Centre for Diffraction Data (ICDD) cards as references. In Figs. 3(a) to 3(c), the unscreened EDTA·Er·H films deposited on quartz glass, stainless steel (304) and aluminum alloy (A5052) exhibited cubic and monoclinic Er2O3 crystalline phases. Er2O3 exhibits three structural polymorphs: cubic, monoclinic, and hexagonal, which are commonly known as C-, B-, and A-type structures, respectively. No apparent phase transformation or decomposition (or element diffusion) occurred after deposition on various substrates. These results imply that the substrate has no effect on the crystal structure of the deposited films.

Figure 4 shows surface SEM images of Er2O3 films deposited from unscreened EDTA·Er·H onto the three blasted substrates. Flattened splats and spherical splashes approximately 1–20 μm in diameter were observed in all sprayed films. In the films deposited on the quartz glass, a number of spherical (i.e., not flattened) splats or splashes, disk-like splats and pores were also observed. Furthermore, small spherical splashes with sizes of approximately 1 μm were also observed in the Er2O3 film synthesized on stainless steel (304) substrate. Finally, a large number of flattened splats and small spherical splashes were observed in the Er2O3 film deposited on aluminum alloy (A5052). When quartz glass was used as the substrate, the degree of flattening was the lowest, as shown in Fig. 4(a). In contrast, splats with the highest degree of flatness (or splatting) were observed in the Er2O3 film on the aluminum alloy (A5052), as shown in Fig. 4(c). Additionally, cracks were clearly observed in the coatings deposited on the quartz glass, as shown in the areas indicated by the arrows in Fig. 4(a1), while the other coatings showed no significant cracks in the surface SEM images. Thus, the choice of the substrate causes differences in the surface morphologies of the deposited Er2O3 films. This may be due to the temperature-sensitivity property of the substrate, which instantly affects the cooling rates of molten droplets that impact the substrate, such as aluminum alloy metal. The resulting deposited coatings appear significantly different. Based on the above conditions, after converting the grayscale image [cross-sectional SEM image as depicted in Figs. 5(a) to 5(e)] to a digitized (black and white) image, the porosity ratio was evaluated, and then a series of erosion dilution operations was applied that enabled the
selection of pores (gaps, globular and elongated) or cracks, as shown in Figs. 5(d) to 5(f). Numerous cracks were found in the films deposited on the quartz glass substrate and fewer in the coatings deposited on the stainless steel (304) substrate. The film deposited on the aluminum alloy (A5052) substrate had the fewest cracks, and exceptionally flat splat morphology [such as thin splats, see Fig. 5(f)] was observed. Table 3 shows the values estimated from the digitized (black and white) images of the average thickness, porosity, number of cracks, and average crack length for the Er$_2$O$_3$ films. Through a comparison of these results, we found that the number of cracks and average crack length were the lowest for the coatings deposited on the aluminum alloy (A5052) substrate, although its film deposition rate was the highest of the three substrates. Additionally, the films on the aluminum alloy (A5052) substrate showed a lamellar structure, but the films deposited on the quartz glass and stainless steel (304) substrates

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Fig. 4. SEM images of the surface of the film deposited from unscreened EDTA-Er-H onto blasted substrates of (a) quartz glass [(a$_1$) magnification image], (b) stainless steel (304), and (c) aluminum alloy (A5052). Cracks were clearly observed in the area surrounded by a dotted line.

Fig. 5. Cross-sectional SEM (a, b, and c) and digitized (black and white) images (24 µm x 32 µm) (d, e, and f) of films deposited from unscreened EDTA-Er-H onto blasted substrates of quartz glass (a and d), stainless steel (304) (b and e), and aluminum alloy (A5052) (c and f).
were quite different, showing a dense structure. It can be concluded that differences in structure occur because of the differences in the morphology of the sprayed Er\textsubscript{2}O\textsubscript{3} splats (such as thin or thick splats and gap size) on different substrates.

As mentioned above, during thermal spray processing, after the raw materials are melted by a high-temperature flame, they are deposited onto the substrate, where they instantaneously change from the molten state to the solid state, generating stress on the other side and causing cracks in the solidified splats.\textsuperscript{23,24} Additionally, we found that the number of cracks and average crack length of the coatings were decreased in films deposited on the substrates ranging from quartz glass to aluminum alloy. Based on these results, the effects of the substrates on the properties of the deposited films are discussed below. Through the CFS deposition process, the chemical reaction of EDTA·M·H (M: metal species) can be represented by Eq. (1).\textsuperscript{18,25} In Eq. (1), for instance, EDTA·Er·H reacts with O\textsubscript{2} to form an Er\textsubscript{2}O\textsubscript{3} film.

\[
2\text{EDTA-Er·H} + 24\text{O}_2 \rightarrow \text{Er}_2\text{O}_3 + 20\text{CO}_2 \uparrow + 13\text{H}_2\text{O} \uparrow + \text{NO}_2 \uparrow \quad (1)
\]

