Bonding characteristics of the Al_2O_3 -metal composite coating fabricated onto carbon steel by combustion synthesis

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Abstract: The fabrication of an alumina-metal composite coating onto a carbon steel substrate by using a self-propagating high-temperature synthesis technique was demonstrated. The effects of the type and thickness of the pre-coated layer on the binding structure and surface quality of the coating were systematically investigated. The macrostructure, phase composition, and bonding interface between the coating and the substrate were investigated by scanning electronic microscopy (SEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectrometry (EDS). The diffraction patterns indicated that the coating essentially consisted of $\alpha\text{-Al}_2\text{O}_3$, Fe(Cr), and $\text{FeO}\cdot\text{Al}_2\text{O}_3$. With an increase in the thickness of the pre-coated working layer, the coating became more smooth and compact. The transition layer played an important role in enhancing the binding between the coating and the substrate. When the pre-coated working layer was 10 mm and the pre-coated transition layer was 1 mm, a compact structure and metallurgical bonding with the substrate were obtained. Thermal shock test results indicated that the ceramic coating exhibited good thermal shock resistance when the sample was rapidly quenched from 800°C to room temperature by plunging into water.

Keywords: carbon steel; combustion synthesis; composite coatings; phase composition; morphology; thermal shock resistance

1. Introduction

As traditional materials, carbon steels experience significant challenges in the environment, enduring wear, corrosion, and oxidation. One of the effective strategies to improve the overall performance of carbon steels is often via surface engineering treatments to deposit ceramic coatings. Of the different materials used for this purpose, Al_2O_3 ceramic is one of the most widely used abrasive materials owing to its high corrosion resistance, excellent wear resistance, and low cost. Given these advantages, Al_2O_3 ceramic has become the material of choice for coating metal substrates to improve their wear and corrosion resistance. Thus far, several methods have been adopted to fabricate Al_2O_3 ceramic coatings. However, these traditional fabrication techniques often involve complex manufacturing processes and expensive equipment. Moreover, the conventional fabrication methods have certain inherent limitations for use in different

applications. Therefore, it has always been a challenging task to identify appropriate methods for depositing Al_2O_3 ceramic coatings onto carbon steel.

Combustion synthesis (CS), also known as self-propagating high-temperature synthesis (SHS), is an effective, low energy consuming, cost-effective method for preparing advanced materials, such as ceramics, inter-metallic compounds, composites, and cermets [1–5]. Recently, there has been an increased interest in the deposition of ceramics, cermets, and inter-metallic coatings onto metal substrates using SHS owing to their potential use in a wide variety of applications [6–9]. In particular, several studies have investigated the dynamic process associated with the SHS coating technology combined with centrifugal technique [10–14]. However, the practical implementation of the SHS technique for coating ceramic materials is greatly limited by complexities and difficulties originating due to the difference in physical, chemical, and mechanical properties between the metal and Al_2O_3 ceramics.

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To this end, in this study, we have made an attempt to deposit the Al₂O₃-metal composite coating onto the steel substrate using the SHS method under static conditions. This does not demand any sophisticated equipment or stringent working conditions. Furthermore, we have systematically investigated the various process parameters and the composition of reaction materials.

2. Experimental method

2.1. Fabrication of ceramic coating

Table 1 provides a detailed summary of the characteristics of the various precursor materials used in the experiment.

Table 1. Characteristics of the precursor materials used in the experiment

Raw material	Fe ₂ O ₃	Cr ₂ O ₃	Al	SiO ₂	NiO	NiCrAl
Purity / wt%	99.0	99.0	99.0	99.0	99.0	—
Particle size / μm	0.2–0.8	0.5–2.0	4–70	5–25	0.3	45–109

In reality, the expansion coefficient and elastic modulus of the ceramic coating is rather different from that of the substrate. Therefore, the NiCrAl or NiAl layer is commonly used as a transition layer between the substrate and the coating during the plasma spraying process in order to improve the bonding performance [15–16].

