

Title	Fundamental Considerations on Plasma Sprayed Ceramic Coating (Report II) : Structural Study of Plasma Sprayed Al <sub>2</sub> O <sub>3</sub>
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# Fundamental Considerations on Plasma Sprayed Ceramic Coating (Report II)<sup>†</sup>

## — Structural Study of Plasma Sprayed $\text{Al}_2\text{O}_3$ —

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### Abstract

*Plasma sprayed alumina was structurally investigated with X-ray diffraction method. Similar diffraction patterns were obtained from plasma sprayed  $\alpha\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  and these sprayed coatings were identified as the mixture of  $\alpha\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$ . From the result of commercial alumina containing silica, it was suggested that silica addition decreased the amount of  $\alpha\text{-Al}_2\text{O}_3$  in plasma sprayed coating. Only unexplained results were obtained from differential thermal analysis on plasma sprayed alumina. From the observation with scanning electron microscope, it was shown that almost all of alumina particles were fully flattened.*

### 1. Introduction

As reported in the previous paper<sup>1)</sup>, plasma spraying is a great promoting method when some protective coating is intended to deposit on the surface of a metal. Especially, the advantages of this method are clearly exhibited in the cases such as versatile deposition of oxide and carbide in order to improve heat- and abrasive-resistance and some other properties of metals. However, state analysis on such sprayed compounds and the interface between substrate and sprayed compound has not fully been performed in spite of their importances. In this paper, state of plasma sprayed alumina was investigated because alumina is one of very popular ceramics as well as zirconia. Although it is well known that alumina is widely used as a fire-resistance material, the formation of metastable phases such as  $\gamma\text{-Al}_2\text{O}_3$  and  $\delta\text{-Al}_2\text{O}_3$  is very significant for the properties of plasma sprayed alumina. For example, the formation of  $\gamma\text{-Al}_2\text{O}_3$  brings about thermal expansion due to the transformation of  $\gamma\text{-Al}_2\text{O}_3$  into  $\alpha\text{-Al}_2\text{O}_3$  in later thermal recycle and the expansion gives great influences upon the strength of alumina coating. Further, it was reported that amorphous alumina was formed at the interface when plasma spraying method was used<sup>2)</sup>. Therefore, it is anticipated that state of plasma sprayed alumina is more complicated. In this study, the clarification of state of plasma sprayed alumina, and the formation of metastable phases and isomorph inversion by annealing were mainly performed.

### 2. Experimental Procedures

Materials used for plasma spraying were reagent grade  $\alpha\text{-Al}_2\text{O}_3$ ,  $\gamma\text{-Al}_2\text{O}_3$  and commercial alumina METCO 105. Plasma spraying equipment used was a plasma gun of METCO 3MB type and plasma spraying conditions were as follows;

Voltage and Current:  $70\text{V} \times 500\text{A}$ ,

Flow gas: Primary Ar, Secondary  $\text{H}_2$ .

All of metal substrates used for plasma spraying were steel rods (SGD-2) with 25 mm in diameter and about 10 mm in thickness. One side of each steel rod was blasted just before plasma spraying. Flame spraying of  $\alpha\text{-Al}_2\text{O}_3$  was also performed with a gun of Mogul 305 and oxygen and acetylene gases were used for combustion.

X-ray diffraction measurement was performed with following conditions;

Target: Cu K $\alpha$  (Ni filtered),

Voltage and Current:  $35\text{KV} \times 10\text{ mA}$ ,

Ditector: Sci., Path: Air.

Differential thermal analysis (DTA) from room temperature to  $1200^\circ\text{C}$  on each specimen, which peeled off from substrate by 1N-HCl aq. and pulverized in a agate mortar and pestle, with following conditions;

Heating rate:  $5^\circ\text{C}/\text{min}$ ,

Sensitivity:  $\pm 10\ \mu\text{A}$ ,

Reference material:  $\alpha\text{-Al}_2\text{O}_3$ .

Sprayed commercial alumina was used for annealing experiment. The furnace was brought to the

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desired temperature before the specimen was inserted. The specimen was kept in Pt-13%Rh crucible for the desired time and was removed into air at the end of the annealing time. Following each calcination, it was reexamined by X-ray diffraction in the same conditions as described above.

