Rare Metal Materials and Engineering
Volume 52, Issue 2, February 2023
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Zhang Zhao, Yin Shuo, Zhu Lin. Synthesis Mechanism of Reactive Plasma Sprayed Al-Fe_2O_3 Composites Under Atmosphere and Low-Pressure Ambient Conditions[J]. Rare Metal Materials and Engineering, 2023, 52(02): 486-492.

ARTICLE

Synthesis Mechanism of Reactive Plasma Sprayed Al-Fe_2O_3 Composites Under Atmosphere and Low-Pressure Ambient Conditions

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Abstract: Reactive plasma spray (RPS) technique is frequently used to prepare high-performance coating materials with different application requirements. Based on the classical thermite reaction, the Al-Fe_2O_3 coatings were fabricated by RPS under atmosphere and low-pressure ambient. The phase compositions and microstructures of the obtained coatings were characterized by XRD, SEM and EDS. Moreover, the reaction mechanisms of thermite reaction of Al and Fe_2O_3 in sintering and RPS process were elucidated. The DTA analysis results indicate that the main sintering products are Fe, Al_2O_3 and FeAl phases under prolongated reaction condition with Ar gas protetion. However, low oxygen partial pressure leads to the formation of $FeAl_2O_4$ hercynite phase as an intermediate product during spraying. In atmosphere-reactive plasma spraying (A-RPS), such phase can be retained in the final coating under extremely fast cooling rate. Furthermore, it can also be continuously reduced to FeAl phase in the low pressure Ar-H_2 ambience due to the deoxidation effect and long in-flight distance of plasma jet.

Key words: reactive plasma spray; low pressure; FeAl; thermite reaction; coating

Reactive plasma spray (RPS) technology, also called plasma spray synthesis[1], has drawn a wide research interest in recent years. This technology can be used to synthesize metastable and/or intermediate phases due to its high deposition rate, flexible process, high pure coating product, low cost and good adherence with substrate, etc[2–6]. In principle, RPS process combines conventional plasma spraying and self-propagation high-temperature synthesis (SHS) [7] to in situ synthesize mono- or multi-phase coating through chemical reactions between the selective raw powder mixture[8] and surrounding reactive gases[9] in the plasma jet. Besides, the ambiance condition also has a great influence on the final coating product, which leads to emergence of two different types of RPS technologies, i. e. atmospheric-reactive plasma spray (A-RPS) and low pressure-reactive plasma spray (LP-RPS). A large amount of novel coating materials have been successfully obtained by these technologies and dedicated to different application requirements, thanks to their thermal and environmental protective ability[10–11], electrical and mag-netic performances[12–13], super-hardness, wear and corrosion resistances[14–16], etc.

FeAl intermetallic coating is a desirable structural coating due to its relatively low cost and excellent high-temperatures properties, such as high corrosion resistance, excellent oxidizing resistance and mechanical properties[17]. However, the fabrication of uniform FeAl coating is not well established. It is reported[18] that the reactions between metals are generally less exothermal than that between metals and non-metals or oxides, resulting in relatively low adiabatic temperature (below FeAl melting point). Thus, self-sustaining reaction is not readily feasible if Fe and Al particles are used as raw materials for spraying directly.

Received date: May 23, 2022
Foundation item: Fundamental Research Program of Shanxi Province (202103021223193)
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It is well-known that the Al-Fe_2O_3 reaction as a simple and classical thermite system has been deeply investigated by different processing routes. And it is also very important in the synthesis of composites[19] for the wide-ranging applications[20–21]. Taking advantages of the strong redox reaction between Al and Fe_2O_3 can realize the formation of dense FeAl coating. Meanwhile, the reductive effect of H_2 or Ar-H_2 atmosphere in the plasma jet can contribute to fabrication of spinel or intermetallic phases. However, the formation mechanism of Al-Fe_2O_3 coatings fabricated by RPS technology is uncertain because of the complexity of RPS process, including ultra-fast reaction, deposition and cooling processes. Therefore, this work aimed at clarifying the formation mechanism of the RPS coatings under different ambiance conditions (atmosphere and low pressure), which is beneficial to the control of RPS process and high-quality coating products.

