Rare Metal Materials and Engineering
Volume 50, Issue 8, August 2021
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Cheng Taotao, Wang Zhiping, Dai Shijie, et al. Influence of SiC Whiskers on Microstructure of APS YSZ Coating[J]. Rare Metal Materials and Engineering, 2021, 50(08): 2700-2707.

ARTICLE

Influence of SiC Whiskers on Microstructure of APS YSZ Coating

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Abstract: Agglomerated YSZ (Y_2O_3 partially stabilized ZrO_2) particles with 0wt%, 1wt%, 2wt% and 3wt% of whiskers (named as 0#, 1#, 2# and 3# powders, respectively) were prepared by spray granulation technology. Four groups of coatings (0#, 1#, 2# and 3# coating) were prepared by APS (atmospheric plasma spraying). The dispersion and quantitative characterization of SiC whiskers, morphology of agglomerated particles and microstructure of the coatings were studied by SEM (scanning electron microscopy) and light-optical microscopy, and the forming process of the coating containing SiC whiskers was analyzed. The result shows that as the stirring time increases to 5 h, the whiskers show better dispersion and the corresponding area percentage of whiskers of the specimen is 11.03%. The particles containing whiskers are mainly "droplet shaped" and "spindle shaped", and the percentage of these two streamlined particles in 1#, 2# and 3# powders is 16.5%, 22.7% and 39.3%, respectively. Due to the obstructing effect of non-horizontal state whiskers on impacting and spreading process of unmelted raw powders, the porosity increases as the whiskers content increases. The porosity of 0# coating is 3.89%, while the porosity of 1#, 2# and 3# coatings is 3.15, 4.17 and 7.52 times larger than that of 0# coating, respectively.

Key words: SiC whiskers; APS; YSZ coating; microstructure

Application of thermal barrier coating is a practical way to increase the servicing temperature of aero-engines[1-3]. Thermal barrier coating is generally a complex multilayered composite system, including nickel-based superalloy substrate, superalloy transition layer (BC layer), thermal growth oxide layer (TGO layer), and YSZ ceramic coating[4-6]. The multilayered metal/ceramic coating systems and work environment may lead to failures of the coating system in service. The most significant reason is the fatigue cracking of ceramic coating during thermal cycling[7-10]; it leads to direct failure of the thermal barrier coating system and results in an unreliable life, and has become an urgent problem in the application of thermal barrier coating.

Up till now, the thermal cycling life has been improved mainly by optimizing the microstructure of YSZ coating. Early researchers used electron beam physical vapor deposition (EB-PVD) to prepare ceramic coating with "columnar" structure, which exhibits a good thermal cycling life via the effective release of residual stress during thermal cycling through numerous longitudinal micro-cracks between columns[11]. The suspension plasma spraying (SPS) and plasma spray physics vapor deposition (PS-PVD) techniques proposed in recent 10 years can prepare ceramic coating with similar "columnar" structure, which can improve the thermal cycling life of thermal barrier coating to various levels[12,13]. In the past 5 years, a method to release the residual stress of YSZ coating by longitudinal crack was proposed[14]. A surface heating method was used to generate a longitudinal crack perpendicular to the direction of the coating. The residual stress in the thermal cycling process can be released through the longitudinal crack, thus improving the thermal cycling life. However, the above methods confront several obstacles, including high cost, difficult preparation, low production efficiency and poor performance stability. Therefore, researchers still explore new micro-structural optimization methods to improve the thermal cycling life of YSZ coating.

Received date: August 25, 2020
Foundation item: National Natural Science Foundation of China (51501222)
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The researches[15-17] in the field of ceramic sintering showed that the fracture toughness of ceramic block materials prepared by sintering method can be significantly improved by whiskers (nanometer sized short fibers growing from single crystal) toughening technology. The toughening mechanism mainly includes crack deflection effect, micro-crack effect, whiskers pulling effect and crack bridging effect. The general process of ceramic sintering is as follows: first the blank is molded by physical or chemical methods and then processed at high temperature to obtain the ceramic material. Similarly, the process of APS ceramic coating is as follows: the spraying powders prepared by granulation are heated to molten or semi-molten state by plasma arc, and then the powders are deposited on the substrate to obtain ceramic coating. Based on the similarity between spraying and sintering, whisker toughening technology in ceramic sintering process is applied to the process of APS.

