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# Fundamental Considerations on Plasma Sprayed Ceramic Coating (Report I)<sup>†</sup>

## —Problems of Plasma Sprayed Zirconia—

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### Abstract

*Properties of commercial zirconia for plasma spraying were investigated. It was shown that particle size distribution has an important effect on the content of stabilizer such as CaO or MgO. After plasma spraying, increase of 150 ppm to 1200 ppm in nitrogen quantity was found and it was suggested that investigation on the effect of other impurity elements on the mechanical properties of sprayed zirconia is necessitated. From SEM observation and line analysis with XMA, the region which seems to be black zirconia or nonstoichiometric zirconia was found but identification remains unclear. Lowering of porosity of plasma sprayed zirconia could not be achieved by addition of pyrex glass and philogopite. It is found that preliminary oxide with about 1 μ or less was effective on the deposition of zirconia.*

### 1. Introduction

Recently, the use of only a material is insufficient to satisfy more severe requirements for materials. Metals are widely used by virtue of their excellent mechanical properties but they can not give fully satisfaction for recent various requirements such as heat-, corrosion- and abrasion-resistance. In order to satisfy these requirements and make wider uses of metals possible, much endeavour has been performed by various treatments on a surface of metal. For example, excellent materials which can be used at a high temperature such as 1000°C or over are required in nuclear reactor and iron- and steel-making with atomic energy. In such cases, it is necessary to treat a surface of a metal with both hardly oxidizable and infusible materials and it is easiest to coat the surface with a ceramic material such as Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub>. However, it was difficult to carry out ceramic coating such as ZrO<sub>2</sub> before 1950's because of its high melting point. Versatile coating of high temperature materials became first possible by establishment of plasma spraying method which was devised in the second half of the 1950's. At present, ceramic spraying is widely used in ocean development or aircraft manufacturing because it can remarkably improve various properties of metal.

In spite of the widely application of ceramic spraying, however, physico-chemical investigation on ceramic sprayed coats has not fully been performed. Especially, state analysis on ceramic-metal interface has

scarcely been investigated. First of all, extensive knowledges related to metallurgy and compound chemistry are necessitated. Insufficient establishment of adherence mechanism in porcelain enamel or glass to metal seal also produces many problems. Furthermore, inexperienced phenomena are produced by rapid quenching from a temperature of about 10<sup>4</sup> °C or over.

In this study, in order to improve the adherence of plasma sprayed zirconia coat, which is used as extensively as Al<sub>2</sub>O<sub>3</sub>, physical and crystallographical properties of powder stabilized zirconia, state of steel-plasma sprayed zirconia interface and an effect of pre-oxidation on steel surface before plasma spraying were investigated. Further, the influence of a few oxide addition was also investigated to decrease the porosity of plasma sprayed zirconia layer.

### 2. Experimental Procedures

Stabilized zirconia made in Bay State Abrasives Co. Ltd. (U.S.A.) and Nippon Kagaku Togyo Co. Ltd. (Japan) were used for plasma spraying. The composition of steel used as substrate material was shown in Table 1. Philogopite used was natural products with

Table 1 Chemical composition of steel used as substrate

Substrate	Chemical composition (wt %)				
	Fe	C	Mn	P	S
S G D 4	Bal.	0.20~0.25	0.30~0.60	<0.045	<0.045

† Received on March 31, 1977

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325 mesh or under and pyrex glass 7740 was used. In sintering experiment, special grade reagent  $\text{SiO}_2$  and  $\text{Na}_2\text{CO}_3$  were used for additional materials to stabilized zirconia. Screening of zirconia powder was performed by hand with one minute period method<sup>1)</sup> and specimen weight was always fixed to be 100 gram. Specimen powder was finally divided into eleven parts in the range from 80 mesh over to 400 mesh under. Longer and shorter diameters of a hundred particles from among specimen powders in each part were measured under a microscope. Arithmetic average of these diameters in a particle was determined as the diameter of the particle and average value of these average diameters was adopted as average diameter of particles in each part. The weight percentage value of powder in each part was plotted for the average diameter as shown in **Fig. 1**.