1 Experiment

1.1 Preparation of composite powder

The raw powders of Al (5 μm in size, 99.5% purity) and Fe_2O_3 (1 μm, 99% purity) were purchased from Anshan Iron and Steel Fine Aluminum Powder Co., Ltd, China and Tianjin Third Chemical Reagent Co., Ltd, China, respectively. For preparing the powder feedstock, Al and Fe_2O_3 were weighed with the mole ratio of 2:1 and subsequently mixed and stirred into absolute ethyl alcohol for 24 h to achieve complete dispersion. Afterwards, the mixed powders were dried in an oven at 60 °C. Finally, an agglomerant of 5% polyvinyl alcohol aqueous solution was added and homogeneously blended. Then the mixture was spray dried at 100 °C, and the obtained composite powder was collected after sieving.

1.2 Coating process

The substrate samples were made of stainless steel sheet with the dimension of 100 mm×35 mm×2 mm. Prior to spray deposition, the substrate specimens were degreased and grit-blasted using corundum to make a clean and rough surface. A controlled ambiance plasma spray system (100 Pa to 100 kPa) was employed to perform A-RPS and LP-RPS process, in which the Ar and H_2 mixture was selected as reactive gas. The configuration of RPS system is illustrated in Fig. 1a. The plasma torches F4-MB and F4-VB (Sulzer Metco, Switzerland) mounted on a 6-axis robot (ABB, IRB 1400) were used to spray the Al-Fe_2O_3 composite powder under atmosphere and low pressure, respectively. As shown in Fig.1b, the anode of the torch F4-VB designed exclusively for LP-RPS process is a little longer than that of the torch F4-MB. In comparison to A-RPS process, the plasma jet is extensively expanded in the low-pressure condition (as shown in Fig. 1c and 1d). Additionally, for the LP-RPS process, the chamber was pumped to the working pressure, and the substrate was preheated to about 1000 °C by the plasma jet as controlled by a calibrated infrared detector. The spraying parameters are listed in Table 1.

1.3 DTA analysis

In order to investigate the reaction mechanism of the composite powder, the differential thermal analysis (DTA) measurement was carried out for the raw materials. Al/Fe_2O_3 composite powder was mechanically mixed and compressed into cylindrical pellet with 4 mm in diameter and 2 mm in thickness at a pressure of 5 MPa. The DTA test was performed at 1100 °C with a heating rate of 20 K/min, and subsequently cooled down to room temperature. The sintering procedure was carried out under a constant flow of highly pure argon gas.

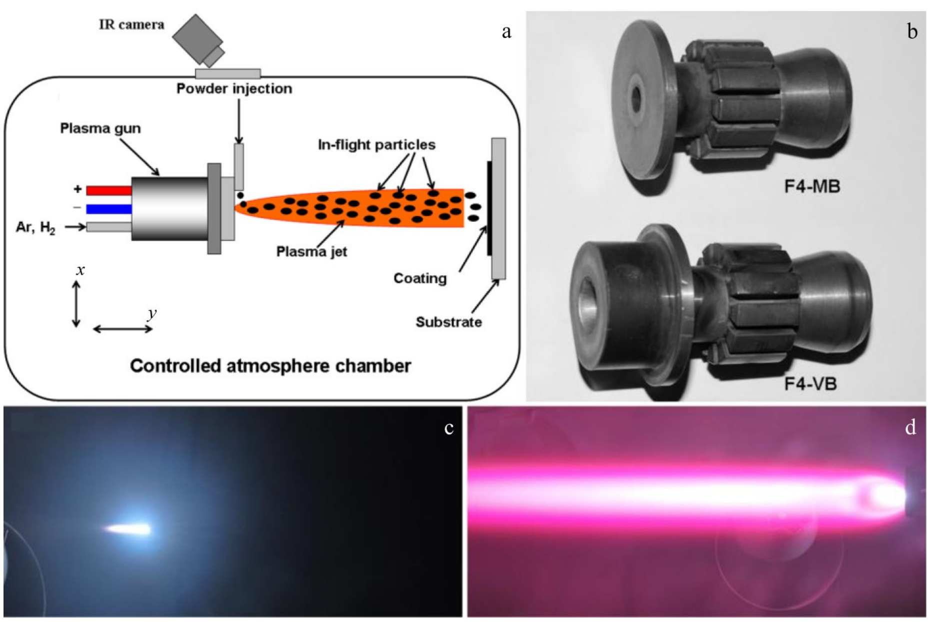

Fig.1 Schematic of controlled atmosphere plasma spraying system (a); anodes of the plasma torches F4-MB and F4-VB (b); image of plasma jets expanding at atmosphere (c) and low pressure (100 Pa) (d)

