

# Basic Study of Plasma Spray Synthesis —Synthesis of BaTiO<sub>3</sub> from BaCO<sub>3</sub> and TiO<sub>2</sub>\*—

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## ABSTRACT

A limiting feature of the plasma spray synthesis is the need for powders to melt and react each other during its passage through the plasma flame. In case of using the mixtures of ordinary sized powders, it is quite impossible to obtain coatings with new compositions.

Agglomeration techniques were used to prepare the fine powders of BaCO<sub>3</sub> and TiO<sub>2</sub>. BaTiO<sub>3</sub> (Barium Titanate) coatings were produced by plasma spraying of the agglomerated powders. The formation of BaTiO<sub>3</sub> were established by X-ray diffraction.

## 1. INTRODUCTION

Plasma spraying is a well-accepted technological process in which protective coatings are deposited at high velocities from plasma torch. Ceramics and metallic coatings have mainly found in the fields of corrosion protection, wear resistance, and thermal barrier coatings. However, only a few application studies have been conducted in plasma spray synthesis.

Some nitrides (AlN, TiN) were formed by the reaction between the particle of corresponding metals (Al, Ti) in flight into the nitrogen plasma jet and the excited nitrogen.<sup>(1),(2)</sup>

In plasma sprayed  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> onto substrate, the cooling rate will be of the order of 10<sup>3</sup> - 10<sup>6</sup>°C/sec. So the occurrence of metastability is expected by quenching the molten state because rapid cooling of the molten particles prevents the ordering of oxygen and aluminium ions into the stable  $\alpha$  phase. The experiment with thermally sprayed Al<sub>2</sub>O<sub>3</sub> deposits showed that the metastable,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> high temperature phases were produced rather than the stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.<sup>(3)</sup>

Compounds or ceramics can be synthesized in the plasma by injected the raw material in some form into the plasma gas or with another raw material which is also injected into the plasma. In that case, the powder preparation is most important. Empirically, it is found that the best powders for coating have spherical particles of 50  $\mu$ m or some what smaller diameter. In

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synthesis, fine powder is more desired. However, powders which are too fine are not properly intrained: larger powder particle are not wholly melted in flight.

In this study the plasma spray synthesis of  $\text{BaTiO}_3$  (Barium titanate) from  $\text{BaCO}_3$  and  $\text{TiO}_2$  is described. The starting powders are agglomerated by use of suitable organic binders to achieve fluidity and chemical homogeneity. The products are characterized by X-ray diffraction analysis.

## 2. PLASMA SPRAYING PROCESS

In the plasma spraying process a D.C. plasma jet is used as a heat source to melt and accelerate the injected powder particles which subsequently impinge and solidify on a given substrate.

Fig. 1 shows a schematic cross section through a typical commercial version of a non-transferred plasma torch. An electrical discharge is created between a tungsten cathod and a copper anode of internally water cooled nozzle in the presence of a working gas such as argon or nitrogen. The temperature in the core region of the plasma flame is of the order of  $10^4\text{K}$  and it falls rapidly with distance from the nozzle exit. Since the effective temperature used in melting the particles is in the range of 3000 to 8000 K,

