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ARTICLE

Effect of Heat Treatment on $LaTi_2Al_9O_{19}$-$Zr_{0.92}Y_{0.08}O_{1.96}$ Composite Coating Powders by Air Plasma Spraying

Yang Zesheng[1], Zong Pengan[1,2], Huang Muzhang[1], Han Yi[1], Zhou Huajian[1], Feng Yingjie[1,2], Zhang Peng[1], Wan Chunlei[1]

[1] State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China; [2] College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211816, China

Abstract: The nano/submicron scaled spraying powders of lanthanum titanium aluminum oxide $LaTi_2Al_9O_{19}$ (LTA) toughened by yttria stabilized zirconia $Zr_{0.92}Y_{0.08}O_{1.96}$ (YSZ) were prepared via spray drying and then calcined at different temperatures. The effect of heat treatment on the flowability, apparent density, and morphology of the spray-dried powders was investigated. Results show that the spray-dried powders have loose structure with the size of 40~80 μm. The cohesion between LTA-YSZ particles becomes stronger after calcination. The spray-dried powders calcined at 1100 °C achieve the optimal spraying characteristics and morphology, and therefore are deposited via air plasma spraying (APS) to obtain LTA-YSZ coatings which show a good lamellar structure with defects.

Key words: spray drying; sol-gel; flowability; apparent density; coating

The thermal barrier coating (TBC) systems, mainly consisting of ceramic top coats, thermally grown oxides (TGOs), bond coats, and metallic substrates, are widely used to protect the hot components of turbine engines[1-4]. The operating temperatures of gas turbine engines are more than 1100 °C, which exceeds the upper service temperature limit of metallic hot components. TBC systems can protect those engines to work at higher temperatures, consequently improving the thermal efficiency[5-8].

The state-of-the-art ceramic top-coat material is yttria stabilized zirconia $Zr_{0.92}Y_{0.08}O_{1.96}$ (YSZ), which has low thermal conductivity, high coefficient of thermal expansion (CTE), and excellent mechanical properties. However, YSZ cannot be used at higher temperatures (above 1200 °C) due to the severe sintering behavior and phase transformation. Therefore, novel TBC materials are increasingly required for application at higher temperatures, and they should fulfil the following requirements: (1) high melting point; (2) low thermal conductivity; (3) suitable CTE; (4) no phase transformation; (5) good thermochemical stability; (6) good sintering resistance; (7) good corrosion and erosion resistance[9-14]. Some new materials have already been studied for potential TBC applications[15-17].

Recently, an alternative refractory material $LaTi_2Al_9O_{19}$ (LTA) attracts much attention as a new ceramic top-coat material[18-20]. The huge unit cell with a complex crystal structure of LTA shows great potential to achieve the low thermal conductivity. Compared with YSZ coatings, LTA coatings have lower thermal conductivity, better phase and thermochemical stability, and better sintering resistance with comparable mechanical properties and CTE. However, the fracture toughness is inferior for basically all the TBC materials.

In the past few decades, ceramic toughening is a crucial research issue[21]. Due to the transformation toughening and ferroelastic toughening mechanism, the tetragonal phase ZrO_2 is widely used to toughen many kinds of ceramics, such as alumina, mullite, and cordierites[22,23]. The tetragonal YSZ toughened LTA was studied in Ref. [19]. Compared to single LTA, LTA-YSZ ceramic composites have lower thermal conductivity, better sintering resistance, and comparable CTE, which is a very promising TBC material.

Since the flowability of nanomaterials is poor due to the irregular shape of powders caused by agglomeration, the granulation is an important method to improve the flowability

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Corresponding author: Zhang Peng, Ph. D., State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, P. R. China, Tel: 0086-10-62788645, E-mail: peng.zhang.11@hotmail.com

of ceramic powders at the submicron scale and nanoscale for a better thermal spray processes, especially for the air plasma spraying (APS) process. The suitable powders should have fine sphericity, weak agglomeration, and uniform size of 20~125 μm. The organic binder is usually added to the slurry of spray drying to connect the nanoparticles via interfacial binding, thereby forming the compact spherical powders. However, those powders cannot be fed into the plasma plume because their interfacial binding is not large enough. The powders cannot undergo the airflow and vibration during feeding, and some of them even break. Thus, the heat treatment is used to remove the organic binder and to change the connecting method. In this research, LTA-YSZ ceramic composite powders were granulated by spray drying followed by heat treatment at different temperatures. The spraying characteristics of calcined spray-dried powders were investigated, including the flowability and apparent density. LTA-YSZ composite coatings were then prepared via APS using the calcined spray-dried powders with the optimal spraying characteristics. The morphology of the as-sprayed coating was then analyzed.

