



# Zircon-Based Ceramics Composite Coating for Environmental Barrier Coating

M. Suzuki, S. Sodeoka, and T. Inoue

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Studies on plasma spraying of zircon ( $ZrSiO_4$ ) have been carried out by the authors as one of the candidates for an environmental barrier coating (EBC) application, and had reported that substrate temperature is one of the most important factors to obtain crack-free and highly adhesive coating. In this study, several amounts of yttria were added to zircon powder, and the effect of the yttria addition on the structure and properties of the coatings were evaluated to improve the stability of the zircon coating structure at elevated temperature. The coatings obtained were composed of yttria-stabilized zirconia (YSZ), glassy silica, whereas the one prepared from monolithic zircon powder was composed of the metastable high temperature tetragonal phase of zirconia and glassy silica. After the heat treatment over 1200 °C, silica and zirconia formed zircon in all coatings. However, coatings with higher amounts of yttria exhibited lower amounts of zircon. This resulted in the less open porosity of the coating at elevated temperature. These yttria-added coatings also showed good adhesion even after the heat treatment, while monolithic zircon coating peeled off.

**Keywords** environmental barrier coating (EBC), plasma spray, yttria, zircon, zirconia

## 1. Introduction

Zircon ( $ZrSiO_4$ ) is widely used as a refractory material, because of its excellent mechanical and chemical properties at high temperature. As far as plasma spraying of zircon is concerned, however, only some studies had been reported since 1970s (Ref 1-4). As shown in Fig. 1 (Ref 5), zircon has a dissociation line at 1676 °C, so that it is not possible for zircon to be formed from liquid phase, but via solid-solid reaction of zirconia and silica. Wong et al. reported that zircon was dissociated into zirconia and glassy silica in the plasma-processed powder (Ref 1). Kuroda et al. reported on the microstructure and wear property of the plasma-sprayed zircon coating (Ref 2). Addition of other oxides, such as yttria (Ref 3) and alumina (Ref 4), to zircon was examined to obtain new structure and feature in plasma-sprayed zircon coating. Yttria addition resulted in the composite of yttria-stabilized zirconia and silica, and addition of alumina formed mullite. However, none of these reports referred to the long time stability and durability at elevated temperature.

Environmental barrier coating (EBC) is one of a key factor to improve efficiency and durability of jet engines and gas turbines. Many materials were examined as candidates for EBC, which are expected to prevent

oxidation degradation of SiC-based composite components (Ref 6-9). The authors have selected zircon as a candidate material for an EBC, and have studied the coating structure of plasma-sprayed zircon coating. Zircon dissociates into amorphous silica and zirconia during the plasma spray process (Ref 10). Zircon is formed out of zirconia and silica in the coating via solid-solid reaction after the heat treatment at 1400 °C. This reaction is accompanied with a large volume shrinkage (around 25%) causing the formation of voids (up to 10% in volume) in the coatings.

The authors also revealed that the higher substrate temperature during the spray is one of the key factors to obtain dense and adhesive coating (Ref 11). Open porosity of the coating obtained with substrate temperature of 1200 °C was as low as 2%, thus the structure of the as-sprayed coating was improved significantly. However, the reaction to form zircon took place by the heat treatment in these dense coatings. Thus voids are also formed in the coatings, no matter what the substrate temperature was. This volume shrinkage must be overcome to apply plasma-sprayed zircon-based coating to high-temperature application such as EBCs. In this study, 3-20 mol.% of yttria ( $Y_2O_3$ ) was added to spraying powder of zircon, and the effect of yttria addition on the stability of the coating structure after the heat treatment was evaluated.

## 2. Experimental

### 2.1 Powder Preparation

Plasma spray parameters are shown in Table 1. Spraying powders were granulated by means of spray drying method in four different amount of yttria addition:

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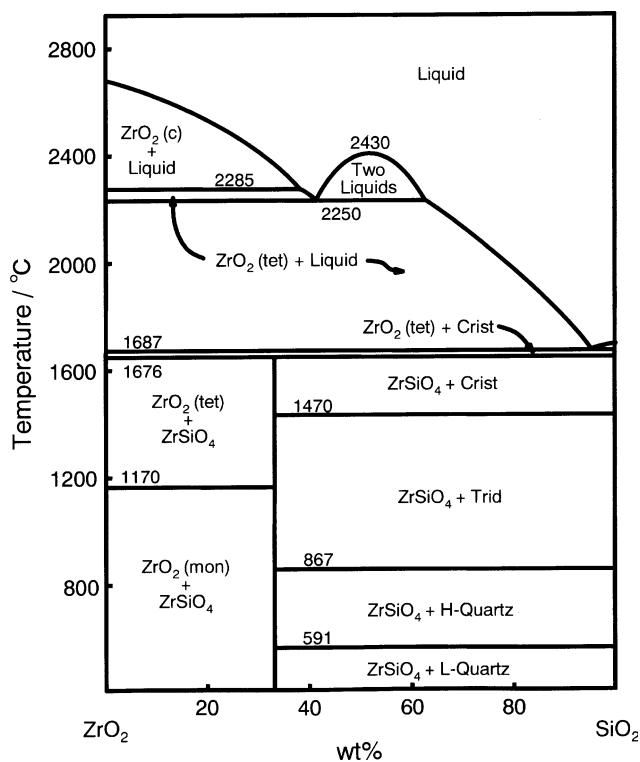


Fig. 1 Phase diagram of  $ZrO_2$ - $SiO_2$  system (Ref 5)

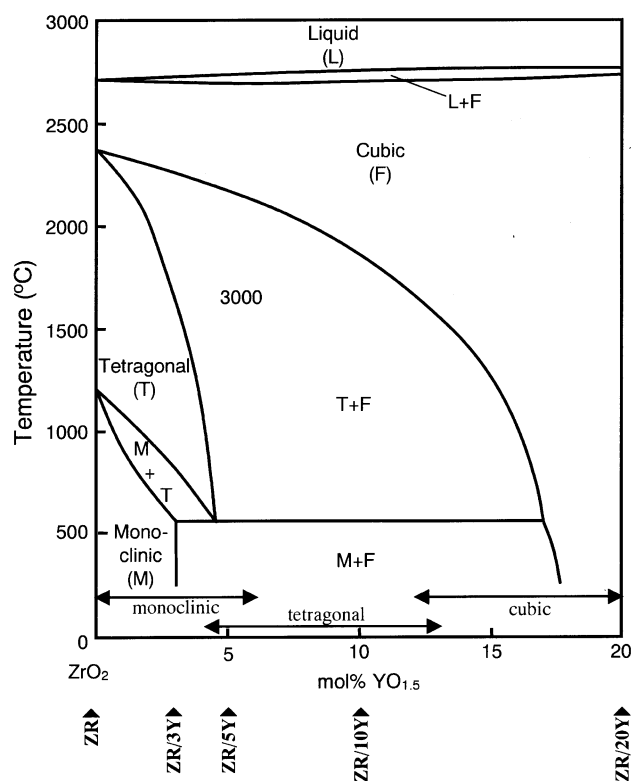


Fig. 2 Phase diagram of  $ZrO_2$ - $Y_2O_3$  system and the composition of the prepared powders (Ref 12)

Table 1 Plasma spray parameters

Starting powder	$ZrSiO_4$ ; Saint Gobain Ceramic Materials, PC-ZR/#VF $Y_2O_3$ ; Nihon Yttrium, Fine Powder (ave. 0.4 $\mu m$ )
Spraying powder	Granulated, +37-63 $\mu m$ 3, 5, 10, and 20 mol.%- $YO_{1.5}$ + $ZrSiO_4$ F4VB with APS Nozzle, Sulzer Metco
Plasma gun	Ar: 50 L/min. $H_2$ : 10 L/min.
Plasma gas	40 kW
Power input	125 mm
Spraying distance	Ar (500 mbar)
Ambient gas	1200 °C
Substrate temperature	Graphite plate (10 mm in thickness) SiC plate (sintered, 5 mm in thickness)
Substrate	In air, 1200 and 1400 °C for 20-72 h
Heat Treatment	

3, 5, 10, and 20 mol.% of  $YO_{1.5}$  into  $ZrSiO_4$ . These compositions are decided from the phase diagram of  $ZrO_2$ - $Y_2O_3$  system shown in Fig. 2 (Ref 12). Hereafter, the coating samples will be described as ZR for monolithic zircon, ZR/3Y, 5Y, 10Y, and 20Y for yttria-added zircon depending on its composition, respectively.