In thermal spray field, researchers[18,19] have demonstrated that SiC whiskers in coating can increase the porosity, and improve the thermal cycling performance. However, the porosity increase mechanism and the law of SiC whisker on the coating deposition process have not been deeply analyzed. In this study, the whisker dispersion process and quantitative characterization method were studied, and the law of different whisker contents on the microstructure of YSZ coating was analyzed.

1 Experiment

SiC whiskers were highly oriented short fiber mono-crystalline materials with diameters ranging from nanometers to micrometers, characterized with high chemical impurity, no grain boundary, fewer defects in crystal structure, and uniform composition of crystal phase. Therefore, the strength is close to the binding force between atoms, so SiC whiskers possess high specific strength and specific elastic modulus.

SiC whiskers were manufactured by Qinhuangdao ENO High-Tech Material Development Co., Ltd, and the whiskers line-up rate was 80%. Fig. 1 shows the morphologies of SiC whiskers before dispersion. It can be seen from Fig. 1a (500× magnified) that the whiskers are twined together in batt state, and Fig. 1b (6000× magnified) shows that in addition to fine needle-shaped SiC whiskers, there are also some granular and short bar state SiC whiskers.

The microscopic morphology of YSZ raw powders (Shanghai Shuitian Material Science and Technology Co., Ltd) is shown in Fig. 2. The powders were white, with purity of 99.9%, and particle size range of 1~10 μm.

The dispersants and adhesives used in the spray granulation process are shown in Table 1.

SiC whiskers were dispersed mechanically, followed by stirring with dispersants. Spray granulator was used to aggregate YSZ powders with different whisker contents. The coating was prepared by APS. The microstructures of agglomerated powders and coating were characterized and analyzed by SEM and light-optical microscopy.

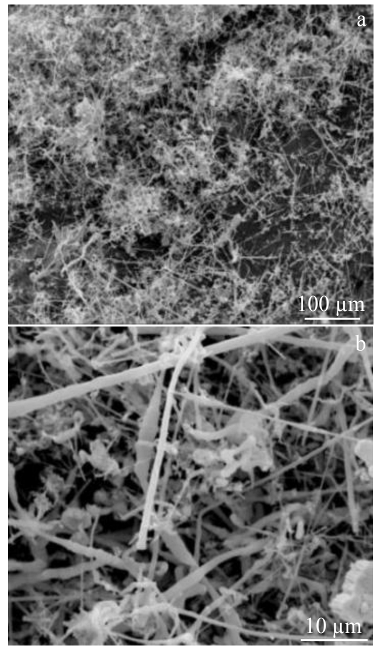

Fig.1 SiC whiskers before dispersion magnified at 500× (a) and 6000× (b)

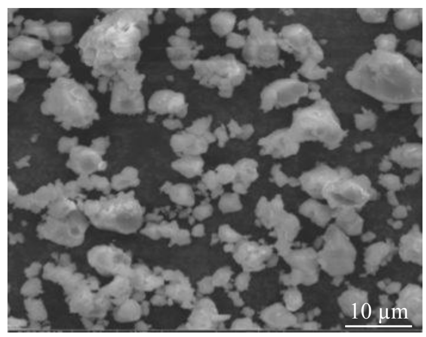

Fig.2 YSZ raw powders before granulation

2 Results and Discussion

2.1 Dispersion technology and quantitative characterization of SiC whiskers

Main components of agglomerated powders are listed in

Table 1 Dispersants and adhesives

Material	Manufacturer	Purity	Function
Sodium hexametaphosphate	Shandong Yousuo Chemical Technology Co., Ltd	Analytically pure	Dispersants
Polyethylene glycol (PEG)	Wuxi Yatai United Chemical Co., Ltd	Analytically pure	Dispersants
Polyvinyl alcohol (PVA)	Shanghai Yingjia Industrial Development Co., Ltd	≥97.0%	Adhesives

Table 2. The content of SiC whiskers (SiC_w) in the agglomerated powders is 0wt%, 1wt%, 2wt% and 3wt%, labeled as 0#, 1#, 2# and 3# powders, respectively.

