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# Improving the Hot Corrosion Resistance of Nanostructured ZrO<sub>2</sub>-7wt.%Y<sub>2</sub>O<sub>3</sub> Thermal Barrier Coatings Fabricated by Plasma Spraying

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**Abstract.** Conventional and nanostructured  $ZrO_2$ -7wt.% $Y_2O_3$  thermal barrier coatings (TBCs) were prepared by plasma spraying technology. Microstructure and hot corrosion resistance of two TBCs in 75%Na<sub>2</sub>SO<sub>4</sub>+25%NaCl (mass fraction) mixed molten salt under 850 °C were compared. Meanwhile, hot corrosion failure mechanisms of TBCs were investigated. Results demonstrated that both conventional and nanostructured TBCs were typical lamellar stacking characteristic. However, compared with conventional TBC, the nanostructured TBC presented the base phase which is gained from recrystalization of fully melted nano-particles as well as the embedding phase of partially melted nano-particles. The nanostructured TBCs, hot corrosion failure is caused by partial transformation of tetragonal phase (t-ZrO<sub>2</sub>) into monoclinic-phase (m-ZrO<sub>2</sub>) martensite as a response to the consumption of the stabilizer  $Y_2O_3$ . However, the nanostructured TBC generally has lower degree of hot corrosion and better protection to the metal bonding layer and matrix compared with conventional TBC.

## 1. Introduction

Thermal barrier coatings (TBCs) are the fourth generation of high-temperature coatings [1]. A typical two-layer system TBC is composed of metal bonding layer and surface ceramic layer. TBCs have significantly better heat-insulating performance and stronger resistance to high temperature oxidation than the previous three generations of high-temperature coatings. As a result, TBC have been widely applied in hot-end parts, such as turbine engine. TBCs are often exposed to high-temperature oxidation, hot corrosion and washout during services. In particular, Na and S in fuels may cause molten salt hot corrosion to coatings on gas turbine. They are an important factor to shorten its service life [2]. Therefore, it is very necessary to study hot corrosion performance of TBCs.

Due to characteristics of simple operation, low cost and good heat-insulating performance, plasma spraying technology is the most common method to prepare TBCs [3]. However, the spraying layer is in typical stratified structure with more pores. Spraying layer diffuses to the metal bonding layer through pores and holes in coatings and thereby penetrate into the base metal, thus accelerating corrosion and further cause fast failure of TBCs. Currently, immersing sealing, spark plasma sintering [4] and laser remelting [5] are common measures to improve performance of TBCs prepared by

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plasma spraying. In addition, preparing nanostructured coating is also viewed an effective method to improve the performance [6,7].

In this study, conventional and nanostructured  $ZrO_2$ -7wt.% $Y_2O_3$  TBCs were prepared by plasma spraying. A contrastive study of two TBCs in structure and resistance to hot corrosion in 75%Na<sub>2</sub>SO<sub>4</sub>+ 25%NaCl (mass fraction) mixed molten salt under 850 °C was carried out. The hot corrosion failure mechanism was analyzed and influences of nanostructure on hot corrosion of TBCs were investigated.

# 2. Experimental

 $\gamma$ -TiAl based alloy (20 mm×20 mm×8 mm) which was smelted by High-temperature Material Center of Iron and Steel Research Institute was applied as the base material in the experiment. The nominal chemical components of  $\gamma$ -TiAl based alloy were Ti-46.5Al-2.5V-1Cr (mole fraction, %). The metal bonding layer MCrAlY applied the NiCoCrAl superalloy powder which was produced by Metal Material Center of Beijing General Research Institute of Mining and Metallurgy through diffusion of Y<sub>2</sub>O<sub>3</sub>. Granularity of the NiCoCrAl superalloy powder was 45~105 µm. Irregular commercial powder which was crushed conventionally into granularity of 20~74 µm which was produced by Shenyang Ronghua Company was used as conventional ceramic material. Nanostructured agglomerated powder used the Nanox 4007 powder with a granularity of 40~100 µm (Inframat, USA). The nominal component of two materials was ZrO<sub>2</sub>-7wt.%Y<sub>2</sub>O<sub>3</sub>. The morphologies of corresponding powders are shown in figure 1.



Figure 1. SEM morphologies of ceramic powder: (a) conventional powder and (b) nanostructured agglomerated powder.