Table 1 Plasma spray parameters

Parameter	A-RPS	LP-RPS
Chamber pressure/kPa	98	0.1
Current/A	550	700
Power/kW	32	44
Ar flow/L·min^{-1}	32	45
H_2 flow/L·min^{-1}	8	10
Standoff distance/mm	110	600
Substrate preheating temperature/°C	-	1050

1.4 Characterization

The microstructure of raw composite powder, in-situ synthesized coatings and DTA reactive products was characterized by optical microscope (OM) and scanning electron microscopy (SEM, JEOL JSM-5800LV). The size of powder particles was measured using a laser particle size analyzer (MASTERSIZER 2000, Malvern Instruments Ltd, UK). The phase composition of coatings and the DTA sintered sample was examined by X-ray diffractometer (XRD) with a Cu Kα radiation (JEOL 2500, Japan). The element composition and mapping of coatings were analyzed by an energy-dispersive X-ray spectrometry (EDS) associated with SEM.

2 Results and Discussion

2.1 Composite powder characterization

The morphologies of the Al/Fe_2O_3 composite powder are characterized by SEM and OM, as shown in Fig. 2. The composite powders present a globular shape in the agglomerated state (Fig.2a and 2b). The OM image (Fig.2c) of cross-section of the composite powder illustrates that the globular Al particles are dispersed and cladded by ultra-fine Fe_2O_3 powder. Some Al particles are removed during polishing due to the relatively weak bonds in the agglomerates. The particle size distribution is measured for composite powder and a normal distribution is found in the range of 10 – 50 μm, which is centered around 30 μm. It implies an agglomerated structure and homogeneous size distribution of the composite powder waste, which is contributed to the complete reaction between Fe_2O_3 and Al particles.

2.2 Phase and microstructure observation

The XRD patterns of the as-synthesized Al/Fe_2O_3 coatings prepared by A-RPS and LP-RPS are shown in Fig. 3a and 3b, respectively. It is found that the A-RPS coating is principally composed of Fe, Al_2O_3, $FeAl_2O_4$ spinel, and a small amount of FeO wustite. In comparison, only FeAl phase can be detected in the XRD pattern of Al/Fe_2O_3 coating fabricated by LP-RPS process. It is indicated that the oxidation phenomenon occurring during spraying is partially avoided in low pressure ambience compared to in atmospheric condition. In addition, no residual Al or Fe_2O_3 phases are detected in both patterns, implying that the thermite reaction is completed.

The SEM back-scattered electron images of the cross-section microstructures of the coatings are presented in Fig. 4. For the coating sample fabricated by A-RPS process, a compact microstructure with the mean thickness of about 120 μm forms, as shown in Fig. 4a and 4b. It is inferred that the typical stacking of splats is originated from high-velocity semi-melted or melted droplet deposition. Whereas, some defects can be observed from the high-magnification image (Fig.4b), as pointed by white arrows.

Furthermore, it is obvious that the coating is composed of four different hues, including white, grey, black and dark grey which merge uniformly with each other. The EDS analysis

