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Fundamental Considerations on Plasma Sprayed Ceramic Coating (Report III)†

— Effects of Zircon Addition on Zirconia —

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Abstract

Structural properties of plasma sprayed zircon sand and zirconia containing some zircon sand were investigated with X-ray diffraction and SEM observation. From the results of X-ray diffraction analysis, sprayed zircon sand was identified as tetragonal zirconia with some undecomposed zircon sand and a small quantity of monoclinic zirconia whereas sprayed zirconia containing 20 wt% zircon sand was cubic zirconia with very small quantity of zircon sand and unknown materials. SEM observation found out black region at interface but the identification did not succeed. Zircon sand addition to zirconia showed good effect on lowering the ratio of open pores to closed pores in sprayed coating and it was suggested that plasma sprayed zirconia containing some zircon can be applied a new ceramic coating material.

1. Introduction

When some improvements of the properties of a material are desired in order to satisfy recent severe requirements, plasma spraying has many advantages as described in previous report[1]. However, the wide application of ceramic plasma spraying is prevented on account of following faults[2),3)];

(1) insufficiency of adherence at the interface between substrate and coating,
(2) structural change of sprayed ceramics before and after spraying and in thermal recycle,
(3) existence of inherent penetrating pores.

To improve the insufficiency of adherence, many trials such as the undercoating of substrate with alloy and the multi-coating with metal-cermet-ceramic[4] have been performed. When plasma sprayed zirconia is considered from the standpoint of crystallography, large thermal expansion coefficient of stabilized zirconia produces many difficulties for wider utilization. Further, lowering of porosity, especially complete elimination of open pores, can never be ignored when main purpose is the corrosive-resistance.

In this study, effects of zircon sand addition to zirconia on lowering of porosity and some other crystallographical properties of sprayed coating were investigated because zircon was following advantages[5),6)];

(1) fairly cheep raw material,
(2) no structural transformation up to about 1540°C,
(3) lower thermal expansion coefficient than stabilized zirconia,
(4) high resistance for thermal shock,
(5) existence of SiO_2.

2. Experimental Procedures

Materials used for plasma spraying were commercial stabilized zirconia (METCO 201 and BAY STATE PP-42) and natural product zircon sand (made by Nippon Kagaku Togyo Co, Ltd.). The typical analysis data and particle size distributions are given in **Tables 1-(a)** and **1-(b)**. Zircon sand was divided by screening with one minute period method[7] after it was milled in a alumina mortar and pestle, and was mixed with commercial stabilized zirconia in the ratio

Table 1 (a) Typical analysis data on powders for spraying
(b) Particle size distributions of spraying powders

(a)

	Raw materials	
Impurities	METCO 201 (stabilized ZrO_2)	Zircon sand (A)(B)(C)
SiO_2	0.4	
CaO	5.0	
Al_2O_3	0.5	0.2 ∼ 0.8
P_2O_5		0.005 ∼ 0.02
Fe_2O_3		0.03 ∼ 0.08
TiO_2		0.12 ∼ 0.28
other oxide	1.1	HfO_2(?)

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(b)

MESH	METCO 201	BAY STATE PP-42	Zircon sand (A)	Zircon sand (B)	Zircon sand (C)
70 ~ 80	–	Tr.	–	–	Tr.
80~100	–	Tr.	–	–	0.6
100~120	–	Tr.	–	–	1.7
120~145	Tr.	0.1	–	–	16.3
145~200	0.1	16.2	–	–	45.2
200~250	0.5	29.0	–	} 100.0	10.3
250~270	5.6	29.3	–		8.1
270~300	2.4	5.6	–	–	6.9
300~325	6.8	7.5	5.6	–	4.5
325~400	14.2	6.7	19.1	–	1.9
under 400	70.3	5.5	75.3	–	4.4
Total (%)	99.9	99.9	100.0	100.0	99.9

and composition as shown in **Table 2.**

Plasma spraying equipment used was a plasma gun of METCO 3MB type and spraying conditions were as follows;

Spraying Voltage and Current; 70–80V×500A
Flow Gas; Primary Ar, Secondary; H_2.

