

Nano-structured SiC reinforced plasma sprayed zirconia based thermal barrier coating

Joo Won Lee, Chang Hee Lee* and Hyung Jun Kim^a

Ceramic Processing Research Center (CPRC), Division of Materials Sci. & Eng., Hanyang University, 17 Haengdang-dong seongdong-ku, Seoul, South Korea

^aResearch Institute of Industrial Science and Technology (RIST), Center for Advanced Plasma Surface Technology (CAPST)

Plasma sprayed zirconia-base coatings are of general interest as thermal barrier coatings in diesel and gas turbine engines. However, residual pores and cracks in these coatings decrease the mechanical properties. Therefore the improvements to $ZrO_2-25CeO_2-2.5Y_2O_3$ (CYSZ) coatings by SiC impregnation were studied. The effect of the nano-SiC sealing on the wear properties was also studied. The coatings were produced by an atmospheric plasma spraying process. The YYSZ coatings were sealed by repeated polycarbosilane (PCS) solution infiltration and pyrolysis. Through thermogravimetry analysis, the PCS precursor solution started to decompose at 100°C and finished at 800°C. After 800°C pyrolysis process, the SiC phase was amorphous. DSC analysis revealed that the crystallization of the amorphous silicon carbide started at about 1030°C and finished at 1100°C. The mean grain size determined using the Sherrer and Wilson formula from the breath of the SiC(220) line was not larger than 5 nm. Under dry condition sliding wear against sintered $ZrO_2-8Y_2O_3$ (YSZ), weight losses were markedly decreased by SiC sealing. The sealing resulted in the wear transition, which corresponded to the change in the mechanism from a brittle fracture mode causing sever wear to a plastic deformation mode causing mild wear. The friction coefficient was also decreased by both the surface smoothing effect of the SiC sealing and the possible excess carbon of the non-stoichiometric SiC due to SiC sealing. During sliding wear of unsealed and sealed coatings, a stress induced tetragonal to monoclinic martensitic phase transformation, which deteriorates wear resistance, was not observed.

Key words : Air plasma spray, YYSZ, PCS sealing, Nano SiC, Porosity, Wear resistance.

Introduction

Partially stabilized zirconia (PSZ) thermal spray coatings are of general interest as thermal barrier coatings in both diesel and turbine engines [1]. In general, a duplex structural thermal barrier coating system consists of a thick layer of PAS plasma sprayed coating over the substrate to be protected with an intermittent layer of MCrAlX (M=Ni and/or Co, X=Y, Hf, Ce and Yb) as a bond coat. Thermal Barrier Coating (TBC) can allow an increase in the operating temperature without increasing the temperature of the underlying metal substrate or an decrease of the cooling gas consumption and thus it can promote the thermal efficiency of the engine and improve the engine durability and lifetime [1, 2].

However, plasma sprayed ceramic coatings inevitably contain pores and usually also cracks. Open or closed pores in plasma sprayed coatings can originate from several different sources [2]. These are inadequate flow during the spreading of impacted molten or partially melted droplets or fragmentation of

the molten particles at impact, shadowing effects due to lower than optimum angle deposition, and entrapped gas. High cooling rates of the individual splats and poor inter-lamellar bonding result in vertical and horizontal cracks or voids. These pores and cracks make both a positive and a negative contribution to the TBC system. The positive ones are to a decrease in the thermal conductivity and an increase in the thermal shock resistance of the TBC. But the presence of pores and cracks allows corrosive compounds to enter the coating and deteriorate the corrosion resistance of the metal bond coat and substrate. These defects also cause a decrease in mechanical properties inducing debonding or spallation due to thermal and mechanical stress.

Post-treatments of the plasma sprayed coating such as laser remelting, HIP, CVD, and impregnation are used to enhance the chemical and mechanical properties by closing the open pores and cracks [3]. Among these methods, impregnations are widely used. Commercially-developed sealants are usually based on polymers, inorganic solutions, or even molten metals. Because the working conditions of the TBC system are very severe; high temperature, corrosive and high stress conditions, sealants for TBC should have sufficient thermal, chemical, and mechanical stability. However, commercially-developed sealants are not

*Corresponding author:
Tel : +82-2-2290-0388
Fax: +82-2-2290-0389
E-mail: chlee@hanyang.ac.kr

ideal for TBC's. Another sealing method is using pre-ceramic precursor solutions, such as polycarbosilane (PCS). PCS converts into fine crystalline silicon carbide after a pyrolysis process. Pre-ceramic polymer solutions with low viscosity, which can be obtained from organic solvents, can be easily infiltrated into the pores and cracks [4]. Usually silicon carbide has been used because of its excellent properties, especially strength and oxidation resistance at high temperature.

