

Research on Using Plasma Thermal Spraying Technology for Enameling

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Abstract

The article is a brief introduction of the technical theories, features and functions of plasma thermal spraying. The authors study on which porcelain enamel frits and powders were suitable for plasma thermal spraying and what the related technical parameters were. The research results showed that it was possible to use the plasma thermal spraying method on thick steel plate surfaces by using special porcelain enamel powders. This technology is particularly suitable for surface enameling on large pieces requiring porcelain enameling.

Keywords: thermal spraying, enameling, porcelain enamel, powder

Plasma Thermal spraying is a kind of technology for metal surface protection and strengthening. It plays an important role in improving the product's reliability and prolonging the service lives of components. There is a lot of research on the plasma spraying technique today since it has the potential to improve the hardness, wear resistance, corrosion resistance, and other physical and chemical performance of the component's surface [1]. Thermal spraying materials are considered as the "food" or material basis of such technology. Many materials, such as metal, ceramic, nanometer and composites, could be coated by using plasma spraying [2]. At present, plasma spraying powders are mainly alloy and ceramic materials in the domestic and overseas applications. The Atomizing Method is mostly adopted for the applications. Powder materials and the coating technology, has become very mature, but it still cannot be widely applied, due to the high price of powder materials.

With the features of corrosion resistance, wear resistance, heat resistance and decorating properties, porcelain enamel materials can meet all the requirements of powder materials for plasma thermal spraying, and have been widely used in industry because of their low price [3]. However, there have been few research studies about using plasma spraying technology for enameling [4]. Plasma thermal spraying technology has great practical and economic value since it not only lowers spraying cost, simplifies and improves the enameling process, but also reduces the dependence on furnaces which require high energy consumption, increasing costs. Compared with furnace firing, plasma spraying technology could make coating thickness easy to be controlled, the coating process finished at once, usage of clay and other mill-addition reduced, and finally, physical and chemical properties would be greatly improved.

1. Plasma Spraying

The technology and application of plasma spraying has been rapidly developed since 1950, and especially since 1970. It has been widely adopted because of its features of wear-resistance, heat resistance, and antioxidant corrosion. The technology of spraying on heat resistant ceramics is the focus of development at the present time, but composite materials and metallic compounds are very popular as well.

1.1 Fundamentals

Plasma spraying is a kind of thermal spraying with plasma arc as the heat source, metal ceramic powders are melted by using a high temperature, high speed and high enthalpy flow flame to obtain high quality composite coatings [5]. Spraying fundamentals are: The nozzle [anode] and the tungsten electrode [cathode] come close together and they create a high frequency spark which acts as an igniter. The nitrogen or argon which has entered into pores of the spraying gun ionizes and turns into a plasma. The high frequency circuit could be cut off when the electric arc is ignited, since by this time the powder materials, fed by a pipe to the spray gun, are rapidly heated to a molten state by flame flow, and stick to surface of target surfaces by high speed spraying. Finally, a layer of coating will be formed after a certain time of spraying.

1.2 Main features

Compared with PVD, CVD, bead welding, flame spraying and other surface coating technologies, plasma spraying has many outstanding features, such as fast deposition, efficient production, a wide range of applications, etc. Major advantages are as follows:

- 1) No distortion for components. As the body is electrically neutral and does not melt, even though the temperature of the flame is very high, and the temperature on the component will not exceed 200°C when the process is controlled properly, and therefore the body will not distort. With this feature, plasma spraying is especially applicable for the plungers, slender weld materials, thin components and precision parts processing and repairing.
- 2) Stable processing. The parameters for spraying materials are different according to different requirements, but they can be quantitatively controlled to achieve stable processing and high reproducibility. The flying speed of the plasma molten particles generally is 180-480 m/s and the flame spraying speed is 45-120 m/s, so the molten particles distort when hitting the body, and finally they adhere to the body tightly and the coating is formed. Normally the adhesive strength is 45-75 N/mm². Because we can control the gas it is easy to control the oxidized and nitrate levels.
- 3) Wide range of coating materials.

The temperature of the plasma spraying flow is very high, therefore, general refractory materials with properties of wear-resisting, heat-resisting, oxidation resistance at high temperature and insulating properties can be coated.

