Research on Thermal Conductivity of Organosilicone Anticorrosive Coating Modified by Thermal Conductive Particles

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Abstract: In order to strengthen the utilization of boiler flue gas waste heat, an anticorrosive coating is applied to the heat exchange surface of ordinary metal heat exchangers. Graphene and boron nitride were added to the coating to enhance its thermal conductivity. The thermal conductivity of composite coating samples was studied, and the influence of sample forming pressure on thermal conductivity was studied. The results show that the organic silicon coating can work in an environment above 200℃,and the addition of graphene and boron nitride will enhance its heat resistance to a certain extent; the best experimental effect is when the molding pressure of the sample is 20KN; Both graphene and boron nitride will enhance the thermal conductivity of the coating, and the effect of graphene is better than boron nitride.

1. Introduction

The flue gas contains a large amount of SO_2 and SO_3, which form sulfuric acid vapor with water vapor. When sulfuric acid vapor condenses, it will cause corrosion of the metal heat exchanger. The acid dew point of the flue gas is the temperature at which the sulfuric acid vapor condenses. To prevent corrosion of the metal heat exchanger, the boiler exhaust gas temperature is generally about 10°C higher than the flue gas dew point temperature, but this method causes a waste of energy. If the waste heat of the boiler flue gas can be fully utilized and the boiler flue gas emission temperature can be reduced, it will greatly promote energy saving, emission reduction and efficient use of energy.

Spraying anti-corrosion coating on the wall of metal heat exchanger is one of the common anti-corrosion measures[1]. Anti-corrosion coating can significantly prevent the corrosion of heat exchangers, and has good economic efficiency, so it has attracted wide attention. Among them, environmentally-friendly anti-corrosion coatings have become a research hotspot[2]. Some scholars use silicone modified epoxy resin as the base material to prepare coatings[3,4], grafting organosilicon into epoxy resin not only ensures the anti-corrosion performance of the coating, but also improves its heat resistance, so that it can work in a certain high temperature environment. The organic silicon modified coating uses the chemical bond Si-O as the molecular backbone, and the bond energy is much higher than that of the C-O bond and the C-C bond. It has stable properties and good heat resistance and corrosion resistance. However, the silicone anticorrosive coating also has the disadvantage of poor thermal conductivity. After the metal heat exchanger is coated with the silicone coating, the thermal conductivity of the heat exchanger will be reduced. Relevant research shows that the thermal conductivity of the anticorrosive coating is improved by adding thermal conductive materials. Single-walled CNTs are doped into epoxy resin. When the mass content is 1wt% and the temperature is 40K, the thermal conductivity of the composite material is increased by 70 %[5].

Graphene not only has good corrosion resistance and mechanical properties, but because of its special structure, the carbon atoms are connected in sp^2 hybrid mode, so it also has excellent thermal conductivity; Boron nitride is a crystal composed of nitrogen atoms and boron atoms. Its crystal structure is similar to graphite. Both are layered structures and have good thermal stability and good thermal conductivity.

At present, most domestic researches on anticorrosive coatings for flue gas heat exchangers focus on the corrosion resistance of the materials, while the thermal conductivity of anticorrosive coatings is less concerned. In this paper, graphene and boron nitride are added to organic silicon coatings, and their temperature resistance and thermal conductivity are measured and analyzed experimentally to strengthen the utilization of flue gas waste heat.

2. Experiment

2.1. Experimental Sample Preparation

The metal substrate Q235 carbon steel is sprayed with organosilicon anticorrosive coating and organosilicon coating with different mass fractions of thermal conductivity materials added. Before spraying, the surface of the substrate is repeatedly polished with dry sandpaper, 400#, 600# sandpaper, and roughened, then cleaned with deionized water, scrubbed with acetone, and placed in a desiccator for 60 minutes.

Prepare the silicone coating and curing agent at a ratio of 10:1 and mix them thoroughly with a mixer; Graphene is added to the coating with mass fractions of 1%, 5%, 10%, 15%, and 20%, and boron nitride is added to the coating with mass fractions of 5%, 10%, 15%, and 20%, and the magnetic mixer is used for stirring at constant temperature for more than 120 minutes until the powder boron nitride filler and silicone coating are fully mixed.

Air compressor is used to spray the coating under high pressure. When spraying, the distance between the spray gun and the metal substrate shall be kept 300mm, and the spraying pressure shall be 0.5MPa.