The precursors used in the SHS system are based on the chemical reactions shown in Eqs. (1)–(3). Moreover, Al powders are added in excess to ensure the successful completion of the reaction. Accordingly, the molar ratio of Fe₂O₃:Cr₂O₃:Al is typically 6:4:21, and the molar ratio of NiO:Al is 3:2. In the typical process, raw powders were mixed for 6 h in a ball-mixed mill. Carbon steel Q235 in dimension of 50 mm × 40 mm × 6 mm was used as the substrate. Prior to coating, the carbon steel substrate was sand-

blasted and cleaned. Subsequently, the ball-milled powders were pre-coated onto the blasted steel substrate, forming a structure as shown in Fig. 1. Following that, the powders were ignited using magnesium ribbon as the ignition agent. Fig. 2 shows the protocol adopted in this process.

Fig. 1. Schematic of the coating deposited using the SHS process.

Fig. 2. Protocol showing the sequence of steps adopted in the SHS process.

Furthermore, a transition layer was deposited to ensure the effective bonding between the substrate and the ceramic material. Table 2 summarizes the different materials and thickness of the transition layers deposited in this study.

Table 2. Parameters of different samples

Sample	Type of the pre-coated transition layer	Thickness of the pre-coated transition layer / mm	Thickness of the pre-coated working layer / mm	Additive
Coating 1	—	0	10	—
Coating 2	NiCrAl	1	10	—
Coating 3	NiO+Al	1	10	—
Coating 4	NiCrAl	1	6	—
Coating 5	NiCrAl	1	3	—
Coating 6	NiCrAl	1	10	5wt% SiO ₂

2.2. Characterization

The phase composition of the coatings was identified by

X-ray diffraction (XRD, Bruker D8-Advance). The surface morphology and microstructure of the coating, and those of the interface between the coating and the substrate, were

observed using a Hirox KH-7700 Digital microscope, Olympus BX51M microscopy (OM), and scanning electron microscopy (SEM, Hitachi S-3400N).

The elemental distribution analysis of the coating was performed by energy-dispersive X-ray spectrometry (EDS, Horiba EX-250). The microhardness at the cross-section of the coating was estimated using a Vickers microhardness tester (HXD-1000TC) with a load of 1.96 N. The final hardness value was determined by averaging the results of 10 measurements.

The thermal shock test was performed according to JIS H8666–1990 [17], in order to evaluate the bonding property between the coating and the substrate. In the typical experiment, the coated sample was heated to 800°C in an electric furnace, and maintained at that temperature for 5 min. Following that, the sample was immersed in water and rapidly quenched to room temperature.

3. Results and discussion

3.1. Coating without the transition layer

Fig. 3 shows the XRD pattern of coating 1 that was fabricated without the transition layer. The diffraction pattern clearly reveals that the coating is composed of α -Al₂O₃, Fe(Cr), and FeO·Al₂O₃. There are no diffraction peaks corresponding to the raw materials, implying the completion of reaction in the designed system.

Fig. 3. XRD pattern of coating 1 fabricated without the transition layer.

The SEM image shown in Fig. 4 presents the microstructure at the interface between the coating and the substrate. As evidenced from the image, there are some microcracks at the interface zone. The bottom of the coating has different phases. Therefore, we performed EDS analysis at the regions designated as zones A and B in Fig. 4, and the

corresponding results are listed in Table 3. Correlating the EDS results shown in Table 3 with the XRD results shown in Fig. 3, it could be concluded that the black zone A has α -Al₂O₃ phase containing traces of Cr and Fe elements in the solution. On the other hand, the bright zone B is a particle of Fe(Cr) solid solution.

Fig. 4. SEM image of the interfacial region in coating 1 fabricated without the transition layer.

Table 3. EDS analysis of regions designated as zones A and B in Fig. 4

Location	at%			
	Al	Fe	Cr	O
A	45.97	0.57	1.11	52.35
B	0	56.36	43.64	0

3.2. Effect of the transition layer

Fig. 5 shows the representative SEM images of the interfacial region in coating 2, which was fabricated with a 1-mm-thick NiCrAl transition layer and a 10-mm-thick ceramic layer, and the interfacial region in coating 3 with a 1-mm-thick (NiO + Al) transition layer and a 10-mm-thick ceramic layer. In the image, the section at the left corresponds to the substrate, while that at the right corresponds to the coating. As is seen, the interface between the coating and the substrate is not a line, but a hackle. This suggests that the steel substrate could have been melted by the reaction heat generated during the SHS process. Therefore, the interface bonding between the coating and the substrate is not only a mechanical bonding but also can be considered partially as a metallurgical bonding. These results substantiate the formation of good bonding in the system [18].