In this study, surface modification of as-sprayed PSZ-TBC through a PCS impregnation method was carried out. The optimization of the impregnation process was based on the formation of nano-structured SiC to enhance the mechanical properties and the control of impregnation depth to minimize the gradient of the thermo-physical properties. Also the resultant wear properties were observed.

Experiments

As a substrate, Ni-based alloy (Inconel 600) in the form of a disk (20 mm diameter by 3 mm thickness) was used. Commercial powders of NiCrAlY, and $ZrO_2-25CeO_2-2.5Y_2O_3$ (CYSZ) were used for bond coating and ceramic TBC material. Both NiCrAlY and CYSZ powders were manufactured by a homogeneous oven spherical powder method (HOSP). The chemical compositions and characteristics of the substrate and starting powders are listed in Tables 1 and 2.

Before plasma spray coating the substrate was ultrasonically cleaned, and grit blasted to enhance bonding strength. A NiCrAlY bond coat with a thickness of

Table 1. Chemical compositions of substrate (%)

Class	Ni	Cr	Fe	Mn	C
Inconel 600	72	14~17	6~10	1	0.15

Table 2. Characteristics of powders

Powder	$ZrO_2-CeO_2-Y_2O_3$	NiCrAlY
Mnufacturing Method	Homogeneous Oven Spherical Powder Method (HOSP)	Gas Atomized
Chemical Composition (wt%)	$ZrO_2-25CeO_2-2.5Y_2O_3$	Ni-22Cr-10Al-1Y
Particle Shape	Spheroidal	Spheroidal
Particle Size (μm)	-90+16 μm	-106+56 μm

Table 3. Parameters for plasma spraying

Coating Materials	Ampere (A)	Voltage (V)	Gas Flow Rate (SCFH)			Feed Rate (g/min)	Spray Distance (mm)
			Primary N2 Gas	Secondary H2 Gas	Carrier N2 Gas		
Ni-22Cr-10Al-1Y	500	74	100	20	12	60	125
$ZrO_2-25CeO_2-2.5Y_2O_3$	500	76	75	20	12	45	10450

about 200 μm , and CYSZ 500 μm were coated by an air plasma spray (APS) system. The optimum spray parameters used for coatings are summarized in Table 3.

Polycarbosilane (PCS) was used as the precursor of SiC. Toluene/PCS 1 : 1 solution was used to impregnate pores and cracks of the TBC. PCS could be directly pyrolysed to form SiC, yielding 60~85% without curing. The pyrolysis process in N_2 was analyzed by using thermogravimetry analysis (TGA) with heating rates 10 and 20°C/min. To measure the crystallization temperature of the SiC formed by pyrolysis of the PCS, DCS was used with heating rate of 10°C/min in N_2 . 50 mass% PCS toluene solution was painted on the surface of the as-sprayed TBC to infiltrate into the pores and cracks by both its own wettability and a capillary effect and then pyrolysed at 800°C with the heating rate of 10°C/min. The impregnation-pyrolysis process was repeated for 6 times to obtain dense SiC. In the 6th process it was pyrolysed at 1100°C in order to crystallize the amorphous SiC.

Reciprocating pin-on-plate wear and friction experiments were performed. The oscillating upper pin, made of sintered $ZrO_2-8Y_2O_3$, was loaded against the stationary plasma sprayed CYSZ coating plate. All the tests were carried out in dry air and at room temperature and 400°C without lubrication. The track length was 9 mm long and the average sliding velocity was 54 $mm s^{-1}$.

The thermal fatigue resistance was evaluated by a thermal cycling test. A thermal cycle consisted of 5 min heating from room temperature up to 1100°C, 10 min holding at 1100°C, and finally cooling to room temperature in a static air condition.

All specimens were sectioned with a diamond saw and epoxy mounted and fine polished to minimize the smearing and pull-out of particles. Optical microscope, scanning electron microscope (SEM) and electron probe microanalysis (EPMA) were used to characterize the microstructure and worn surface. Porosity (area%) was measured using an image analyzer. XRD was used for phase identification. And Vickers micro indentation was used to measure the micro-hardness change after impregnation. A 300 g-load was applied for a 10s loading-unloading cycle and at least 15 points were measured for each specimen.