The observation with scanning electron microscope was performed on sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  and commercial alumina in order to investigate the appearance of sprayed alumina particles. The experimental conditions were as follows;

Voltage and Current: 20KV  $\times$  100–110  $\mu\text{A}$

Tilt angle: 30°

Type of microscope: HSM-2B (Hitachi).

### 3. Results and Discussion

#### 1) X-ray Diffraction Analysis

The existence of many metastable phases in alumina is well known and there are five well-defined intermediate phases with distinct crystal structures, before the alpha form corundum is reached, namely, those described by the prefixed gamma, delta, theta, kappa and chi<sup>(3),4),5)</sup>. According to the previous results on flame or plasma sprayed alumina, the existence of  $\gamma$ -,  $\delta$ - and  $\theta$ - $\text{Al}_2\text{O}_3$  were certified<sup>6)</sup>. However, the effects of impurities or the difference of spraying conditions on structural change of alumina were scarcely been considered. In this study, therefore, the structures of

pure  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  after plasma spraying were investigated. These X-ray diffraction patterns are shown in Fig. 1. As shown in this figure, it can be considered that both plasma sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  essentially change into the mixture of  $\alpha$ - and  $\gamma$ - $\text{Al}_2\text{O}_3$ . The diffraction pattern of sprayed  $\gamma$ - $\text{Al}_2\text{O}_3$  is not shown in Fig. 1 because it is almost same to that of sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$ . In order to compare plasma sprayed with flame-sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$ , X-ray diffraction pattern of flame sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  is also shown in Fig. 1. Although it has been reported that almost all  $\alpha$ - $\text{Al}_2\text{O}_3$  changes into  $\gamma$ - $\text{Al}_2\text{O}_3$  after flame spraying with rod method<sup>6)</sup>, flame sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  with powder method was identified as  $\alpha$ - $\text{Al}_2\text{O}_3$  containing some  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\delta$ - $\text{Al}_2\text{O}_3$ . It was very difficult to certify the existence of  $\delta$ - $\text{Al}_2\text{O}_3$  but its identification was determined by following reasons;

(1) asymmetry of the peak near 38° in  $2\theta$ ,

(2) splitting of the peak near 66° in  $2\theta$ .

A large amounts of  $\alpha$ - $\text{Al}_2\text{O}_3$  in flame-sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  with powder method seems to attribute to the occurrence of unmelted or semifused  $\alpha$ - $\text{Al}_2\text{O}_3$ . Therefore, different results may be obtained when the optimum conditions are obtained. Further, the fact that  $\delta$ - $\text{Al}_2\text{O}_3$  was detected in flame-sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  but not in plasma sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  are supported by schematic transformation diagram by Dragoo and Diamond<sup>7)</sup> as shown in Fig. 2. Reheating effect is also important to the formation of metastable phase because of supply of a large amounts of heat, and, therefore, spraying in this study was performed so that the effect of reheating was as suppressed as possible. Furthermore, the difference of atmosphere between plasma- and flame-spraying is also significant. These problems will be taken up in further investigations.

Subsequently, a commercial material METCO 105 was plasma-sprayed in order to compare a typical commercial alumina with pure  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$ .