2. Plasma Spraying for Porcelain Coating

It is generally known that the whole porcelain enameled piece should be put into furnace for firing during today's ordinary enameling process. It's easy to enamel on small items or pieces,

but difficult for large items such as reaction vessels, which need several firing processes, special requirements for the furnace, and result in a high cost of energy. Now we have plasma spraying technology which is applicable for localized spraying. With this technology, the thickness of the coating is easy to be controlled, the enameling could be finished at one time, the manufacturing process is simplified, costs are saved, and physical and chemical properties, such as corrosion and abrasion assistance will be greatly improved.

2.1 Porcelain materials preparation for plasma spraying

The study of porcelain enameling powder should be combined with the selection of the steel plate, so the authors designed an experiment to study the requirements of the ground coat formula. The expansion coefficient of the enamel was controlled between 280×10^{-7} to 300×10^{-7} and the firing temperature was controlled between 800C to 860C. Three sets of enamel frit formula with different performances were studied in order to make a comparison (shown as 1, 2, and 3). The enamel materials are melted in a high temperature testing furnace. Melting temperature is between 1250°C to 1300°C, and the melting time was 35 to 40 minutes. Below are the chemical compositions of three frits:

Table 1. Range of chemical composition of Frit Formula 1

Oxide	SiO ₂	Al ₂ O ₃	F	B ₂ O ₃	K ₂ O	Na ₂ O	CaO	SrO	CoO	NiO	MnO ₂
Weight(%)	36-42	3-4	3-4	18-21	1-2	17-19	9-10	2-3	0.5	1	2.5

Table 2. Range of chemical composition of Frit Formula 2

Oxide	SiO ₂	Al ₂ O ₃	B ₂ O ₃	K ₂ O	Na ₂ O	Li ₂ O	TiO ₂	P ₂ O ₅	CoO	NiO	MnO ₂
Weight(%)	48-53	1-2	14-17	4-6	9-12	2-3	3-4	1-2	0.5	1	2.5

Formula 3: Use CuO and FeO instead of CoO and NiO in Formula 1 to find whether or not adherence promoter like CoO and NiO has an effect on adhesion for enamel material and steel plates during plasma spraying. It has little influence upon coating physical properties, such as expansion coefficient, surface tension, firing temperature, etc.

Table 3. Technical parameters comparison between Formula 1 and Formula 2 (calculated by Chemical composition theory)

Enamel serial Number	Softening temperature (°C)	Expansion coefficient($\times 10^{-7}$)	surface tension(dyne/cm)
1	600	297	265
2	650	282	298

2.2 Preparation of plasma enamel powder

2.2.1 Powder making

It is known that plasma spraying requires high fluidizing performance for the enamel powder. The surface of the powder particle produced is smoother and more spherical by wet milling compared with dry milling. Based on the above three different enamels, the materials were milled respectively with the right amount of water and a little ethanol to a required fineness, then they were screened and dried at a low temperature. The three powders were distinguished by labeling them Powder 1, Powder 2, and Powder 3.

2.2.2 Coating Treatment

It's not easy to make the powder all into a ball shape for normal plasma spraying equipment. To increase fluidization, a particle coating treatment of liquid or gaseous sedimentation can be used on the particle surface. The coating method of porcelain enamel electrostatic dry powders can be used as a reference that coating the porcelain enamel powders with silicon oil can increase fluidization. By dry milling, the proper amount of silicon oil was added to the above Powder 1, Powder 2, and Powder 3. They were then labeled as A, B and C. The fluidization was tested by the SAMES Fluidization Detector. If the fluidization reached 70, it could meet the requirements of plasma spraying. Powder 1 was milled for the same time with no silicon oil, and was labeled as D to compare the fluidization of D.