Results and Discussion

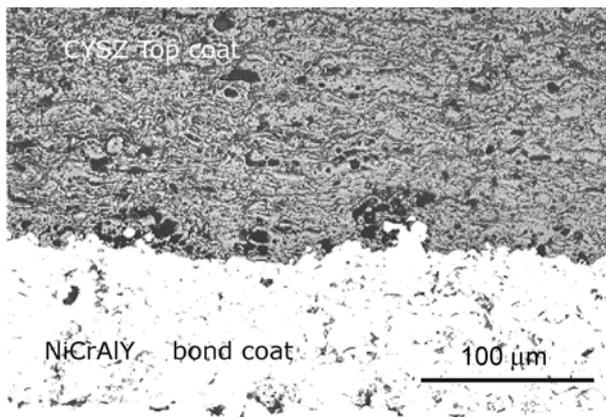


Fig. 1. Cross sectional morphology of the as-sprayed thermal barrier coating system.

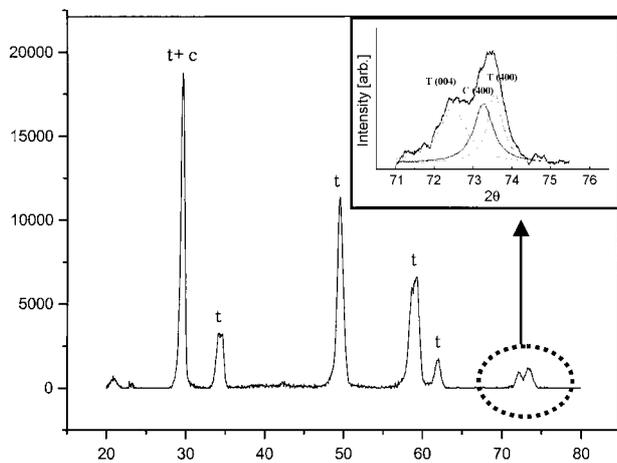


Fig. 2. X-ray diffraction of the as-sprayed CYSZ coating.

Figure 1 shows a cross sectional optical micrograph of the as-sprayed coating. A lamellar structure, typical of thermal spray coating structure, was seen. The CYSZ topcoat shows a lot of pores and unmelted particles as expected. Porosity in topcoat was measured to be 13% (area) by image analysis.

An X-ray diffraction pattern of the as-sprayed CYSZ coating is shown in Fig. 2. Tetragonal and cubic phases were detected but no monoclinic phase was found. This non-equilibrium phase formation was attributed to the rapid solidification process during the deposition of the splat. No further phase change would be expected in this study due to the sluggish diffusion rate below the 1200°C heat treatment. In reality, a higher phase stability of the CYSZ coating than the YSZ coating was observed as previously [5].

Figure 3 shows TGA curves of PCS pyrolysis in an N₂ environment with heating rates of 10°C/min and 20°C/min. It can be seen that the precursor solution lost about 5% of its mass below 250°C and this was attributed to the evaporation of small molecules in the PCS. From 250°C to 350°C, the PCS showed almost no change in weight. However above 400°C, PCS began

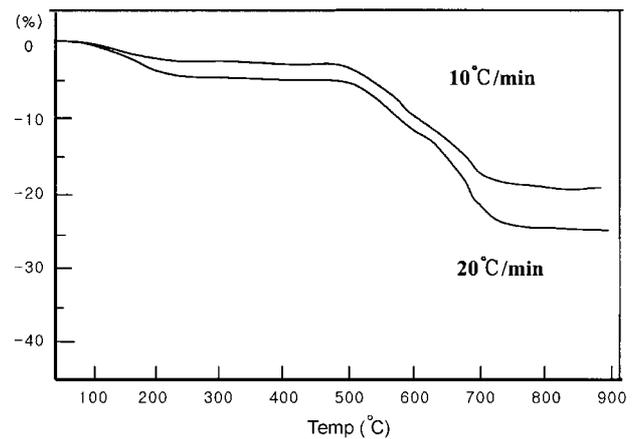


Fig. 3. TGA analysis of PCS decomposition.

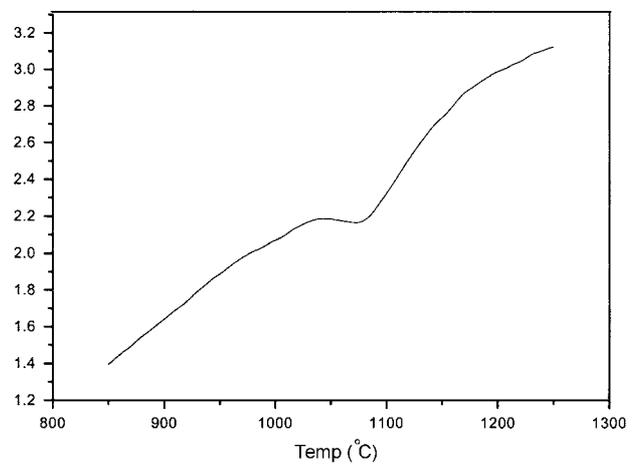


Fig. 4. DCS analysis of SiC crystallization.

to decompose and its weight decreased sharply until about 800°C. After which the weight of the PCS residue was almost constant. This implied that the decomposition had almost finished. The ultimate pyrolytic yield was about 80%. This high yield may be excellent as a use of TBC sealant. However, the pyrolytic yield at 20°C/min heating rate were about 68%. It was considered that a trace of oxygen made PCS cross linked at about 200 through 300°C, and thus the reduced amount of gas emitted by the decomposition of PCS at the slow heating rate [6].