The samples used in this instrument are all in powder form. Select the sample plate with uniform coating, scrape the coating surface gently with a tool knife, dry it in a tubular vacuum furnace at 150 °C for 24 hours, and then take it out and crush it with a multifunctional pulverizer.

2.2. Experimental Apparatus

The density of the sample was measured with the MDY-1 electronic density/specific gravity meter produced by Shanghai Fangrui Instrument Co., Ltd.

The samples were analyzed by STA 449 F3 thermogravimetry analyzer (Netzsch Instrument Manufacturing Co., Ltd.), then the curves of thermogravimetry (TG) and differential scanning calorimetry (DSC) were obtained. The first derivative of TG curve was used to obtain the DTG curve.

The thermal diffusivity of the sample is measured by the LFA-457 laser thermal conductivity meter (German Netzsch Instrument Manufacturing Co., Ltd.). The sample of this instrument needs to be made into a cylindrical shape, and the sample diameter is generally 12.2mm~12.7mm.

2.3. Experimental Methods

2.3.1. Heat Resistance Test of Coating

TG curve and DSC curve can be obtained by STA 449 F3, and the heat resistance of the coating can be obtained by analyzing the curve.

The samples were weighed 6-10mg each time and placed in the aluminum crucible. The combustion atmosphere was set as dry synthetic air, and nitrogen was set as protective gas with a flow rate of 20ml/min. The temperature range was set at 40-500°C and the temperature rise rate was 10K/min.

2.3.2. Heat Resistance Test of Coating

The thermal conductivity of the coating was calculated by formula (1), the specific heat capacity of the coating was measured and analyzed by STA 449 F3, and the thermal diffusion coefficient was measured by LFA-457.

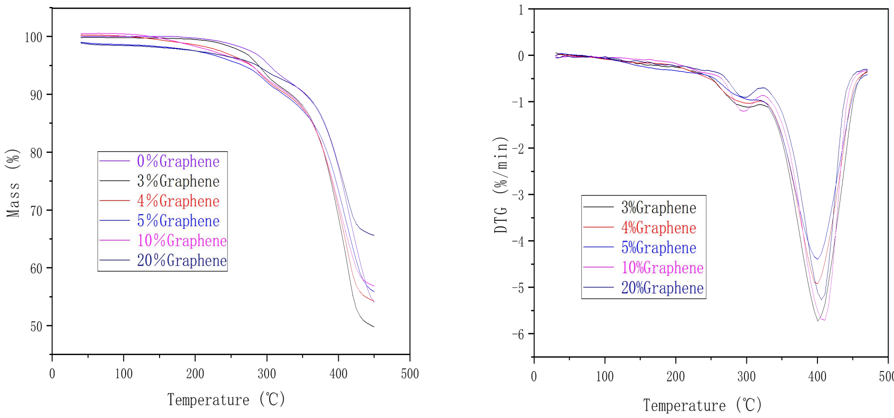
$$\lambda(T)=\alpha(T)\cdot\rho(T)\cdot Cp(T) \qquad (1)$$

In the formula: $\alpha(T)$ is the coefficient of thermal diffusion, mm^2/s; $Cp(T)$ is the specific heat capacity, $J/(g\cdot k)$; $\rho(T)$ is the density, g/cm^3;

3. Experimental Results and Discussion

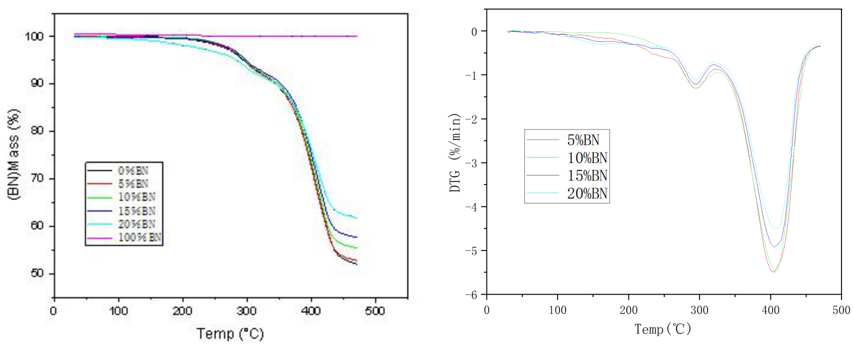
3.1. Heat Resistance of Coating

It can be seen from Figure 1 that the TG curve of the silicone anticorrosive coating has not changed before 200°C, indicating that it can work at 200°C. With the increase of the graphene mass fraction in the coating, the maximum weight loss of the coating decreases and the maximum weight loss rate of the coating decreases, and the maximum weight loss temperature moves to the right, indicating that the temperature resistance of the coating is enhanced by the addition of graphene. TG-DTA test results show that the composite graphene modified organosilicone coating has better thermal stability.



