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Property of TiO₂-15MgAl₂O₄ Electrical-Heating Coating Prepared by Atmospheric Plasma Spraying and Hydrogen Heat Treatment

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Abstract: Using TiO₂-15MgAl₂O₄ mixed powder as spray-feed, an electrical-heating coating was successfully fabricated by atmospheric plasma spraying technology. The phase composition, microstructure, and electrical-heating performance of the coating were characterized by XRD, SEM, and cyclic electrification tests, respectively. The coating samples were heat-treated at 350 °C in a hydrogen atmosphere. The results show that TiO₂-15MgAl₂O₄ coating can be heated over 300 °C within 30 m at 55.1 V which preserves heat for a long time. Before heat treatment, the available heating temperature of the coating decreases significantly with electrification cycles. The resistivity of coating rises rapidly during the cyclic electricity test. After hydrogen heat treatment, the electrical-heating property of coatings is significantly enhanced.

Keywords: TiO₂-15MgAl₂O₄ coating; electrical-heating property; atmospheric plasma spraying; resistivity; hydrogen heat treatment

1. Introduction

Heating rollers are widely used in plastic calendar, film lamination, paper drying, deep processing of non-woven materials and laser anti-counterfeiting printing. The traditional heating roller is mainly a fluid heating system. Oil and steam are used as the medium to heat the roller. Problems such as high maintenance cost, poor temperature uniformity, large energy loss, and potential safety problems lead to its elimination. The electromagnetic heating roller based on magnetic induction heating has the advantages of good temperature distribution and no pollution. However, it needs to heat within a cavity, and the heat is transmitted to products through the wall metal. This results in low thermal conversion efficiency and high energy consumption. In addition, its complex structure design increases costs.

The electrical-heating coating roller is a new type of heating roller which uses a thermal spraying method to spray electrothermal materials on the surface of the roller. It can be heated on the surface of the roller and directly conduct heat to products. It greatly enhances the heating efficiency of the heating roller. Recently, researchers used carbonaceous materials as heating elements to fabricate heaters, including carbon nanotubes (CNTS), graphene, and carbon fiber [1–3]. The carbonaceous composite material electrical heaters are mainly applied in flexible conductors and low-power applications, including wearable heating equipment, defogger devices, and indoor climate control heater [4–6]. The common metal electrical-heating materials include nickel-chromium alloy, iron-aluminum alloy, copper-based alloy, etc. [7]. Due to the low resistivity of metal electrical-heating materials, the metal



layer is usually thin and complex in structure (spiral or coil) in order to achieve the resistance required for a certain level of heat energy [8]. This will lead to a serious inductive effect, resulting in energy loss. On the other hand, metal electrical-heating materials will inevitably be oxidized in the process of electrified heating, which results in increased resistance and locally elevated temperature of metal layer [9]. To overcome the problems above, the ceramic electrical-heating materials have attracted much more attention because of its controllable resistivity, good oxidation resistance, and stable chemical properties [10–14].

Recent photocatalysis research has focused on TiO_2 because of its excellent photochemical properties [15–18]. There has been little reported on using TiO_2 as electricity-driven resistive heaters. TiO_2 is an excellent thermal spraying material with good thermal stability, high spraying deposition efficiency, tight coating-bonding, and low cost [19]. Stoichiometric TiO_2 is not conductive. Rutile TiO_2 is an insulator at room temperature, but non-stoichiometric TiO_{2-x} is a p-type semiconductor material [20,21] whose conductivity is attributed to oxygen vacancies. Toma et al. fabricated TiO_2 - Cr_2O_3 coating by an atmospheric plasma spraying method. The coatings are prone to re-oxidization when the temperature exceeds 300 °C [22]. Recent studies by Bobzin have shown that anisotropic cracks in TiO_2 - Cr_2O_3 coating lead to inhomogeneous temperature distributions on the surface of the coating [23].

In this paper, the composite powder of TiO_2 and $MgAl_2O_4$ is used as electrical-heating material to prepare coating by atmospheric plasma spraying. $MgAl_2O_4$ is included in the design as the insulating layer. On the one hand, the gradient change of composition between the heating layer and the insulating layer can reduce the thermal stress caused due to different thermal expansion coefficients, enhancing the bonding strength of different layers. On the other hand, non-conductive $MgAl_2O_4$ can regulate the resistivity of TiO_2 coatings in order to meet the requirements of high voltage and low current in industrial applications. The hydrogen heat treatment was used to improve the electrical-heating property of the coating.

