Mechanism of Vertical Microcracking in $\text{CaO}\cdot\text{SiO}_2\text{-CaO}\cdot\text{ZrO}_2$ Sprayed Thermal Barrier Top Coating

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The durability of thermal barrier coatings (TBCs) at gas turbine has been improved substantially by instituting more strain tolerant zirconia-ceramic top coatings with vertical cracks artificially, such as $\text{ZrO}_2\text{-Y}_2\text{O}_3$ plasma-sprayed coating with purposely segmentation. Under the necessity of TBCs with thermal shock resistance and durability at high temperature, we have developed the top coating of $2\text{CaO}\cdot\text{SiO}_2\text{-10}\sim 30\text{mass}\%\text{CaO}\cdot\text{ZrO}_2$ ($\text{C}_2\text{S-10}\sim 30\%\text{CZ}$) with many vertical microcracks that is formed with the spraying process only, namely one vertical microcrack does not pierce through the sprayed layer but remains within a single flattened ceramic particle of the top coating. In order to discuss the mechanism of the vertical microcracking, the flattening-solidification behavior of the $\text{C}_2\text{S-10}\sim 30\%\text{CZ}$ sprayed splat was investigated. Microcrack was observed within the splat of $\text{C}_2\text{S-10}\sim 30\%\text{CZ}$ particle after solidification on the polished SUS304 stainless steel. It is assumed that spraying particle liquefied in plasma flame collides and strongly adheres on the substrate or the accumulated particles and change the phase from liquid to brittle solid due to rapid cooling, at the same time, the tensile stress is generated on the external surface of the particle and fine vertical microcrack occurs in the particle which could not withstand this stress. From strong correlation between the vertical microcracking and amorphous like behavior of the $\text{C}_2\text{S-10}\sim 30\%\text{CZ}$ coating, the liquid phase of $\text{C}_2\text{S-10}\sim 30\%\text{CZ}$ particle sublimated some CaO in plasma flame is considered to take an important role in vertical microcracking formation due to shrinkage during the cooling and solidifying process.

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1. Introduction

Modern land based gas turbines bring increased output and high thermodynamic performance. In addition to these, from the view of lightening the burden imposed on earth environment, it becomes very important to develop technology to allow higher turbine inlet gas temperature, which directly links to high efficient power generation mainly with the combined cycle gas turbine system.¹⁾

ZrO_2 -base sprayed coatings can effectively protect the base metal of hot section component of gas turbines exposed to high temperatures though comparatively thin; consequently it is commonly used as the thermal barrier coating (TBC).^{2,3)} Conventional $\text{ZrO}_2\text{-Y}_2\text{O}_3$ coatings, however, do not have sufficient thermal shock resistance and it is still necessary to improve the quality of ZrO_2 -base ceramic coatings.

So far, various researches have been intensively carried out to improve thermal shock resistance of sprayed coatings,⁴⁾ for example, partially stabilized zirconia producing microcracks in the coating by its phase transformation,⁵⁾ improvement of its stabilizer components,^{6,7)} the graded coating in which the compounding ratio is gradually and continuously changed from the MCrAlY ($\text{M}=\text{Co}, \text{Ni}$) bond coat to the oxide ceramic top coat,⁸⁾ release of residual stress in the coating by heat treatment,⁹⁾ and the microcracking to the coating by laser irradiation.¹⁰⁾ Recently, in order to release the residual stress caused by the difference of thermal expansion between the base metal of turbine components and the coating materials under high and low temperatures repeated, TBC in which vertical cracks are artificially made have been developed, such as $\text{ZrO}_2\text{-Y}_2\text{O}_3$ sprayed dense coating with segmentation cracks purposely made¹¹⁾ and columnar crystalline $\text{ZrO}_2\text{-Y}_2\text{O}_3$ coating made by electron beam physical

vapor deposition (EB-PVD),¹²⁾ and some of them have been already put to practical use.

From the necessity of TBC with thermal shock resistance and durability in high temperatures, we have developed the sprayed coating of $2\text{CaO}\cdot\text{SiO}_2\text{-10}\sim 30\text{mass}\%\text{CaO}\cdot\text{ZrO}_2$ ($\text{C}_2\text{S-10}\sim 30\%\text{CZ}$) in which numerous vertical microcracks formed with the spraying process only.¹³⁻¹⁵⁾

Sprayed coatings are the aggregate of flattened particles and peculiar porous constitute that consist of fine texture with the typical lamella structure. So, the coating structure has been eagerly investigated through the behavior of sprayed particle splats in the elementary process of impinging-flattening-solidification.¹⁶⁾

At this time, we will report on the discussion about the mechanism of the vertical microcracking in the newly developed $\text{C}_2\text{S-10}\sim 30\%\text{CZ}$, based on the investigation of flattening-solidification behavior of the sprayed splats and growing behavior of the vertical microcracks due to heat load in the coating, comparing with C_2S , CZ sprayed coatings and commercially available $\text{ZrO}_2\text{-Y}_2\text{O}_3$ sprayed coating.