1 Experiment

In this research, LTA-YSZ composite powders were synthesized via the hybrid Pechini sol-gel method[24]. In order to obtain the powders with suitable size for APS process, the as-synthesized powders were granulated by spray drying, and the related process parameters are listed in Table 1. For binder decomposition and densification, the spray-dried powders were then calcined in a furnace at different temperatures from 1000 °C to 1300 °C with an interval of 50 °C.

The flowability and apparent density of spray-dried powders were measured by the Hall flowmeter funnel method, as shown in Fig. 1[25]. The apparent density (AD_H) could be calculated by Eq.(1), as follows:

$$AD_H = M/V \quad (1)$$

where M is the mass of powders in the density cup and V is the volume of density cup (25 ± 0.03 cm^3).

The morphologies of powders and as-sprayed coatings were characterized by scanning electron microscope (SEM, XL-30 FEG, Philips). The ceramic coatings and bond coat (Ni/Al) were prepared by APS through the Model PARXAIR 3710 plasma system, and the related parameters are shown in Table 2.

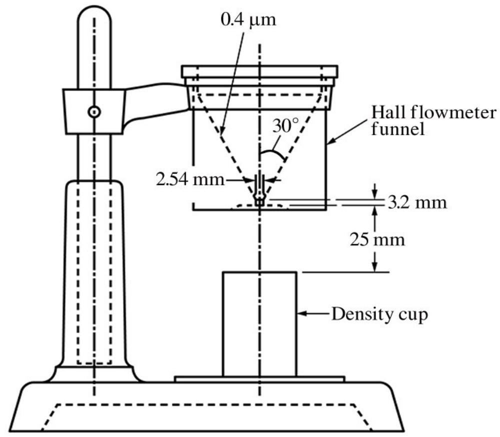

Fig.1 Schematic diagram of Hall flowmeter funnel method[25]

Table 2 APS process parameters

Coating	Current/A	Voltage/V	Spray distance/mm
Ni/Al	500	60	100
LTA-YSZ	550	70	80

2 Results and Discussion

2.1 Morphology of spray-dried powders

The morphologies of synthesized and spray-dried powders are shown in Fig. 2. It can be seen that the synthesized powders after ball milling mainly consist of submicron circular particles of approximately 200 nm in size and large irregular agglomerations, which are not suitable for APS process. The spray-dried powders have loose structure with the size of 40~80 μm, and are formed by massive small particles bound by organic binder. Fig. 2b also displays some non-sphericity powders caused by the inhomogeneous heating of fog drops and migration of small particles in fog drops during spray drying.

Table 1 Spray drying process parameters

Parameter	Value
Feed rate/mL·h^{-1}	500
Inlet temperature/°C	220
Outlet temperature/°C	120

The morphologies of spray-dried powders after heat treatment at different temperatures are shown in Fig. 3~Fig. 5. Compared with the spray-dried powders, the calcined powders are coarser due to the removal of organic binder. The nano/submicron scaled particles are connected by the grain boundary binding force instead of the interfacial binding force, which are compact and cannot break during feeding, and thereby are suitable for thermal spraying process.

It can be seen from Fig. 3 that the powder is around 60 μm in size and maintains good sphericity after heat treatment. The nano/submicron scaled particles grow into polygonal particles with the particle size of less than 1 μm (for majority particles), and start to connect with each other via grain boundary binding force.

According to Fig. 4b, the nano/submicron scaled particles after heat treatment at 1200 °C become the micron scaled ones, and most of the particles are connected to each other tightly. Ref. [19] reported that YSZ particles are much smaller than LTA particles and tend to locate between LTA particles, which is beneficial to the particle binding.

The spray-dried powders after heat treatment at 1300 °C are severely invaginated, as shown in Fig. 5a. In Fig. 5b, the nano/submicron scaled particles grow rapidly into strip shape and obvious sintering neck can be found. Some particles are severely sintered and even become polygonal plate-like shape.