Figure 4 shows the DSC curve of the amorphous SiC, which is formed after PCS pyrolysis at 800°C, with a heating rate 10°C/min. It can be seen that the crystallization of the amorphous SiC started at about 1030°C and finished at about 1100°C.

X-ray diffraction patterns of products of the respective PCS pyrolysis processes at 800°C and 1100°C are shown in Fig. 5. It can be seen that the pyrolytic product of PCS at 800°C was completely amorphous, while that at 1100°C exhibited a broad peak from SiC. The broad peaks indicate that the crystallite size of the SiC was very small. A mean grain size was determined by the Sherrer-Wilson formula from using the SiC

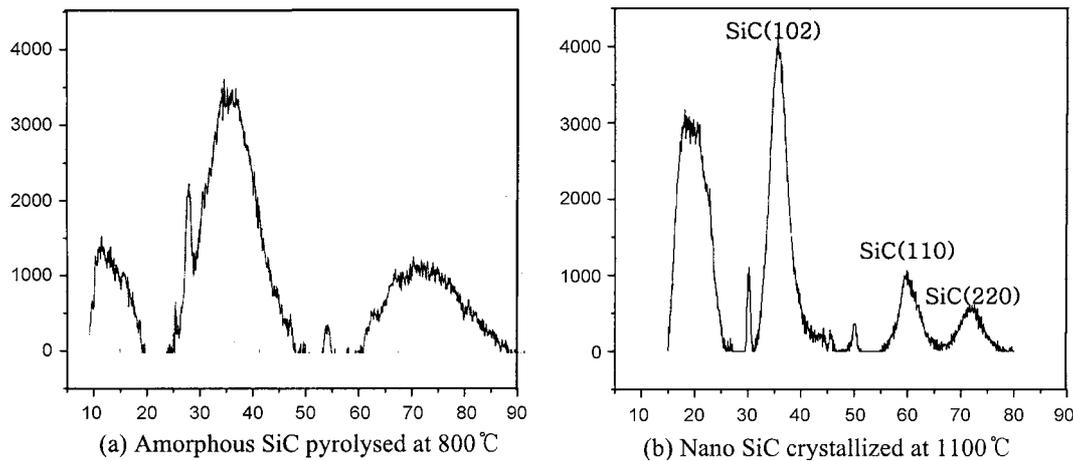


Fig. 5. X-ray diffraction of pyrolysed PCS.

(220) peak [7]. It had a minimum of peak asymmetry due to one dimensional disordering. The Wilson method was used to the correct mean grain size for error due to microstrain line broadening. The calculated mean grain size for the pyrolysed PCS at 1100°C was not larger than 5 nm.

Figure 6 shows cross sectional micrographs of the coating, sealed with SiC, after 6th times impregnation and pyrolysis processes. It can be seen that dense SiC was formed in pores and cracks. The average impregnation depth was approximately 150 μm of the 500 μm CYSZ TBC coating. The sealing process increased the hardness of the CYSZ plasma spray coating from Hv 480 to Hv 550 under a 300 g-force.

Cross sectional microstructures of thermally shocked coatings of both as-sprayed and SiC sealed coatings are seen in Fig. 7. Both as-sprayed and sealed coatings had similar lifetime and fracture behaviors. Generally pores and vertical cracks in the TBC enhance thermal shock resistance, but in this work no distinguishable difference between sealed and unsealed coatings in terms of thermal shock resistance was found. This is due to the controlled sealing depth. In the 500 μm CYSZ TBC coatings, the sealed portion was only about 150 μm at the top of the TBC, so the reduction of the porosity by sealing concerned with the thermal shock resistance can be minimized by impregnation depth control.

Figure 8 shows the variation in weight loss with an increase of the sliding wear time of the as-sprayed coatings and sealed coatings under the different load conditions (0.5, 1.0, and 1.5 MPa). Sealing improved the wear resistance markedly. The weight loss of sealed coatings was reduced by more than 50% of the as-sprayed coating. The presence of pores and cracks generally has negative influences on the mechanical properties, since pores can cause stress concentration, resulting in low strength [8]. The presence of pores and cracks, distributed at grain and splat boundaries, weakens the bonding strength and leads to a reduction of fracture energy. It is known that for TZP (tetragonal

zirconia phase) ceramics the variation of fracture energy, Young's modulus and fracture toughness according to the residual porosity follows an exponential relation. Wear characteristics can be also affected by the residual porosity. Therefore, sealing reduces porosity and increases fracture energy.