2. Test Materials and Experimental Procedure

As the spraying materials, $2\text{CaO}\cdot\text{SiO}_2\text{-20mass}\%\text{CaO}\cdot\text{ZrO}_2$ ceramic powder containing 20% of $\text{CaO}\cdot\text{ZrO}_2$ was used. Figure 1 shows the Scanning electron microscope (SEM) image of $\text{C}_2\text{S-20}\%\text{CZ}$ spraying material produced with $\gamma\text{-C}_2\text{S}$ and CZ fine particles by the spray dried process. The powder particles are spherical bodies 20 to 50 μm in diameter. As the vertical microcracking appears particularly on $\text{C}_2\text{S-10}\sim 30\%\text{CZ}$ sprayed coating only, spraying materials made of similar components; C_2S , $\text{C}_2\text{S-50}\%\text{CZ}$, and CZ spray dried powders (C, S, and Z mean CaO , SiO_2 , and ZrO_2 , respectively) and $\text{ZrO}_2\cdot 8\text{mass}\%\text{Y}_2\text{O}_3$ (8YZ) fused-crushed

Fig. 1 Powder morphologies.

material generally used in TBC were also tested for the comparative discussion.

As the substrate material of test specimens Type 304 stainless steel (50 mm × 50 mm × 5 mm) was used and its surface was polished to mirror finish with 0.3 μm diamond paste for the observation of flattening behavior of the particles, other test specimen was blasted with WA60# alumina grid for actual coating before spraying.

As the way of sprayed splats capture, carbon steel plate with a 0.5 mm-wide slit was put 10 mm ahead of the substrate surface as shown in Fig. 2 and plasma gun set up on a robot was traversed one pass with 750 mm/s, and the melted

particles passed through the slit of the steel plate were collected on the mirror polished substrate.

In order to observe the behavior of the splats on lamination a test coupon was made by spraying with the plasma gun traversed 5 passes on the same track.

To investigate the relationship between the base material temperature and the morphology of the splat the substrate was preheated up to the specified temperature with a commercially available hot plate and controlled by *in-situ* temperature measurement with an infrared thermometer. Temperatures of the substrates were kept at room temperature (293 K), 353 K, and 453 K, respectively.

The actual coating was applied to the substrate preheated to 453 K. As the temperature of the substrate rises during the spraying work, the substrate should be cooled so as to keep the temperature of the substrate within 453–503 K. The F-4 plasma gun (Plasma Technik AG) was employed to spraying. The spraying conditions are summarized in Table 1.

From X-ray diffraction results of C₂S-10~30% CZ sprayed coating shown in Fig. 3,¹³⁾ amorphous-like-behavior specific to the composition is estimated to largely participate with vertical microcracking peculiar to the coating. So, the differential thermal analysis of C₂S-20% CZ coating was carried out from the room temperature to 1673 K at the heating rate of 10 K/min by TG-TDA2000S (Mac Science Co., Ltd.). Then, in order to investigate the relationship

Fig. 2 Experimental set-up for splat collecting.

Table 1 Ceramic materials and spray parameters.

Materials	Composition (mass%)	C ₂ S, C ₂ S-20% CZ, C ₂ S-50% CZ, CZ, 8YZ (C:CaO, S:SiO ₂ , Z:ZrO ₂ , Y:Y ₂ O ₃)
Spray parameters		
Spray process		Atmospheric Plasma Spray
Spray gun		Plasma Technik Type F4
Plasma gas		Ar/H ₂
Power (kW)		43
Spraying distance (mm)		120
Gun traverse (mm/s)		750 (with Robot)
Substrate Temperature K		293, 353, 453

Fig. 3 X-ray diffraction pattern of as-sprayed C₂S-CZ coating.

between the exothermic reaction and the vertical micro-cracking phenomenon, X-ray diffraction on C₂S-20%CZ coatings was carried out after the coatings were held for 10.8 ks in the electric furnaces of the temperatures, 1023 K and 1123 K, respectively.

3. Experimental Results and Discussion

3.1 SEM observation of C₂S-CZ and 8YZ splats and cross-section structure of the sprayed coatings

SEM image of these splats with the substrate temperature of 453 K is shown in Fig. 4. C₂S-CZ series splats show disc-like flat pattern though a few splash appears on outer edge. Smooth flat deposit provides the basis for the fact that the splats had high viscosity on deposition. Whereas, 8YZ splats have splash patterns where numerous reticulated fine cracks are clearly exist.