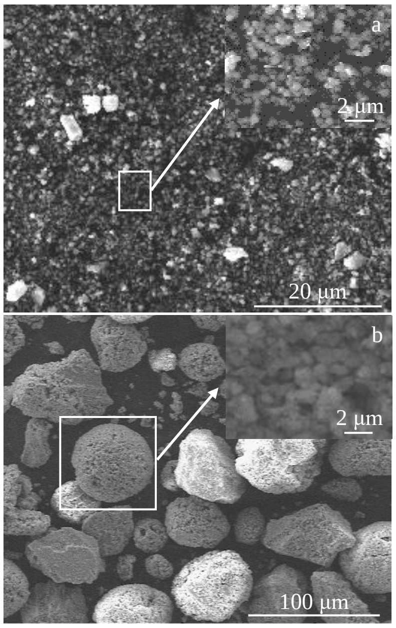

Fig.2 Morphologies of powders before (a) and after (b) spray drying

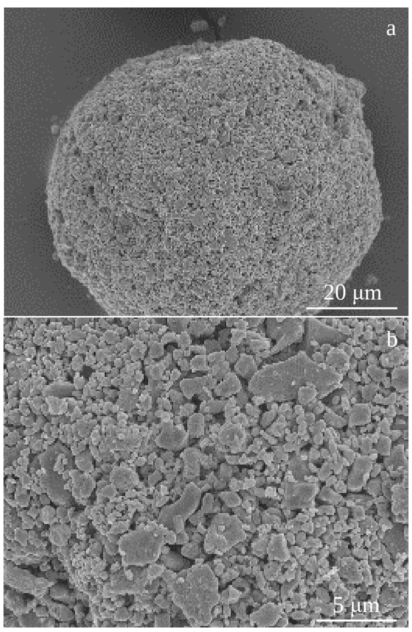

Fig.3 Appearance (a) and morphology (b) of spray-dried powders after heat treatment at 1100 °C

In brief, the heat treatment temperature should not be above 1200 °C.

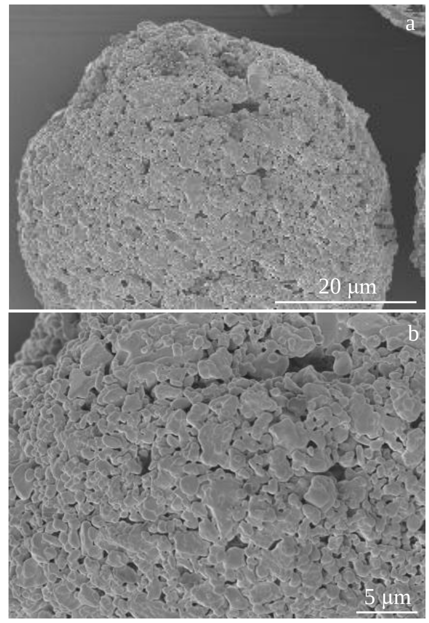

Fig.4 Appearance (a) and morphology (b) of spray-dried powders after heat treatment at 1200 °C

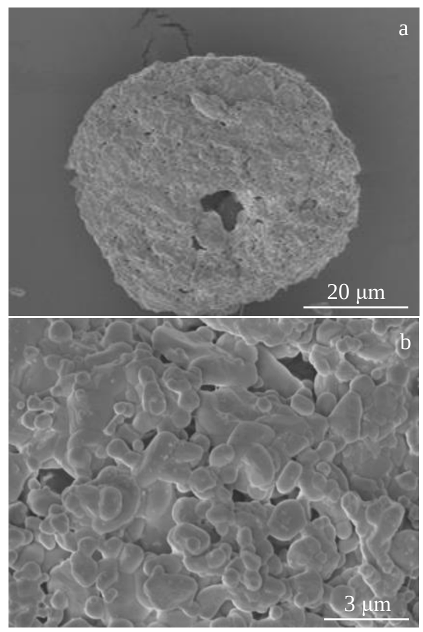

Fig.5 Appearance (a) and morphology (b) of spray-dried powders after heat treatment at 1300 °C

2.2 Spraying characteristics of spray-dried powders

The flowability and apparent density of different LTA-YSZ powders are shown in Table 3. The larger the flowability value, the worse the flowability performance. The flowability of synthesized LTA-YSZ powders cannot be measured due to the small particle size and irregular geometry. The smaller the particle size, the larger the specific surface area, consequently the larger the frictional force, and the more inferior the flowability of powders. The geometry also strongly affects the rolling movement of flowing powders, thereby influencing the flowability. LTA-YSZ powders obtained by sol-gel method are severely agglomerated, leading to irregular geometry of powders which produces large frictional force and hinders the rolling movement of powders, therefore decreasing the flowability of LTA-YSZ powders.