2. Experimental Procedure

2.1. Experimental Materials

In this experiment, the composite coating system was sprayed on 310S stainless steel pipes (φ 23 mm × 294 mm) and 310S stainless steel disc substrates (φ 25.4 mm × 6 mm), respectively. As shown in Figure 1, the coating system consists of three layers. The bottom layer is a bonding coating, which decreases the thermal stress caused by different thermal expansion coefficient and improves the bonding strength between the coating system and the substrate. The top layer is the electrical-heating coating, which is used as a heat source after it is electrified. The middle layer is an insulating coating, which is used to insulate the heating layer and the substrate. There is a pair of copper hoops at two edges of the pipe which is used to load voltage and operates as an electrode.



Figure 1. Structure schematic diagram of the coating system sprayed on steel pipe.

The feedstock of the bonding coating is Ni-Al alloy powder (particle size 45–95 μ m, purity > 99%). Ni-Al coating matches well with the steel matrix in thermal and physical properties, which is beneficial for enhancing the bonding strength between the coating system and matrix [24]. The feedstock of the insulating coating is comprised of MgAl₂O₄ powder (particle size 10–45 μ m, purity > 99%). Compared with Al₂O₃, MgAl₂O₄ has no phase transition during the spraying process and has better performance for temperature and humidity [25]. A mixture of commercial black TiO₂ powder (particle size 15–45 μ m, purity > 99%) and MgAl₂O₄ powder (particle size 10–45 μ m, purity > 99%) were used as spray-feed to produce the heating coatings. Previous exploratory experiments showed that when the addition of MgAl₂O₄ was 30%, the resistance of the coating increased, resulting in lower working current and joule heat. In this study, TiO₂-15MgAl₂O₄ (TM15) powder was mixed at a mass fraction ratio of 85:15 to fabricate electrical-heating coating.

2.2. Preparation of Coating and Hydrogen Heat Treatment

Before spraying, the substrate was degreased by gasoline ultrasonic and then cleaned by alcohol. The substrate was sandblasted by #46brown corundum under pressure of 0.4 MPa. The oil and oxide on the surface of the substrate were removed. The roughness was increased to enhance the bonding strength between the coating and the substrate. The bonding layer, insulating layer, and the heating layer were all prepared by atmospheric plasma spraying. The spraying equipment used was the MF-P1000 atmospheric plasma spraying system (GTV) attached with an F6 gun (Oerlikon-Metco). The parameters used for the spraying process are shown in Table 1.

Coating	Current/A	Voltage/V	Distance/mm	Flux of Ar L/min	Flux of H ₂ L/min	Powder Feed Rate g/min
Ni-Al	600	70	110	45	8	25
$MgAl_2O_4$	630	75	110	40	9	33
TM15	580	79	110	41	11	30

Table 1. Atmospheric plasma spraying parameters.

The pipe and disc samples were heat-treated at 350 $^{\circ}$ C at a heating rate of 7 $^{\circ}$ C /min and cooled to room temperature in a vacuum furnace. The corresponding holding time was 6 h. The heat treatment was operated under a hydrogen flow rate of 100 mL/min.

2.3. Performance Characterization of Coatings

The phase composition of powders and coatings was examined by X-ray diffraction (XRD, Smartlab 9 kW, RIGAKU) (Tokyo, Japan using Cu K_{β} radiation at a scanning rate of 10°/min at Bragger angle (2 θ) between 10° and 90°. The microstructure and chemical composition of the coatings were characterized by scanning electron microscopy (SEM, Nova-Nona-430, FEI) equipped with an energy dispersive spectrometer (EDS).

The electrical-heating property of TM15 coating was researched by a cyclic electrification test. DC stabilized voltage power supply (KXN-6020D) (Shenzhen, Guangdong, China was selected for the power equipment. The power supply voltage was kept stable at 55.1 V during the electrification test. A cycle of electrification test comprises of heating the coating from room temperature to maximum temperature and then turning off the power to cool to room temperature after holding for 11 h. The temperature of the heating layer was measured by an infrared thermometer (UNI-T, UT303D) (Shenzhen, Guangdong, China. The temperature distribution of coating was observed through infrared thermal imager (UNI-T, UTi80) (Shenzhen, Guangdong, China. The resistance of the coating (R) was calculated by Equation (1) using the online voltage and current displayed on the power supply,

$$R = \frac{U}{I}$$
(1)

where U denotes the loading voltage and I the working electricity. Furthermore, the resistivity (ρ) can be calculated by

$$\rho = \frac{R \cdot S}{L} \tag{2}$$

where S represents the cross-sectional area of heating coating perpendicular to the electrical current and L the length of the heating coating in the direction of the electrical current.