All of metal substrates used for plasma spraying were steel rods (SGD-4) with 25 mm in diameter and about 20 mm in thickness and one side of each steel rod was blasted just before plasma spraying. Apparent porosities of plasma sprayed coatings were measured with Archmedean method as described in the previous paper[1]. The measurements of true density of plasma sprayed coatings were performed with pycnometer method and pulverized specimen with 200 mesh or under was used because closed pores seem to have a great influence on density measurement. As immersion liquid, distilled water was used. Closed pores, which are one of important quantities in plasma sprayed ceramic coating, were determined by following equations[8];

$$P_{ap}(\%)=\left(1-\frac{\text{bulk density}}{\text{apparent density}}\right)\times 100$$

$$P_t(\%)=\left(1-\frac{\text{bulk density}}{\text{true density}}\right)\times 100$$

$$P_c(\%)=P_t-P_{ap}$$

where P_{ap}, P_t and P_c are open pores, total pores and closed pores (% of bulk volume), respectively. Further, in order to identify the structure of plasma sprayed ceramics, X-ray diffrcation was carried out by following conditions;

Target: Cu K_α (Ni filtered),
Voltage and Current: 35KV×15 mA
Method: Fixed time (40 sec×2),
Ditector: S.C., Path: Air.

Furthermore, appearance of interface between steel substrate and sprayed ceramics was observed with a scanning electron microscope (Hitachi, HSM-2B). The experimental conditions were as follows;

Voltage and Current: 20KV×100–110 μA,
Sensitivity in XMA: 30 cps or 100 cps.

DTA from room temperature to 1200°C were performed on a few pulverized coatings prepared by plasma spraying with following conditions;

Heating rate: 5°C/min,
Sensitivity: ±50 μV,
Reference material: α-Al_2O_3,
Atmosphere: Ar.

3. Results and Discussion

1) X-ray diffraction analysis

It is well known that crystal structures of sprayed ceramics are often transformed into another structures before and after spraying. Taking an example, it was reported that α-Al_2O_3 sprayed with combustion flame changed into γ-Al_2O_3 with some α-Al_2O_3 and θ-Al_2O_3 whereas α-Al_2O_3 sprayed with plasma flame was transformed into θ-Al_2O_3 or δ-Al_2O_3 with some α-Al_2O_3 and γ-Al_2O_3[9]. Likewise, N.N. Ault reported that zircon changed into cubic zirconia with broad peaks from X-ray diffraction analysis when zircon rod was flame-sprayed, and that both glassy and crystalline phases were observed in sprayed zircon coating from microscope examination, therefore, concluded that the glassy phase increased closed pores in the coating[10].

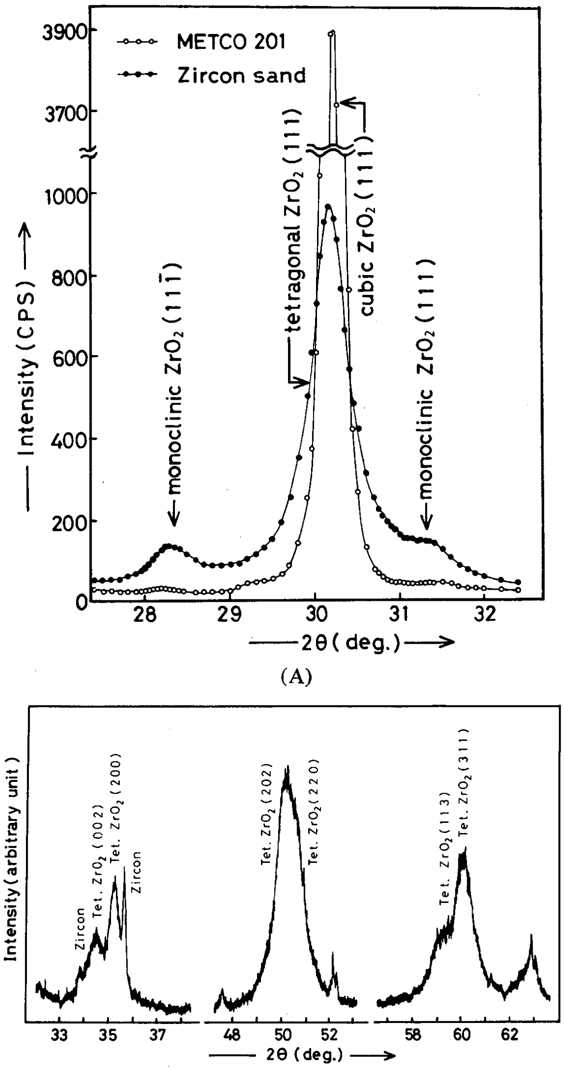
As is generally, the earnest requirements for the