As described in Eq. (1), the H\textsubscript{2}–O\textsubscript{2} flame reacts with O\textsubscript{2}, and the precursor melts and thermally decomposes to produce the gases CO\textsubscript{2}, H\textsubscript{2}O, and NO\textsubscript{2}, resulting in the formation of molten liquid Er\textsubscript{2}O\textsubscript{3} particles that are sprayed onto substrates. The molten particles continue to impact and deposit on the substrate as the substrate temperature rises. Under these conditions, upon molten particle deposition on the substrate, or rather on the coating surface, thermal dissipation occurs from the splats into the surface, which is accompanied by a shrinkage of the splats due to the change in temperature and phase transitions during solidification. Therefore, for the temperature-sensitive aluminum alloy substrate,\textsuperscript{26} the molten particle impacts the substrate and forms a thin splat due to the rapid diffusion of the particle temperature. Hence, the irregular splats were responsible for the formation of interlayer gaps and reduced cracks of the thin splat. The temperature of the deposition on a substrate with low thermal conductivity was assumed to be high enough to retain the molten state for a while, and additional molten droplets impacted the fused deposition to form a dense structure. However, splat solidification (or shape) is affected not only by the above conditions (temperature or thermal conductivity) of the substrate but also by the wetting ability and thermal contact of the substrate.\textsuperscript{27} It is expected that a further series of studies will be performed.

### 3.2 Characterization of Er\textsubscript{2}O\textsubscript{3} coatings with various raw material particle sizes

The XRD patterns were used to determine the phase structure of the coatings deposited on the quartz glass and A5052 substrates, as shown in Figs. 6 and 7. The samples can be identified using ICDD card Nos. 01-073-6274 (cubic Er\textsubscript{2}O\textsubscript{3} phase) and 01-077-6226 (monoclinic Er\textsubscript{2}O\textsubscript{3} phase) without any significant differences. In the case of

| Substrate          | Average thickness (\(\mu\text{m}\)) | Cross-sectional porosity (%) | Number of cracks | Average crack length (\(\mu\text{m}\)) |
|--------------------|-------------------------------|-----------------------------|-----------------|------------------|
| Quartz glass       | 13.5                          | 2.0                         | 39              | 1.2              |
| Stainless steel    | 12.7                          | 3.7                         | 20              | 1.3              |
| Aluminum alloy (A5052) | 14.3                      | 6.9                         | 13              | 1.0              |

Table 3. Estimated average thickness, porosity, number of cracks, average crack length, and number of cracks per unit area in Er\textsubscript{2}O\textsubscript{3} films deposited from unscreened EDTA-Er·H onto blasted substrates of quartz glass, stainless steel (304), and aluminum alloy (A5052).
particle sizes of 45-μm-on/pass as the raw material, the peak at approximately 45° was not detected in the other films on the quartz substrate [Figs. 6(d) and 6(e)]. As a result, the raw material particle size had no obvious effect on the phase structure of the Er₂O₃ coatings.

Figures 8 and 9 show Er₂O₃ film surfaces, with Fig. 8 showing SEM images of the Er₂O₃ films deposited on quartz glass and Fig. 9 showing the coatings on aluminum alloy (A5052). Each top row shows a different powder size. The Er₂O₃ films deposited on quartz glass had flattened spherical splats. A number of spherical (or lowest degree of flatness) splashes or splats were observed for particle size 75 μm on, and cracks occurred on the coating surface, as indicated by the arrows in Fig. 8(b). The films deposited from the raw material with a particle size of 53-μm-on still had cracks that can be discerned in the surface SEM image. Furthermore, there were no obvious differences in the surface morphology obtained with powder sizes of 53-μm-on, 45-μm-on and 45-μm-pass, which may be due to the smaller particle size [Figs. 8(c) to 8(e)]. In addition, spherical splashes or splats approximately 1–4 μm in diameter were observed in the surface images [Figs. 8(b) to 8(d)]. We found that for the same raw material particle size, the extent of the flattened particles in the Er₂O₃ film
deposited on aluminum alloy (A5052) was greater than that on the quartz glass substrate, especially for 75-μm-on particles, as shown in Fig. 9(g). Additionally, the films obtained from unscreened 75-μm-on raw material had cracks visible in the surface SEM images. Further, more small spherical splashes with a size below 1μm in diameter were also seen on the film surface, as shown in the area highlighted by the dotted line in Figs. 9(f), 9(i), and 9(j). In contrast, the presence of spherical small-splash particles in the surface images [Figs. 9(g) and 9(h)] after screening was not significant. Thus, the comparison of the SEM images of the Er2O3 film surfaces indicated significant differences in the size of the spherical splats or splashes. In general, the solidification speed of the molten droplets affects the degree of spattering of the accelerated droplets. This may be the reason for the more noticeable formation of small splats by the splashes of spayed molten particles on the aluminum alloy substrate that were not obvious on the quartz glass substrate.