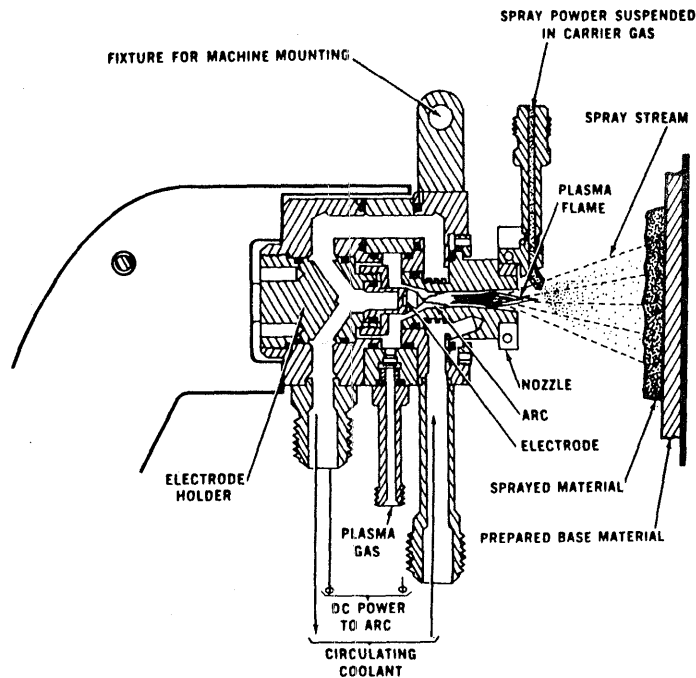


Fig. 1 Schematic of plasma spray torch.<sup>(5)</sup>

the applicable plasma field is confined in small region.

The microstructures of the coating layer are strongly influenced by the various plasma spraying parameters. Some of the most important parameters are:

- 1) distance between the nozzle exit and substrate
- 2) plasma torch power (current and voltage of the discharge)
- 3) particle size and its distribution
- 4) particle shape
- 5) powder feed rate
- 6) surface preparation of substrate
- 7) location and angle of powder injection
- 8) working gas compositions
- 9) spraying circumstances (in air or in a protective atmosphere).

### 3. EXPERIMENTAL PROCEDURE

#### 3.1 POWDER PREPARATION

Plasma spray powders were prepared through the agglomeration of fine powers of the starting materials. An illustration of how this technology would be applied is shown in Fig. 2.

Equimolar quantities of  $\text{BaCO}_3$  and  $\text{TiO}_2$  were mixed for 3 hours with PVA (Poly Vinyl Alcohol) binder solution in a polyethylene jar containing ceramic balls. The slurry was then dried, granulated with a mortar and pestle. The particle size distribution of the powders was determined by sieving in sieves. The agglomerated particle-size range was from 53 to 250  $\mu\text{m}$  in diameter.

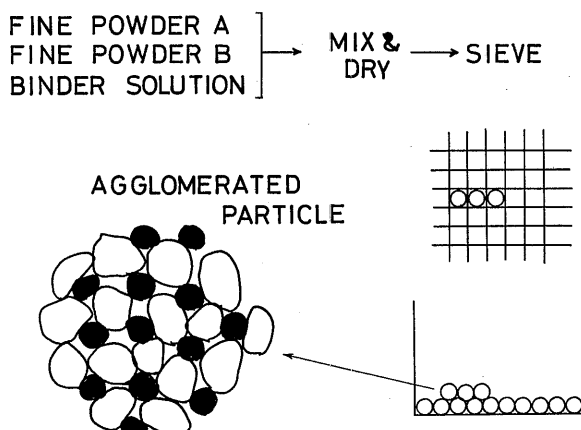


Fig. 2 Illustration of agglomeration.

These powders were then sprayed with conventional plasma spray equipment.

### 3.2 PLASMA SPRAY CONDITION

Plasma spraying was carried out with a commercial D.C. plasma torch (Metco 7MB) working in air with nitrogen and hydrogen gas mixture. Arc current and voltage were set at 500 A and 70 V, respectively. A grit blusted steel with 2 mm thick, was employed for substrate. The substrate was maintained at room temperature by attaching copper plate cooled by water to the back surface of the substrate while spraying. The spraying distance was kept at approximately 8 cm and powder feed rate was 20 g/min. An air jet blown onto the coating while spraying in order to cool it.

### 3.3 MICROSTRUCTURE

Crystal structure was determined by X-ray diffraction analysis. The polished and free surface of samples were studied using a SEM (Scanning Electron Microscopy). The polished surface were obtained by using various SiC and Al<sub>2</sub>O<sub>3</sub> polishing compounds, and finally using 0.05 μm Al<sub>2</sub>O<sub>3</sub> to obtain optical finish.

Charging problems in the secondary electron imaging mode were prevented by using a thin film of gold deposited onto the specimen's surface.