(a) (b)

Figure 1: (a) The TG curves of Graphene modified coating. (b) The DTG curves of Graphene modified coating.



(a) (b)

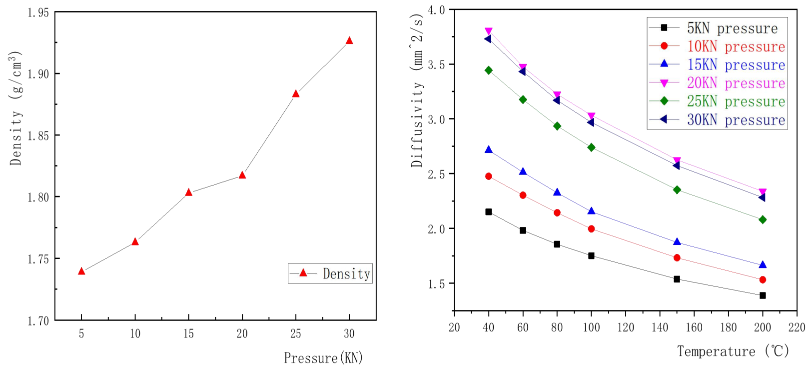
Figure 2: (a) The TG curves of Boron nitride modified coating. (b) The DTG curves of Boron nitride modified coating.

It can be seen from Figure 2 that with the increase of the mass fraction of boron nitride filler in the coating, the maximum weight loss rate and the maximum weight loss rate of the coating decrease, and the maximum weight loss temperature moves to the right, indicating that the addition of boron nitride has enhanced the temperature resistance of the coating. The boron nitride modified silicone coating can also work at least 200°C.

3.2. Effect of Sample Forming Pressure on Thermal Conductivity of Coating

In order to measure the thermal diffusivity of coating by LFA-457, the sample should be made into a cylinder, so the powder sample should be compacted. Fig. 3 shows the molding materials under different pressures. It can be seen that with the increase of molding pressure, the material surface becomes smooth and the molding effect is better. When the molding pressure is 5KN, the edge of the material is fragile and the surface is rough.

Figure 3: Experimental samples under different forming pressures.



(a) (b)

Figure 4: (a) Density of coating under different forming pressure. (b) Thermal diffusivity of coatings under different molding pressures.

It can be seen from Figure 4 that the material density increases with the increase of molding pressure, which is due to the decrease of porosity between material particles. The thermal diffusion coefficient of the coating changed little when the forming pressure was 20KN to 30KN, and when the pressure was less than 10KN, the porosity of the sample was larger, which was easy to cause the inaccuracy of density measurement. Therefore, 20KN molding pressure was selected for the experiment.

3.3. Thermal Conductivity of Coatings Modified with Different Mass Fraction of Thermal Conductive Materials

It can be seen from Figure 5 that the addition of graphene increases the thermal diffusivity and thermal conductivity of the composite coating. At 80 °C, the thermal conductivity of the silicone coating without graphene is 0.188W/(m•K); when the mass fraction of graphene is 1%, the thermal conductivity of the composite coating is 0.34W/(m•K), increasing by 80.8%;At 80°C, the thermal conductivity of the composite coating with a graphene mass fraction of 15% was 1.591W/(m•K), which increased by 746.3% compared with the organic silicon coating without graphene.

It can be seen from Figure 6 that the addition of boron nitride also increases the thermal diffusion coefficient and thermal conductivity of the composite coating. At 80°C, when the mass fraction of boron nitride was 5%, the thermal conductivity of the composite coating was 0.243(W/m· K), which increased by 29% compared with that of the silicone coating without boron nitride; when the mass fraction of boron nitride was 20%, the thermal conductivity of the composite coating was

0.48W/(m·k), which increased by 155.3% compared with the organic silicon coating without boron nitride. Under the same conditions, the thermal conductivity of boron nitride composite coating is lower than that of graphene composite coating.