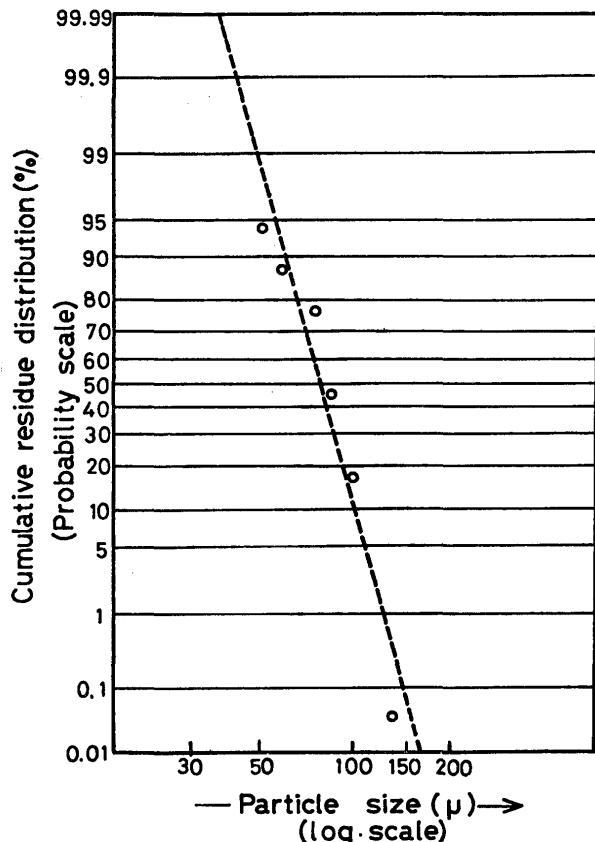


Fig. 1 Particle size distribution of raw material zirconia made in U.S.A.

Experimental conditions of plasma spraying were as follows;

Arc Current: 500 A, Arc Voltage: 70–80 V.  
For the preparation of some specimens, following conditions;

Arc Current: 700 A, Arc Voltage: 35 V.

Determination of lattice constant of zirconia was

performed with X-ray diffraction method. Experimental conditions were as follows;

Target:  $\text{CuK}\alpha$ , Voltage and Current: 35 KV  $\times$  10 mA, Filter: Ni, Ditector: S.C., Path: Air.

DTA measurement was performed with following conditions;

Elevating Velocity of Temp.: 10°C/min.,  
Sensitivity:  $\pm 50 \mu\text{V}$ ,  
Standard Material:  $\alpha\text{-Al}_2\text{O}_3$ .

Nitrogen quantity of each specimen was measured with resistance heating method. In each measurement, standard electrolysed iron powder was added in a ratio of one hundred times to zirconia quantity.

Measurement of porosity was performed with following method. First of all, specimen was dried at 120°C for 1 hr or over and weighed after cooling down in a desiccator. Then, the same specimen was immersed into distilled water and voiled for 1 hr or over to remove air in open pores. The specimen was weighed in leaving it into water. Finally, the specimen was taken out water and quickly wiped off water drops on its surface with a piece of wet absorbent cotton. Then, the specimen was quickly weighed. Therefore, apparent of specimen,  $P_{ap}$ , was calculated from following equation:

$$P_{ap} = \left( 1 - \frac{W_1 - W_2}{W_3 - W_2} \right) \times 100 (\%)$$

where  $W_1$ ,  $W_2$  and  $W_3$  are weights of specimen in air, in distilled water and with water in open pores in air.

Observation of SEM and line analysis with XMA were performed under following conditions:

Voltage: 20 KV, Current: 100  $\mu\text{A}$ ,  
Tilt angle: 30°, Sensitivity: 30 cps or 100 cps.

Preliminary oxide of each specimen was formed in air at 500°C for 10 min to 45 min.