MCrAlY metallic bond coating and conventional and nanostructured ZrO<sub>2</sub>-7wt.%Y<sub>2</sub>O<sub>3</sub> ceramic top coatings were prepared by plasma spraying successively. The coating equipment applied the 3710 plasma spraying system produced by Praxair (America). Plasma spraying parameters are listed in Table 1. Samples were preprocessing by polishing, degreasing and abrasive blasting before the coating. **Table 1.** Plasma spraying parameters employed in spraying thermal barrier coating.

Process parameters	MCrAlY	Conventional	Nanostructured
		$ZrO_2$ -7wt.% $Y_2O_3$	$ZrO_2$ -7wt.% $Y_2O_3$
Current (A)	710	920	950
Voltage (V)	42	42	42
Primary gas, Ar (PSI)	65	45	45
Secondary gas, He (PSI)	115	150	150
Carrier gas, Ar (PSI)	45	45	45
Powder feed rate (rpm)	2	3	3
Spray distance (mm)	110	100	100
Traverse speed (mm $\cdot$ s <sup>-1</sup> )	100	100	100
Coating thickness (µm)	~100	~350	~350

In the present study, a fast immersing hot corrosion test was carried out. The molten salt was composed of 75% Na<sub>2</sub>SO<sub>4</sub>+25% NaCl (mass fraction). A hot corrosion test was implemented in a SX2-4-9 chamber electric furnace under 850 °C. Samples were immersed in molten in a crucible and taken out every 5 h to the bolted water to remove surface salt. After being dried, a  $10^{-4}$  g FA1004 analytical balance was used to weigh samples. A corrosion kinetic curve between mass fraction of samples per unit area and time was drawn (all results were mean of three samples). New salt was changed for the next periodic test and the total corrosion time was 50 h.

Morphologies of TBCs before and after the hot corrosion were observed by a JSM-7100F (JEOL) field emission scanning electron microscope. Phase analysis was carried out by a Rigaku D/max2500 X-ray diffractometer (XRD).

### 3. Results and discussions

### 3.1. Microstructures of TBCs

The X-ray diffraction analysis results of conventional and nanostructured TBCs which are prepared by plasma spraying are shown in figure 2. Conventional TBC contains tetragonal phase (t-ZrO<sub>2</sub>) and monoclinic phase (m- $ZrO_2$ ). Tetragonal phase takes the dominant role. This is because all phases of powder are transformed into tetragonal phase and cubic phase  $(c-ZrO_2)$  by high-temperature heating of plasma flame. However, there's inadequate content of the stabilizer yttrium oxide to make tetragonal phase maintained to room temperature during fast consolidation and cooling process after particles impact onto the matrix. Instead, transformations from cubic phase to tetragonal phase or cubic phase to tetragonal phase and then to monoclinic phase occur. The transformation from cubic phase to monoclinic phase belongs to a martensite transformation, which is related with not only grain size and chemical components, but also cooling speed. Generally speaking, temperature in the beginning of phase transformation is low and temperature at the end of transformation is high, which is attributed to the increase of cooling speed. In other words, the temperature interval from tetragonal phase to monoclinic phase is narrowing, and the transformation volume decreases. Plasma spraying is a process of collision between melted powder and base, flattening of transverse flowing and fast cooling and consolidation. In this process, the cooling speed is relatively high and finally only few monoclinic phases are produced in the final coating.



Figure 2. XRD analysis results of TBCs: (a) conventional TBC and (b) nanostructured TBC.

TBCs which are prepared by plasma spraying only contains non-equilibrium tetragonal phase (t'- $ZrO_2$ ), but involves no monoclinic phase. This is significantly different from conventional TBCs. During plasma spraying some stable  $ZrO_2$  onto  $Y_2O_3$  layer, only tetragonal phase with grain size higher than the critical size can be transformed into monoclinic phase. This is because the smaller grain size, the higher the interface energy and phase transformation resistance will be. However, nanostructured agglomerated powder is composed of nano-particles with small grain size. It is

believed that nano agglomerated composed of fine crystals is the main cause of tetragonal phase in coatings.