2.1.1 Dispersion of SiC whiskers

It can be seen from Table 2 that SiC whisker content in 3# powders is the largest. Therefore, 3# powders are chosen for the dispersion process analysis. In the dispersion process, the solid content of spray granulation slurry is set to 33.33%. The total mass of raw materials is 200 g, including 194 g raw YSZ powders and 6 g SiC whiskers. In addition to 400 g distilled water, 6 g sodium hexametaphosphate and 10 mL PEG are required. Ambient temperature is 80 °C and the stirring speed is 600 r/min. Whiskers are extracted by dipping the conductive tape into the mixed solution after 1, 3 and 5 h, and the dispersion results are shown in Fig.3.

Fig.3 illustrates that the dispersion degree of SiC whiskers increases gradually with prolonging stirring time. As the stirring time increases to 5 h, the whiskers have a better dispersion degree. Considering the test efficiency, the stirring time is set to 5 h.

2.1.2 Quantitative characterization of dispersion degree

The dispersion degree of SiC whiskers, which represents the dispersion and uniformity of whiskers in the mixed solution, directly affects the distribution of whiskers in agglomerated particles, and determines the microstructure of the coating containing whiskers. Therefore, it is of great significance to quantify the dispersion degree of SiC whiskers.

The quantitative characterization method of dispersion degree is divided into the following three steps. Firstly, during the whiskers dispersion process and at the corresponding 1, 3 and 5 h time nodes, the conductive tapes are immersed into the dispersion solution with tweezers, kept for 5 s, and then taken out. Secondly, for the samples prepared above, SEM is used to observe them and images of 3 fields at the same magnification 500× are randomly collected. Lastly, image analysis software is employed to measure the percentage of whiskers in each field, and the average value is calculated.

Table 2 Components of agglomerated powders (wt%)

Powder	YSZ	SiC_w
0#	100	0
1#	99	1
2#	98	2
3#	97	3

The average area percentages of whisker content obtained by the above method are used to quantitatively characterize the degree of whisker dispersion. Table 3 shows the area percentage of whisker with different dispersion time measured by the above method. It can be seen that as the stirring time increases to 5 h, the average percentage of whiskers is 11.03%. The average value of whisker content directly reflects the degree of whisker dispersion, i. e. the larger the average value, the worse the dispersion, and vice versa.

2.2 Preparation and microstructure of agglomerated powders

The solid content is set to be 33.33%, inlet temperature is 310 °C, and outlet temperature is 110 °C. YSZ agglomerated powders containing 0wt%, 1wt%, 2wt% and 3wt% SiC whiskers (marked as 0#, 1#, 2# and 3# powders, respectively) are prepared by spray granulator. The contents of each component in the slurry are shown in Table 4.

After vacuum densification at 1000 °C for 2 h, the micromorphology images of the four powders are shown in Fig. 4, which illustrate that the agglomeration effect of the four powders is good, and the addition of whiskers has a great influence on the morphology of the agglomerated particles. Fig. 4a shows that 0# powders without whiskers exhibit the best sphericity, with only globular agglomerated particles. After adding SiC whiskers in 1#, 2# and 3# powders (Fig.4b~4d), besides globular agglomerated particles, the powders also contain agglomerated particles which are "droplet shaped" (Fig.4e) and "spindle shaped" (Fig.4f).

Fig. 5 shows the cross-section morphologies of the three typical morphology particles above. It can be seen that the agglomerated spherical, "droplet" and "spindle" particles are all in solid state with high density. In the spray granulation process, fog droplets without whiskers become spherical due to surface tension. Meanwhile, due to the large surface area of the droplet, the water rapidly evaporates and dries, and finally shrinks into compact and dry spherical particles (Fig. 5a). However, for fog droplets containing SiC whiskers, raw powders in the droplet will shrink and dry around the whisker.

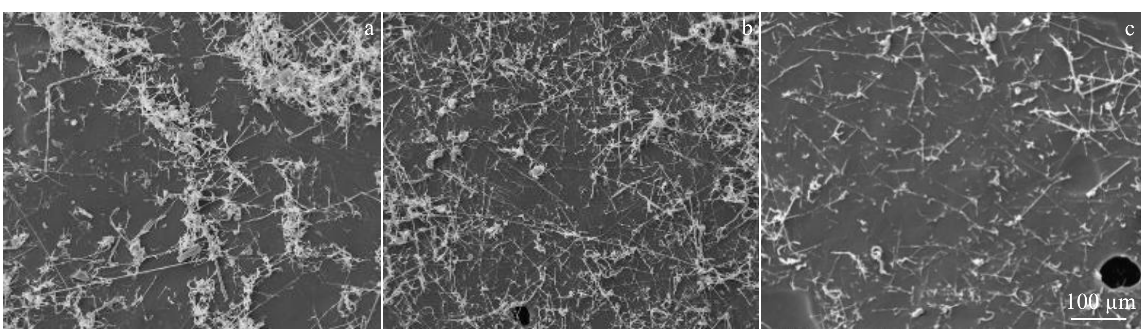

Fig.3 Dispersed SiC whiskers with stirring time of 1 h (a), 3 h (b), and 5 h (c)