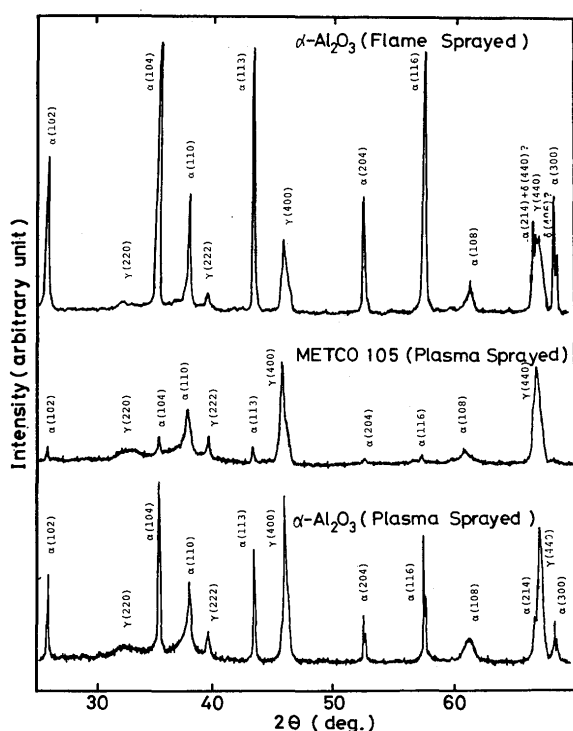


Fig. 1 X-ray diffraction patterns of plasma sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  and commercial alumina, and flame-sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$

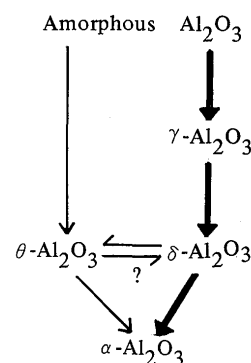


Fig. 2 Transformation diagram of amorphous alumina to  $\alpha$ - $\text{Al}_2\text{O}_3$  after Dragoo and Diamond<sup>7)</sup>

As shown in Fig. 1, sprayed commercial alumina changed into a large amount of  $\gamma$ - $\text{Al}_2\text{O}_3$  with a small quantity of  $\alpha$ - $\text{Al}_2\text{O}_3$ . It can be considered that this attributes to the occurrence of glassy silica, that is, to the phenomenon that viscous glassy silica reacts with alumina and coats the surface of alumina particle and thus the migration of alumina are retarded. Such consideration was also performed by Iler<sup>8)</sup> in order to explain the stabilization of metastable phases by silica addition. However, the effect of silica addition on the stabilization of metastable phases in sprayed alumina must be investigated on account of insufficient data. Other possible impurities in commercial alumina are  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ . These impurities may improve the adherence at the interface but seem to have little influence on stabilization of metastable alumina because these are less viscous than silica.

Furthermore, some investigators<sup>2)</sup> reported that amorphous alumina was detected at the interface in plasma sprayed alumina. Therefore, the detection of amorphous alumina was performed with simple X-ray diffraction method though the identification by electron diffraction may be considered to be better approach. As shown in Fig. 3, it was difficult to detect amorphous pattern on account of the high background due to  $\gamma$ - $\text{Al}_2\text{O}_3$ . The difference of the amount

of  $\gamma$ - $\text{Al}_2\text{O}_3$  between surface and interface could only be detected. Therefore, further investigation with other methods are desired.

## 2) Differential Thermal Analysis

DTA from room temperature to  $1200^\circ\text{C}$  were performed on plasma sprayed  $\alpha$ -,  $\gamma$ - $\text{Al}_2\text{O}_3$  and commercial alumina, METCO 105. DTA patterns of plasma-sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  and commercial alumina are shown in Fig. 4. DTA patterns of sprayed  $\gamma$ - $\text{Al}_2\text{O}_3$  was abbreviated because it was similar to the pattern of sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$ . The peak near  $840^\circ\text{C}$  corresponds to the transformation of  $\gamma$ - to  $\delta$ - $\text{Al}_2\text{O}_3$  according to the result by Dragoo and Diamond<sup>7)</sup> whereas it corresponds to the transformation of  $\gamma$ - to  $\theta$ - $\text{Al}_2\text{O}_3$  according to the result by Iler<sup>8)</sup>. It is considerably difficult to distinguish  $\delta$ - $\text{Al}_2\text{O}_3$  with  $\theta$ - $\text{Al}_2\text{O}_3$  though, in this study, the formation of  $\delta$ - $\text{Al}_2\text{O}_3$  was supported from X-ray diffraction result. Therefore, it would be reasonable to consider that the peak near  $840^\circ\text{C}$  caused mainly by the transformation of  $\gamma$ - to  $\delta$ - $\text{Al}_2\text{O}_3$  and partly by the transformation of  $\gamma$ - to  $\theta$ - $\text{Al}_2\text{O}_3$ . Secondly, it can be considered that the peak near  $1000^\circ\text{C}$  corresponds to the transition of  $\delta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  though the temperature was  $50^\circ\text{C}$  higher than that reported by Dragoo and Diamond<sup>7)</sup>. Lastly, the peak near  $1150^\circ\text{C}$  could not be explained if this did not attribute to  $\theta$ - $\alpha$  transition. Iler<sup>8)</sup> reported that the temperature of  $\theta$ - $\alpha$  transition was  $1150^\circ\text{C}$  whereas Dragoo and Diamond<sup>7)</sup> reported that it was