Morphologies of conventional and nanostructured TBCs prepared by plasma spraying are shown in figure 3. It can be seen from figure 3(a) that the conventional ceramic coating prepared by plasma spraying has lamellar stacking structures of countless deformed particles and shows typical stratified structure of plasma spraying state in wave mode [8]. Most lamellas are composed of columnar crystals which are approximately perpendicular to base surface. In the plasma spraying, powder is melted and impact onto the base or paved and re-crystallized on the subsided surface. In the process of crystallization, the growth direction of crystals is corresponding to the direction with the fastest heat conduction. Nevertheless, crystal growth perpendicular to this direction is restricted to some extent. There's the maximum heat flux along the normal direction (perpendicular to base) of paving of molten drops. Hence, columnar crystals in lamellas basically grow along the direction perpendicular to the base [8]. Moreover, lamellas are not bonded tightly, but there are some pores or holes. Performance of TBCs is closely related with content, shape and distribution of pores. Pores can decrease ceramic density and heat conductivity, but increase the thermal shock performance [8]. However, pores are stress concentration regions and might be further developed to cracks directly, thus decreasing strength of the ceramic layer. If there are excessive pores on the ceramic layer, these pores are easy to be connected into penetrability cavities. Corrosive media are easier to arrive at the interface between the ceramic layer and the transition layer under hot corrosion conditions, thus accelerating growth of oxidation film on the transition layer surface and increasing thermal stress. Hence, the coating is easy to crack and peel off.



**Figure 3.** Cross-section morphology of TBCs prepared by plasma spraying: (a) conventional TBC and (b) nanostructured TBC.

In figure 3(b), the nanostructured ceramic coating prepared by plasma spraying consists of fully melted region of nano-particles and partially melted region. The partially melted region is enclosed by fully melted regions. The whole coating has a base phase which is gained from recrystallization of fully melted nano-particles and the embedding phase of partially melted nano-particles. This conforms to the research results of Lima et al [9]. The fully melted region presents a typical stratified structure, which is basically consistent with the structure of conventional coating which is prepared by plasma spraying. The partially melted region is formed by melted or non-melted nano-particles. Structure of this partially melted region is very similar with the original  $ZrO_2$  nano-powder, showing typical nano-powder aggregate has experience high temperature during the plasma spraying, powder stays in efflux very shortly. The driving force for combination and growth of crystal boundaries of partially melted region on the sprayed coating still maintains some growing nano-particles. It is compared with internal morphology of the original nano-powder aggregate and finds

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that density is increased significantly after high-temperature sintering by plasma flame in the plasma spraying process.

### 3.2. Hot corrosion resistance performance

The corrosion kinetic curves of the prepared conventional and nanostructured TBCs in  $75\%Na_2SO_4+25\%NaCl$  molten salt under 850 °C are shown in figure 4. Corrosion mass of both conventional and nanostructured TBCs is positively related with time. The kinematics curves are approximately parabolas, indicating strong resistance to hot corrosion of TBCs. Generally, corrosion mass gain of the nanostructured TBC is kept smaller than that of the conventional TBC. After hot corrosion for 50 h, weights of the conventional and nanostructured TBCs are increased by 6.92 mg·cm<sup>-2</sup> and 5.83 mg·cm<sup>-2</sup>, respectively. Obviously, the nano coating can improve resistance to hot corrosion of TBC to a limited extent. The improvement of resistance to hot corrosion of nanostructured TBC might be attributed to the increase of density of the coating. On the one hand, the increased density narrows corrosion area. On the other hand, it decreases penetrations of melted salt into metal bonding layer and base, thus weakening the corrosion behavior.



Figure 4. Kinetic curve of hot corrosion on TBCs.

## 3.3. Hot corrosion mechanism

XRD analysis results of the prepared conventional and nanostructured TBCs after hot corrosion are shown in figure 5. Compared with the original coating, monoclinic phase in the conventional TBC is increased significantly, whereas tetragonal phase is decreased accordingly. Moreover, an evident Ni(Co)Cr<sub>2</sub>O<sub>4</sub> spinel diffraction peak is observed. Some new partially monoclinic phases are produced in the nanostructured TBC, but there's no spinel peak in conventional TBC.



Figure 5. XRD analysis results of TBCs surface after hot corrosion: (a) conventional TBC and (b) nanostructured TBC.