### 3. Results and Discussion

#### 1) Estimation of zirconia before and after plasma spraying

It is well-known that zirconium oxide shows monoclinic structure at room temperature and is transformed into tetragonal structure at the temperature near 1170°C. Therefore, pure zirconia can not be used as high temperature material because the abrupt transformation brings about thermal expansion or contraction. In order to use for practical needs, compulsory transformation of zirconia into cubic structure is always performed with addition of 10 mole% to 30 mole%  $\text{MgO}$ ,  $\text{CaO}$  or  $\text{Y}_2\text{O}_3$ .<sup>2)</sup> As zirconia par-

ticles are exposed to a very high temperature such as  $10^4$  °C in plasma spraying, vapourization of additional components comes into one of essential problems. Consequently, it is expected that concentrations of these additional components differ from those in starting material. Therefore, these vapourization behaviours of additional components can, though indirectly, be presumed with the measurement of lattice constant of zirconia. **Table 2** shows lattice constants

**Table 2** (a) Lattice constants of zirconia before and after plasma spraying  
(b) Lattice constants of zirconia with different particle size

Specimen		Lattice constant(Å)
Cubic $\text{ZrO}_2$ (after P. Duwez)		5.075
Bay State Abrasives (made in U.S.A.)	before spraying	5.114 <sub>4</sub>
	after spraying	5.118 <sub>0</sub>
Nippon Kagaku Togyo (made in Japan)	before spraying	5.122 <sub>9</sub>
	after spraying	5.122 <sub>4</sub>

(a)

Specimen		2θ	d value(Å)	Lattice constant(Å)
Nippon Kagaku Togyo (made in Japan)		13.80	2.95 <sub>8</sub>	5.12 <sub>3</sub>
Bay State Abrasives (made in U.S.A.)	under 200mesh up 250mesh	13.89	2.93 <sub>9</sub>	5.09 <sub>0</sub>
	under 400mesh	13.83	2.95 <sub>2</sub>	5.11 <sub>2</sub>
Plasma sprayed		13.81	2.95 <sub>6</sub>	5.11 <sub>9</sub>

$\lambda = 0.71069\text{ Å}$  (Mo Kα), (h k l) = (1 1 1)

(b)

of zirconia under several conditions. It was found from this table that the smaller zirconia particle is, the larger lattice constant of zirconia becomes. Lattice constants of zirconia produced by Bay State Co. Ltd. before and after spraying also showed similar inclination whereas those produced by Nippon Kagaku Togyo Co. Ltd. did not show remarkable change. The reasons of the former phenomenon can be explained as follows;

(1) main additional components in zirconia are CaO and MgO as shown in the result with spectrophotochemical analysis (see **Table 3**)

**Table 3** Result of emission spectrophotocatalytic analysis of raw material zirconia made in U.S.A.

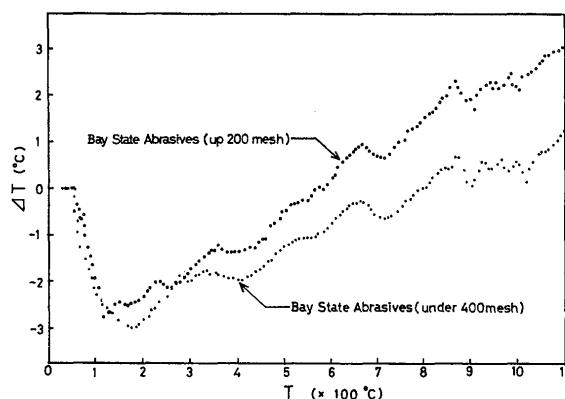
Specimen	Element							
	Ca	Mg	Al	Si	Fe	Ti	Cu	Y
Nippon Kagaku Togyo (made in Japan)	2	3	Tr.	Tr.	Tr.	—	—	—
Bay State Abrasives (made in U.S.A.) (up 200 mesh)	3	3	1	—	Tr.	1	Tr.	—

5 > 4 > 3 > 2 > 1 > Tr. > ? > —

- (2) MgO can vapourize more easily than CaO
- (3) the addition of MgO to  $\text{ZrO}_2$  decreases the lattice constant of  $\text{ZrO}_2$  whereas the addition of CaO increases it.<sup>3)</sup>

These considerations are good agreement with experimental results. The reason of latter seems to attribute to somewhat smaller quantity of CaO than the former. In order to discuss quantitatively, direct investigation on vapourization behaviours of additional components is desired.