3. Results and Discussion

3.1. Phase Composition and Microstructure

Figure 2 shows the XRD pattern of TM15 raw powder and coating. It can be seen from the pattern that the TM15 mixed powders include rutile TiO₂, Ti₃O₅, MgAl₂O₄, Ti₇O₁₃, and a series of other sub-stoichiometric titanium oxides. This is because the employed black TiO_2 powders are agglomerated and sintered in a vacuum environment, inducing the complex lattice anoxia of TiO₂. The peak intensities of the powder XRD pattern indicate that the rutile TiO_2 has the highest content. There are Ti₃O₅, rutile TiO₂, Ti₄O₇, MgAl₂O₄, and TiO phases in the TM15 coating. The peak intensity corresponding to the Ti₃O₅ phase in TM15 coating is the strongest, which indicates that the content of the Ti₃O₅ phase is the highest in TM15 coating. The sub-stoichiometric phase of powders reduced titanium oxides of more anoxia after spraying, e.g., $2\theta = 29^{\circ}$ (Ti₇O₁₃ to Ti₄O₇), 36° (Ti₅O₉ to Ti₃O₅), 41° (Ti₇O₁₃ to Ti₃O₅), 56° (Ti₇O₁₃ to Ti₃O₅). As for Ti_nO_{2n-1}, the lower the n, the more anoxia is induced in titanium oxides and the greater the conductivity. In the process of thermal spraying, the molten TiO₂ particles caused lattice anoxia in the high-temperature flame flow under low oxygen partial pressure [26]. In addition, hydrogen plasma has a strong reduction effect on TiO_2 , promoting the formation of anoxic phase in the coating during the spraying process [27]. Diffraction peaks of MgAl₂O₄ could be detected in both coatings and powders, but no peaks of other phases of Mg and Al elements. This indicates that the structure of MgAl₂O₄ is stable and phase transformation will not occur during spraying.



Figure 2. XRD patterns of TiO₂-15MgAl₂O₄ powder and coating.

Figure 3 shows the surface morphology of the TM15 coating. In Figure 3a, under low magnification, the coating surface is rough, which is composed of a melting zone and an incomplete melting zone. The coating is in the shape of high and low peaks. Figure 3b shows, under high magnification, that the splats in the melting region have spread completely and are smooth. Some reticular cracks are observed in the melting region, which is caused by the residual thermal stress released at the interface of molten particles during the cooling process of the coating [28,29].



Figure 3. SEM images of TiO₂-15MgAl₂O₄ coating surface. (a) low magnification; (b) high magnification.

Figure 4 shows the polished cross-section of the whole electrical-heating coating system. It can be seen from the figure that the electrical-heating coating system has a dense structure, uniform thickness, and close bonds without cracks. The average thickness of the bonding layer, insulation layer, and heating layer is about 65, 260, 320 μ m, respectively. The cross-sectional microstructure shows that the coating has a dense stacking structure (Figure 4). The black phase is distributed evenly in a wavy form in the gray phase matrix, with obvious phase interface. In the spraying process, the feedstock is heated by a plasma jet at a temperature of up to 15,000 K and then melted into a droplet or semi-molten particle, which impacts the substrate at a velocity of up to 800 m/s. Molten droplets or semi-molten particles deform and spread on the substrate due to the kinetic energy impact, accumulating on the substrate and solidifying rapidly into a stacking structure [30,31]. From the analysis by EDS, it can be determined that the black phase in SEM imaging is MgAl₂O₄. It can be evaluated that the gray matrix phase is TiO_{2-X}, containing a large amount of anoxia as determined from BSE imaging and the EDS analysis in Figure 5.



Figure 4. Cross-sectional morphology of electrical-heating coating and EDS analysis.





Figure 5. Backscatter electron imaging of TiO₂-15MgAl₂O₄ coating and EDS analysis.

