Effect of Thermal Treatment on the Grain Growth of Nanostructured YSZ Thermal Barrier Coating Prepared by Air Plasma Spraying

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Abstract: A nanostructured thermal barrier coating is prepared by air plasma spraying using the 8wt% Y2O3 partially stabilized zirconia nano powder with an average grain size of 40 nm. The microstructure and phase composition of feedstock nano powder and coating are investigated using SEM, TEM and XRD. It is found that the as-sprayed zirconia coating has an average grain size of 67 nm and mainly consists of metastable tetragonal phase, together with some monoclinic phase and tetragonal phase. Thermal treatment results show that the grains of the nanostructured coating grow slightly below 900°C, whereas over 1000°C they grow rapidly and monoclinic phase noticeably appears.

Key words: nanostructure; thermal barrier coating; air plasma spraying

Thermal barrier coatings (TBCs) have been used to provide thermal protection for hot sections in the turbine engine for several decades[1,2]. The development of high efficient engine requires the TBCs to have lower thermal conductivity and higher temperature reliability. It is reported that the development of yttria stabilized nanostructured zirconia coatings may enhance the performance of the TBCs due to its low thermal conductivity, high coefficient of thermal expansion and excellent mechanical properties of this kind of coating[3-6].

There are two great challenges in thermal spraying nanomaterials. One is how to spray the nanomaterials onto the substrate successfully. Individual nanoparticles cannot be successfully thermal sprayed because of their low mass. Thus, they do not have the inertia required to cross the streamlines in the spray jet and would be segregated to its periphery without depositing on the substrate. The other is how to retain the existing nanostructure of the feedstock. During thermal spraying process, the heat of the plasma gas will damage the existing nanostructure.

Therefore, it is very necessary to use agglomerate particles. At the same time, in order to retain the pre-existing nanostructure, a lower power should be employed. In addition, larger feeding rate is beneficial to getting nanostructured TBCs. However, the nanostructure will develop at high temperature in service, and this will damage its excellent properties, so the investigation on the stability of the nanostructured coatings at high tem-
perature becomes necessary.

The objective of this work is to investigate the thermal treatment effect on the grain growth. It will be beneficial to further understanding of the stability of the nanostructured coatings in service.

1 Experiment Procedures

An 8 wt% Y$_2$O$_3$ partially stabilized nanostructured zirconia, having grain size of 35-45 nm, is sprayed in air on the Ni-base superalloy. The substrate is prepared by mini-cutting with size of 12 mm $\times$ 15 mm $\times$ 2.5 mm. In order to enhance the adhesion of the coating, the substrate is blasted with alumina and washed with supersonic wave. During thermal spraying process, the compressed air is used to cool the surface of the coating. The thickness of the ceramic coating is appropriately 300 $\mu$m. The spraying parameters are listed in Table 1.

The thermal treatments are performed in an air open furnace at 600, 800, 900, 1000 and 1100 $^\circ$C respectively for 15h.

The microstructure analysis is performed via scanning electron microscope (SEM) (JSM-5800, JEOL), field electron scanning electron microscope (FESEM) (JSM-6301F, JEOL) and transmission electron microscope (TEM) (H-800, Hitachi).

X-ray diffraction (XRD) (D/max 2200pc, Rigaku) is employed to establish the phase composition of the feedstock and coatings.

XRD is also used to estimate the average grain size of the feedstock and coatings$^{[7,9]}$. The obtained average grain size is compared to the results of TEM.

Table 1 Plasma spray parameters for nanostructured zirconia coating

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>28</td>
</tr>
<tr>
<td>Current (A)</td>
<td>560</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>50</td>
</tr>
<tr>
<td>Primary gas (Ar) (slpm)$^*$</td>
<td>60</td>
</tr>
<tr>
<td>Secondary gas (H$_2$) (slpm)$^*$</td>
<td>1</td>
</tr>
<tr>
<td>Carrier gas (Ar) (slpm)$^*$</td>
<td>5</td>
</tr>
<tr>
<td>Spraying distance (mm)</td>
<td>80</td>
</tr>
<tr>
<td>Feed rate (g/min)$^{-1}$</td>
<td>25</td>
</tr>
</tbody>
</table>

$^*$ slpm: standard liter per minute

2 Results and Discussion

2.1 Microstructure analysis

Fig. 1 (a) presents the external morphology of the starting powder agglomerated by spray drying. It can be seen that the particles have a loose structure, which can be separated into little parts by exploding in plasma spraying. The loose structure is disadvantageous for heat transfer, so it is more likely for agglomerated particles to have less molten part than the traditional whole body, therefore the original nanostructure of some particles is retained in the thermal spraying process. Fig. 1 (b) shows the TEM image of the feedstock. It reveals that the feedstock particles are composed of fine grains with size ranging from 30 to 40 nm.

![Fig. 1 Morphology of the nanostructured feedstock particles](image)

(a) the external morphology of the agglomerate entity

(b) the TEM image of the feedstock particles

Fig. 2 (a) and (b) show the typical morphology for plasma sprayed nanostructured zirconia coating. It can be seen that there are two kinds of structure in the coating. One is the continuous molten phase, which is similar to the traditional
coatings, and the other is the loosely contacted phase that retains the nanostructure of the starting powder. During the plasma spraying, the inert plasma gas explodes the agglomerate feedstock particle, and the little particles then adhere to the previous layers. Fig. 2(b) reveals that some particles are partially melted, which have a smooth surface, and the molten parts bond each other to form dense structure.