A great difference of raw material zirconia between Japan and U.S.A. is the addition of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  as shown in **Table 3**. However, influence of these additional components on plasma sprayed zirconia remains unclear. Distribution of particle size of zirconia used is shown in **Fig. 1**. Particles of 80 mesh to 400 mesh in size accounted for 94%. It can be expected that the distribution of particle size has important effects on the properties of plasma sprayed zirconia because vapourization behaviour of additional component depends on particle size as shown in **Table 2**. The result of differential thermal analysis on particle with different size is shown in **Fig. 2**. Although no difference between thermal properties of each particle with different size seems to be shown, it is necessary to investigate the dependence of additional components or impurity upon size distribution. In this study, for an example, nitrogen contents in zirconia before and after spraying were measured. The result is shown in **Table 4**. The increase of 150 ppm to 1200 ppm was observed after plasma spraying though their accuracy must be reconsidered. Behaviours of another components except stabilizer or of impurity during plasma spraying are also desired in further investigations.



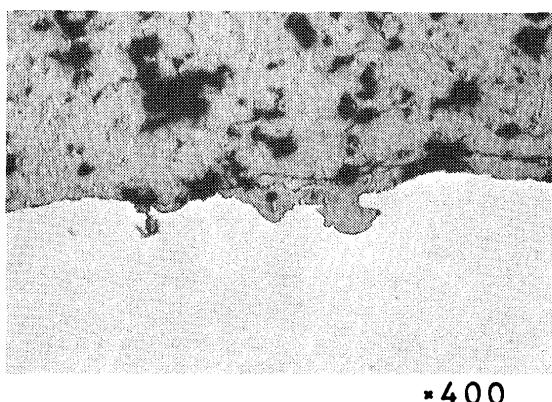
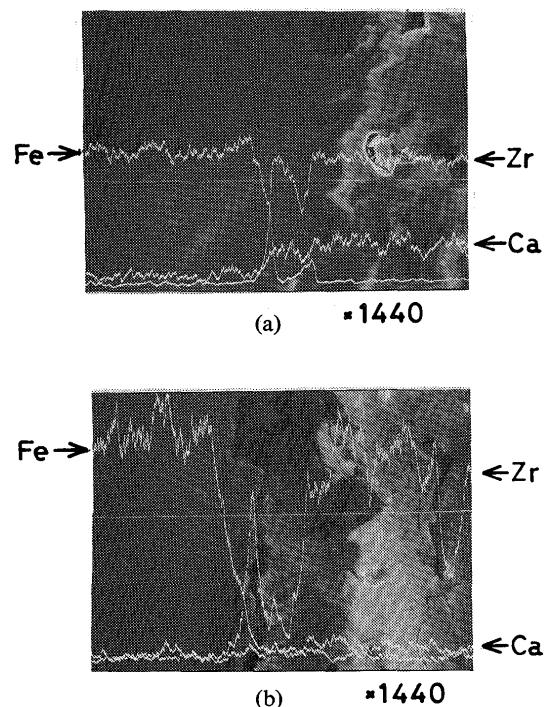
**Fig. 2** Differential thermal analysis of raw material zirconia made in U.S.A.

**Table 4** Nitrogen contents before and after plasma spraying

Nitrogen content (P.P.M.)		
No.	before spraying	after spraying
1	1052.4±100.1	1219.9±163.5
2	627.4±74.5	1838.7±348.7
3	1244.9±124.1	1459.2±180.1