Table 3 Area percentage of SiC whisker content with different dispersion time (%)

Dispersion time/h	Viewing field			
	1	2	3	Average value
1	28.25	36.15	35.62	33.34
3	24.83	18.96	20.16	21.32
5	8.59	13.24	11.25	11.03

Table 4 Contents of main components in slurry

Powder	YSZ/ g	SiC_w/ g	Distilled water/g	Sodium hexameta-phosphate/g	PEG/ mL
0#	200	0	400	0	10
1#	198	2	400	2	10
2#	196	4	400	4	10
3#	194	6	400	6	10

If the whisker is not completely surrounded with raw powders in the droplet, the "droplet shaped" particle is obtained after shrinking and drying (Fig. 5b), and if the whisker is evenly surrounded with raw powders in the droplet, the "spindle shaped" particle can be obtained (Fig.5c).

With increasing the whisker content, the proportion of "droplet shaped" and "spindle shaped" agglomerated particles in the powders gradually increases. For 1#, 2# and 3# powders, three fields are randomly selected, and the ratio of "droplet shaped" and "spindle shaped" agglomerated particles to the total number of particles is calculated in each field, i.e., their average proportion is 16.5%, 22.7% and 39.3%, respectively.

2.3 Micro-morphology and microstructure of coating

2.3.1 Micro-morphology of coating

The micro-morphology of the four groups of coating is shown in Fig. 6. The coating of 0# does not contain SiC whiskers, and the surface is relatively dense, and presents typical spreading morphology of thermal spraying coating, which shows that the morphology of all regions is uniform. When the whisker content gradually increases, different degrees of "rough area" appear in 1#, 2# and 3# coating. Among them, rough area percentage of 3# coating ranks the first, followed by 2# coating and 1# coating.

Fig. 7 demonstrates high-magnification images of the surface micro-morphology of 3# coating. The surface morphology in Fig. 7a is characterized by spreading morphology and rough area, while Fig. 7b shows that some SiC whiskers are found in the rough area.

2.3.2 Section microstructure of coating

The section morphologies of the four groups of coating are shown in Fig.8. The hole size in 0# coating without SiC whiskers is smaller, while that in 1#, 2# and 3# coatings containing whiskers is larger. As can be seen from Fig. 8b~8d, the microstructures of the coating containing whiskers consist of dense region and large-size hole regions. Fig. 8e illustrates that SiC whiskers acting as reinforcing bars are found in large-size hole region, similar to those in reinforced concrete structures.

Porosity of 0#,1#, 2# and 3# coatings is measured by image analysis software, for which five fields are measured and the average values are taken. The results are shown in Table 5, which shows that the porosity of the coating increases significantly with the increase of whiskers content.