As well as measuring the weight loss, the worn surfaces of the coatings were examined by SEM to indicate the main wear mechanisms. Figure 9 shows the worn surface of an unsealed coating. Plastic deformation is the most widely reported wear mechanism in zirconia sliding wear mechanism on zirconia. However, on the unsealed coatings most of the mass loss was found to occur by a fracture wear mechanism. Intergranular fractures (A region) and spallations (B region) can be observed in Fig. 9. Local plastic deformation (C region) wear can be also observed. During the sliding of CYSZ coatings plastic deformation manifested itself as the plastic flow of the surface, the smearing of wear debris and groove formation [9, 10].

Figure 10 shows the worn surface of a sealed coating. Little fracture wear, shown in Fig. 9, was found. Most of the wear was occurred by the deformation wear mechanism. The sealing resulted in the transition of the wear mechanism, which corresponded with the change in mechanism from the brittle fracture mode causing severe wear to the plastic deformation mode causing mild wear. We can expect that the porosity decrease due to sealing increased the fracture energy of the CYSZ top coat, so sealed coats were not fractured until sufficient surface deformation had been occurred.

Figure 11 shows the friction coefficient variations with increase of the sliding time of both unsealed and sealed coatings. Sealed coatings had a smaller friction coefficient, because they are not only less rough but also lubricated by excess carbon in the pyrolyzed SiC. Silicon carbide formed by pyrolysis of PCS was found to have a reasonably high content of excess carbon (C/Si=1~1.4), as compared with stoichiometric SiC [4].