## 2) Observation of plasma sprayed zirconia-steel interface

Although it is generally believed to adhere mechanically in sprayed ceramic to metal bonding, it is still expected that state analysis on interface gives many suggestions to the achievement of good adherence. Typical appearance of plasma sprayed zirconia-steel interface is shown in **Fig. 3**. Dark spots correspond to voids due to cutting or polishing of specimen. A typical interface observed with SEM is shown in **Fig. 4** and distributions of zirconium, calcium and iron were also measured with XMA. As shown in **Fig. 4**, strong signal of zirconium  $L_{\alpha, \beta}$  characteristic X-ray was obtained from dark region in the interface. In this study, identification of the dark region was not tried. As most easily anticipation, it is possible to connect this region with black zirconia reported by Kingery.<sup>4)</sup> It can also be considered to relate to the formation of nonstoichiometric compound such as black rutile in  $TiO_2$  spraying.<sup>5), 6)</sup> It is also necessary to consider the influence of impurity. In further investigations, it is desired to identify the dark region upon adherence strength in plasma sprayed zirconia-steel interface.

**Fig. 3** Typical appearance of plasma sprayed zirconia-steel interface with optical microscope

**Fig. 4** Plasma sprayed zirconia-steel interface with SEM and line analysis with XMA  
 (a) No oxide layer at the interface  
 (b) With about  $4\mu$  oxide layer at the interface

## 3) Effect of additional materials on porosity of zirconia

It is very important to lower porosity of plasma sprayed coat for the perfect protection of metal. When some materials having lower melting temperature than  $ZrO_2$  are added, it is expected that the porosity of plasma sprayed zirconia can be lowered because these melts easily fill up voids in zirconia. In use under conditions necessitating good thermal impact or durability, however, it is undesirable to transform into monoclinic zirconia as a result of the reaction between zirconia and additional material. Therefore, it is required that zirconia still remains stabilized even if lowering of porosity is desired.

In this study, though sintering experiment, the addition of  $SiO_2$  or  $Na_2O + SiO_2$  mixture was performed to lower the porosity of zirconia. As shown in **Table 5**, it was indicated that the addition of these materials can generally lower the porosity of zirconia after sintering at  $1500^{\circ}C$  for 1 hr. Abnormal behaviour of specimen (3) seems to depend on influence of  $CO_2$  gas produced from  $Na_2CO_3$ . The difference, though not remarkably, was found in comparison between specimen (2) and

**Table 5** Effects of  $\text{SiO}_2$  and  $\text{Na}_2\text{O} + \text{SiO}_2$  addition on apparent porosity of sintered zirconia

Composition (mole%)	Bulk specific gravity	Apparent specific gravity	Apparent porosity (%)	Structure
(1) 90% $\text{ZrO}_2$ 10% $\text{SiO}_2$	4.18	5.04	17.12	monoclinic $\text{ZrO}_2$
(2) 80% $\text{ZrO}_2$ 20% $\text{SiO}_2$	4.48	4.49	0.11	monoclinic $\text{ZrO}_2$
(3) 10% $\text{SiO}_2$ 3% $\text{Na}_2\text{O}$	3.51	5.05	30.49	monoclinic $\text{ZrO}_2$ + cubic $\text{ZrO}_2$
(4) 20% $\text{SiO}_2$ 3% $\text{Na}_2\text{O}$	4.17	4.20	0.54	monoclinic $\text{ZrO}_2$
100% $\text{ZrO}_2$	4.02	5.57	27.71	cubic $\text{ZrO}_2$

Compacting pressure & time : 3 ton/cm<sup>2</sup> & 30sec.

Sintering temperature & time : 1500°C & 1 hr.

(4). Although the addition of  $\text{SiO}_2$  or  $\text{Na}_2\text{O} + \text{SiO}_2$  mixture was able to lower the porosity of plasma sprayed zirconia, cubic zirconia was transformed into monoclinic in all cases. As one of reasons, it is suggested that  $\text{CaO}$  or  $\text{MgO}$  in zirconia rapidly diffuses and dissolves into silica or soda silicate glass. However, the existence of cubic zirconia in specimen (3) suggests that  $\text{Na}_2\text{O}$  has an inclination to suppress the lowering of  $\text{CaO}$  or  $\text{MgO}$  in zirconia.