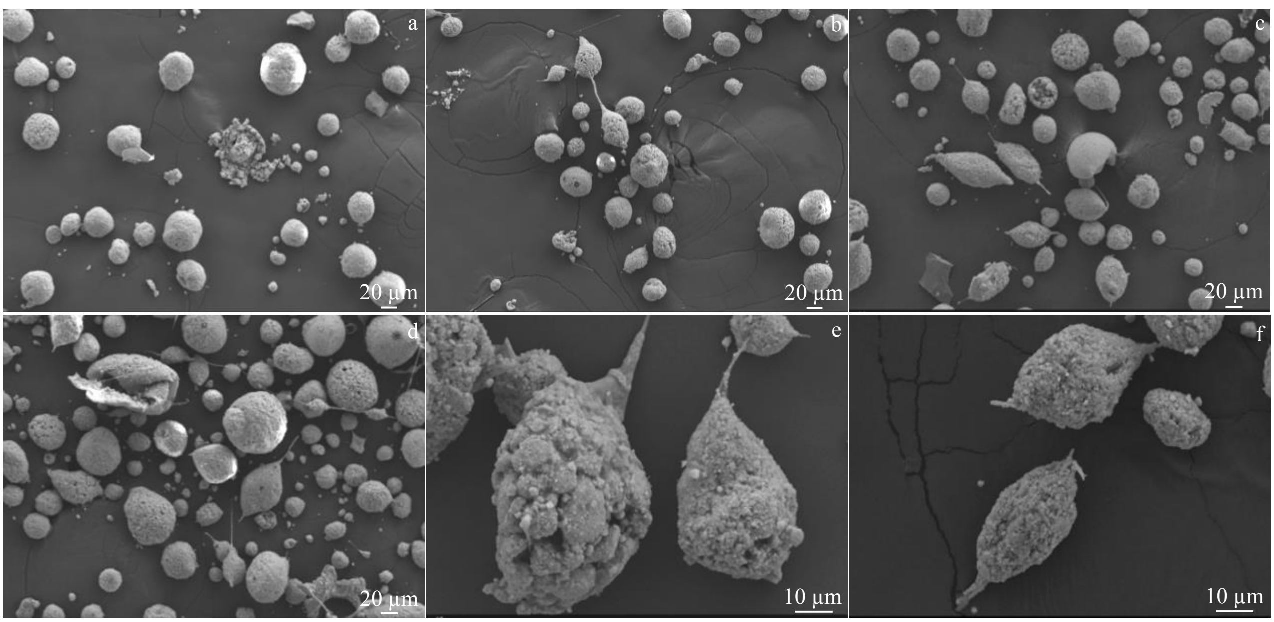

Fig.4 Micro-morphologies of agglomerated powders after densification: (a) 0#, (b) 1#, (c) 2#, (d) 3#, (e) "droplet shaped" particles, and (f) "spindle shaped" particles

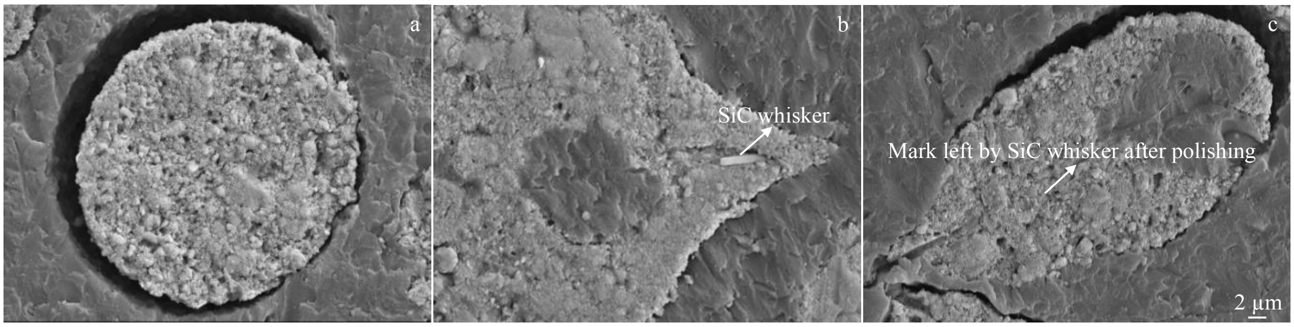

Fig.5 Cross section morphologies of agglomerated powders: (a) spherical particle without whiskers, (b) "droplet shaped" particle, and (c) "spindle shaped" particle