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The increase of monoclinic phase in coatings is related with the relieved corrosion of  $Y_2O_3$  in TBC. There are following reactions in melted salts [10]:

$$Na_2SO_4 \to Na_2O + SO_3 \tag{1}$$

$$Y_2O_3 + 3SO_3 \to Y_2(SO_4)_3 \tag{2}$$

As the hot corrosion goes on, content of the stabilizer  $Y_2O_3$  in  $ZrO_2$ -7wt.% $Y_2O_3$  TBCs is decreased. Some tetragonal phases are transformed to monoclinic phases, accompanied with volume expansion of the coating. As a result, tensile stress in coatings is transformed to a pressure stress, resulting in cracks on the stratified structure after hot corrosion. Some seriously damaged regions have been peeled off from the surface and cavities are produced (figure 6(a)). Since the reaction product  $Y_2(SO_4)_3$  is dissolved in melted salt, no  $Y_2(SO_4)_3$  phase is detected from XRD analysis of TBCs corrosion.

The production of Ni(Co)Cr<sub>2</sub>O<sub>4</sub> spinel structure in conventional TBC is related with corrosion of the metal bonding layer. In the melted Na<sub>2</sub>SO<sub>4</sub>+NaCl solution, since samples are isolated from the external air, solubility and diffusion velocity of oxygen in melted salt are very limited. Hence, oxygen supply mainly depends on decomposition of Na<sub>2</sub>SO<sub>4</sub>. This implies that SO<sub>3</sub> produced by the equation (1) further makes the following thermal equilibrium [10]:

$$2SO_3 \to 2S + 3O_2 \tag{3}$$

Due to high porosity in conventional TBC, corrosive media are easy to be penetrated in and make oxidization reaction with elements in the metal bonding layer:

$$2Ni(Co) + O_2 \to 2Ni(Co)O \tag{4}$$

$$4Cr + 3O_2 \rightarrow 2Cr_2O_3 \tag{5}$$

The product Ni(Co)O further reacts with Cr<sub>2</sub>O<sub>3</sub>, producing Ni(Co)Cr<sub>2</sub>O<sub>4</sub> spinel:

$$Ni(Co)O + Cr_2O_3 \to Ni(Co)Cr_2O_4 \tag{6}$$

Some precipitated Ni(Co)Cr<sub>2</sub>O<sub>4</sub> spinels are recrystalized onto local surface of TBCs (figure 6(b)).



**Figure 6.** SEM images of corrosion surface of conventional TBC: (a) Stratified structure fracture and cavities on coating surfaces and (b) Spinel structure on coating surfaces.

Nanostructured TBC surface after corrosion is shown in figure 7. Compared with the conventional TBC, the nanostructured TBC has broken stratified structure and fewer cavities, indicating the light degree of hot corrosion. Besides, no spinel structure similar with figure 6(b) is detected, indicating that the nanostructured TBC can protect the metal bonding layer during hot corrosion better. This is mainly because the high specific surface area and strong activity of nano-powder aggregate make it easier to

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be heated and melted during plasma spraying. The powder surface is melted well and deformed significantly upon impact onto the base or deposited surface. The pavement performance of nano-powder aggregate is significantly better than that of conventional powder, resulting in the lower porosity and higher density. These are conducive to decrease penetration of corrosion solution during hot corrosion, that is, reducing corrosion and protecting metal bonding layer and base effectively.



Figure 7. SEM image of nanostructured TBC after hot corrosion.

## 4. Conclusions

A conventional and nanostructured  $ZrO_2$ -7wt.% $Y_2O_3$  TBCs are prepared by plasma spraying technology. Their microstructures and resistances to hot corrosion in 75%Na<sub>2</sub>SO<sub>4</sub>+25%NaCl (mass fraction) mixed melted salt under 850 °C are compared.

(1) The conventional  $ZrO_2$ -7wt.% $Y_2O_3$  TBC shows typical lamellar stacking characteristic of plasma spraying. The nanostructured  $ZrO_2$ -7wt.% $Y_2O_3$  TBC shows a base phase which is gained from recrystallization of fully melted nano-particles and an embedding phase of partially melted nano-particles. The nanostructured  $ZrO_2$ -7wt.% $Y_2O_3$  TBC has lower porosity and higher density compared with conventional  $ZrO_2$ -7wt.% $Y_2O_3$  TBC.

(2) For both conventional and nanostructured  $ZrO_2$ -7wt.% $Y_2O_3$  TBCs, the hot corrosion failure mechanism is manifested by transformation of partial tetragonal phase into monoclinic martensite as a response to consumption of the stabilizer  $Y_2O_3$ . However, degree of hot corrosion of nanostructured TBC is generally lower compared with that of conventional TBC, indicating the better protection to metal bonding layer and base.

## 5. Acknowledgments

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