3.2. Electrical-Heating Properties

Figure 6a shows the pipe sample of TM15 electrical-heating coating. The sprayed TM15 coating is shown as a gray-black color. Figure 6b shows the infrared thermal imaging picture of TM15 coating in the holding stage. From the temperatures shown, it can be seen that the surface temperature of the heating pipe is relatively uniform. The temperature difference in the middle of the pipe is no more than 20 °C. The temperature difference between the edges and middle of the pipe is mainly due to the heat loss by thermal radiation and convection [22,32].



Figure 6. Photograph of electrical-heating coating sample (**a**) and infrared thermal image of coating during the holding stage (**b**).

Figure 7 shows the temperature–time curve of TM15 coating tested by five cycles of electrification. The indicated temperature is the highest temperature on the coating surface, which is basically in the middle of the pipe. It can be seen from the figure that the temperature of the pipe rises rapidly in the heating stage. It can be heated to the highest temperature within 30 min. The temperature in the holding stage can remain stable for a long time. However, as the cycles of electrification increases, the highest heating temperature gradually decreases and changes greatly. During the first and second electrical-heating tests, the heating pipe can be heated to 321 and 312 °C respectively. However, in the next three electrification cycle tests, the heating pipes can only be heated to 273, 224 and 218 °C, respectively. According to Equation (3), at a constant voltage and increased resistance, decreased power was loaded on the coating. According to Equation (4), for the same electrification times, the temperature of the coating has a positive correlation with the joule heat. The increased resistance results in the decline of thermal effect. For the same heating pipe, the cross-sectional area and length of the heating pipe are identical. According to Equation (5), the resistance of the heating pipe is directly determined by the resistivity of the conductive layer. It seems that the available heating temperature of the coating is linearly related to the resistivity. However, the actual situation does not support this inference. Figure 8 shows the coating resistivity of five cycles in the heat preservation stage. Comparisons show that the resistivity increases with electrification cycles. The resistivity value of the fifth cycle is 5.59 times higher than that of the first cycle while the temperature is 321/218. It must be also considered that the temperature of the coating surface is not uniform as shown in Figure 6. Furthermore, there are some inherent defects in the coating, such as pores and micro-cracks, and changes have occurred in these defect areas during the cyclic electrification tests. This is discussed in detail in Figure 11.

$$P = U I = \frac{U^2}{R}$$
(3)

$$T \propto Q = P t \tag{4}$$

$$R = \rho \frac{L}{S} \tag{5}$$



Figure 7. Temperature-time curves of electrical-heating coating cyclic electrification tests.



Figure 8. The coating resistivity of five electricity tests in the heat preservation stage.

Figure 9b shows that the resistivity of TM15 coating decreases rapidly with time in the heating stage of 0–30 min. As electrification time increases, the coating attains more joule heat increasing the temperature. Therefore, electrons of the coatings move more intensively and move out of their original orbit easily. With the help of the heat energy introduced into the coating, more electrons gain energy and transit to higher energy levels, which is called the conduction band. When an electron transits to the conduction band, an electron hole remains behind. The electron from neighboring atoms tends to fill the electron hole. This will lead to the movement of more electron holes. In the case of TiO₂, electron holes are attributed to oxygen vacancies. In Figures 4 and 5, the MgAl₂O₄ is distributed uniformly in TiO_{2-x} as many wavy strips. MgAl₂O₄ is not conductive. When an oxygen vacancy moves to encounter MgAl₂O₄, it is impossible to move across through MgAl₂O₄ directly, but it moves along with the meander interface. This increases the motion path of the electron hole effectively so that the coating has a certain resistance for joule heat. As the temperature increases, oxygen vacancies move faster, sharply decreasing resistivity. After 30 min, the temperature of the coating fails to increase. The concentration and transfer rate of oxygen vacancies reach stability and the resistivity no longer changes.

Figure 10 shows the resistivity–temperature curve at different cyclic electrification tests in the heating stage. From the graph, it can be observed that the resistivity of TM15 coating decreases with the temperature, showing a negative temperature coefficient of resistance (NTC), which is similar to semiconductor materials. The resistivity of TM15 coating decreases slowly with temperature in the first cycle. As the number of cycles increases, resistivity declines faster. The cyclic electrification test is a kind of heat treatment in an atmospheric environment for TM15 coatings. The coatings need to undergo rapid heating, long-term heat preservation, air cooling, and multiple cycles. The anoxic phase is prone to oxidization in this process [33]. In the present study, this statement has been further verified. Figure 11 shows the cross-sectional morphology of electrical-heating coating after a cyclic electrification test. It can be observed that there are more pores and micro-cracks in the cross-section of coating than as-sprayed coatings. The size of pores and cracks are about 0.1–0.5 μ m in diameter, 2–5 μ m in length, respectively. The pores and cracks distribute mostly in TiO_{2–X} matrix. It is worth noting that the average ratio of oxygen atoms in the TiO_{2–X} matrix has increased by 10%, from 36% in Figure 5 to 46% in Figure 11. Particularly, the ratio of oxygen atoms in the areas near pores and cracks is higher