Fig. 6 displays the influence of heat treatment temperatures on the flowability of LTA-YSZ powders. The flowability of powders is enhanced after spray drying because of the improved geometry. Compared with spray-dried powders, the

Table 3 Spraying characteristics of LTA-YSZ powders

Specimen	Calcination temperature/°C	Flowability/ s·(50 g)$^{-1}$	Apparent density/ g·cm^{-3}
Spray-dried powder	-	50.76	1.30
Spray-dried powder after heat treatment	1000	60.83	1.31
	1050	61.25	1.28
	1100	63.68	1.25
	1150	65.47	1.23
	1200	68.25	1.22
	1250	60.11	1.48
	1300	55.37	1.63

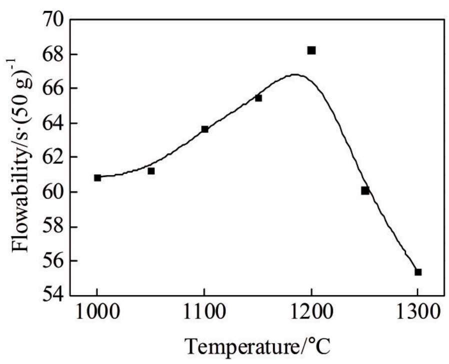

Fig.6 Influence of heat treatment temperatures on flowability of LTA-YSZ powders

flowability performance of heat-treated powders is all deteriorated. The effect of organic binder removal to reduce the surface smoothness of granulated powders after heat treatment at 1000~1200 °C is the main cause for decreasing the flowability. The further densification of granulated powders after heat treatment at 1200~1300 °C may be the main cause for inferior flowability of heat-treated powders, compared with that of spray-dried powders.

The apparent density of LTA-YSZ powders is decreased gradually after heat treatment at 1000~1200 °C, and then increased rapidly after heat treatment at 1200~1300 °C, as shown in Fig.7. The apparent density of powders is decided by several factors: geometry, size, density, and the stacking methods. After heat treatment at 1000~1200 °C, LTA-YSZ powders maintain the good geometry, but do not contract obviously. The powders do not connect tightly, so the main stacking method is bridging, and consequently the apparent density is decreased. After heat treatment at 1200~1300 °C, the powders contract severely, which increases the single powder density. As the contraction rate of powders is not the same, the main stacking method changes to filling instead of bridging, and thus the apparent density is increased rapidly. According to above analyses, LTA-YSZ powders calcined at 1100 °C have the optimal sphericity and superior spraying characteristics, which is beneficial to further thermal spraying.

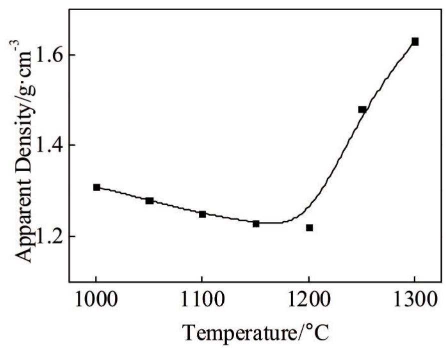

Fig.7 Influence of heat treatment temperatures on apparent density of LTA-YSZ powders

Therefore, the heat treatment temperature for spray-dried LTA-YSZ powders should be 1100 °C.

2.3 Morphology of LTA-YSZ coatings

Fig. 8a displays the cross-section morphology of LTA-YSZ coatings, which shows a typical TBC cross-section morphology, including a substrate, bond coat, and TBC. TGO is discontinuous and cannot be clearly seen in spray-dried LTA-YSZ coatings. Many cavities can be observed on ceramic