## 2.2 Sample Preparation

Coating samples were prepared by a low-pressure plasma spray (LPPS) technique with the plasma preheating, where the substrate temperature was kept above 1200 °C as reported in the previous study (Ref 11). Graphite plates and sintered silicon carbide (SiC) pellets were used as

substrates for the coating structure evaluations and the heat exposure test, respectively. The coating samples were annealed in air at 1200 and 1400 °C for 72 h. Open porosity was measured by means of the Archimedeian method. Crystalline phases were indexed by X-ray diffraction (XRD) measurement (MXP3A, Bruker AXS K.K., Japan). Cross sections of the coatings were observed by scanning electron microscope (SEM; JEOL-6300F, JEOL, Japan). Heat exposure test was carried out at 1400 °C (20 h) in conventional electric furnace for the coatings prepared on the SiC sintered pellets to evaluate adhesion after heat exposure.

## 3. Results and Discussion

### 3.1 Crystalline Phase Analysis

Figures 3-5 show the XRD profiles of the ZR, ZR/5Y and ZR/20Y coatings, respectively. All as-sprayed coatings were composed of  $ZrO_2$  and glassy  $SiO_2$ . However, three different zirconia phases were formed in each coatings; metastable high-temperature phase (tetragonal) in ZR, yttria-stabilized tetragonal phase (t-YSZ) in ZR/5Y and yttria-stabilized cubic phase (c-YSZ) in ZR/20Y, respectively. Thus it is revealed that the added yttria mainly dissolved in zirconia during plasma spray. After the heat treatment, formation of zircon took place in all coatings. Peak height of zircon in the yttria-added coatings