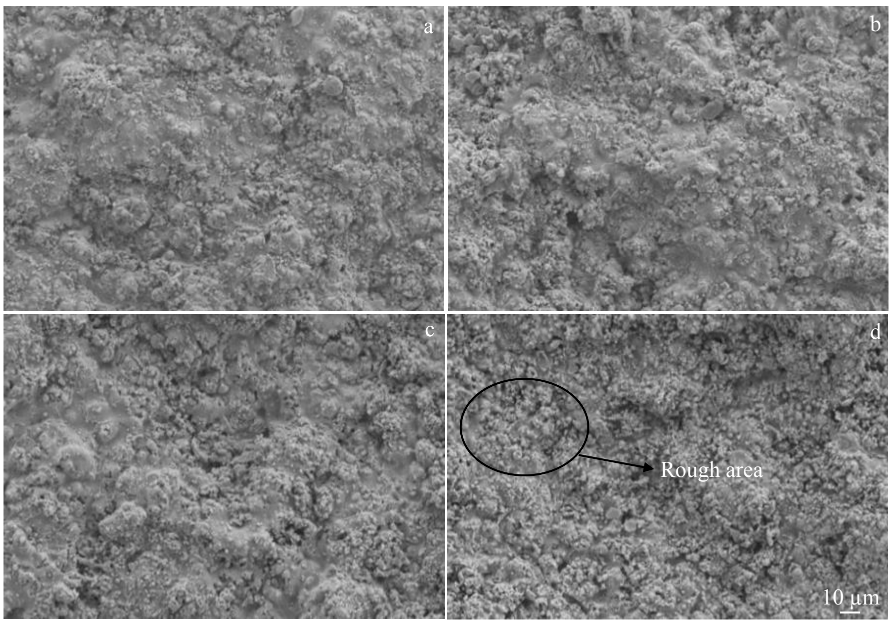

Fig.6 Micro-morphologies of coatings with different SiC whisker contents: (a) 0#; (b) 1#; (c) 2#; (d) 3#

2.4 Effect of whiskers on microstructure of coating

2.4.1 Impacting and spreading morphology of agglomerated particles

Fig. 9 shows the spreading morphology of agglomerated particles on substrate. As can be seen from Fig.9a, the agglomerated YSZ particles without whiskers spread well on substrate. The flying time of particles in plasma arc is at the millisecond level[20], while unavoidably, some raw powders that are not completely melted remain in the spread YSZ sheet, and those powders are uniformly distributed in molten

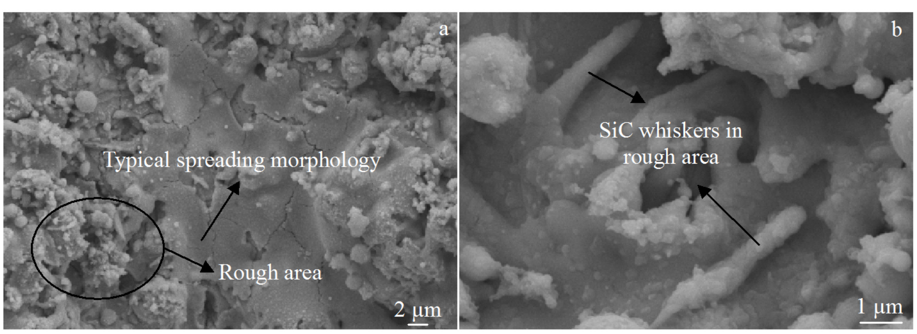

Fig.7 Surface morphologies of 3# coating: (a) spreading morphology and rough area at 2000× and (b) rough area at 10000×