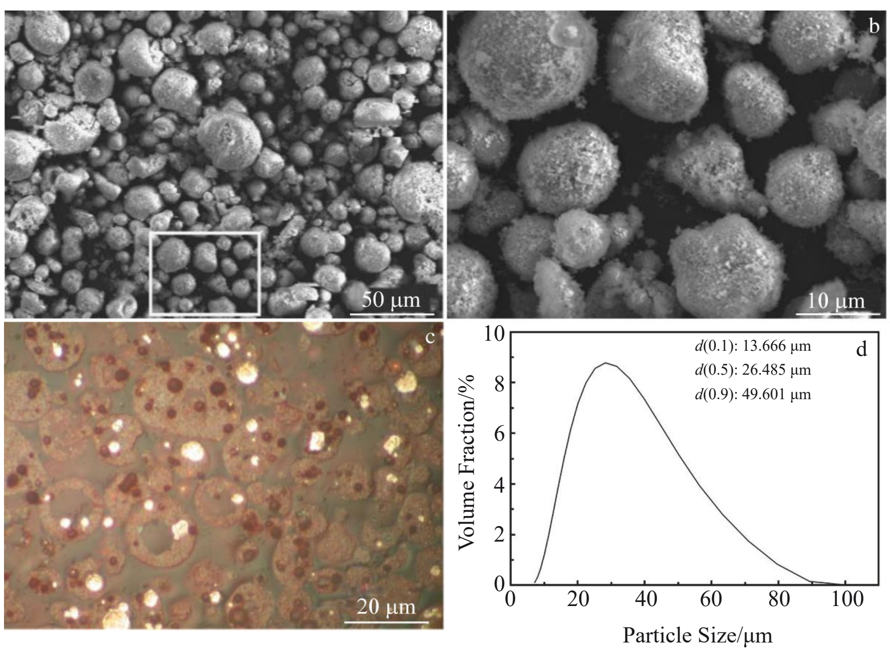

Fig.2 SEM morphologies (a, b), OM image of cross-section (c), and particle size distribution (d) of Al/Fe_2O_3 composite powder

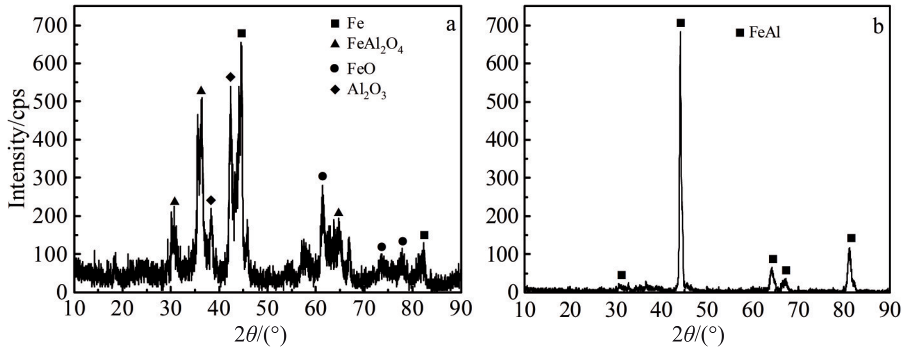

Fig.3 XRD patterns of A-RPS (a) and LP-RPS coatings (b)

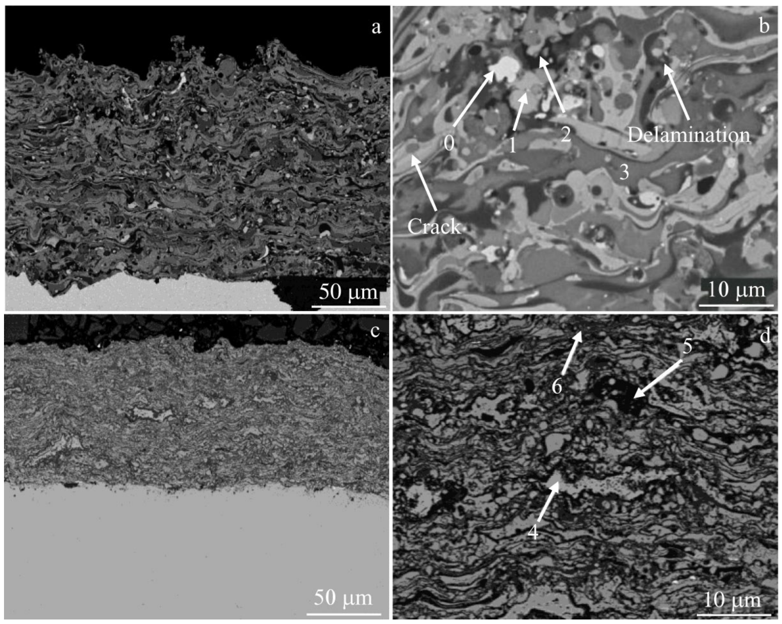

Fig.4 SEM back-scattered electron images of cross-sectional microstructures of A-RPS coating (a, b) and LP-RPS coating (c, d)

was used to determine the element composition of these phases, and the results are listed in Table 2. The region 0 corresponding to the white phase is considered as a Fe-rich phase with a small amount of oxide; the grey phase in region 1 is probably assigned as $FeAl_2O_4$ phase; the black phase in region 2 is confirmed as Al_2O_3 phase; the region 3 with dark grey hue is mainly composed of Al_2O_3 phase and a small amount of iron oxide. Therefore, the formation of the composite coating can be constructed in light of BSE observation. The $FeAl_2O_4$ phase as the fundamental structure of the coating displays a lamellar splat microstructure. Some olive-like or ball-like metal particles and smaller black splats of Al_2O_3 phase are embedded into the $FeAl_2O_4$ framework.