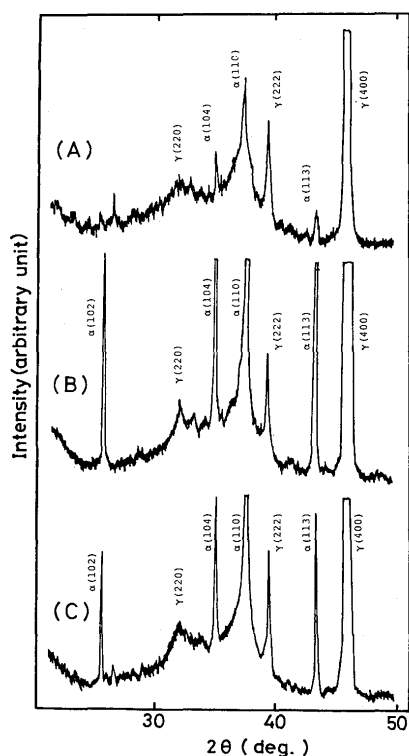


Fig. 3 X-ray diffraction patterns of plasma-sprayed aluminas measured from surface or interface side ((A) commercial alumina METCO 105, interface, (B)  $\alpha$ - $\text{Al}_2\text{O}_3$ , surface, (C)  $\alpha$ - $\text{Al}_2\text{O}_3$ , interface)

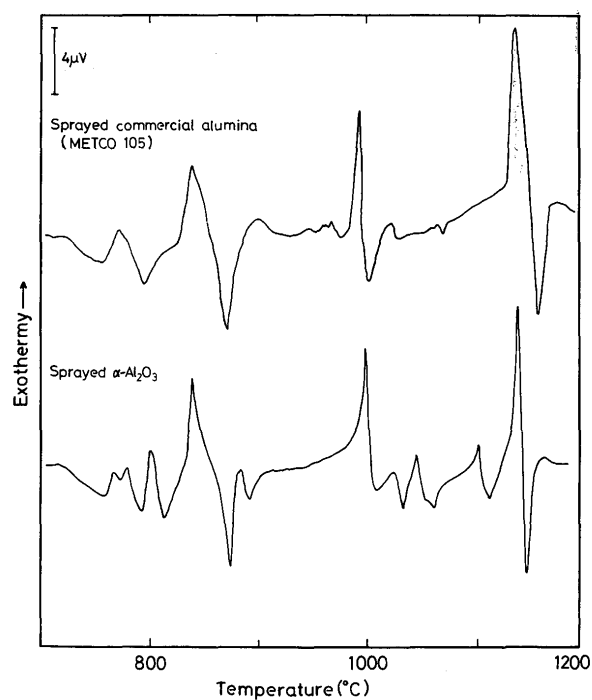


Fig. 4 DTA on plasma sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  and commercial alumina, METCO 105

1070°C. If the latter result is ignored, it may be possible to explain our data as follows;

- (1) lowest peak attributes mainly to  $\gamma$ - $\delta$  transition and partly to  $\gamma$ - $\theta$  transition
- (2) middle peak attributes to  $\delta$ - $\alpha$  transition.
- (3) highest peak attributes to  $\theta$ - $\alpha$  transition.

However, many weak points are found in this interpretation. For example, every peaks were shown in both endothermic and exothermic sides. Further, a lot of small peaks or turbulence in base line were found in all DTA patterns. The latter seems to originated in noise or the retardation of transformation of metastable phases. It must be also considered that transformation in DTA are generally detected at higher temperature than that obtained by isothermally annealing experiment. However, the former could not be explained in this study. Thus, there are many questionable behaviours in DTA result. Conclusively, it is difficult to give clear assignment to each peak in DTA on plasma sprayed alumina.