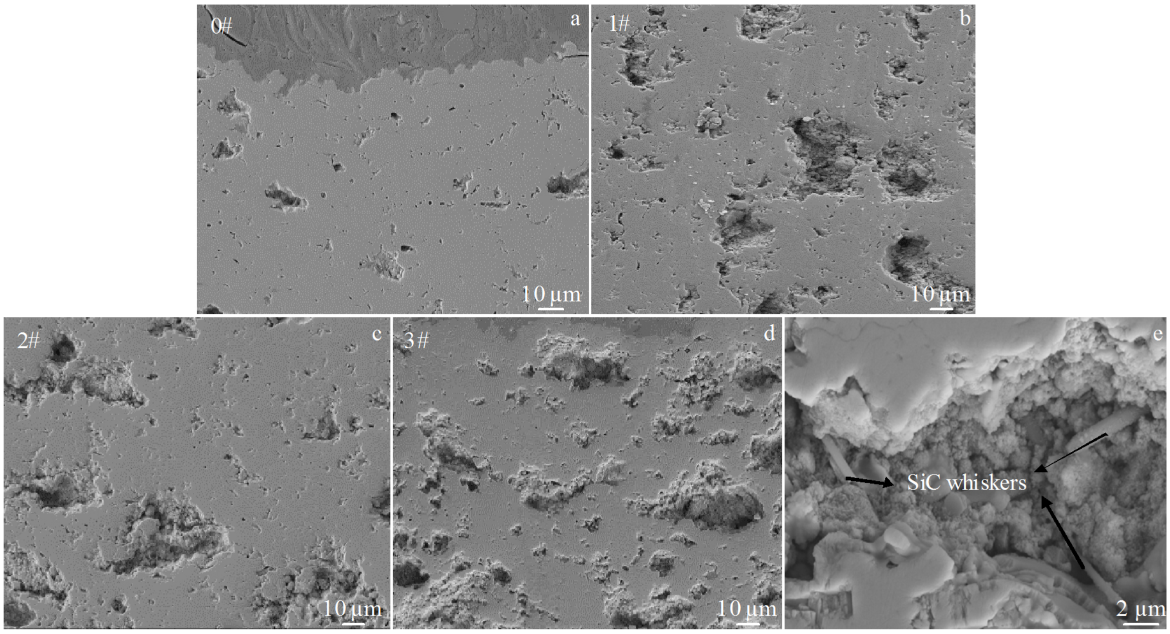

Fig.8 Section microstructures of coatings (a~d) and large-size hole region (e)

Table 5 Porosity of coatings (%)

Coating	0#	1#	2#	3#
Porosity	3.89	12.34	15.74	29.41

sheets. Fig.9b and 9c demonstrate agglomerated YSZ particles containing SiC whiskers, and the spreading morphology can be divided into two types, including horizontal whisker sheet and non-horizontal whisker sheet according to whether the whisker is distributed horizontally in molten sheet. As can be seen from Fig. 9b, when the whisker is in a horizontal state, YSZ sheet is in a good spreading state, and some raw powders which are not completely melted are distributed evenly in the sheet. While in Fig. 9c, when the whisker is in a non-horizontal state, the spreading condition of YSZ sheet is comparatively worse. Because when YSZ particles impact substrate and if the whisker and the substrate are not parallel, it will inevitably restrict the subsequent impacting of the raw

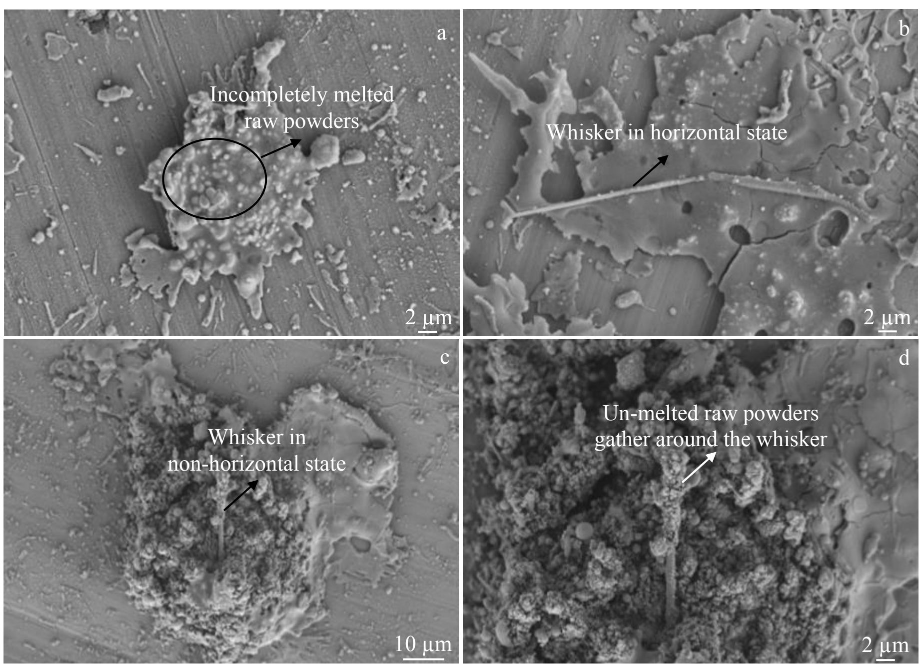

Fig.9 Spreading morphologies of YSZ particles on substrate: (a) sheet without whisker, (b) sheet contains horizontal whisker, and (c, d) sheet contains non-horizontal whisker