Table 2 The mixing ratio of zircon sand to commercial zirconia and its composition

Zircon sand / Zirconia	Zircon sand (A)	Zircon sand (B)	Zircon sand (C)
METCO 201	5/95, 10/90, 20/80	–	50/50
BAY STATE PP-42	–	5/95, 10/90, 20/80	50/50

properties of sprayed ceramics are to lower their porosities and to improve their thermal properties due to transformation of metastable phases. From these points of view, first of all, X-ray diffraction measurements of plasma sprayed zircon sand and zirconia were performed. **Figs. 1-(A)** and **1-(B)** shows diffraction patterns produced by sprayed zircon sand (**C**), which is typical specimen in this study. Whether main phase after spraying cubic or tetragonal structure is difficult by following reasons;

(1) (1 1 1), (2 0 0), (2 2 0) and (3 1 1) peaks in cubic zirconia are detected in very similar position to (1 1 1), (0 0 2) (2 0 0), (0 2 2) (2 2 0) and (1 1 3) (3 1 1) peaks in tetragonal zirconia,
(2) every peak after spraying was generally broad,
(3) the existence of monoclinic zirconia and undecomposed zircon sand.



(A)

(B)

Fig. 1 Typical X-ray diffraction patterns
(A) for sprayed zircon sand and METCO 201 with fixed time method
(B) for sprayed zircon sand (only stronger peaks)

However, the identification of main phase as tetragonal zirconia was supported by following results;

(1) shift of the peak due to (1 1 1) planes to lower angular position,
(2) the existence of two peaks near 35° and 60° in 2θ,
(3) asymmetry of peak near 50° in 2θ,

In order to identify main phase as tetragonal zirconia, result (1) is very weak because the peak due to (1 1 1) planes of stabilized zirconia can shift to both higher and lower angular positions. That is, the peak due to (1 1 1) shifts to higher angular position when zirconia is stabilized by MgO whereas it can shift to lower angular position when zirconia is stabilized by CaO[11]. However, to identify main phase as tetragonal zirconia was strongly supported by results (2) and (3). Thus, three results described above suggested that main phase in plasma sprayed zircon sand was tetragonal zirconia but no existence of cubic zirconia was not proved. Perhaps, a little quantity of cubic zirconia must be contained. According to the above discussion, it is concluded that sprayed zircon sand is tetragonal zirconia containing some undecomposed zircon sand and a small quantity of monoclinic zirconia. Further, existences of glassy SiO_2 and cubic zirconia are not always rejected from the results studied in this paper.

C.E. Curtis and H.G. Sowman[12] reported that zircon was thermally decomposed into monoclinic zirconia and either an amorphous form of SiO_2 or a highly siliceous glass. As described above, however, amorphous SiO_2 was scarcely detected in plasma sprayed zircon sand coating. As the causes of SiO_2 disappearance, vapourization of SiO_2[13] or existence in the form of very small particle or any other form can be considered. Further, the disappearance of SiO_2 seems to be related to the formation of tetragonal zirconia. According to R.S. Roth[14], it was reported that solid-state reaction of zirconia with oxides of the larger tetravalent ions, such as CeO_2[15] and UO_2, might result in tetragonal zirconia solid solutions which existed at room temperature. However, it is well-known that compounds $TiZrO_4$[16] and $ZrSiO_4$ are formed by the addition of TiO_2 or SiO_2 to zirconia. Therefore, it seems to be difficult to consider that the formation of tetragonal zirconia is attributed to any effect of SiO_2.

Subsequently, supercooling of tetragonal zirconia can be considered because quenching velocity is very high in plasma spraying. As reported by G.M. Wolten[17] and L.L. Fehenbacher and J.A. Jacobuson[18], however, it is well established that monoclinic-tetragonal transformation in zirconia is diffusionless and is only dependent on the temperature. Thus, it is questionable that the formation of tetragonal zirconia is originated in supercooling only.