To further investigate the microstructures in Er2O3 films deposited on different substrates with various sizes of EDTA·Er·H particles, cross-sectional SEM and digitized (black and white) images, as shown in Figs. 10 and 11, were analyzed. Figures 10(a) and 10(b) show the cross-sectional SEM and digitized (black and white) images of Er2O3 films deposited on a quartz glass substrate with various sizes of EDTA·Er·H particles. The microstructures of the cracks, pores and gaps can be clearly seen in Fig. 10 (digitized images). Large pores and isolated cracks were observed in the Er2O3 film deposited using the raw material size 75-μm-on. Furthermore, it was found that the numbers of pores in the Er2O3 films synthesized using the raw materials unscreened, 53-μm-on, and 45-μm-on/pass were lower, and the crack length was shorter. Table 4 shows the thicknesses, porosities, numbers of cracks, and average crack lengths of the films. The porosities were determined by analyzing SEM images of the films. This analysis method can be used to determine the numbers of both open and closed pores.10) The Er2O3 film obtained using raw unscreened material had an average thickness of 13.5μm, porosity of 2.0 % and number of cracks of 39. In the case of the screened raw materials 75-μm-on, 53-μm-on and 45-μm-on/pass, the thickness changed by 9.7–14.2μm, the porosity changed by 1.6–4.9 %, and the number of cracks changed by 29–51. The Er2O3 film was densified, and fewer cracks were observed in the screened raw material 45-μm-pass when using the quartz glass substrate.

Figures 11(f) to 11(j) show the cross-sectional SEM and digitized (black and white) images of Er2O3 films deposited on aluminum alloy (A5052) substrate with various sizes of EDTA·Er·H particles. By comparing Fig. 11 with Fig. 10, it is obvious that the cross-sectional images for the deposited films on aluminum alloy (A5052) substrate are significantly different. The Er2O3 films (all samples) deposited on an aluminum alloy (A5052) substrate reveal a lamellar structure with typical microstructures, such as layers, layer gaps and a variety of pores, as shown in Fig. 11. Furthermore, the microstructure can be clearly observed, such as flattened splats (or thin splats) with sizes of approximately 3–8μm. In addition, the inner layer and outer layer splats are almost identical in shape, as shown in Figs. 11(f) to 11(j). Table 4 shows the results for the Er2O3 films synthesized on the A5052 substrate. Tables 4 and 5 show that the Er2O3 films deposited on aluminum alloy were more porous than those deposited on quartz glass and had fewer cracks.

However, there is no significant change in the microstructure and calculation results on the same substrate using different particle sizes, except for the particle size of 75-μm-on. The structures suggest that the effects (temperature and velocity of the infallight particles) could have occurred during the deposition processes. With respect to thermal spraying, knowing the temperature and velocity of the infallight particles is useful for determining their impact behavior, which affects the splat shape and morphology of the deposited films.28,29 Table 6 shows the average diameters of raw material particles and the infallight particle velocities and temperatures during the CFS deposition process when the nozzle-substrate distance was 150mm.
The velocities of the unscreened particles were 87.1 m/s, and the inflight particle temperature was 2803 K. As the particle size decreased, the velocity and temperature of the inflight particles were 90.3–104.1 m/s and 2863–2933 K, respectively. The thermal energy \( Q \) and kinetic energy \( E \) of the particles can be calculated as shown in Eqs. (2) and (3):

\[
Q = mT
\]
\[
E = \frac{1}{2}mv^2
\]

where \( Q \) is the thermal energy (kJ), \( m \) is the mass of the sample (kg), \( T \) is the temperature of the inflight particle (K), and \( v \) is the velocity of the inflight particle. Equations (2) and (3) show that the mass of the EDTA·Er·H particles influences the thermal energy \( Q \) and kinetic energy \( E \) with similar values for the temperature and velocity of the different particle sizes. Therefore, using larger particles would improve the porosity of the films in this study.

4. Conclusions

To investigate the effect of substrate type and raw material particle size on the cross-sectional structure of \( \text{Er}_2\text{O}_3 \) films deposited by the CFS method, EDTA·Er·H powder was used as the raw material. Analyses of photographs, XRD patterns, and surface, cross-sectional SEM and digitized (black and white) images suggested that the films contained cubic and monoclinic crystalline phases of \( \text{Er}_2\text{O}_3 \) films deposited from fully reacted liquid erbia particles. The films directly deposited on the aluminum alloy (A5052) substrate showed typical lamellar structures with few cracks. The densest films were obtained on quartz glass. Small, uniform raw material particles resulted in dense coatings. The CFS method, a new type of flame spray technique, has great potential for rapidly and conveniently forming films from a variety of engineering materials.

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