The morphologies of the LP-RPS coating are shown in Fig.4c and 4d. A uniform lamellar structure with the thinner thickness of about 80 μm is observed. The interface between splats is compressed and imporous which cannot be distinguished easily. The obtained coating is denser than that fabricated by A-RPS. Such ultra-dense microstructure is rather similar to the microstructure of sintered FeAl alloy products[22]. Except

Table 2 EDS results of diffent regions A- and LP-RPS coatings marked in Fig.4 (at%)

Element	A-RPS coating				LP-RPS coating		
	0	1	2	3	4	5	6
Al	2.65	21.45	43.8	35.4	19.1	44.6	58.4
Fe	93.7	36.89	1.87	9.41	74.4	38.6	32.2
O	3.56	41.66	54.2	55.1	6.45	16.7	9.25

for region 4, the atom ratio of Al and Fe is nearly equivalent, which is consistant with the XRD results.

2.3 Analysis of formation mechanism

To clarify the transformation process between Al and Fe_2O_3 with the increase in temperature, the composite powder was compressed into cylindrical pellet and subjected to DTA measurement. The obtained DTA curve is illustrated in Fig.5. It is found that there are two distinct thermic peaks in the curve. The endothermic peak at 660 °C is corresponding to the melting of aluminum powder. The exothermic peak initiated at 900 °C and topped at around 1000 °C can be attributed to the

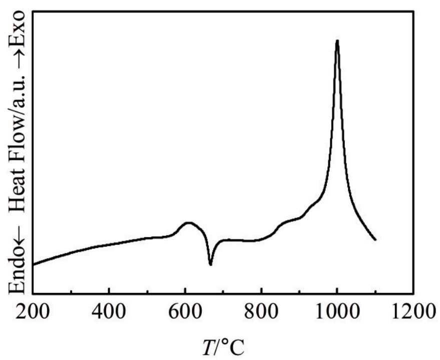

Fig.5 DTA curve of compressed Al and Fe_2O_3 pellet

thermite reaction between Al and Fe_2O_3, as follows:

$$2Al+Fe_2O_3=Al_2O_3+2Fe\ (-849.77\ kJ/mol) \tag{1}$$

Accompanying a large amount of heat emitted by the thermite reaction, the actual temperature of the reactants is dramatically increased, which results in the melting of iron. Theoretically, the reaction product is Al_2O_3 and Fe in the equilibrated process of Eq.(1). Whereas, with the increment of holding temperature at 1100 °C for 0.5 h, FeAl phase is detected in the sintered sample. As shown in Fig.6, the sample after DTA test is composed of Al_2O_3, α-Fe and FeAl phases. The formation of FeAl is attributed to the prolongation of reaction time and elevated temperatures, which promotes the interaction of molten Al and Fe.

The effect of the sintering process on the microstructure was also investigated by SEM (Fig.7). A great number of FeAl grains with a round shape are homogenously dispersed in the sample, which is verified by EDS analysis (point 7 in Table 3). In the high-magnification image (Fig.7b), there are also a lot of tiny particles embedded onto the round grain (point 8). Combining the EDS with XRD analyses, we found that the tiny particles with typical crystalline structures are Al_2O_3 particles. The surface of the Al_2O_3 grains is covered with a thin layer, which is assumed to be molten Fe after thermite reaction. It is consistent with XRD results that molten iron tends to surround the particles and solute molten Al with prolonging reaction time. Furthermore, the elevated temperature also affects the morphology of the Al_2O_3 particles. It is found from Fig.7c and 7d that some column-shaped Al_2O_3

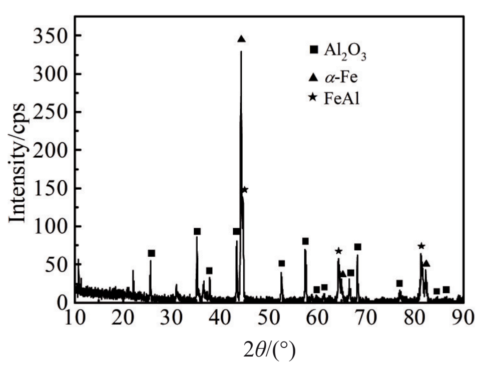

Fig.6 XRD pattern of obtained product by sintering Al/Fe_2O_3 composites

nano-wires grow out of the grains. The perpendicular growth of Al_2O_3 crystalline is attributed to the molten aluminum at high temperature.