Fig. 2 Surface morphology of the nanostructured YSZ coatings

(a) the exploding particle area

(b) the partially molten particle area

Fig. 3 presents the FESEM image of the coating surface. In Fig. 3(a), there are many little particles with the size below 100 nm. These little particles contain large volume fraction of micro pores, which can decrease the thermal conductivity of the zirconia coating and the thermal mismatch. However, the relatively loose structure let the corrosion gas pass through easily, which may induce unexpected early stage degradation. Fig. 3(b) shows a structure that is alike to the traditional coating, where large particles are packed together to form dense layers. It is noted that using this method can avoid mistaking the nanostructure sources. The nanostructure in the coating has two sources, one is the starting feedstock, and the other is the molten droplet. In the thermal spraying process the molten droplet experiences high rate quenching, but the latter will appear in the traditional TBCs. By TEM observation it cannot discern the source of nanostructure.

Fig. 3 FESEM microstructure of the as-sprayed nanostructured zirconia coating

(a) the nanostructure of the coating

(b) the microstructure similar to the traditional TBCs

2.2 Phase determination via XRD

Fig. 4 (a) and (b) show the XRD patterns of the feedstock powder and zirconia coatings. The nanostructured feedstock exhibits the presence of the monoclinic, tetragonal and/or cubic phase. It can be calculated that the feedstock powder contains about 35% monoclinic phase, and there is no metastable tetragonal t' phase in the starting powder. It should be noted that the t' phase is typical of
thermally sprayed zirconia, which is formed due to quenching of droplets at the substrate\textsuperscript{[10]}. The tetragonal \(t\) phase can be distinguished from the transformable tetragonal phase with respect to the martensitic transformation to the monoclinic phase of zirconia\textsuperscript{[10]}. During thermal spraying, there are some partially molten particles, which form the small amount of monoclinic phase. As a consequence, the coating (Fig. 4(b)) consists of three phases: metastable tetragonal, monoclinic and tetragonal phase.

2.3 Effect of thermal treatment temperature on the growth of grain size

The average grain size of the as-sprayed coating and the samples treated at 600, 800, 900, 1000 and 1100\(^\circ\)C for 15h are determined from XRD peak broadening using the Scherrer equation\textsuperscript{[7, 11]}

\[
B_p(2\theta) = \frac{0.9 \lambda}{D \cos \theta}
\]

where \(D\) is the average dimension of crystallite; \(B_p(2\theta)\) is the broadening of the diffraction line measured half maximum intensity; \(\lambda\) is the wavelength of the X-ray radiation and \(\theta\) is the Bragg angle.

The Scherrer equation is deduced under the assumption that only a small grain size is responsible for peak broadening. Strain effects, which may influence the peak broadening, are not taken into account. In this study, the instrumental broadening has been removed by measuring the coarse crystalline zirconia with a diameter larger than \(10^{-4}\) cm.

\[\text{Relative intensity} = \begin{cases} m - \text{monoclinic} \\ t - \text{metastable tetragonal} \\ c - \text{cubic} \end{cases}\]

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According to Ref. [10], (222) at \(2\theta (\sim 63^\circ)\) is the most appropriate peak for average grain size.
determination for all these samples. All the data calculated by Scherrer equation come from the peak of (222).

Table 2 lists the average grain size of as-sprayed coatings and that of the coatings after thermal treatment at different temperatures. The thermal treatment below 900°C has a little effect on the grain growth, but above 1000°C the grain growth becomes significant. During the thermal treatment, the grain boundary begin to move, and large grains are formed step by step. At lower temperature, the growth rate is very slow, so the average grain size has a little difference with that of the as-sprayed coatings. However, when the temperature is higher than 1000°C, the atom near the grain boundary moves quickly, which results in the rapid grain growth. As time go on, the grain become larger and larger, the nanostructure of the coating is damaged, and it tends to be like traditional coating structure. When the temperature is higher than 1000°C, even in a very short period of thermal treatment, the grains grow greatly. Therefore, in order to obtain high temperature stability, some phase stabilizer must be doped into the starting powder.

Table 2  The average grain size of zirconia coating for heat treating at different temperatures for 15h

<table>
<thead>
<tr>
<th>Heat treatment/°C</th>
<th>Average grain size/ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As sprayed state</td>
<td>67</td>
</tr>
<tr>
<td>600</td>
<td>72</td>
</tr>
<tr>
<td>800</td>
<td>78</td>
</tr>
<tr>
<td>900</td>
<td>90</td>
</tr>
<tr>
<td>1000</td>
<td>110</td>
</tr>
<tr>
<td>1100</td>
<td>158</td>
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</tbody>
</table>

3 Conclusion

(1) The starting powder exhibits the mixture of tetragonal phase and monoclinic phase. After thermal spraying, the coating consists of the metastable tetragonal , monoclinic and tetragonal phase.

(2) Using the FESEM technique to observe the grain size of thermal sprayed coatings with comparing the result of XRD is powerful to determine the nanostructure of the feedstock preserved in the coating.

(3) Thermal treatment below 900°C has little effect on the grain growth, but treatment above 1000°C can make the grain grow rapidly.

References


Biography:

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