Impurity effects are also expected because Al_2O_3 and TiO_2 in raw material are contained at the content of 0.1 to 0.8 wt%. However, the effect of trivalent oxide such as Al_2O_3 can not expected because solid-state reactions of zirconia with the very smallest trivalent ions like Al^{3+} did not yield cubic zirconia solid solutions. Further, if the effect of TiO_2 is expected, the effect of SiO_2 must be regarded as more important because on account of its very larger content. Conclusively, the effect of SiO_2 is most expectable to the occurence of tetragonal zirconia. One of the expectable reasons is that glassy SiO_2 was scarcely detected and its whereabouts is unknown. Another reason is that SiO_2 belongs to the group in which CeO_2 and UO_2, which can lower the temperature of monoclinic-tetragonal transion, are included.

Furthermore, the gaseous component such as nitrogen and hydrogen can also be considered because fairly higher content of nitrogen was obtained after spraying as reported in the previous paper[1]. However, detailed discussion could not performed in this study on account of insufficient data.

2) Porosity measurement

In order to obtain the porosities of sprayed specimen, true, apparent and bulk densities were measured. These results are shown in **Fig. 2** and **Table 3.** The minimum ratio of open pores to closed pores was 1.53 in the coating produced from the mixture of METCO 201 with zircon sand, and this is lower value than that (=8.97) of specimen which was prepared by plasma spraying METCO 201. Thus, addition of zircon sand to zirconia was considerably effective to lower the ratio

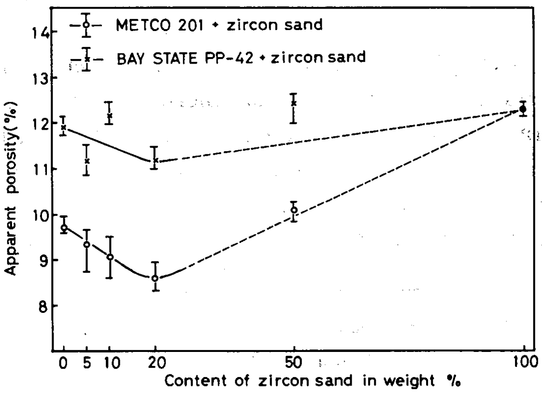


Fig. 2 The effect of zircon sand on lowering apparent porosity of sprayed coating

of open pores to closed pores in the coating. The sealing effect on open pores was not well interpreted but the most possible interpretation is that the sealing effect attributes to glassy SiO_2 produced by thermally decomposed zircon though its identification could not certified in this study. According to the result by N.N. Ault[10], it was reported the value 0.87 in the ratio of open pores to closed pores was obtained from zircon coating which was prepared by combustion flame spraying method using zircon rod. This value is fairly lower than that obtained in this study. However, it would be needless and impossible to discuss this difference because each specimen was prepared by quite difference method.

The addition of zircon sand to zirconia was performed on the expectation that apparent porosity of coating decreased with increasing zircon sand content. However, minimum apparent porosity of the coating was obtained at the content of 20 wt% zircon sand, as shown in Fig. 2. The increase in apparent porosity of zirconia coating contained over 20 wt% zircon sand seems to originate in the deviation from the optimum spraying condition. For example, the un-

Table 3 Ratio of open pores to closed pores in each coating

Density \ Specimen	METCO 201	BAY STATE PP-42	Zircon sand	METCO 201 + 20w/o Zircon sand
True density (before spraying)	–	–	4.6_2	–
True density (after spraying)	5.8_2	–	4.4_7	5.6_5
Bulk density (after spraying)	5.1_9	5.0_1	3.6_0	4.8_4
Apparent density (after spraying)	5.7_5	5.6_8	4.1_1	5.3_0
open pores / closed pores	8.9_7	–	1.7_6	1.5_3

expected result may attribute to the unsuitable particle size distribution (see Table 1-(b)). Therefore, the effect of 20 wt% or more zircon sand addition to zirconia on decreasing apparent porosity of coating must be reinvestigated.