## 4. RESULTS AND DISCUSSION

The plasma spray synthesis was carried out on the formation of BaTiO<sub>3</sub> from equimolar BaCO<sub>3</sub> and TiO<sub>2</sub> (anatase) mixture.

Fig. 3 shows the X-ray diffraction pattern of the deposited coating using the stainless steel substrate maintained room temperature. As expected, the X-ray diffraction analysis of the coating confirms that BaTiO<sub>3</sub> is the main constituent synthesized during the reaction of the agglomerated powders through the plasma.

X-ray diffraction analysis also shows that small amount of BaCO<sub>3</sub> and TiO<sub>2</sub> (anatase) are retained in their elemental form. It can be seen that, for optimum flow rate, most of the particles pass through the hot core region of the plasma. The remaining particles travel in the periphery of the core. So that they have a low velocity, they are not melted, not reacted each other. Intermediate phase Ba<sub>2</sub>TiO<sub>4</sub> is also identified in X-ray diffraction pattern of the coating.

The question then arises as to the nature of the BaTiO<sub>3</sub> formation. How much does these raw materials react directly with each other at the surface contact during their flight? If the BaTiO<sub>3</sub> formation occurs during the plasma flame, the products could easily be collected by rapid quenching of

the melt-atomised particles.

Fig. 4 illustrates the X-ray diffraction pattern of what the melt-atomised powder was directly quenched into the distilled water. The plasma

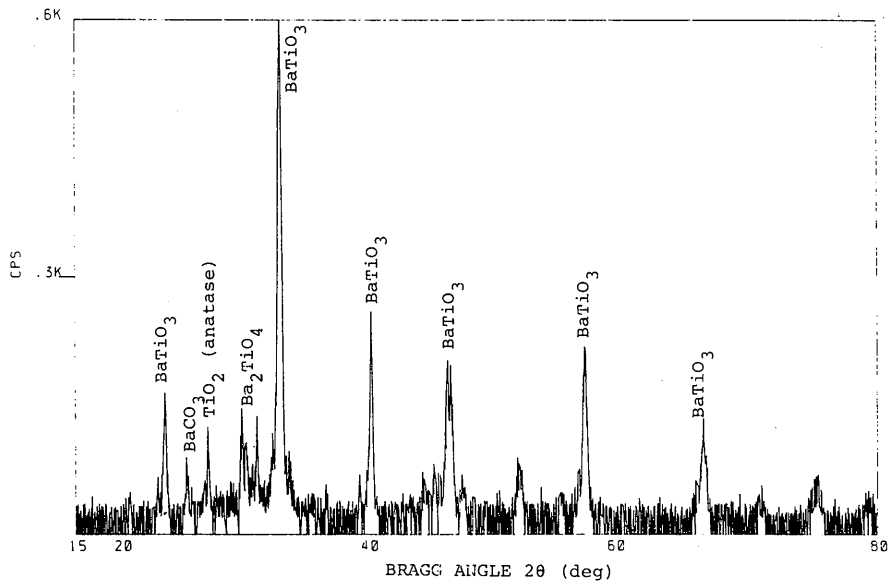


Fig. 3 X-ray diffraction pattern of the deposited coating using equimolar  $\text{BaCO}_3$  and  $\text{TiO}_2$  mixture powder.