2.3 Coating Testing

Plasma thermal spraying equipment, which was made in China, was used in the tests. Ar and H₂ were used as testing gas. The gas pressure of Ar was 0.88 MPa. The gas pressure of H₂ was 0.88 MPa. The plasma current was 500A. The plasma voltage was 50V. The base material was No.45 steel. The spraying material was the above A, B, C, and D powders. Spraying specification: the powder sending speed was 62 g/min. The delivery gas was N₂, whose flow was 800 L/min. The spraying used water for cooling, with a flow of 20 L/min. The distance between base material and nozzle was 50mm. The spraying speed was 10mm/s. The testing was as follows:

2.3.1 Preparation of Base Material

No.45 steel was chosen as the base material. The steel was cut to sample size with a wire cutting machine.

2.3.2 Base Material Surface Pre-treatment

Put the sample into a NaOH solution with a density of 50g/L and soak for 30 minutes. The temperature of the solution was about 80°C, to remove residual oil and other contamination on the base material from the ground finish. After cleaning and drying, the material surface was sand blasted to coarsen the material surface.

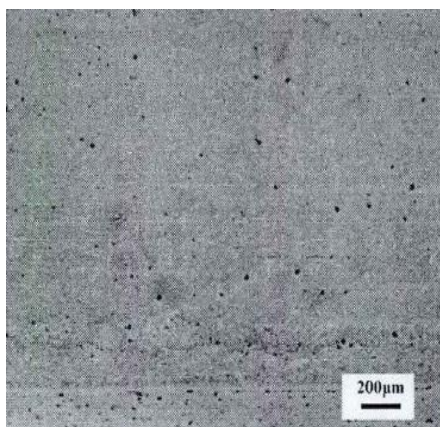
2.3.3 Base Material Surface Preheat

The purpose of preheat was to remove surface water and moisture, reinforce surface vitality, increase interface temperature between spraying particles and material, decrease coating

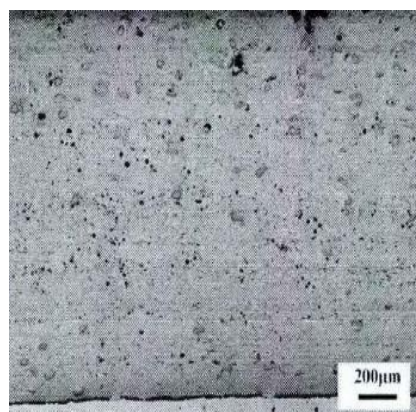
stress from the material thermal expansion, and increase bonding strength between the coating and base material. The plasma spraying gun was used for the preheating. First, the powder feeder was closed. Then plasma spraying with a neutral flame was used to heat the base material evenly. High local temperature will lead to an oxidation film on the surface and should be avoided. Oxidation film affects the combination of coating and base material.

2.3.4 Coating Testing

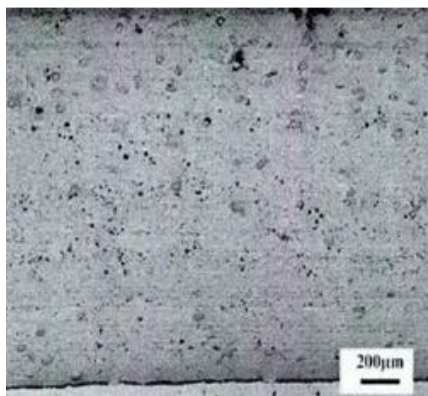
The prepared powder was put into the powder feeder. The main power supply, DC power, water cooler, argon, hydrogen, etc were turned on successively. After preheated, the powder feeder was turned on and the flow speed was adjusted. When spraying, the testing samples were placed in order on the working platform. Spraying gun moved in a straight line, back and forth in a prescribed distance, until the coating thickness is reached. After spraying, the power supply was turned off and the powder feeder was cleaned. Then the second powder was sprayed as before, and all powders were repeated with the same process. The spraying efficiency and quality is relative to power voltage, power current, gas flow, coating distance and other parameters. When confirming the spraying parameter, both good powder melting and proper power should be taken into careful consideration. Too much power would lead the powder to overheat and burn. The A, B, C, and D powders were sprayed according to the above process and the sprayed plates were labeled as Sample A, Sample B, Sample C, and Sample D.