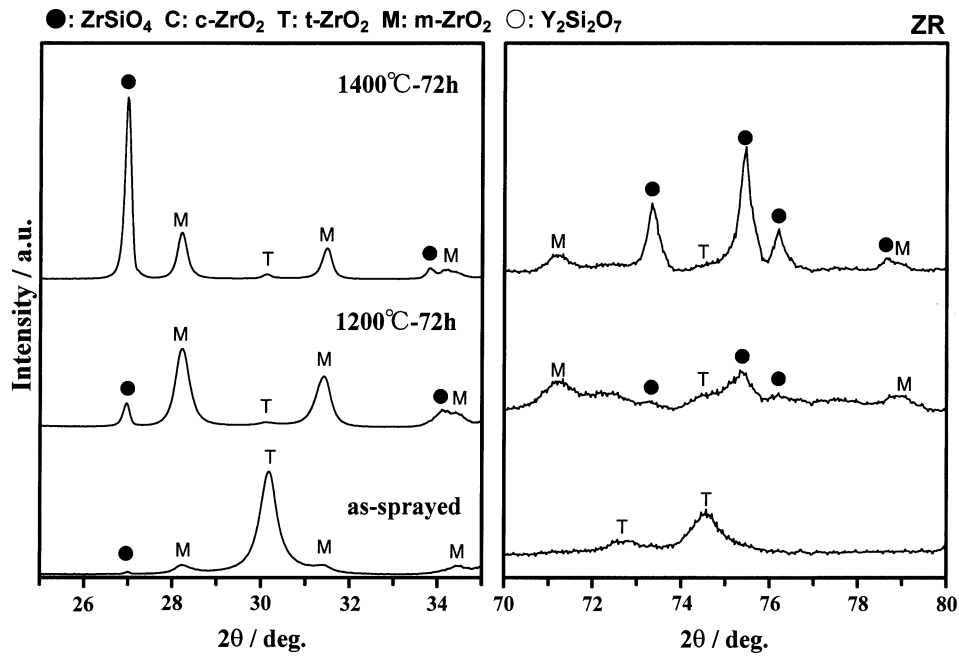


Fig. 3 XRD profiles of the ZR coatings

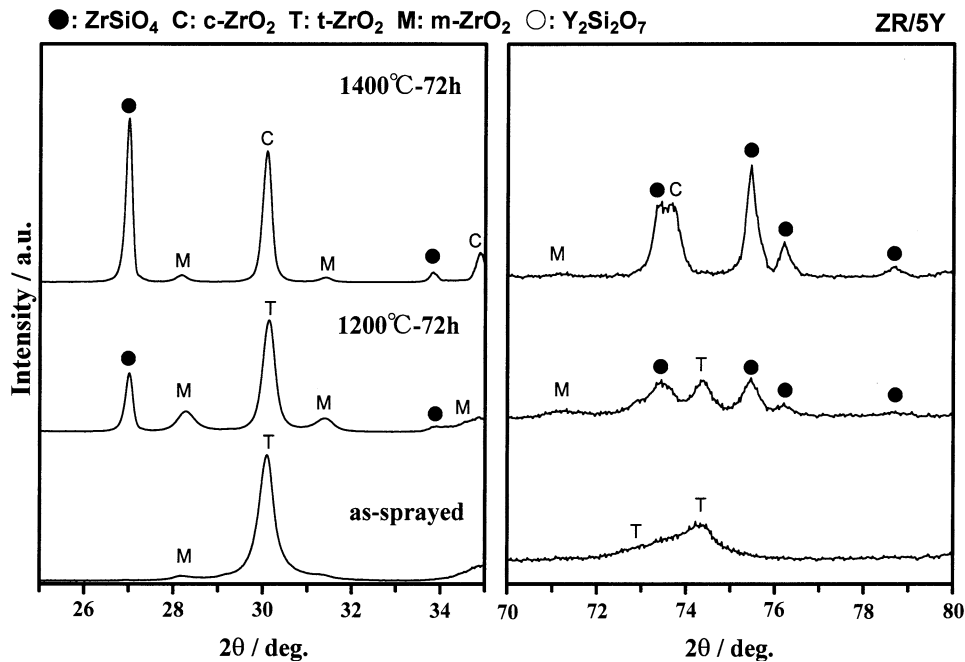


Fig. 4 XRD profiles of the ZR/5Y coatings

(ZR/5Y and 20Y) was lower than that in the ZR coating. At 1400 °C, the ZR/5Y and ZR/20Y coatings were composed of c- $ZrO_2$  and  $ZrSiO_4$  (and also  $Y_2Si_2O_7$  in ZR/20Y). Peak intensity ratio of these coatings is shown in Fig. 6. In the ZR coating, most of  $ZrO_2$  reacted with  $SiO_2$  to form  $ZrSiO_4$  by the heat treatment. This reaction took place in the ZR/5Y and 20Y coatings as well, however the

amount of  $ZrSiO_4$  phase decreased with the increase of  $Y_2O_3$  addition. As a result, the c-YSZ phase remained as a dominant phase in the  $Y_2O_3$ -added coatings. In the ZR/5Y coating, zirconia phase transformed from t-phase to c-phase by the heat treatment at 1400 °C, so that the peak intensity of  $ZrSiO_4$  increased. On the other hand, the zirconia phase and the peak intensity did not vary in the

