Improvement of Plasma Sprayed CeO_2-ZrO_2 Coatings by Heat Treatment†

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Abstract

Plasma sprayed coatings in the system CeO_2-ZrO_2 have been developed for the modification of the mechanical properties of their coatings. The Vickers hardness and the fracture behavior of the 15mol%CeO_2-ZrO_2 (ZC15) coating have remarkable been improved due to the precipitation and the dispersion of a compound after heat treatment. We have succeeded in indicating that the mechanical properties of the coating is modified by simple procedure such as heat treatment.

KEY WORDS : (Plasma Spraying) (Coatings) (Zirconia) (Surface Modification) (Characterization) (Heat Treatment)

1. Introduction

Plasma sprayed ceramic deposits are widely used as thermal barrier coatings (TBCs) for gas turbine or other engine components[1)]. The TBCs provide both a thin insulating layer that reduces the underlying metal surface temperature and a barrier to the ingress of corrosive species from gas phase[2)].

CeO_2-, Y_2O_3- and MgO-stabilized zirconia have been proposed for use as the TBCs[3)]. Especially, it is reasonable to expect that CeO_2-ZrO_2 system may have not only properties of partially stabilized ZrO_2 such as high temperature toughness but also properties of CeO_2, such as small termal conductivity and large thermal expansion[4)]. Several studies have proved that CeO_2 is a better sintering dopant than Y_2O_3 is tetragonal zirconia from the viewpoint of thoughness[5)] and thermal stability[6)]. The phase diagram of the system CeO_2-ZrO_2 was reinvestigated in details[7)]. Unfortunately, this CeO_2-ZrO_2 system is lacking in accumulation of many data applied for TBCs.

It is well know that lowering of the high functional properties of the coatings aries from various defects in the coatings such as micro-structures, -porosities, -cracks, nonbonded area between plasma sprayed particles, etc. Therefore, it is necessary to improve of the properties of the coatings in order to make greater use of the coatings.

In this study, plasma sprayed CeO_2-ZrO_2 TBCs have been developed, and the microstructures and the mechanical properties, such as hardness and fracture behavior, of the coatings have been improved by heat treatment and laser surface treatment. Some results of the surface modification by heat treatment will be mainly described in this paper.

2. Experimantal

Analytical grade reagent powder CeO_2 and ZrO_2 were used for plasma spraying, and SUS304 stainless steel plates were used as substrate metals. The four coatings in the system CeO_2-ZrO_2 were developed as indicated in **Table 1**. One side of the surface of each steel plate was blasted with Al_2O_3 sand before plasma spraying. The CeO_2-ZrO_2 coatings were fabricated using the plasma spraying conditions given in Table 1.

20kgf Vickers hardness indentation were made in the

Table 1 Plasma spraying conditions

Plasma spraying eguipment	METCO 9M type
Voltage and current	65V and 500A
Arc gases	
primary (flow)	Ar (80l/min)
Secondary (flow)	H_2 (151l/min)
Powder materials	
ZC5	5mol % CeO_2 − ZrO_2
ZC10	10mol % CeO_2 − ZrO_2
ZC15	15mol % CeO_2 − ZrO_2
ZC20	20mol % CeO_2 − ZrO_2
Substrate	SUS 304 stainless steel
Spray distance	80mm
Thickness of coatings	200 μm

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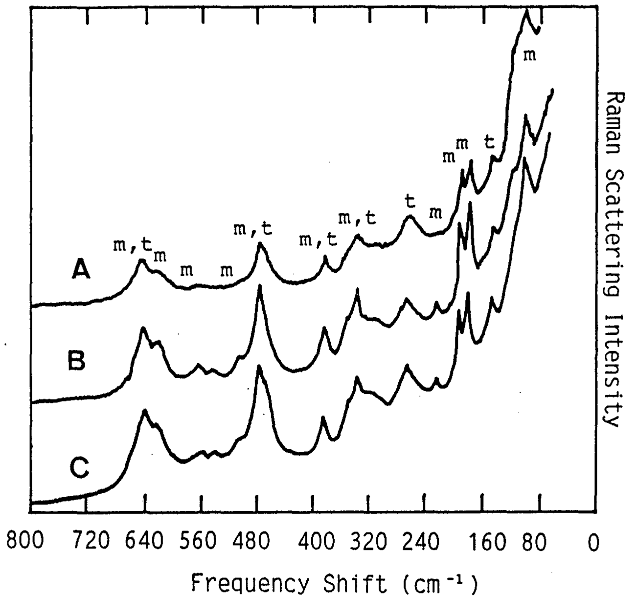

Fig. 1 Raman spectra of plasma sprayed (A) 5mol%CeO_2-ZrO_2 (ZC5), (B) 10mol%CeO_2-ZrO_2 and (C) 15mol%CeO_2-ZrO_2 (ZC15) catings.
m: monolinic phase; t: tetragonal phase

surfaces to produce five well-defined indentations per square millimeter. The crack formed by Vickers indentation was a square with a side about 240 μm long. The heat treatment of the coatings were carried out in vacuum (1×10^{-5} torr) at the temperature range from 800°C to 1200°C for 1 hour.