Fig. 6 shows the elemental distribution map at the interfacial region in coating 3, as determined by EDS. Results indicate the diffusion of Fe, Ni, and Al elements between the two sides, once again verifying the formation of metallurgical bonding at the interface.

Fig. 5. SEM images of the interface area in coating 2 (a) and coating 3 (b).

Fig. 6. EDS analysis at the interface of coating 3.

According to the nickel-iron phase diagram, Fe and Ni can form infinitely mutual solid solution. Therefore, during the liquid-solid transformation at the interface, Ni and Fe atoms will tend to diffuse across the interface. Accordingly, the corresponding EDS pattern shows gradual variations. This confirms the formation of metallurgical bonding at the interface.

3.3. Effect of the thickness of the ceramic layer

According to the study reported by Merzhanov and An [19–20] the SHS reaction would take place spontaneously, only under the condition that the adiabatic temperature is higher than 1800 K. The adiabatic temperature calculated for the reactions (1), (2), and (3) are 3135, 2654, and 3514 K, respectively. It can be realized that the adiabatic temperature is much higher than the melting points of Al₂O₃ (2327 K), Fe (1808 K), Cr (2130 K), and Ni (1728 K). Therefore, with the increase in the thickness of the reaction compact, the reaction system will release more heat. Fig. 7 shows the surface macrograph of the coating with different thicknesses of the pre-coated working layers. When the thickness of the pre-coated working layer is of the order of 3 mm, the surface of the SHS coating is characterized by discrete, dispersive, and uneven island-shaped products. Moreover, the surface of coating 5 reveals several metal particles. Fur-

thermore, with an increase in the thickness of the pre-coated working layer from 3 to 10 mm, the surface of the SHS coating becomes smooth with fewer holes. In addition, the spreadability of the coating is better, as shown in Fig. 7. With a further increase in the thickness of the working layer to 10 mm (Fig. 7 (c)), we could obtain a smooth, complete, and uniform coating. Based on these results, it can be concluded that the increase in the thickness of the working layer results in the release of more reaction heat. Correspondingly, the liquidity of the reaction products was improved, leading to the formation of a smooth surface as mentioned above.

Fig. 8 shows the representative SEM images of the interfacial region in the coatings with different thicknesses (from 3 to 10 mm) of the pre-coated working layer. The cross-sectional SEM image of the coating with a pre-coated working layer of 3 mm in thickness reveals several big pores closer to the interface. With an increase in the thickness of the pre-coated working layer to 6 mm, we could not observe any big pores, although few fine cracks were observed. With a further increase in thickness to 10 mm, we could observe effective binding at the interface, without any pores or cracks.

3.4. Effect of SiO₂ additives

According to Rice and McDonough, the coatings formed by the SHS reaction are associated with two kinds of porosity, namely, extrinsic and intrinsic. The extrinsic porosity typically originates from the pores that are initially present in the green compact, as well as from the vaporization of impurities or low melting point phases at high temperatures. On the other hand, intrinsic porosity is formed due to the intrinsic differences between the products and the starting reactants, wherein the final products are denser than the starting reactants [21]. However, according to previous studies [22–23], the porosity of the coating could be greatly reduced by using SiO₂ as an additive in the raw materials. Fig. 9 shows the representative SEM images of coating 2 and coating 6 with 5wt% SiO₂. As is seen, the porosity of

Fig. 7. Surface macrographs of the coatings with different thicknesses of the pre-coated working layer: (a) coating 5; (b) coating 4; (c) coating 2.