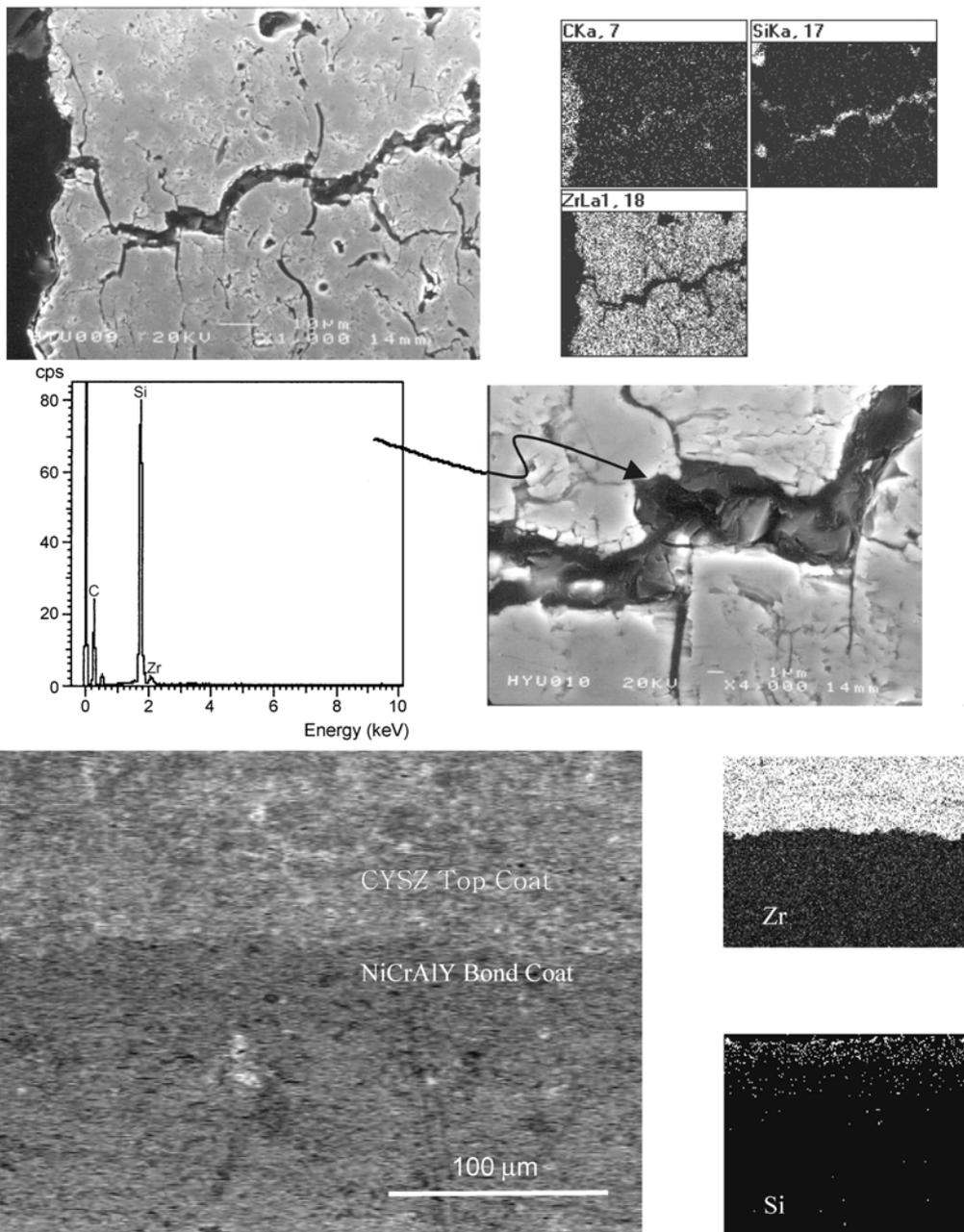


Fig. 6. SEM & EDS analysis of sealed coating.

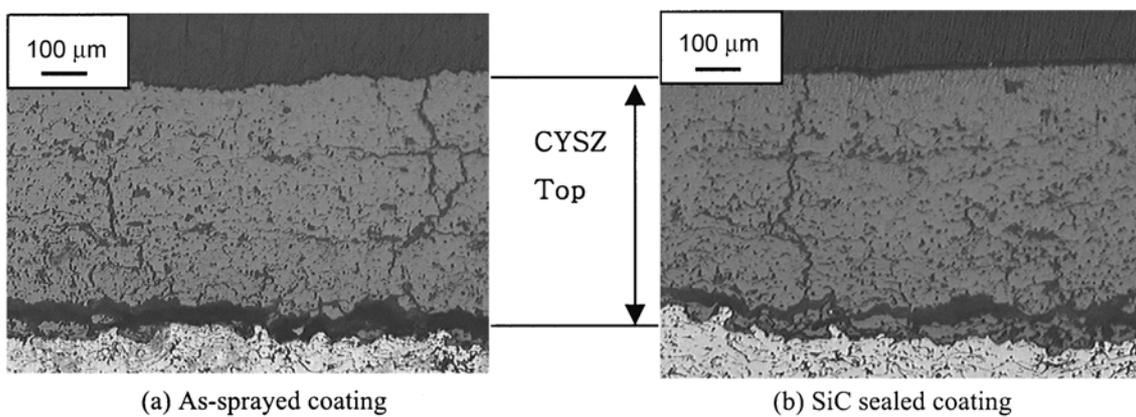


Fig. 7. Cross sectional microstructure of thermal shocked coatings.

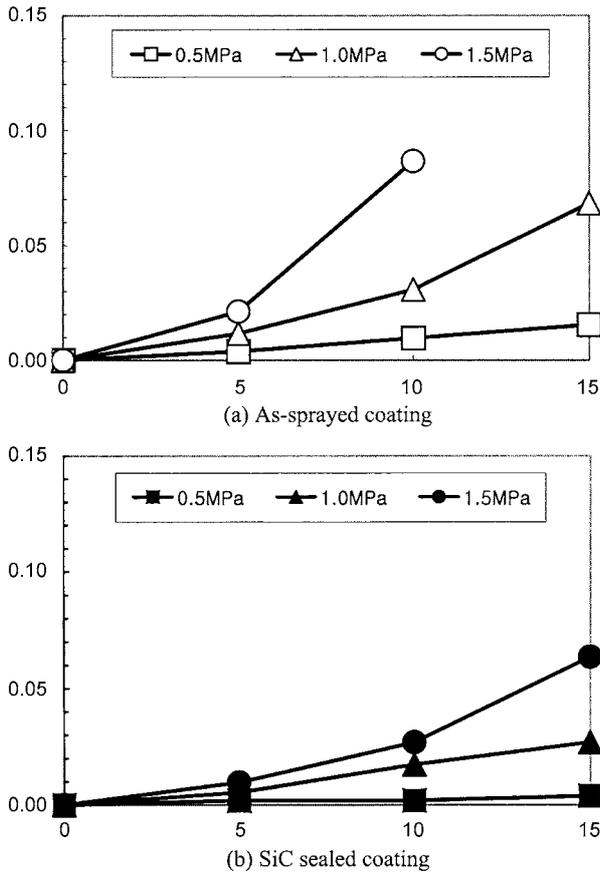


Fig. 8. Variation in weight loss with sliding wear time at room temperature.

This is because the precursor polymer, polycarbosilane, has a high carbon content. This excess carbon content varies with the pyrolytic atmosphere. The excess carbon content can vary the mechanical properties of SiC. But in this study this excess carbon may act as a lubricant in this sliding wear.