### 3) Isomorph Inversion of Plasma Sprayed Alumina by Heat Treatment

Up to present time, numerous investigations on thermally transformation of metastable alumina have been performed but, in most cases, hydrate such as gibbsite, diaspore or boehmite was used as a starting material. In several cases, amorphous alumina prepared by sputtering or electron beam heating was utilized. One of most important properties in plasma sprayed coating is that sprayed coating are stable during heat treatment. Accordingly, phase transition of plasma sprayed alumina by heat treatment was investigated with X-ray diffraction method. In this experiment, commercial alumina METCO 105 was intentionally used instead of pure alumina. The results are shown in Figs. 5 and 6. Existence ratio of  $\alpha$ - $\text{Al}_2\text{O}_3$  was semi-quantitatively decided by three main peaks of (113) in  $\alpha$ - $\text{Al}_2\text{O}_3$ , (440) in  $\gamma$ - $\text{Al}_2\text{O}_3$  and (406) in  $\delta$ - $\text{Al}_2\text{O}_3$ . As shown in Fig. 5, existence ratio of  $\alpha$ - $\text{Al}_2\text{O}_3$  could not show any change even after an-

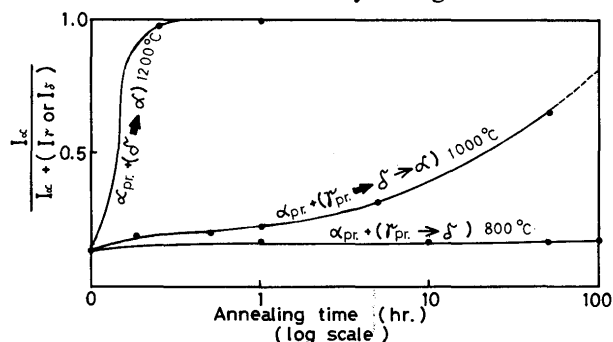


Fig. 5 Alumina forms obtained from commercial alumina, METCO 105, annealed after plasma spraying

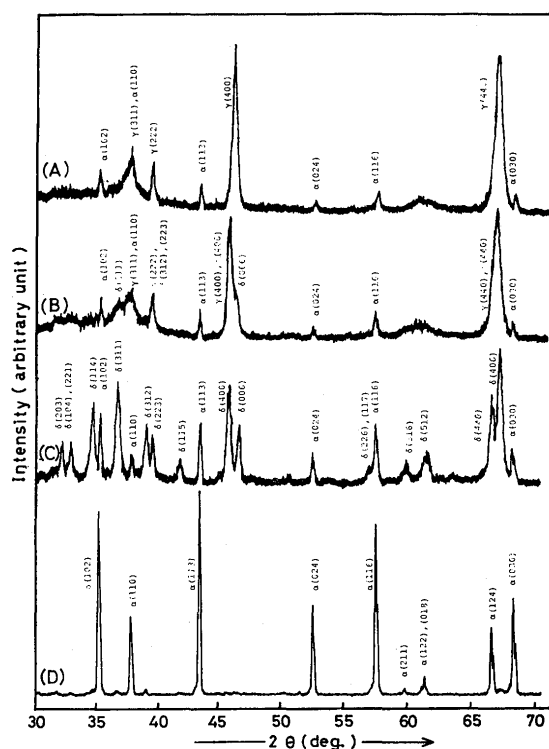


Fig. 6 X-ray diffraction patterns of plasma-sprayed commercial aluminas annealed on various conditions

- (A) as sprayed,
- (B) annealed at 800°C for 100 hr
- (C) annealed at 1000°C for 5 hr
- (D) annealed at 1200°C for 10 min