Based on the above characterizations, the sintering process of Al and Fe_2O_3 composite can be described as follows: the state of composite is constant until the temperature reaches 660 °C. The Al powders start to melt and to infiltrate into the sample. When the temperature increases to around 900 °C, the thermite reaction is carried out with the formation of Al_2O_3 and Fe phases. With the increase in temperature, the reaction proceeds and emits a large amount of heat. The actual temperature of reactants dramatically increases, which results in the melting of iron as well as the extremely high exothermic peak in the DTA curve. With the temperature held at 1100 °C, FeAl phase forms via the interaction of molten Al and iron.

In comparison with the equilibrium reaction during sintering, RPS technology is known as non-equilibrium reactive process. As indicated in previous XRD results, $FeAl_2O_4$ and FeAl are the major phases in the A-RPS and LP-RPS coatings, respectively. Generally, the retention of intermediate phases is attributed to the ultra-fast cooling characteristic of plasma jet. Furthermore, the atmosphere and processing duration of the RPS technology are responsible for the final products.

For the sample fabricated by A-RPS process, the coating is composed of Fe, Al_2O_3, $FeAl_2O_4$ spinel and FeO wustite. On the base of DTA analysis, it is reasonable to assume that some other reactions occur besides thermit reaction. The initial molar ratio of Al and Fe_2O_3 in feeding powder is 2:1. Theoretically, the RPS process can convert Al and Fe_2O_3 into Al_2O_3 and Fe, whereas the evaporation of aluminum during spraying cannot be ignored. The temperature of plasma jet is much higher than the boiling temperature of aluminum (2520 °C). The evaporation of aluminum leads to excessive Fe_2O_3 in reaction. The chemical reaction of Eq.(2) will occur.

$$2Al+3Fe_2O_3=FeAl_2O_4+5FeO\ (-863.4\ kJ/mol) \tag{2}$$

It is interesting to note that $FeAl_2O_4$ and FeO phases are only detected in the product of A-RPS process instead of sintered sample. There are two reasons for this phenomenon. Firstly, the sintering temperature during DTA test is not high enough for the boiling of aluminum. Meanwhile, the composite powder is compressed, which also avoids the possible evaporation of aluminum. Secondly, $FeAl_2O_4$ and FeO are intermediate phases which are not stable in equilibrium process. The RPS process can retain the intermediates phases due to its ultra-fast cooling rate. The disturbed microstructure of the A-RPS coating layer (Fig.4b) also indicates that these products are more likely to generate from the solidification of liquid phases.

In contrast, FeAl phase emerges as the dominant phase in LP-RPS coating. The main difference of these technologies is the pressure in plasma chamber. Low pressure Ar-H_2 atmosphere can provide a reductive environment for plasma spray synthesis. According to the phase diagrams of FeO-Fe_2O_3 at different partial pressures of oxygen, it is reported