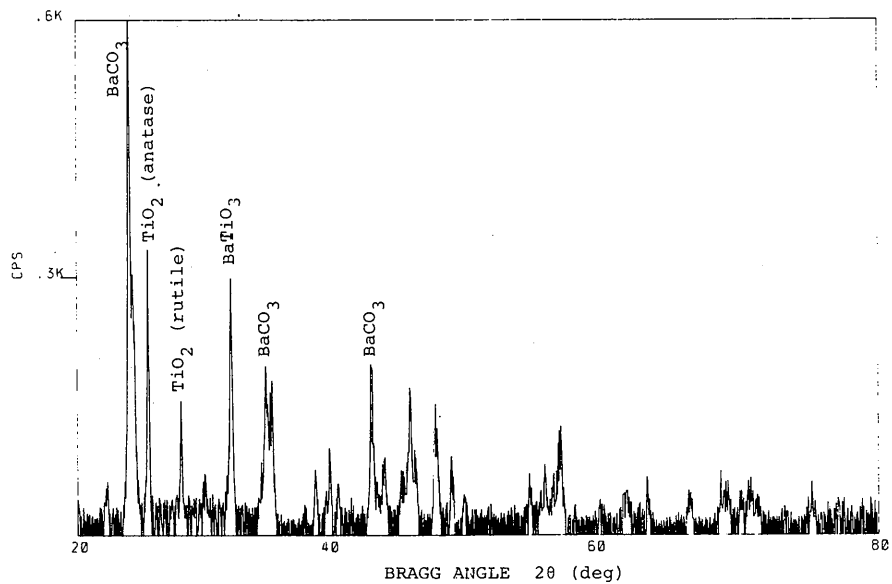


Fig. 4 X-ray diffraction pattern of water quenched sample.

spraying parameter was used the same condition as coating ones. As shown in Fig. 4, the X-ray diffraction pattern of the water quenched sample is completely different from that of coating. In this case, a small amount of  $\text{BaTiO}_3$  is formed and some  $\text{TiO}_2$  is changed antase\* to rutile structure. Almost raw materials, however, are retained.

This result indicates that the reaction of the two raw materials does not

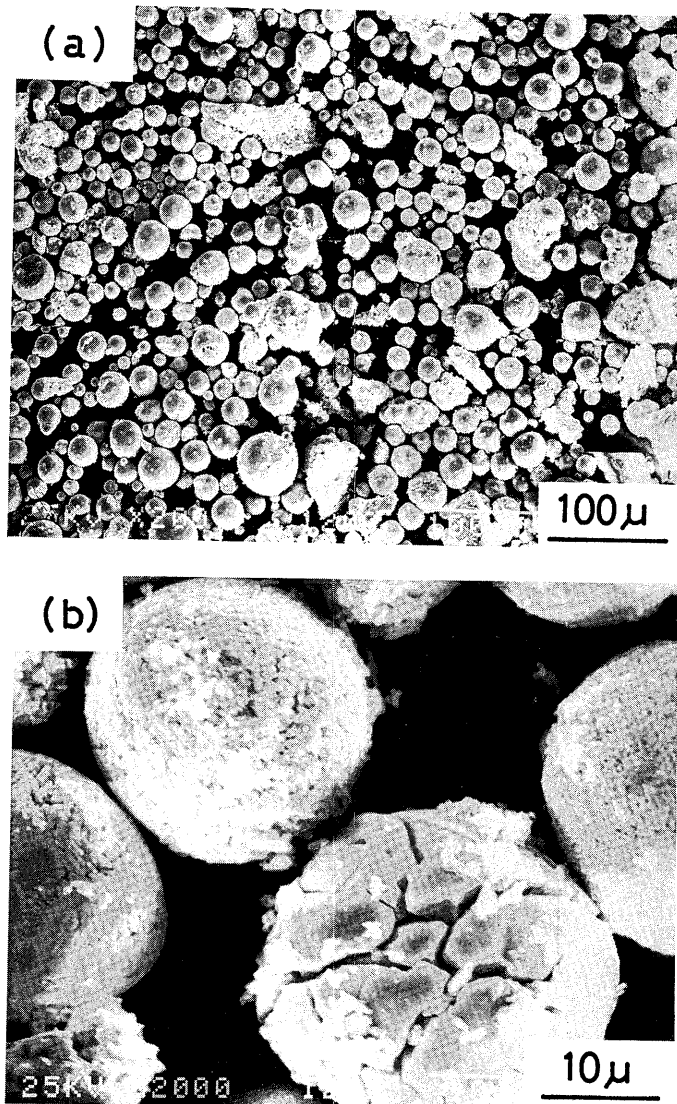


Fig. 5 SEM micrographs of the water quenched particles using  $\text{BaCO}_3$  and  $\text{TiO}_2$  mixture powder.