3.2 Relationship between substrate temperature and form of splats

Flattening degree of C₂S-20CZ splats at various temperatures of the substrate is shown in Fig. 5. At the substrate temperatures, room temperature and 353 K, not all the C₂S-20CZ splats deposit completely. It is recognized that some splats collapse during the impinging-flattening-solidification process and some splats fall off the substrate. These facts show that the splats are lacking in adhesive ability. When the substrate temperature is 453 K, though splash occurs partially, spraying particles adhere on the substrate forming disc-like flat splats in almost completely melted state. As many researchers pointed out, splat state of this material also depends on the substrate temperature.¹⁷⁾

3.3 Behavior of C₂S-20%CZ splats on lamination

As shown in Fig. 6, in C₂S-20%CZ flat splats comparatively large cracks are introduced across inside of a single particle and vertical cracks occur in laminated splats. Cracks in C₂S-20%CZ splats are larger than those in ZrO₂-Y₂O₃ splats, but number of cracks in the former is less than the latter, that is, a few cracks are observed on single particle within the view field under this microscope.

3.4 Behavior of vertical cracks in C₂S-20%CZ coating kept at elevated temperatures

From the results of differential thermal analysis of C₂S-

Fig. 4 Splat morphologies of various material particles on the polished stainless steel at 453 K and SEM micrographs of the cross sectional structure of the coatings.

20%CZ coating shown in Fig. 7, exothermic reactions are observed around 1110 K and it is estimated that the re-crystallization occurs accompanied with disappearance of the amorphous like phase. Figure 8 gives the results of the X-ray diffraction on each coating after kept at high temperatures up to 1023 K and 1123 K, respectively, which was carried out taking the exothermic reaction temperature into account.

As-sprayed coating shows the broad curve indicating the existence of amorphous like phase. When it is heated up to 1023 K the broad curve disappears, which suggests re-crystallization of the coating is progressing at lower temperature than that of exothermic reaction. As shown in Fig. 9, the vertical cracks in the coating become remarkably larger and clearer with increasing temperature at which the coating is held. However, there is no interrelation between the cracking behavior and the exothermic reaction recognized in the differential thermal analysis, and it is hardly considered that the vertical cracks are related to disappearance of the amorphous like phase and resulting re-crystallization.

Fig. 5 Splat morphologies of $\text{C}_2\text{S-20CZ}$ on the polished stainless steel at different temperature.

Fig. 6 SEM images of overlapping $\text{C}_2\text{S-20CZ}$ splats on the polished stainless steel substrate at 453 K.

3.5 Mechanism of vertical microcracking in $\text{C}_2\text{S-20CZ}$ coating

Vertical microcracking in $\text{C}_2\text{S-20CZ}$ is obviously recognized within the specific region of composition containing 10–30 mass% of CZ in the material agglomerated $\gamma\text{-C}_2\text{S}$ and CZ fine particles by the spray dried process as shown in Fig. 1. As judged from the cross-sectional micrographs shown in Fig. 9, the vertical microcracks occurring in the as sprayed coating do not pierce through the whole coating layer but is limited within one single flattened particle.

The $\text{C}_2\text{S-20CZ}$ coating has sufficient density due to the adhesion between each particle resulting in strong bonding with few pores among the flattened particles. While, in the

Fig. 7 Result of differential thermal analysis of $\text{C}_2\text{S-20CZ}$ coating.

Fig. 8 X-ray diffraction pattern of $\text{C}_2\text{S-CZ}$ coatings after holding at different temperature for 10.8 ks.

Fig. 9 SEM micrographs of cross-section of C_2S -20CZ coatings after keeping at different temperature for 10.8 ks.

flat splats sprayed on the substrate at 453 K a crossing crack occurs in a single flattened particle surface and when splats are laminated the crossing cracks dividing single flattened particle form clearly. From these results, vertical microcracks are estimated to generate in extremely short time of impinging-flattening-solidification process of the spraying particles on the substrate after the agglomerated particles melted in the plasma flame.

From the broad pattern of the X-ray diffraction analysis shown in Fig. 3, the amorphous phenomenon specific to the composition seems to be largely concerned with the occurrence of vertical microcracks peculiar to C_2S -10~30% CZ coating. Essentially C_2S -CZ system oxides are on the co-existent line as shown in Fig. 10,¹⁸⁾ so it is considered to be theoretically impossible to produce any double oxide. In spite of them, the amorphous phenomenon was confirmed as

Fig. 10 The compatible triangles in the system ZrO_2 - CaO - SiO_2 at 1673–1773 K.

the experimental fact. This phenomenon is the important factor that cannot be ignored for the estimation of the occurrence mechanism of the vertical microcracks in the C_2S -10~30% CZ coating.