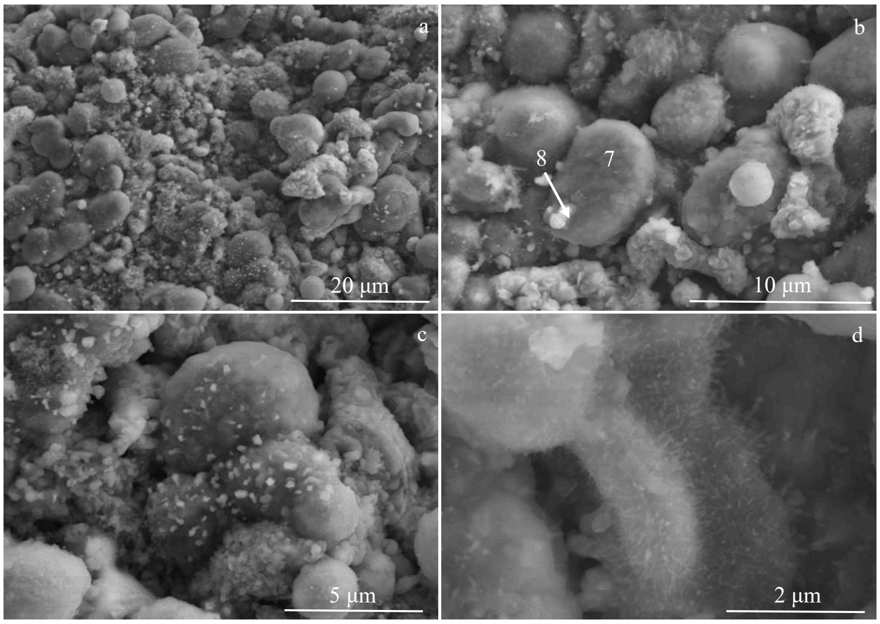

Fig.7 SEM morphologies of sintered powder (a, b) and column-shaped Al_2O_3 particle (c, d)

Table 3 EDS results of point 7 and point 8 marked in Fig. 7b (at%)

Element	Point 7	Point 8
Al	41.81	36.60
Fe	41.01	11.58
O	17.18	51.81

that iron oxides become liquid Fe-O phase at high temperature and low oxygen partial pressure[23]. The high temperature inside the plasma jet induces the melting and decomposition of iron oxides $FeAl_2O_4$ and FeO, which are likely to be reduced into metallic state under such reductive atmosphere. Moreover, the longer in-flight distance of LP-RPS during spraying (Fig. 1d) also provides a sufficient reaction time for the reduction reaction between composite powder and H_2 ambiance in the jet. The above DTA analysis proves that prolongation of reaction time and elevated temperature can promote the interaction between molten Al and iron, resulting in the formation of FeAl. In summary, the low pressure Ar-H_2 atmosphere and longer in-flight distance of LP-RPS lead to the decomposition and reduction of iron oxides, which further results in the formation of FeAl phase.

3 Conclusions

1) The Al/Fe_2O_3 coatings can be fabricated by reactive plasma spraying (RPS) technique under atmosphere and low-pressure ambient. The reaction mechanisms of thermite reaction of Al and Fe_2O_3 in sintering and RPS process are clarified. The reaction of Al/Fe_2O_3 spray-dried composite powder in finely agglomerated state with the diameter of 10–50 μm can be completed in RPS process. Fe-Al_2O_3-$FeAl_2O_4$ and FeAl coatings can be synthesized using Al/Fe_2O_3 composite powder by A-RPS and LP-RPS process.

2) DTA results confirm that the major sintered products are Fe and Al_2O_3 phases during a quasi-equilibrium reaction. The prolongation of reaction time induces the formation of FeAl phase. The RPS process can retain the intermediates phases due to its ultra-fast cooling rate. The formation of $FeAl_2O_4$ and FeO phases in the A-RPS coating is due to the evaporation of aluminum, which results in the side reaction. However, in the LP-RPS process, the low pressure Ar-H_2 atmosphere may lead to reduction and decomposition of the $FeAl_2O_4$ and FeO phases, and the long in-flight distance of plasma jet can promotes the formation of FeAl phase.

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常压和低压环境下反应等离子喷涂 Al/Fe_2O_3 复合材料的合成机理

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摘　要：反应等离子喷涂（RPS）技术被广泛用于制备不同使用需求的高性能涂层材料。基于经典的铝热反应原理，采用反应等离子喷涂技术分别在近常压和低压环境下制备了 $Al\text{-}Fe_2O_3$ 涂层，通过XRD、SEM和EDS等分析方法对所制备涂层的相组成和显微结构进行了表征。阐明了Al和 Fe_2O_3 在加热和反应等离子喷涂过程中的反应机理。DTA分析结果表明，氩气氛下长时间热处理产物主要为Fe、Al_2O_3 和FeAl相。然而，在等离子喷涂过程中，低氧分压环境导致中间产物 $FeAl_2O_4$ 铁尖晶石相的生成，由于近常压等离子喷涂过程的冷却速度极快，该相可以保留在最终涂层结构中。而低压反应等离子喷涂等离子体射流飞行距离长，还原性气氛和较长的反应时间将其进一步还原为FeAl相。

关键词：反应等离子喷涂；低压；铝铁合金；铝热反应；涂层

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