\* Transforms to rutile at about  $800^\circ\text{C}$ .

completely finish in the plasma flame, but the lamellae of melting particles as they strike the substrate surface has a strong influence on the reactivity of coating.

Fig. 5 illustrates scanning electron micrographs of the water quenched particles using  $\text{BaCO}_3$  and  $\text{TiO}_2$  mixture. As shown in Fig. 5, quenching of the powders by plasma spraying into water resulted in spherical particles. Most of the particles were less than  $50 \mu\text{m}$  in diameter. There were less than the original agglomerated powder size.

As usual for plasma-sprayed coatings, the ceramic deposits have an

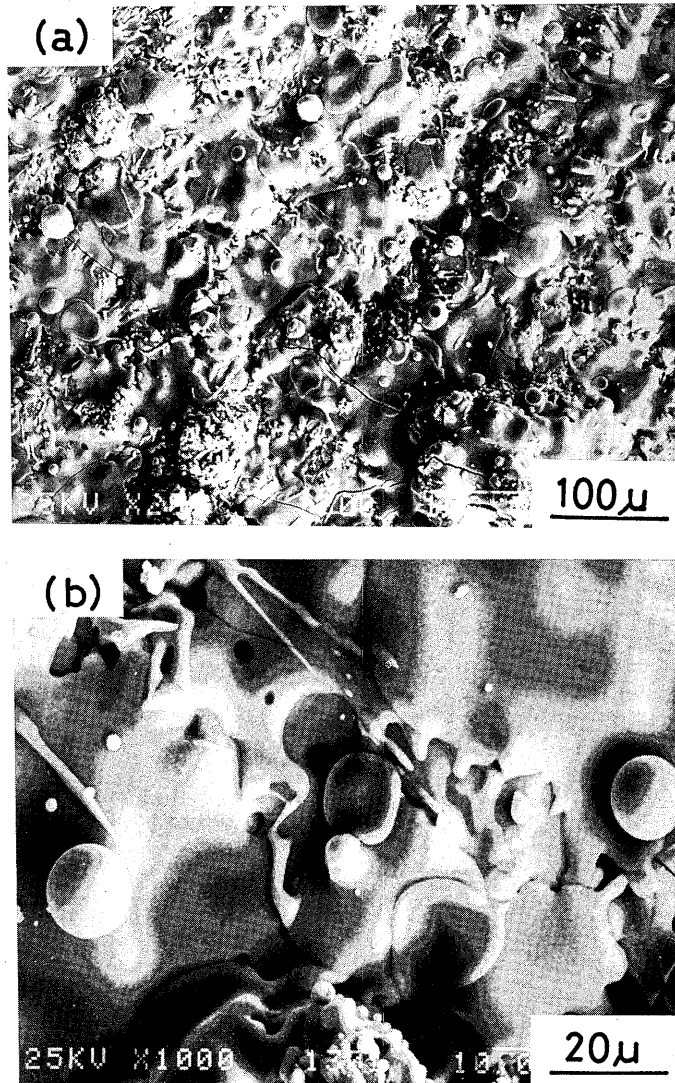


Fig. 6 SEM micrographs of  $\text{BaTiO}_3$  coating surface.

anisotropic layered structure, with dense array of microcracks.<sup>(4)</sup> Example of microcracks are shown in Fig. 6.

Fig. 7 illustrates the SEM micrograph of polished cross section of plasma sprayed  $\text{BaTiO}_3$  coating layers on steel. A lot of porosities are existed.

The micrograph in Fig. 8 shows the influence of after heat treatment. The coating layer has a large crack caused by internal stress.