On the basis of the above described results in sintering experiments, the effect of pyrex glass or philogopite on plasma sprayed zirconia was investigated. The effect of pyrex glass on porosity is shown in Table 6. It was found from the result that the addition of pyrex glass is not always effective to lower the porosity of plasma sprayed zirconia. This is contrary to the result that the addition of pyrex glass was able to lower the porosity of zirconia in flame spraying.<sup>7)</sup> Further, this shows no agreement with the result in sintering experiment described above, though the difference of component must be considered. The contradiction in latter case seems to attribute to small

content of  $\text{Na}_2\text{O}$  in pyrex glass. The difference between plasma and flame spraying also seems to be related to thermal effect but was not investigated in this study. Furthermore, it must be reconsidered whether the condition carried out in this study is optimum. Further investigation on the effect of additional materials, especially  $\text{Na}_2\text{O}$ , is also desired.

**Table 6** Effect of pyrex glass addition on apparent porosity of plasma sprayed zirconia

Pyrex content added (w/o)	0	1	5	20
Bulk specific gravity	4.72	4.59	4.31	3.65
Apparent specific gravity	5.60	5.60	5.2626	4.61
Apparent porosity (%)	15.75	18.01	18.13	20.73
Structure	Cubic $\text{ZrO}_2$	—	Cubic $\text{ZrO}_2$	Cubic $\text{ZrO}_2$

#### 4) Influence of preliminary oxide film

In porcelain enamel, oxide promoting adherence such as  $\text{CoO}$  or  $\text{TiO}_2$  plays important roles to good adherence, and pre-oxidation of base metal generally has a great influence to glass to metal seal.<sup>8)</sup> In this study, the effect of preliminary oxide thickness on adherence of plasma sprayed zirconia was investigated. Extensive previous results support that good adherence can not be obtained in  $\text{FeO}$ -steel interface, so that it is undesirable to form too thick iron oxide film in plasma sprayed coat. However, it is anticipated that proper thickness of preliminary oxide film produces good result because of improvement of wettability on a metal surface.

In this study, the effect of iron oxide which was formed in air was investigated. Appearances of plasma sprayed zirconia on steel with various oxide thickness are shown in Fig. 5. The result showed that the strength

Thickness of oxide film ( $\mu$ )	0.0	0.1	1.0	4.0 *
Appearance				
Weight of adherent particles ( $\text{g/cm}^2$ )	Tr.	Tr.	1.08 <sub>0</sub>	2.32 <sub>3</sub>

Fig. 5 Effect of preliminary oxide on the deposition of sprayed zirconia

\* Spraying condition was somewhat different because spray was stopped just before sprayed zirconia peel off

in iron-iron oxide interface can not withstand thermal construction when the thickness of iron oxide layer reaches to about  $4\text{ }\mu$  or over. Apparent quantity of zirconia deposited on steel plate decreased with decreasing the thickness of iron oxide. Conclusively, preliminary oxide film up to about  $1\text{ }\mu$  thickness seems to be effective on good adherence of plasma sprayed zirconia. Effects of other iron oxide such as  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  or of insert metal such as Ni or Ti must be considered in further investigations.

#### 4. Summary

Properties of commercial zirconia for plasma spraying were investigated. Behaviours of stabilizers added to zirconia before and after plasma spraying were presumed from the measurement of lattice constant of zirconia with X-ray diffraction method and it was suggested that vapourization behaviours of stabilizers, especially  $\text{MgO}$ , must be directly measured. Further, it was indicated that the difference of particle size distribution and the effect of trace elements must be investigated. In this study, nitrogen quantities before and after plasma spraying were investigated and increase of 150 ppm to 1200 ppm was found, whereas the effect of size distribution on thermal behaviour was not shown. From SEM observation and line

analysis with XMA, the region which is presumed as black zirconia or nonstoichiometric zirconia was found in plasma sprayed zirconia-steel interface but the identification of the region requires further investigations. Lowering of porosity in plasma sprayed zirconia was not realized by addition of pyrex glass or philogopite. However, it is necessary to reconsider plasma spraying conditions, particle size distribution and difference between specific gravities of powders. Finally, it was found that preliminary oxide with about  $1\text{ }\mu$  or less can improve the deposition of zirconia.

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