Laser Raman spectroscopy is a powerful technique for phase analysis in the plasma sprayed zirconia coatings[8]. Therefore, the microstructures of the as-sprayed, heat- and surface-treated coating were examined by laser Raman spectroscoy and Raman microprobe. Raman spectra were measured on a JASCO R-800 doublegrating spectrometer at a scattering angle of 90°. The excitation source was the 488nm line of a NEC GLG-3300 Ar^+ ion laser at a power from 300 to 500mW. The beam diameters were about 1 mm and 1 μmϕ for normal Raman spectroscopy and Raman microprobe, respectively. X-ray diffraction (X.R.D.) was also performed on the phases analysis.

Scratch testing for adhesion of the coating-substrate was carried out with a scratch testing unit designed by the Laboratoire Suisse de Recherches Horlogerès. The unit has a diamond stylus in the form of a Rockwell C120 cone with an indenter tip of radius 0.2mm. The scratch equipment was fitted with an acoustic signal detector in the form of an accelerometer mounted just above the diamond stylus.

3. Results and Discussion

Figure 1 shows the Raman spectra of the as-sprayed

Table 2 Phase fraction of the plasma sprayed CeO_2-ZrO_2 coatings indentified by laser Raman spectroscopy

Coating sample	$R(\frac{C_t}{C_t + C_m})$
5mol % $CeO_2 - ZrO_2$ (ZC5)	
As-spraying	0.65
After indentation	0.36
Heat treatment	0.25
10mol % $CeO_2 - ZrO_2$ (ZC10)	
As-spraying	0.51
After indentation	0.22
Heat treatment	0.47
15mol % $CeO_2 - ZrO_2$ (ZC15)	
As-spraying	0.67
After indentation	0.49
Heat treatment	0.30

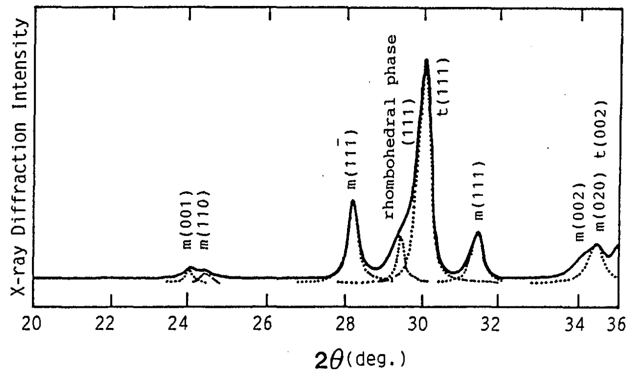

Fig. 2 X.R.D. pattern of a plasma sprayed 15mol%CeO_2-ZrO_2 (ZC15) coating.
m: monoclinic phase; t: tetragonal phase

CeO_2-ZrO_2 coatings. The Raman bands obtained from the monoclinic, tetragonal phases are in good agreement with our previous Raman results[8]. As can be seen in this figure, there is some overlap of the monoclinic and tetragonal Raman bands for the frequency shifts of beyond 300cm^{-1}, but over the range from 100cm^{-1} to 300cm^{-1} these bands are well separated (monoclinic bands, 181 and 192cm^{-1}; tetragonal bands, 148 and 264cm^{-1}). Since the intensity of a Raman band is directly proportional to the concentration of scattering species, we can therefore apply it to the determination of the fractions of the monoclinic and tetragonal phases in terms of the Raman intensities using the following equation[9]:

$$R[\frac{C_t}{C_t + C_m}] = \frac{I_t(148) + I_t(264)}{I_t(148) + I_t(264) + I_m(181) + I_m(192)}$$

,where C_m and C_t are the concentration of monoclinic and tetragonal phases, respectively. The Raman results are given in **Table 2**. This indicates that these coatings consist of the monoclinic and tetragonal phases produced by nonequilibrium processing of the plasma spraying, as opposed to the prediction from the phase diagram[7]. The tetragonal phase existing in the coatings is a metastable state due to the slow cation diffusions by the freezing of high-temperature equilibrium[10]. We also observe a (111) X.R.D. peak of rhombohedral phase[11] formed from the small amount of cubic zirconia, as shown in **Fig. 2**.