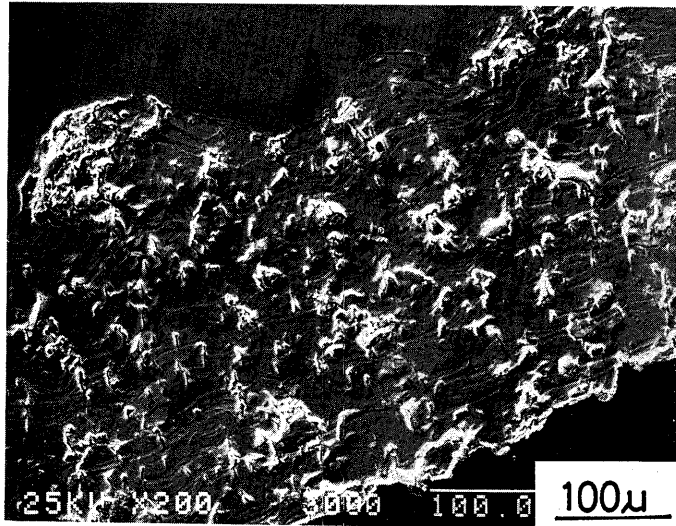


Fig. 7 SEM micrograph of polished cross section plasma sprayed  $\text{BaTiO}_3$  coating layers on steel.

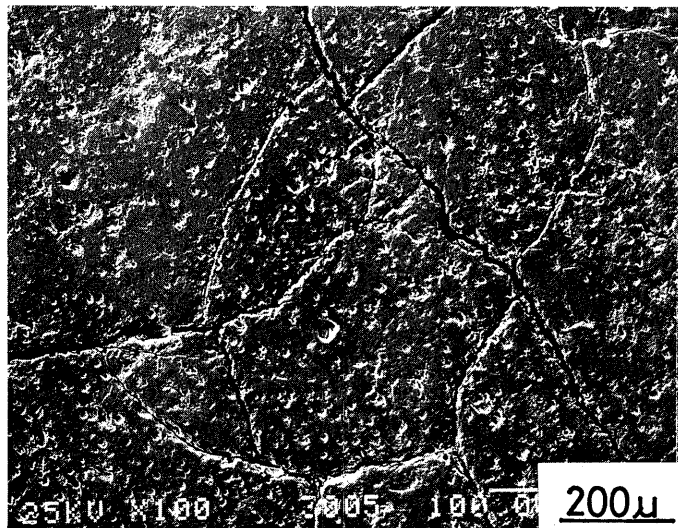


Fig. 8 SEM micrograph of polished surface of  $\text{BaTiO}_3$  coatings after short-time heat treatment by plasma torch.



## 5. CONCLUSION

Plasma spray synthesis using the agglomerated powders of  $\text{BaCO}_3$  and  $\text{TiO}_2$  onto steel substrates results in the formation of  $\text{BaTiO}_3$  materials. In the water quenched sample, however, only a small amount of  $\text{BaTiO}_3$  was formed and almost raw materials were retained in non-reacted conditions. So this means that the melted particles striking the substrate are flattened and form lamellae, and the possibility of reaction between  $\text{BaCO}_3$  and  $\text{TiO}_2$  will rapidly proceed with the increase of the surface area available for diffusion of each elements.

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## REFERENCES

- 1) N. Asahi and Y. Kojima, "Low Pressure Plasma Spray Coating", *Journal of High Temperature Society*, Vol. 10 supplement (1984) pp. 249-256.
- 2) F. Kassabji et al., "Aluminium and Aluminium Nitride Deposition by Low Pressure Nitrogen Arc Plasma Spraying", *Proceedings of the 10th International Thermal Spray Conference, Essen, 1983 in DVS Berichte*, Vol. 80 (1983) pp. 82-84.
- 3) N. N. Ault, "Characteristics of Refractory Oxides Coatings Produced by Flame-Spraying", *Journal of American Ceramic Society*, Vol. 40 (1957) pp. 69-74.
- 4) R. Mcpherson, "The Relationship between the Mechanism of Formation, Microstructure and Properties of Plasmasprayed Coating", *Thin Solid Films*, Vol. 83 (1981) pp. 297-310.
- 5) H. S. Ingham, Jr. and A. P. Shepard, "Flame Spray Handbook", Vol. III, Plasma Flame Process, Metco Inc., Westbury, New York.