3) SEM observation

SEM observation was performed in order to investigate states of surface of sprayed specimen and interface between sprayed ceramic and steel. As shown in **Fig. 3**, the surface of sprayed zircon sand showed spotted pattern. This seems to originate in the easiness of electric conduction of sprayed material. Further, it was suggested from X-ray energy spectrum that the easiness attributes to the difference of SiO_2 content. Besides, the difference in SiO_2 content may produce nonstoichiometry in sprayed zircon sand.

4) Differential thermal analysis

DTA on three kinds of coatings as described above were carried out from room temperature up to 1200°C for the purpose of investigating thermal properties of coatings. All runs were performed in Ar instead of N_2 because zirconium dioxide might form zirconium nitride. These results are shown in **Fig. 4.**

The commercial stabilized zirconia (METCO 201) coating gives exo-endothermic peaks at about 800°C. R.E. Jaeger and R.E. Nickell[19] reported that a fully stabilized zirconia containing 4.5 to 5.0 wt% MgO expanded at a uniform rate and a partial stabilized zirconia containing only 2.8 wt% MgO shrank at the temperature range of 800 to 950°C and of 1100 to 1250°C in thermal expansion measurement. Usually, monoclinic-tetragonal transformation in zirconia occurs at about 1170°C[20]. According to their conclu-