It is widely recognized that an irreversible transformation from the tetragonal to monoclinic phase[12] is caused by mechanical impacts such as fracture, indentation, heating and thermal cycles etc. and markedly affects the various properties of the coatings. **Figure 3** indicates that the tetragonal phase was transformed into monoclinic phase in the indentation. Furthermore, this figure shows that the stress-induced transformation of zirconia was more pronounced near the edge than in the central area. The micro-Raman result are due to the stress concentration at the edge area. It is considered that the stress-induced transformation is closely telated to the tensile stress to the concentrated stress rather than the compressive stress.

Figure 4 shows the Vickers hardness for the adhesion of the four as-sprayed and heat-treated coatings. **Figure 5** shows the distribution of AE signal of the as-sprayed and heat-treated ZC15 coatings with the scratch testing. As can be seen in these figures, it is recognized that the Vickers hardness and the fracture load of the ZC15 coating predominantly increase after heat treatment. It is considered that the great improvement of the mechanical properties of the ZC15 coating after heat treatment is due to the precipitation and dispersion of a $Ce_2Zr_2O_7$/$Ce_{0.75}Zr_{0.25}O_2$ compound in the coating, as indicated in **Fig. 6**. It should be pointed out here that the mechanical properties of the coating is modified by simple procedure such as heat treatment.

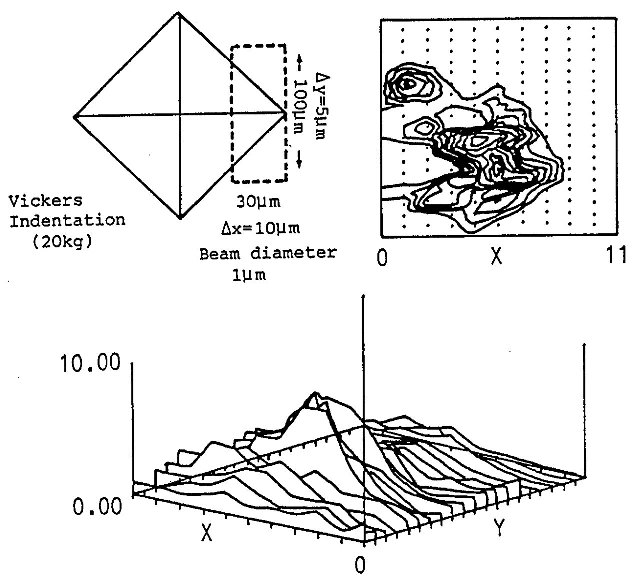

Fig. 3 Monoclinic/tetragonal ratio map and micro-Raman spectra of a Vickers indentation in a 15mol%CeO_2-ZrO_2 (ZC15) coating.

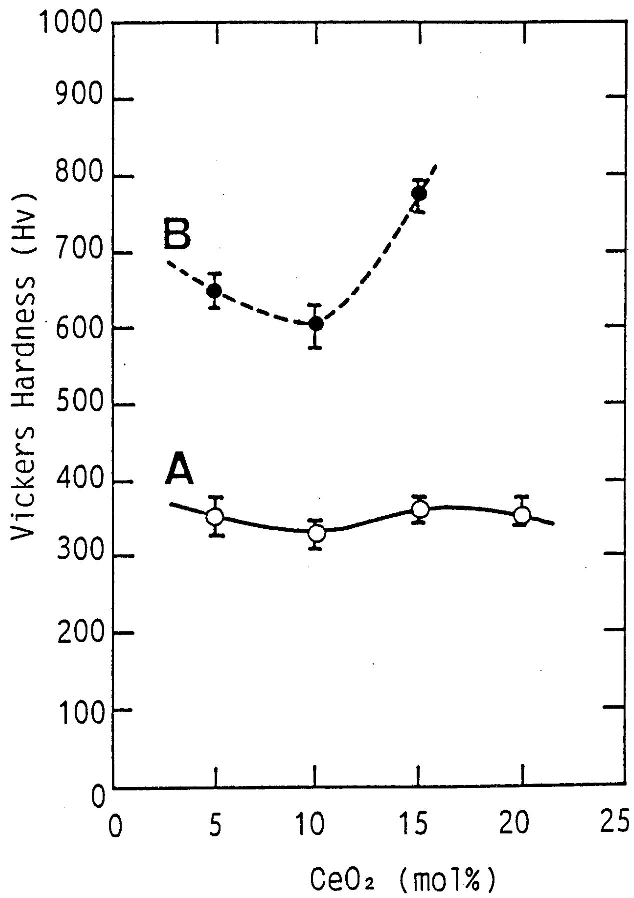

Fig. 4 Vickers hardness of the plasma sprayed coatings in the system CeO_2-ZrO_2.
A: as-sprayed; B: heat-treated