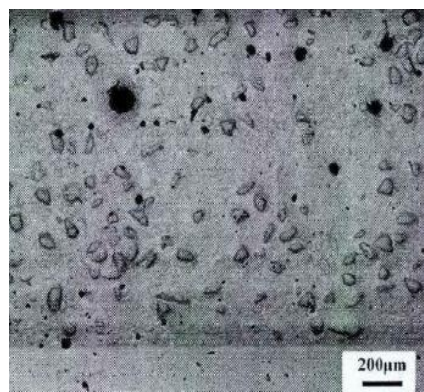
Sample Plate A



Sample Plate B



Sample plate C



Sample Plate D

Picture 1: 4 Samples Under Scanning Electron Microscope

3 Test Results and Discussion of Plasma Spraying

- 1) Powder A, B, C, and D were tested with the same test process. During spraying, it was apparent that Powder A, B, and C flowed out smoothly, continuously and evenly. Their coating thickness was comparatively consistent. Powder D, which had worse fluidization, did not flow out continuously. Powder D sometimes blocked the gun and the coating thickness was obviously not even. It was shown that silicon oil coating of the frit powders can increase fluidization in plasma spraying and achieve an even coating.
- 2) The surface effect of sample plate A and B were compared. The surface of sample A was smooth and didn't have obvious defects. The surface of sample B was not smooth and showed partial crawling. If the frit of sample plate A and B was compared, it can be seen that frit B has larger surface tension and a higher softening temperature. Because the center temperature of the plasma flame is above 15000 K, a 50 degree softening temperature difference would not have obvious impact on spraying. If the frit surface tension is too high, melted particle would shrink too much and will not make a plastic deformation. So melted particles don't spread as a layer evenly and create crawling. Therefore, the surface tension of plasma spraying frit cannot be too large.
- 3) The adherence of sample A and sample C was compared. The adherence of Sample A is level 3. Sample C cannot reach level 4. It is shown that the cobalt nickel adherence material can promote the integration of the enamel powder and steel, and it improves adherence.



Sample Plate A



Sample Plate C

Picture 2: Adherence Comparison of Sample Plate A and Sample Plate C

- 4) A sample with traditional wet enamel spraying with clay was prepared and Formula 2 was used, and then the acid resistance with sample B was compared. The acid resistance of Sample B is obviously better than that of wet enameling. Compared with wet enameling, plasma spraying enameling is better at physical and chemical performance.

4、Summary

Through the above preliminary experiment and research, the following conclusions can be made.

- 1) Porcelain Enamel materials [Frit] can be adapted to the plasma spraying technique, which can then satisfy the technical requirements of parts needing partial enameling. It is hopeful that plasma spraying can solve the problems of the enameling process of reactor vessels and other large pieces.
- 2) Specially designed frits, and frit powders, made by special techniques, are suited for plasma spraying, and can lower the cost of plasma spraying.
- 3) Plasma spraying and cobalt nickel adherence material can improve the adherence to the steel. Silicone oil coating of the frit powder can increase fluidization, which satisfies the plasma spraying specification.
- 4) Compared with traditional wet enameling, plasma spraying can improve the acid resistance of the coating.

Reference

- 1、 Guiyun Chen, Xuke Zhou, Lishi Wen, etc. Microstructure and Properties of Plasma Spraying Nickel Base Alloy Amorphous Coating, Corrosion Science and Protection Technology. 1992,4 (3); 180-184.
- 2、 Huang Chen, Chuanxian Ding, Microstructure Research of Plasmas Spraying Nano Zirconia Coating, Journal of Inorganic Materials, 2002,17 (4) 882-886
- 3、 Pantelis D I,psyllaki P,Alexopoulos N,Tribological behav-iour of plasma-sprayed Al_2O_3 coatings under severe wear condition,Wear,2000,237(2):197-204
- 4、 Militke J,kovaÓ iÓV V,Bajzí K V,Mechanical properties of basaltfilaments, Fibers and Textiles in Eastem Europe January,2007,1595260:64-65
- 5、 Lee K N,Miller R A,Jacos on N S,New generation of plasma sprayed mullite coatings on silicon carbide.J.Am,Ceram,soc,1995,78(3):705-710.
- 6、 Xingzhi Li, Shubing Hu, Development and Application of Plasma Spraying, Journal of Hubei University Of Automotive Technology