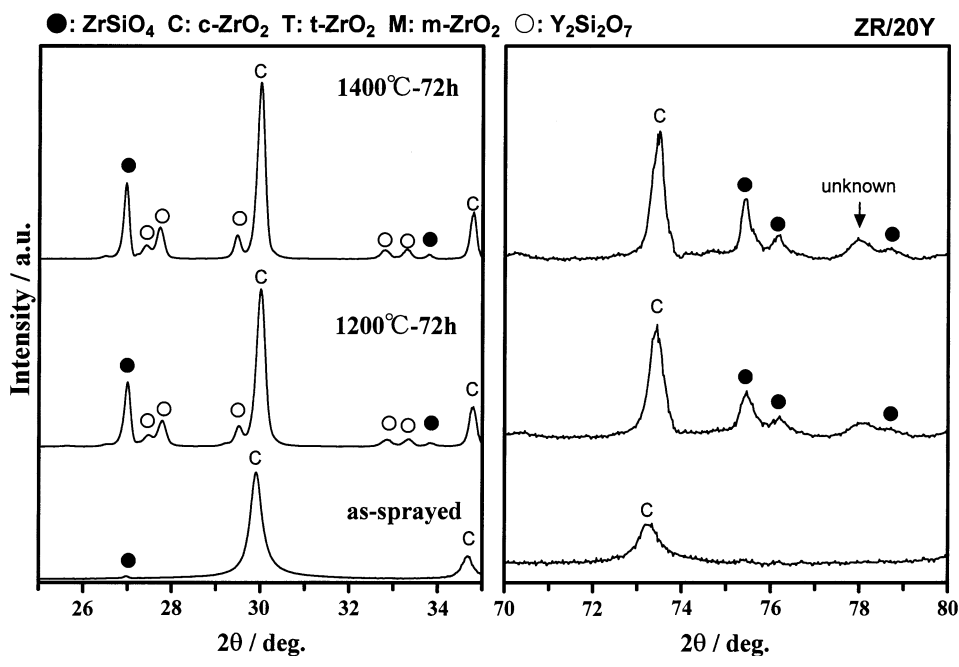


Fig. 5 XRD profiles of the ZR/20Y coatings

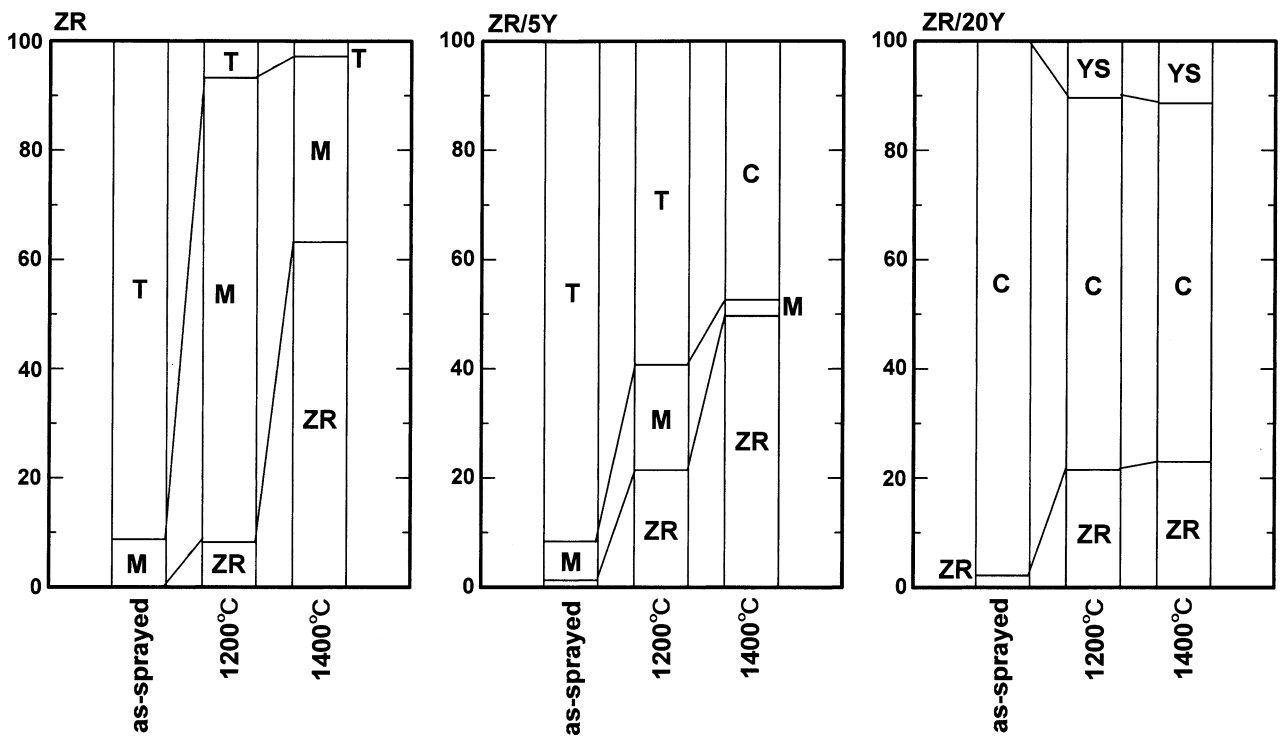


Fig. 6 Change of the crystalline phases in the coatings after the heat treatment. Vertical axis stands for the ratio of the XRD peak intensity of obtained crystalline phases

ZR/20Y coating. From these two facts, it can be said that the adding of  $Y_2O_3$  to form YSZ would reduce the amount of zircon after the heat treatment.

However, the phase diagram of the  $ZrO_2$ - $Y_2O_3$  system shows that t-YSZ dissociates into c- $ZrO_2$  ( $Y_2O_3$ -rich) and m- $ZrO_2$  ( $Y_2O_3$ -poor) (Ref 12), and then this m- $ZrO_2$

might react with  $\text{SiO}_2$  to form  $\text{ZrSiO}_4$ . Thus the formation of t-YSZ phase is not enough to avoid zircon formation, but the formation of the cubic phase of YSZ is significantly effective.