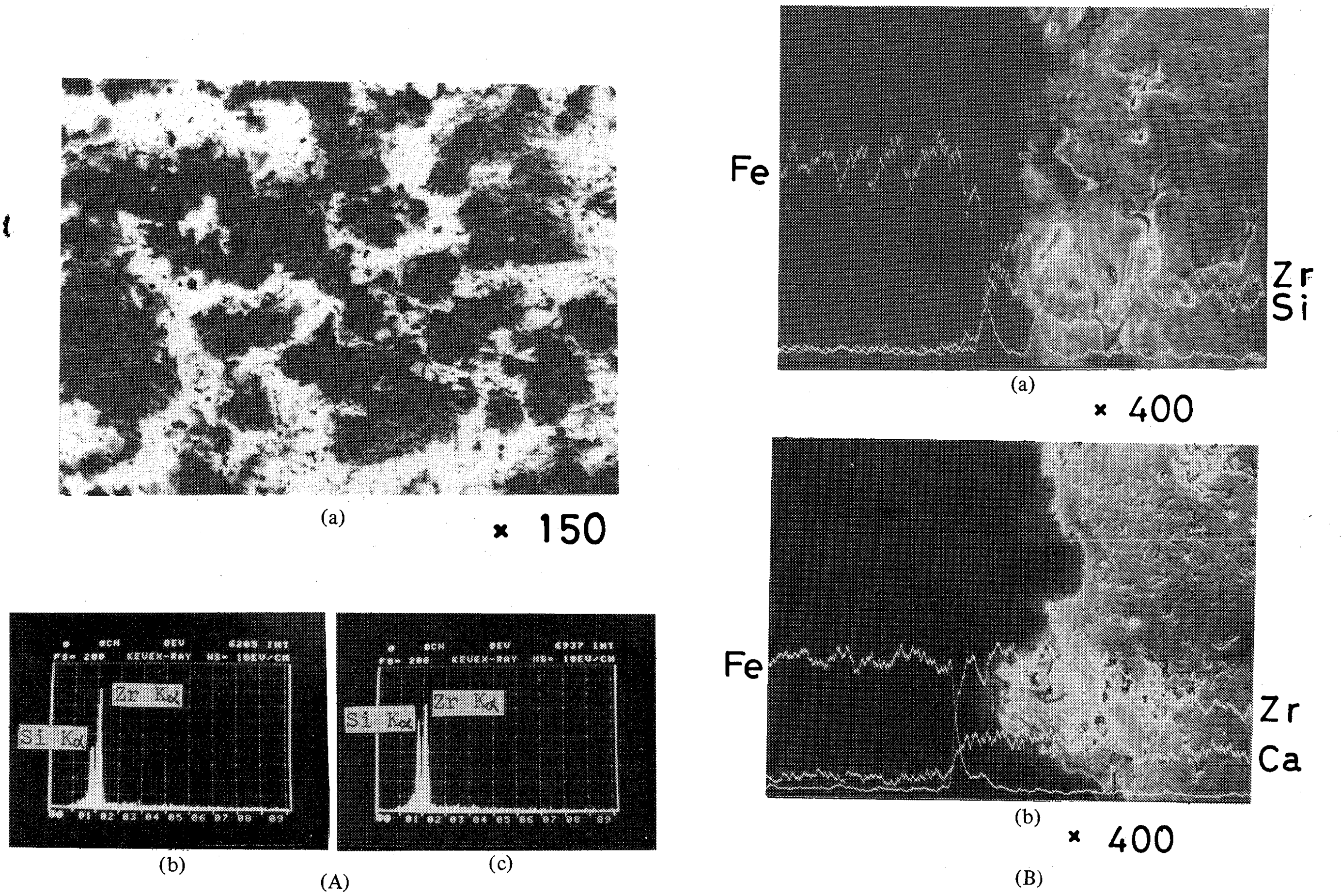


Fig. 3 Results of SEM observation and line analysis with XMA

(A) Surface of sprayed zircon sand
(a) surface of sprayed zircon sand
(b) X-ray energy spectrum at dark region
(c) X-ray energy spectrum at light region
(B) Interface between steel and sprayed ceramic
(a) steel-zircon sand
(b) steel-zirconia containing 20 wt% zircon sand

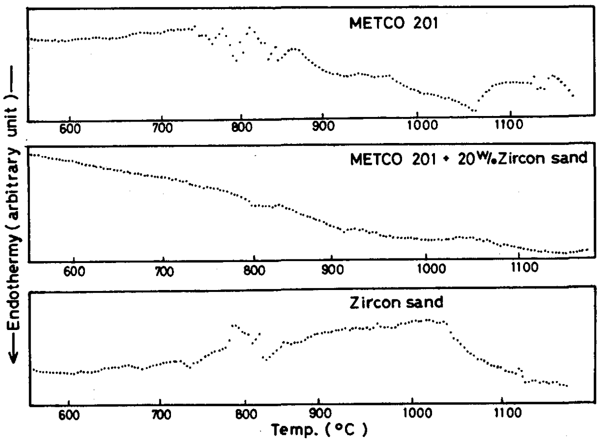


Fig. 4 DTA curves of METCO 201, METCO 201 containing 20 wt% zircon sand and zircon sand coating

sion, in this transformation, it might be expected that this portion of monoclinic phase which might well be left in a stressed condition within the cubic crystal would convert at low temperature, such as the case of a partial stabilized zirconia. The commercial zirconia used in this study is not full stabilized (see Fig. 1-(A)), and it is anticipated that sprayed coatings have high stress. Although it seems to be incorrect to compare their result of thermal expansion measurement with our result of DTA, the anomalous exo-endothermic peaks at about 800°C may be caused by the evidence as described above.

Likewise, zircon sand coating shows exo-endothermic peaks at about 800°C. Although these peaks may originate in reassociation of dissociated zircon or transformation of SiO_2 separated from zircon, they were not identified in this study.

However, METCO 201 containing 20 wt% zircon sand coating apparently gives no peaks. Therefore, it is supposed that this coating has good thermal properties.

4. Conclusion

Plasma sprayed zircon sand and zirconia containing some zircon sand were structurally investigated with X-ray diffraction and SEM observation. From the results of X-ray diffraction measurement, main phase of sprayed zircon sand was identified as tetragonal zirconia with some undecomposed zircon sand and monoclinic zirconia. Although the existence of cubic zirconia and glassy SiO_2 was expected, the certification of these materials were not obtained. Further, sprayed stabilized zirconia containing 20 wt% zircon sand was identified as cubic zirconia with very small quantity of zircon and unknown materials. It is presumed that the occurence of tetragonal zirconia originated in SiO_2 and high quenching velocity. However, further investigations are desired to obtain the certification of this interpretation. Subsequently, the effect of zircon sand addition to zirconia on lowering porosity was investigated and lowering the ratio of open pores to closed pores was realized. This suggests that plasma sprayed zirconia containing some zircon sand can be utilized as a new ceramic coating material. Black region presumed as nonstoichiometric zirconia was found at the interface from SEM observation, but the identification did not succeed. Therefore, structural analysis on the state of interface are also required in further investigations. From the results of DTA, zirconia containing 20 wt% zircon sand coating seems to have better thermal properties than commercial zirconia coating.

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