In order to investigate the porosity content effect on the sliding wear of the CYSZ coating, the CYSZ coat-

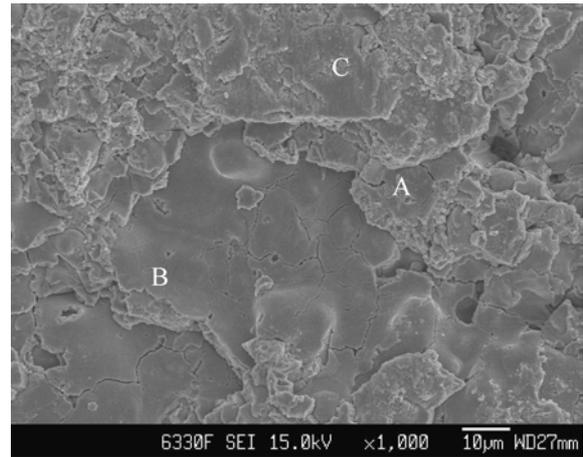


Fig. 9. Worn surfaces of as-sprayed coating.

ing with 8 area% porosity was produced by controlling the coating parameters. Figure 12 shows the variation in weight loss with increase of the sliding wear time of as-sprayed coatings and sealed coatings with the different porosity contents under the 1MPa loading condition. The 8% porosity coat had a smaller weight loss than that of the 13%. However it had a much higher weight loss than the sealed coat. Because porosity

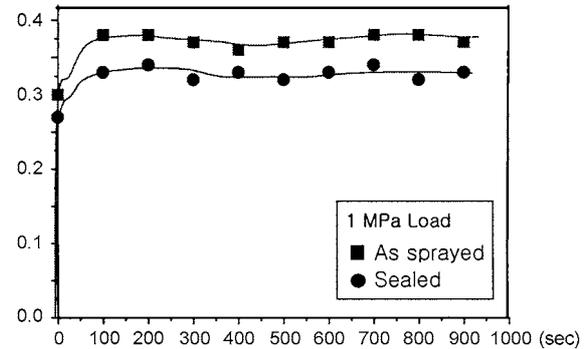


Fig. 11. Friction coefficient variations with the sliding time.

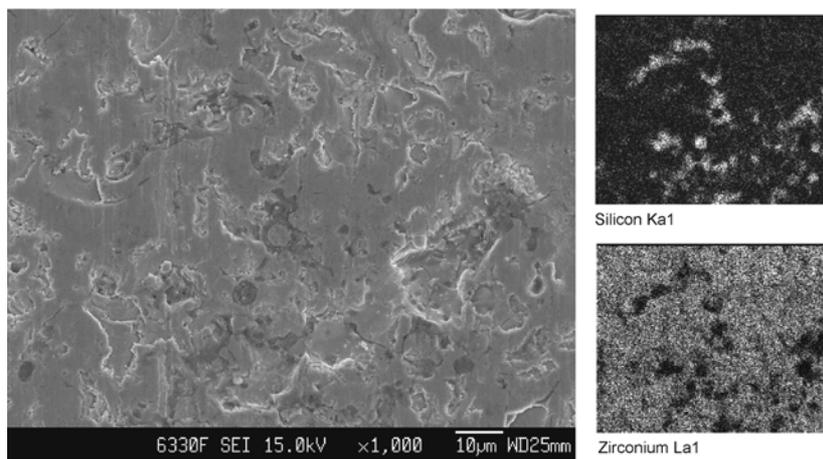


Fig. 10. Worn surfaces of SiC sealed coating.

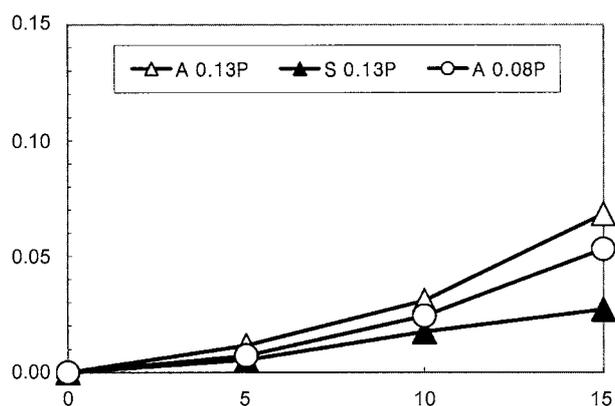


Fig. 12. Variation in weight loss with sliding time (A: as-sprayed, S: sealed & P: porosity).