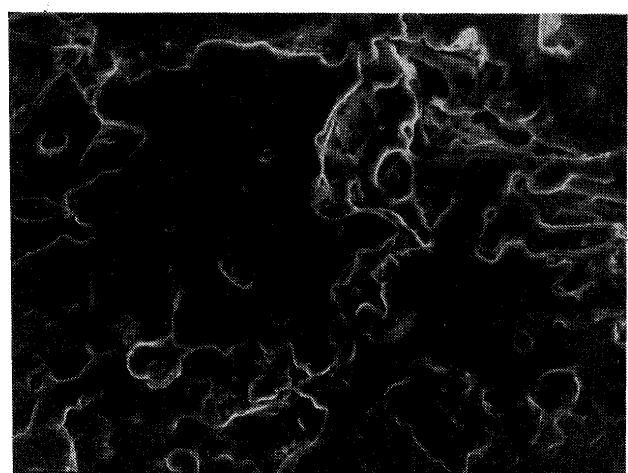
nealing at 800°C for 100 hr. In annealing at 1000°C, however, transformation of  $\gamma$ - to  $\delta$ - $\text{Al}_2\text{O}_3$  or  $\delta$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  rapidly progressed as annealing time increased. The fact that  $\gamma$ - $\text{Al}_2\text{O}_3$  was stable at a little higher temperature than that performed by Dragoo and Diamond seems to originate in the existence of silica. Thus, as indicated in previous papers, it is expected that transition of  $\gamma$ - $\text{Al}_2\text{O}_3$  or other metastable alumina in plasma sprayed coating is inclined to be suppressed by silica addition.

### 4) SEM Observation on Plasma Sprayed Alumina

In order to observe both surface and interface of plasma sprayed alumina, SEM observation was performed. These results are shown in Fig. 7. It was clearly shown from these results that almost all of alumina particles were fully flattened just after each particle was struck on a substrate. Lamellar structure was also observed from the photograph of the interface. Further, high conductive black alumina was also found at the interface as well as in the case of sprayed zirconia.

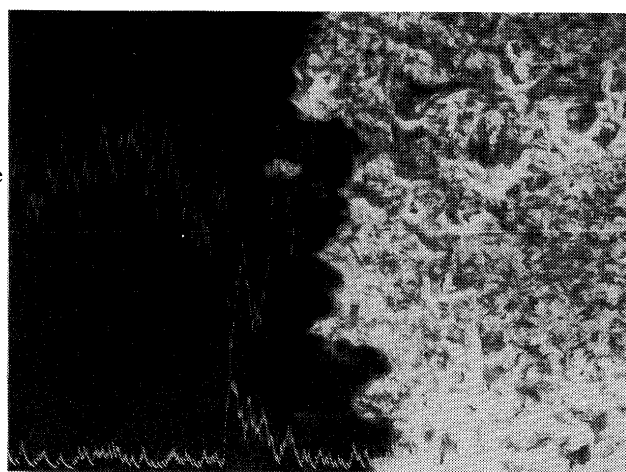
## 4. Summary

Plasma sprayed  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  were structural-



(a) surface

× 800



(b) interface

× 800

Fig. 7 The interface and surface of plasma sprayed commercial alumina with SEM observation

## 5. Acknowledgement

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ly investigated with X-ray diffraction method and similar diffraction patterns were obtained from these sprayed materials. They were identified as the mixture of  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$ . Further, plasma sprayed commercial alumina was also identified as the mixture of  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$ . However, the amount of  $\alpha$ - $\text{Al}_2\text{O}_3$  in sprayed commercial alumina was fairly less than that in sprayed  $\alpha$ - or  $\gamma$ - $\text{Al}_2\text{O}_3$ . It was suggested that the difference in the amount of  $\alpha$ - $\text{Al}_2\text{O}_3$  attributed to additive silica. Only unexplained result was obtained from DTA in the range of room temperature to 1200°C on plasma sprayed alumina. Annealing experiment on sprayed commercial alumina also suggested that transition of  $\gamma$ - $\text{Al}_2\text{O}_3$  or other metastable phases into  $\alpha$ - $\text{Al}_2\text{O}_3$  was suppressed by silica addition and that the addition of silica to alumina may enable sprayed alumina to use at higher temperature in comparison with sprayed alumina containing no silica.