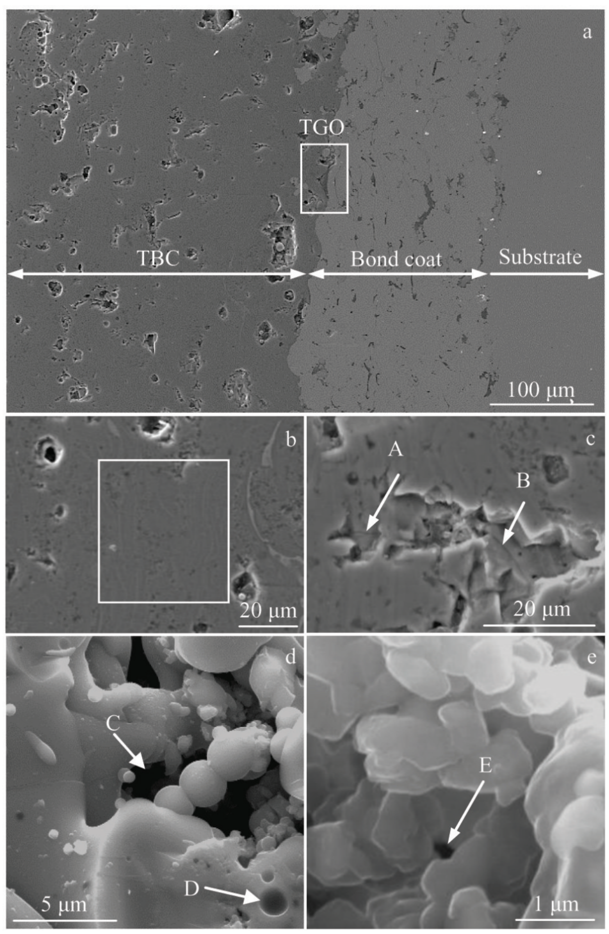

Fig.8 Cross-section morphology of spray-dried LTA-YSZ coating (a); lamellar structure (b), defects in cross-section (c), and defects on surface (d, e) of APS coating

top coat, whereas the lamellar structure cannot be clearly observed. The lamellar structure is clearly shown in the rectangle area and other areas in Fig. 8b. The defects of the crack A vertical to the ceramic coating and the small gap B between two lamellar layers are shown in Fig. 8c. Fig. 8d and 8e show the open pores on the unpolished surface, including the cavity C, void D, and interspace E of the LTA-YSZ coatings.

3 Conclusions

1) The lanthanum titanium aluminum oxide $LaTi_2Al_9O_{19}$ (LTA) toughened by yttria stabilized zirconia $Zr_{0.92}Y_{0.08}O_{1.96}$ (YSZ) particles is granulated by spray drying. The spray-dried powders are calcined at different temperatures to remove the organic binder and become densified.

2) The loose spray-dried powders become more compact after heat treatment, and the particles connect to each other more firmly due to the grain boundary binding.

3) LTA-YSZ powders calcined at 1100 °C have the optimal sphericity and superior spray characteristics, which are beneficial to further thermal spray. The air plasma sprayed LTA-YSZ coatings show the lamellar structure with defects of cracks, gaps, cavities, voids, and interspaces.

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热处理对大气等离子喷涂 $LaTi_2Al_9O_{19}$-$Zr_{0.92}Y_{0.08}O_{1.96}$ 复合涂层粉末的影响

杨泽生[1]，宗鹏安[1,2]，黄慕章[1]，韩　毅[1]，周华建[1]，冯英杰[1,2]，张　鹏[1]，万春磊[1]

(1. 清华大学 新型陶瓷与精细工艺国家重点实验室，北京 100084)

(2. 南京工业大学 材料科学与工程学院，江苏 南京 211816)

摘　要：将纳米/亚微米级 $Zr_{0.92}Y_{0.08}O_{1.96}$（YSZ）增韧稀土复合氧化物 $LaTi_2Al_9O_{19}$（LTA）颗粒通过喷雾干燥制备出喷涂粉体，采用不同温度对其进行煅烧，并研究不同温度的热处理对喷雾干燥粉体的流动性、松装密度和形貌的影响。结果表明：未经热处理的喷雾干燥粉体呈现出疏松结构，粒径为40~80 μm。经过热处理后，LTA-YSZ颗粒之间的结合更加紧密，在1100 ℃下煅烧的粉体具有最好的喷雾特性和形貌。通过等离子喷涂进行沉积制备的LTA-YSZ涂层呈现良好的层状结构，并伴有缺陷。

关键词：喷雾干燥；溶胶凝胶法；流动性；松装密度；涂层

作者简介：杨泽生，男，1996年生，博士生，清华大学新型陶瓷与精细工艺国家重点实验室，北京 100084，E-mail：yzs18@mails.tsinghua.edu.cn