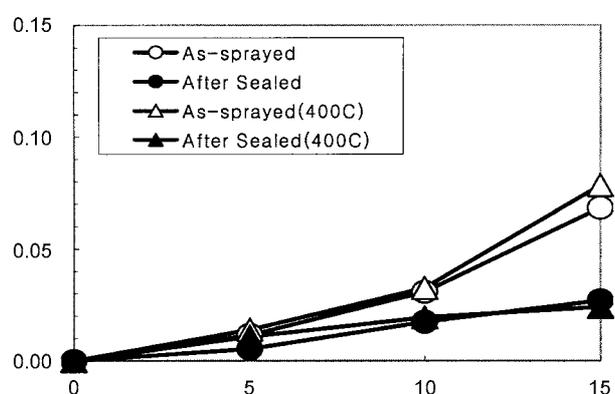


Fig. 13. Variation in weight loss with sliding time at room temp and 400°C.

enhances the thermal shock resistance, for the TBC, a porosity that is less than 8% is not so good. However, it has been observed in this study that a decrease in porosity content increased the mechanical properties. And these contradictory effects of the porosity could be solved by the control of the impregnation depth. Only sealing the upper part of PSZ TBC enhanced the wear property without decreasing the thermal shock resistance.

Figure 13 shows the variation in weight loss with increase of the sliding wear time of as-sprayed coatings and sealed coatings at room temperature and 400°C under the 1MPa loading condition. At 400, the weight loss of the as-sprayed coat was increased relative to that of the room temperature test. This is due to the high friction coefficient of zirconia from 300 through 400°C. This friction coefficient increase was related to the oxygen vacancy content, dislocation movement and lattice vibrations. Because this effect occurred reversibly with temperature, a phase transformation was not related to this. However, in sealed coats no weight loss increase was observed. This is because the lubricant effect of excess carbon diminished the coefficient increase caused by high temperature.

After wear and thermal shock tests, XRD patterns of

sealed and unsealed PSZ coats were the same as before the tests (Fig. 2). During sliding wear of unsealed and sealed coatings no zirconia phase transformations, which deteriorates wear resistance, take place. The stress-induced phase transformations, tetragonal to monoclinic, improve the surface fracture toughness [11]. However, in other literature [12], no improvement in wear resistance was observed. This behavior was attributed to the presence of microcracks due to the volume expansion. Moreover, the monoclinic phase has a lower Young's modulus and hardness than the tetragonal. So tetragonal to monoclinic phase transformation was not good for the sliding wear resistance of the plasma sprayed zirconia based coatings.

Summary

The decomposition of the PCS precursor solution started at 100°C and finished at about 800°C. Silicon carbide formed by 800°C pyrolysis was amorphous. The crystallization of the amorphous silicon carbide started at about 1030°C and finished at 1100°C. The mean grain size determined by the Sherrer and Wilson formula using the SiC (220) peak was not larger than 5 nm. Under the dry condition sliding wear against sintered $ZrO_2-8Y_2O_3$ (YSZ), weight losses were pronouncedly decreased by SiC sealing. The sealing resulted in the transition of the wear mechanism, which corresponded with the change in mechanisms from brittle fracture mode causing severe wear to plastic deformation mode causing mild wear. The friction coefficient was also decreased by the excess carbon of the non-stoichiometric SiC and less rough surface due to SiC sealing. During sliding wear of unsealed and sealed coatings no stress-induced tetragonal to monoclinic phase transformation, which deteriorate wear resistance, took place.

References

1. R. A. Miller, Surf. Coat. Technol. 30 (1987) 1.
2. R. B. Heimann, Plasma-Spray Coating, Principle and Application, VCH, 1996, 164-165.
3. J. Knuutila, P. Sorsa and T. Mantyla, J. Thermal Spray Technol. 8 (1999) 249-257.
4. Michio Takeda, Hiroshi Ichikawa, Composites Science and Technol. 59 (1999) 787-792.
5. H. K. Kim, H. S. Choi and C. H. Lee, Surf. Coat. Technol. 124 (2000) 1-12.
6. Y. Hasegawa, J. Mater. Sci. 24 (1989) 1177-90.
7. H. P. Klug and L. E. Alexander, X-ray Diffraction Procedures for Polycrystalline Amorphous Materials, Wiley, 662.
8. D. H. Buckley, Tribological Properties of Structural Ceramics, in Treatise on Materials Science and Technology, 293-365.
9. A. Tucci and L. Esposito, Wear, 172 (1994) 111-119.
10. J. Breznak, E. Breval and N. H. McMillan, J. Mater. Sci. 20 (1985) 4657-4680.
11. G. de Portu and S. Conoci, J. Am. Ceram. Soc. 80 (1997)

3242-3244.

12. S. Conoci and G. de Portu, *J. Mater. Sci.* 34 (1999) 1009-

1015.