### 3.2 Coating Cross Section Observation

SEM images of the cross sections of the ZR, ZR/5Y, and ZR/20Y coatings before and after the heat treatment at 1400 °C are shown in Fig. 7 (secondary electron images). No major cracking was observed in the microstructures of these coatings. After the heat treatment, many small pores were formed in the ZR coating as shown in the picture with high magnification (left-bottom). This is caused by the volume shrinkage during zircon formation as mentioned above (Ref 4). On the other hand, size of the pores in the yttria-added ZR/5Y and ZR/20Y coatings were larger than the one of the ZR coating.

Open porosity of the coatings before and after the heat treatment is measured by the Archimedeian method and shown in Fig. 8. The more  $\text{Y}_2\text{O}_3$  addition resulted in less porosity after the heat treatment, in general. The ZR/20Y coating showed <4% in open porosity even after the heat treatment at 1400 °C.

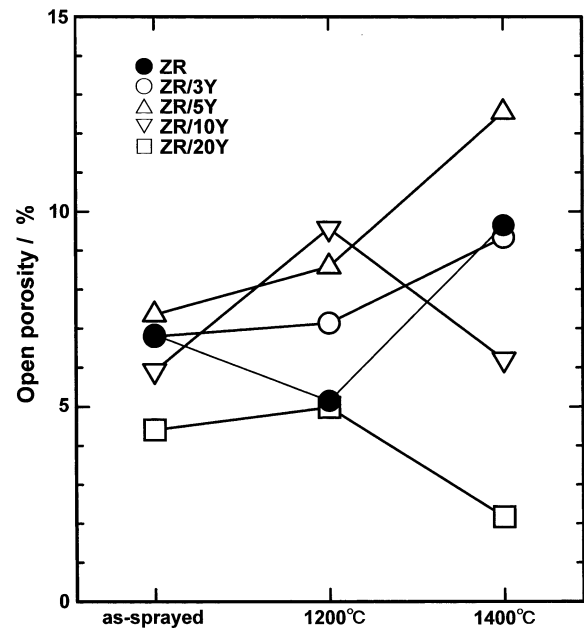


Fig. 8 Open porosity of the coatings before and after the heat treatment

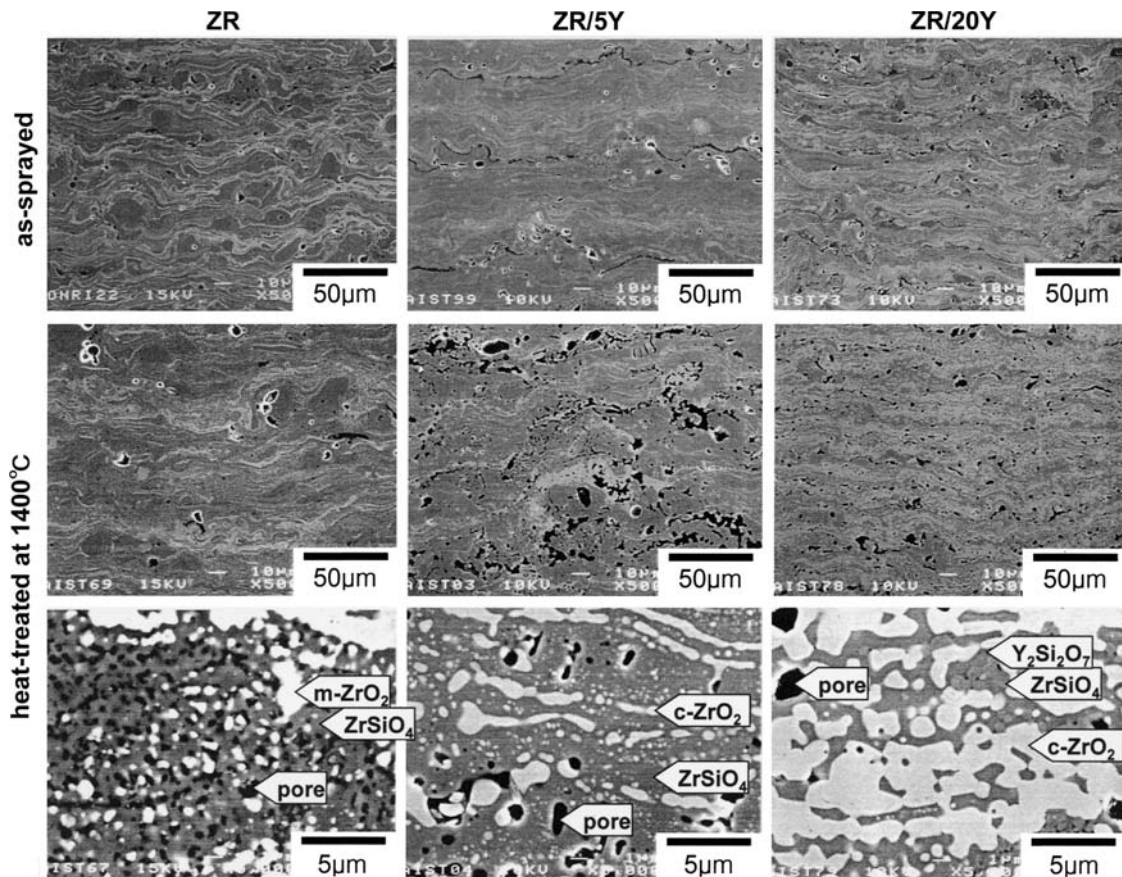
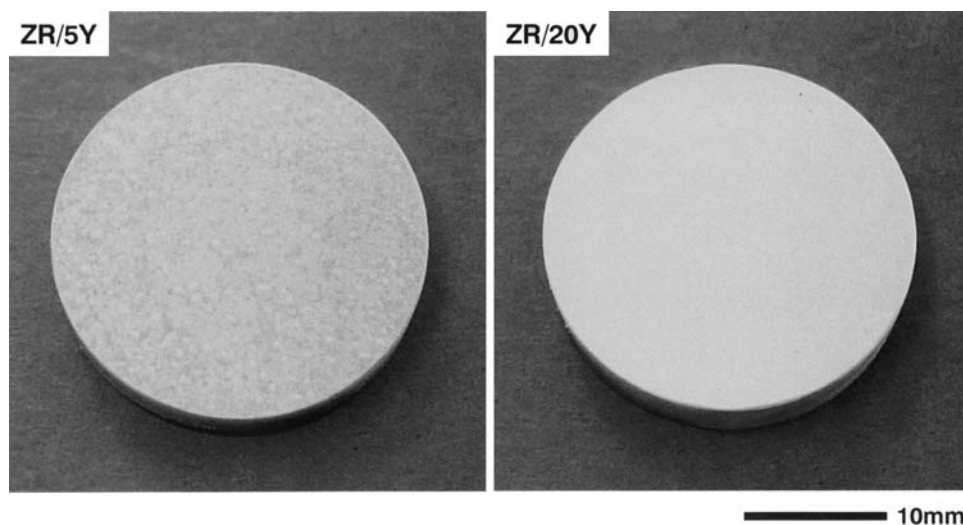


Fig. 7 Cross-sectional SEM images of the ZR, ZR/5Y, and ZR/20Y coatings before and after the heat treatment



**Fig. 9** The ZR/5Y and ZR/20Y coatings after the heat exposure test (1400 °C-20 h)

### 3.3 Heat Exposure Test

Heat exposure test was carried out for the coating samples prepared on the sintered SiC substrates. Figure 9 shows the pictures of the ZR/5Y and 20Y samples after the test. The ZR/5Y sample had a lot of small pieces of coatings peeling off, while the ZR/20Y had no degradation. Because of the decrease of zircon formation caused by an increase of  $Y_2O_3$  addition, the formation of void was avoided resulting in the improvement of the stability and adhesion of the coating at high temperature.

## 4. Summary

Effect of the yttria addition to zircon powder on the coating structure after the heat treatment was evaluated. Obtained results should be summarized as follows:

- (1) As-sprayed coatings are composed of glassy silica and zirconia; however, the tetragonal or cubic YSZ phase was obtained depending on the amount of yttria addition.
- (2) YSZ, zircon, and yttrium silicate are formed in the yttria-added coatings.
- (3) More amount of yttria addition decreases the zircon formation. This results in less porosity in the coating even after the heat treatment at 1400 °C, thereby improving the coating stability and adhesion.

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