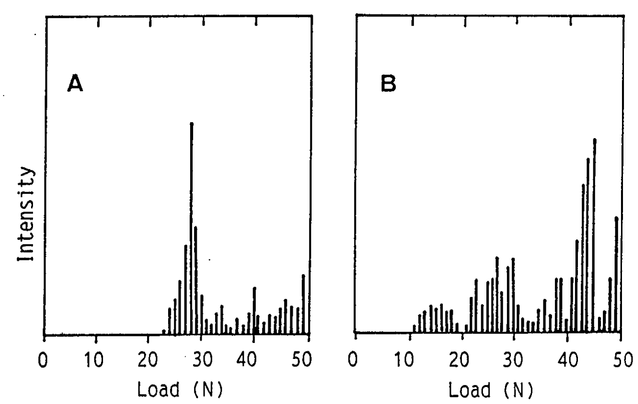

Fig. 5 Distribution of analysis of AE signal of a plasma sprayed 15mol%CeO_2-ZrO_2 (ZC15) coating with scratch testing.
A: as-sprayed; B: heat-treated

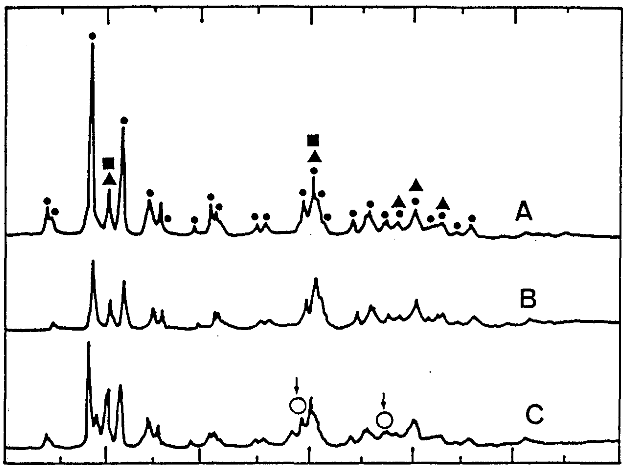

Fig. 6 X.R.D. patterns of heat treated (A) 5mol%CeO_2-ZrO_2 (ZC5), (B) 10mol%CeO_2-ZrO_2 (ZC10) and (C) 15mol%CeO_2-ZrO_2 (ZC15) coating.
● monoclinic ZrO_2;
▲ tetragonal ZrO_2;
■ cubic ZrO_2;
○ $Ce_2Zr_2O_7$/$Ce_{0.75}Zr_{0.25}O_2$

4. Conclusion

In this paper, plasma sprayed coatings in the system CeO_2-ZrO_2 have been developed for the modification of the mechanical properties of their coatings. The Vickers hardness and the fracture behavior of the 15mol%CeO_2-ZrO_2 (ZC15) coating have remarkably been improved due to the precipitation and the dispersion of a $Ce_2Zr_2O_7$/$Ce_{0.75}Zr_{0.25}O_2$ compound after heat treatment. We have succeeded in indicating that the mechanical properties of the coating is modified by simple procedure such as heat treatment.

References

1) L. Kvernes, E. Lugscheider and J. Fairbanks: Advanced Materials Research and Developments for Transports - Ceramic Coatings for Heat Engines, ed. by Kvernes, L., Bank, W.J.G., MRS 1985.
2) Wu Bo-Chen, and E. Chang: J. Am. Ceram. Soc., **72** (1989) 212.
3) R. A. Miller: NASA TM-79205, June 1979.
4) T. Suzuki, H. Takeda and M. Itoh: J. Ceram. Soc. Japan, **94** (1989) 66 (in Japanese).
5) J. G. Duh, W. Y. Hsu and B. S. Chiou: Materials Science Monographs **38B**, ed. by Vincenzini, Elsevier, 1987, pp.1281.
6) T. Sato, S. Ohtaki, T. Endo and M. Shimada: J. Mat. Sci. lett., **5** (1986) 1140.
7) E. Tani, M. Yoshimura and S. Somiya: J. Am. Ceram. Soc., **66** (1983) 506.
8) N. Iwamoto, N. Umesaki and S. Endo: Thin Solid Films, **127** (1985) 129.
9) D. R. Clarke and F. Adar: J. Am. Ceram. Soc., **65** (1982) 284.
10) M. Yoshimura and S. Somiya: "The phase Equilibria in the Zirconia Systems: The Present State and Problem", Zirconia Ceramis, Vol.3, ed. by Somiya, S., and Yoshimura, M., Uchida Rokakudo Publishing Co., 1984, pp.149/74 (in Japanese).
11) H. Hasegawa: J. Mat. Sci. Lett., **2** (1983) 91.
12) E. Subbarao: Proc. Int'l. Conf. on the Science and Technology of Zirconia, ed. by Heuer A. H. and Hobbs, in Advanced in Ceramics, Vol.3, Am. Ceram. Soc., 1981, pp.1.