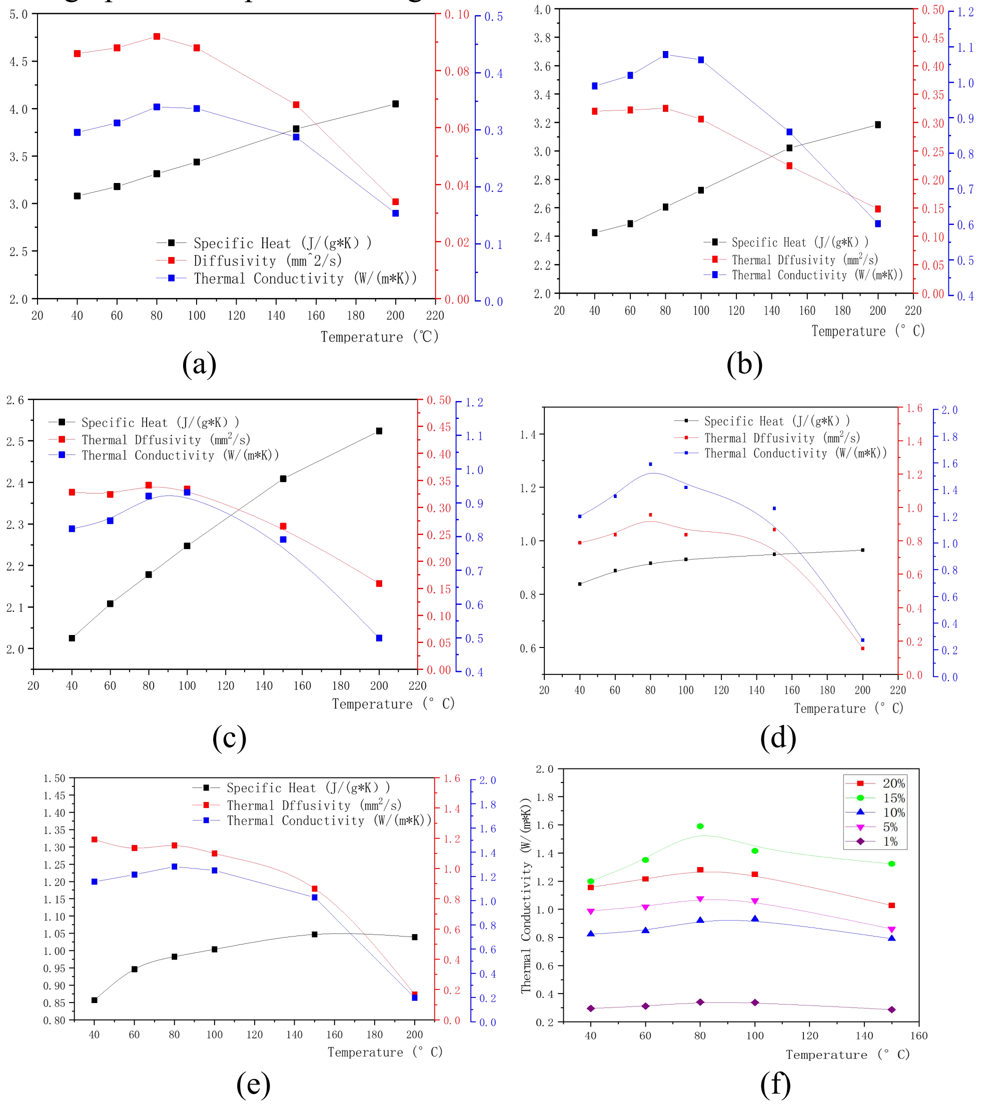


Figure 5: (a) 1% graphene modified silicone coating. (b) 5% graphene modified silicone coating. (c) 10% graphene modified silicone coating. (d) 15% graphene modified silicone coating. (e) 20% graphene modified silicone coating. (f) Thermal conductivity of graphene modified silicone coatings.