than other smooth sections. This demonstrates that the oxidation of TM15 electrical-heating coating during electrification occurs preferentially in the defects of the coating.



Figure 9. Resistivity–time curves of the coating cyclic electricity test (**a**) and graph of the corresponding heating stage 0-60min (**b**).



Figure 10. The resistivity-temperature curves of coating in the heating stage.



Figure 11. Cross-sectional morphology of electrical-heating coating after cyclic electricity test and EDS analysis.

3.3. Effect of Hydrogen Heat Treatment on Coating Electrical-Heating Properties

Some studies [34,35] have shown that a hydrogen atmosphere can promote rutile TiO₂ to form non-stoichiometric TiO₂ (anoxia phases of titanium dioxide). The contents of non-stoichiometric TiO₂ have an important influence on the conductivity of TiO₂ coating. The higher the content of non-stoichiometric TiO₂, the higher the conductivity of TiO₂ coating [36,37]. Figure 12 shows the temperature–time curve of the cyclic electrification test of coatings after 350 °C heat treatment. During 10 cycles of electrification, the coatings can be heated stably to above 300 °C within 30 min and kept for 11 h. Compared to coatings without heat treatment in Figure 7, it can be found that the heat-treated coating can still be heated to 324 °C after 5 cycles of electrification and 310 °C after 10 cycles of electrification, much higher than 218 °C in Figure 7. The heating temperature of heat-treated coatings remains stable from the fifth cycle. It illustrates that the hydrogen heat treatment effectively improves the heating property of TM15 coating.

As is shown in Figure 13, the resistivity of heat-treated TM15 coating decreases rapidly in the heating stage and kept stably in the holding stage, which is consistent with that of TM15 coating without heat treatment. The resistivity of heat-treated TM15 coating after five cycles is lower than that of non-heated ones. It is demonstrated that the conductivity of heat-treated TM15 coating is better than that of non-heat treatment one. After heat treatment, the coating resistivity of the fifth cycle electrification test is only 2.3 times higher than the first cycle and the resistivity of the tenth cycle is only 3.3 times higher than the first cycle. Compared with the TM15 coating before heat treatment, the resistivity stability of heat-treated TM15 coating is greatly improved. After hydrogen heat treatment, the coating resistivity of multiple electrification cycles is lower than that of non-heat-treated coatings, and the variation of resistivity is much smaller. It can be observed that the contents of Ti₃O₅ increases significantly after hydrogen heat treatment in Figure 14. Ti₃O₅ is relatively conductive among sub-stoichiometric titanium oxides. This finding is in accordance with the results in [35,36].



Figure 12. Temperature-time curves of the cyclic electrification test of heat-treated coatings.



Figure 13. Resistivity-time curves of the cyclic electrification test of heat-treated coatings.



Figure 14. XRD patterns of TiO₂-15MgAl₂O₄ coating before and after hydrogen heat treatment.

4. Conclusions

The TiO₂-15MgAl₂O₄ coating for electric heating was successfully synthesized by an atmospheric plasma spraying method. The phase composition, microstructures, and electrical-heating properties were investigated systematically. Some important conclusions can be drawn as follows:

- The phases of atmospheric plasma sprayed TiO₂-15MgAl₂O₄ coating include Ti₃O₅, rutile TiO₂, Ti₄O₇, MgAl₂O₄, and TiO phase. The MgAl₂O₄ distributes uniformly in a wavy strip in the TiO_{2-x} matrix.
- (2) The resistivity of electrical-heating coating rises and the available heating temperature declines during cyclic electrification tests. This is attributed to the increased pores, expanded micro-cracks, and re-oxidized TiO_{2-x}.
- (3) After hydrogen heat treatment, Ti₃O₅ of the electrical-heating coating increases obviously. The available heating temperature and the stability of coating resistivity are significantly improved.

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