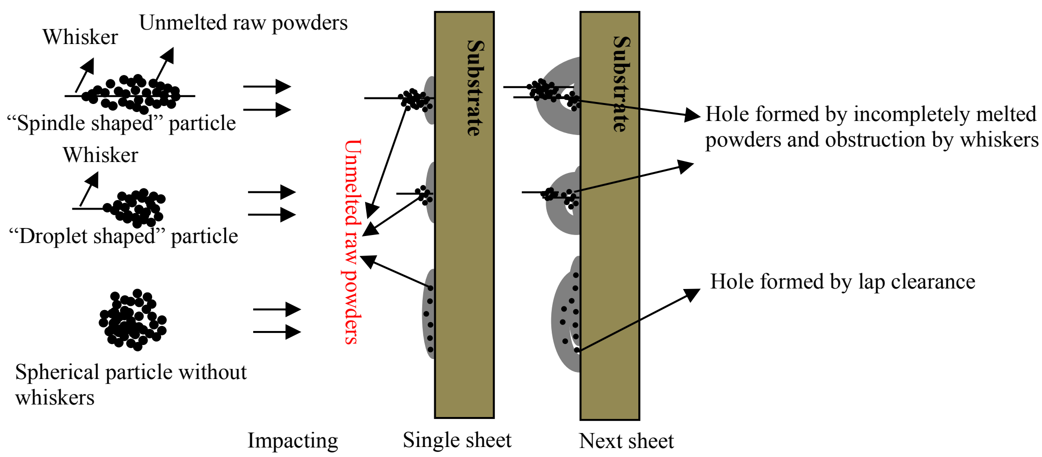

Fig.10 Impacting and spreading model of agglomerated particles

powders surrounding the whisker once the strong whisker contacts the substrate. This can lower impact effectiveness of these raw powders on substrate and they cannot be completely dispersed, thus finally gathering around the whisker, as shown in Fig.9d.

2.4.2 Impacting and spreading model of agglomerated particles

Fig. 10 shows impacting and spreading model of agglomerated particles on substrate. When particles contain whiskers, both "droplets shaped" and "spindle shaped" agglomerated particles are impacting and spreading sheet by sheet, and the non-horizontal state whiskers will restrict the subsequent impacting and spreading process of the raw powders because of the high strength property of whiskers. This can cause raw powders to gather together, thus forming large-size hole and high porosity easily, as shown in Fig. 8e. For agglomerated YSZ particles without SiC whiskers, incompletely molten raw powders can be fully impacted and evenly spread on substrate, and holes in the coating are mainly formed by lap clearance among the sheets, thus resulting in smaller holes and lower porosity in coating, as shown in Fig.8a.

3 Conclusions

1) The dispersion degree of SiC whiskers gradually improves with prolonging the stirring time. As the stirring time increases to 5 h, whiskers show a better dispersion degree, and the corresponding whiskers' area percentage is 11.03%.

2) The agglomerated particles containing SiC whiskers are "droplet shaped" and "spindle shaped". The percentage of these two agglomerated particles in 1#, 2# and 3# agglomerated powders is 16.5%, 22.7% and 39.3%, respectively.

3) The obstructing effect of non-horizontal state whiskers on impacting and spreading process of raw powders causes these powders to gather together, and thus large-size holes and high porosity form easily. The porosity increases as the whisker content increases. 0# coating without whiskers is relatively dense, with the porosity of only 3.89%, while the porosity in 1#, 2# and 3# coatings is 3.15, 4.17 and 7.52 times larger than that of 0# coating, respectively.

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SiC晶须对等离子喷涂YSZ涂层显微结构的影响

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摘　要：为了研究SiC晶须对等离子喷涂YSZ（Y_2O_3部分稳定的ZrO_2）涂层显微结构的影响规律，采用喷雾造粒技术制备了晶须含量分别为0%、1%、2%和3%（质量分数）的团聚YSZ颗粒（0#、1#、2#和3#粉末），利用等离子喷涂技术（APS）分别制备了0#、1#、2#和3#等4组涂层。利用扫描电镜（SEM）及金相显微镜等测试分析设备研究SiC晶须分散工艺和定量表征方法，以及团聚颗粒的形态和涂层的显微结构，并分析了含晶须涂层的成型过程。结果表明：机械搅拌时间增加至5 h时，晶须具有较好的分散程度，对应的晶须面积分数为11.03%。含晶须的团聚颗粒主要呈“水滴状”和“纺锤状”，1#、2#和3#粉末中“水滴状”和“纺锤状”团聚颗粒的数量比例分别为16.5%，22.7%和39.3%。由于非水平态晶须对颗粒中未熔融原粉末在冲击和铺展过程的阻碍作用，涂层的孔隙率随着晶须含量的增加而增加，0#涂层的孔隙率为3.89%，1#、2#和3#涂层的孔隙率分别是0#涂层的3.15倍、4.17倍和7.52倍。
关键词：SiC晶须；等离子喷涂；YSZ涂层；显微结构

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