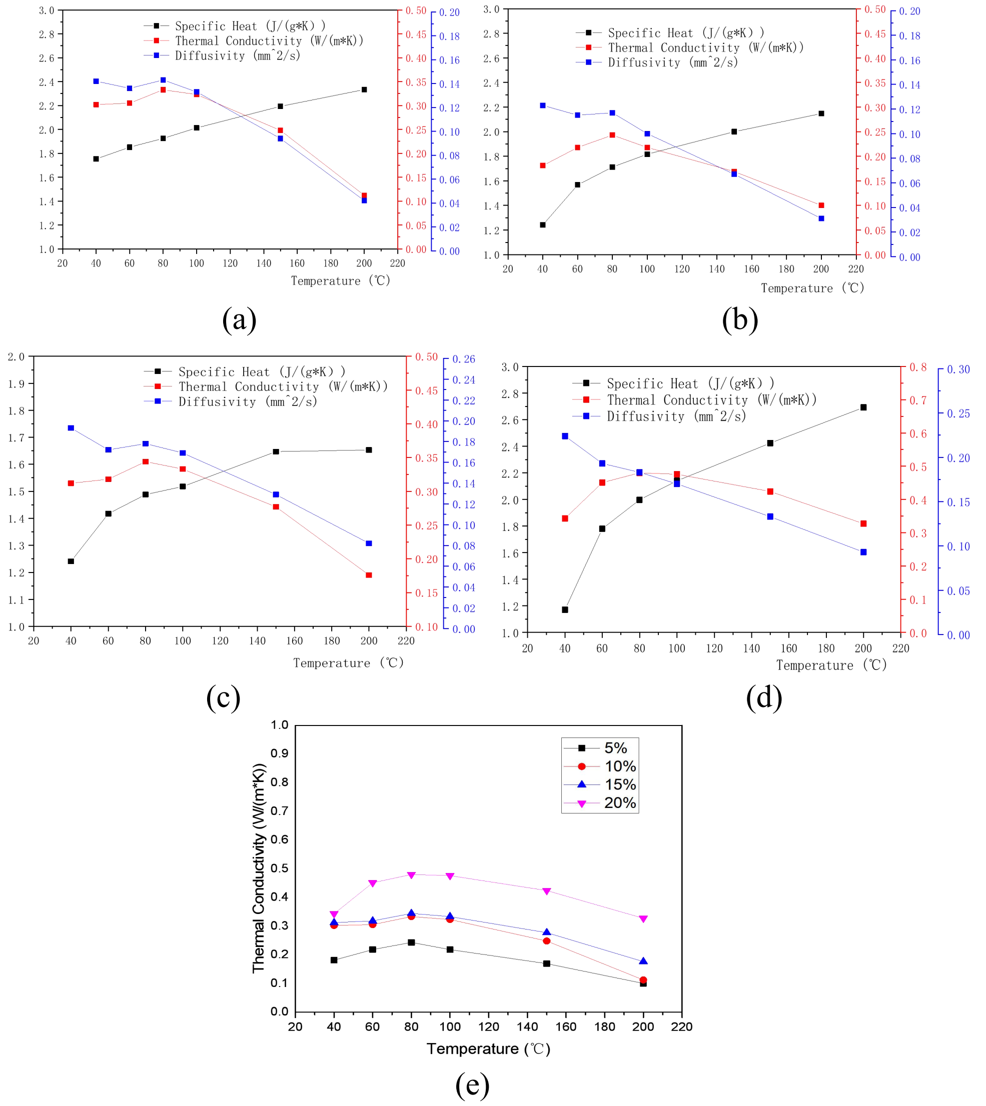


Figure 6: (a) 5% boron nitride modified silicone coating. (b) 10% boron nitride modified silicone coating. (c) 15% boron nitride modified silicone coating. (d) 20% boron nitride modified silicone coating. (e) Thermal conductivity of boron nitride modified silicone coatings.

4. Conclusion

To solve the corrosion problem of medium and low temperature flue gas waste heat exchanger, the prevention method of coating anticorrosive coating is chosen. In this paper, organic silicon coating with excellent corrosion resistance and temperature resistance was selected, graphene and boron nitride were added to improve the thermal conductivity of the coating. The thermal conductivity of the composite coating was analyzed by STA 449F3, LFA-457 and other instruments, and the following conclusions were drawn:

The silicone coating can withstand the temperature of more than 200°C, which can ensure the coating to work in the medium and low temperature flue gas waste heat exchanger, and the addition of graphene and boron nitride can improve the heat resistance of the composite coating; In order to ensure the accuracy of the thermal diffusion coefficient, the forming pressure of the experimental sample was investigated. The results showed that when the forming pressure was 20KN, the surface of the experimental sample was smoother, the edge of the sample was firm, and the thermal diffusion coefficient was higher; The addition of graphene and boron nitride can improve the thermal conductivity of the coating. At 80℃,when the mass fraction of graphene was 15%, the thermal conductivity of the composite coating was 1.591W/(m·k), compared with the organic silicon coating without graphene, the thermal conductivity increased by 746.3%.When the mass fraction of boron nitride was 20%, the thermal conductivity of the composite coating was 0.48W/(m·k). Compared with the organic silicon coating without boron nitride, the thermal conductivity increased by 155.3%; When the mass fraction of graphene and boron nitride are the same, the thermal conductivity of graphene modified coating is higher than that of boron nitride.

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