The cause of the amorphous like phase formation is considered as follows; first, CaO , the main component of C_2S -10~30% CZ material, sublimates in the plasma flame of the ultra high temperature. As the result, the chemical composition shifts in the direction of the arrow described in the phase diagram in Fig. 10, and the three component system of C_2S -CZ- C_3S_2Z , ($CaO=C$, $SiO_2=S$, and $ZrO_2=Z$) is formed. Gitzhofer *et al.* also confirmed the sublimation of CaO during plasma spraying.¹⁹⁾ It is quite probable that the behavior of CaO component whose melting point (2845 K) is close to the sublimation temperature (3123 K) and the presence of SiO_2 with low melting point (1976 K–1986 K) that is liable to turn into glassy state will facilitate the transition of C_2S -10~30% CZ to amorphous like phase. C_2S -CZ- C_3S_2Z three component system thus formed, will decompose into cubic- ZrO_2 (CZ₄), C_2S and liquid phase at a low temperature (1907 K).²⁰⁾ As the cooling rate of the sprayed particles coagulating on the substrate is as large as $10^6 \sim 10^9$ K/s,²¹⁾ it is considered that the melted particles are rapid-quenched to the low temperature region without any time to crystallize from liquid phase and form the amorphous state.

Vardelle *et al.* reported that at the substrate temperature where the disc splats can be formed, while the temperature difference that is the driving force of heat transfer becomes small, at the same time, the thermal resistance at the interface between the flat droplets and the substrate surface extremely decreases, and as the result the cooling rate remarkably increases.²²⁾ It is also reported that the sprayed coating applied under the condition where the disc splats is formed keeps high adhesion property.²³⁾

Here, the liquid phase of C_2Z -CZ spraying material formed in the plasma flame is considered to have the following characteristics:

- (1) Phase transition from liquid to brittle solid occurs momentarily and the residual stresses remains in the flattened particle because of its high viscosity and high temperature range of glass transition due to the contained ZrO_2 with high melting point of 2873 K.
- (2) Quenching effect is remarkable because of high content of CaO with thermal conductivity as high as 14.64 W/m·K.
- (3) Strong thermal stress generates because of comparatively high thermal expansion coefficient of each component (C_2S : $13.5 \times 10^{-6} K^{-1}$, CZ: $10 \sim 14 \times 10^{-6} K^{-1}$) in the system.

C_2S -10~30% CZ particles which has melted in the plasma flame and turned to liquid phase are accelerated by the high-speed plasma flame. In addition to the brittleness of C_2S and CZ materials, these particles colliding with the substrate usually give a brittle flat structure.

As mentioned above, mechanism of vertical microcracking in a single flattened particle is estimated as the illustration in Fig. 11. The melted C_2S -10~30% CZ particles collide on the substrate or existing laminated layer, spread, and are rapidly cooled. As the particles adhere strongly to one another or to

Fig. 11 Schematic illustrations showing mechanism of vertical microcracking formation in a flattened C₂S-20CZ particle.

the substrate, thermal shrinkage of the particle by rapid cooling is confined by the solid surface and so in the coagulated particles the rapid-quenching stress generates that become the tensile stress in the coating.

Kuroda *et al.* calculated the stress corresponding to the temperature difference of 100 K to be 300 MPa.²⁴⁾ As the adhering particles that receive such a strong stress have above-mentioned characteristics of liquid phase, it is assumed that the vertical microcracks occur within a single flattened particle.

As vertical microcracks occurring within a single flattened particle release the internal stress, discontinuous vertical microcracks relaxing thermal stress effectively seem to occur and the vertical microcracks never grow to particle boundary cracks that pass through whole the coating layer.

4. Conclusion

As to 2CaO·SiO₂-10~30mass%CaO·ZrO₂, (C₂S-10~30% CZ) sprayed coating in which numerous vertical microcracks occur through the plasma spraying process only, the mechanism of vertical microcracking was discussed based on

flattening and solidification behaviors of splats. The results obtained are summarized below.

- (1) Spraying particle liquefied in plasma flame collides and firmly adheres on substrate or the deposited particles. The tensile stress generated on the external surface of the sprayed particle due to rapid cooling seems to make microcracking trigger.
- (2) From strong correlation between vertical microcracking and amorphous like behavior it is estimated that C₂S-10~30% CZ spraying material transited the three component system, C₂S-CZ-C₃S₂Z in the plasma flame and then it decomposes into cubic-ZrO₂(CZ₄), C₂S and liquid phase. This liquid phase is considered to take an important role in vertical microcracking due to shrinkage during the cooling and solidifying process.

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