Fig. 8. Cross-sectional SEM images of the SHS coatings with different thicknesses of the pre-coated working layer: (a) coating 5; (b) coating 4; (c) coating 2.

coating 6 (Fig. 9(b)) is significantly reduced compared to that of coating 2 (Fig. 9(a)), due to the inclusion of the SiO_2 additive. For pure Al_2O_3 , the starting and ending points of crystallization occur at a fixed temperature of 2054°C [24]. However, with the addition of SiO_2 , there occurs a difference between starting and ending points of crystallization. In the Al_2O_3 - SiO_2 system, mullite is formed in the meta-stable

phase equilibria, with the crystallization end point of $(1828 \pm 10)^\circ\text{C}$ [25]. These results suggest that the addition of SiO_2 not only lengthens the liquid state time of the product Al_2O_3 , but also favors the escape of gas. The longer the product Al_2O_3 is maintained in the liquid state, the more the pores or porosities are filled up, which will lead to the formation of the coating with a more compact structure.

Fig. 9. SEM images of coating 2 (a) and coating 6 (b) with 5wt% SiO_2 .

Fig. 10 shows the microhardness profile of the coating. With the increase in distance between the interface and the top surface of the coating, the hardness of the SHS coating increases initially. At the distance of 4430 μm , coating 6 reached the maximum hardness of Hv 2203. At the distance of 3330 μm , coating 2 reached the maximum hardness of Hv 2400. The addition of 5wt% SiO_2 decreased the microhardness of the SHS coating to some extent. This could be attributed to the existence of mullite phase, which has a lower hardness than Al_2O_3 .

Fig. 10. Microhardness profile of coating 2 and coating 6.

As suggested by the abovementioned results, coatings 2 and 3 are bonded well to the substrate. This result was further substantiated via thermal shock testing. During the test, the coatings were heated to 800°C, followed by rapid quenching to room temperature by plunging into cold water. The process was repeated until macrocracks were observed in the coatings. Fig. 11 shows the number of thermal shock cycles endured by the six coatings. As is seen, coating 1 yielded earlier to the thermal shock owing to the bad binding of the coating to the steel substrate. Of all the samples, coatings 2 and 3 exhibited the best thermal shock resistance. With an increase in the thickness of the pre-coated working layer from 3 to 10 mm, there was a significant improvement

in the bonding quality. Consequently, the thermal shock resistance of these coatings increased from 3 cycles to 9 or 10 cycles. In simple terms, coatings 2 and 3 featured good metallurgical bonding with the substrate exhibited the best thermal shock resistance. Fig. 12 shows the photograph of coating 3 after 4, 9, and 20 cycles of thermal shock testing. As is seen, cracks did not appear even after 3 cycles of thermal shock. However, after 9 cycles, some small cracks appeared on the surface of the coating. After 20 cycles, the cracks propagated. Nevertheless, the coating did not flake off from the substrate. These results suggest that coating 3 exhibited excellent bonding with the steel substrate and had a very good thermal resistance. In reality, thermal stress tends to develop and increase gradually during the thermal shock test owing to the difference in thermal physical properties between the ceramic coating and the steel substrate. After a certain period of testing, thermal cracks begin to appear on the top ceramic layer or/and at the interface between the top ceramic layer and the transition layer. With further thermal cycling, the cracks tend to propagate and interact with each other. Fig. 13 illustrates the vertical propagation of the cracks in the coating during thermal cycling. Because

Fig. 11. Thermal shock test results of six coatings.

Fig. 12. Crack propagation in coating 3 during thermal shock testing after 4 cycles (a), 9 cycles (b), and 20 cycles (c).

Fig. 13. Schematic illustration of the vertical crack propagation model in the coatings during thermal shock testing.

of the difference in expansion coefficient of the ceramic coating and the steel substrate, a shear stress would be developed at the interface between the coating and the steel substrate. This gets enlarged progressively during the repeated heating-cooling cycles, thereby resulting in the horizontal propagation of the cracks. Finally, the cracks connect together, leading to an interfacial delamination [26]. However, when metallurgical bonding exists at the interface, the bonding is rather strong, and interfacial delamination occurs only after several heating-cooling cycles.

4. Conclusions

(1) A ceramic-metal composite coating was successfully fabricated onto the steel substrate by SHS under normal atmosphere pressure. The coating was pre-coated with a tran-

sition layer of 1-mm-thick NiCrAl powder or (NiO + Al) powder mixture, and a working layer of $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{Al}$ of 10 mm in thickness.

(2) The ceramic-metal composite coating was primarily composed of the $\alpha\text{-Al}_2\text{O}_3$ matrix, Fe–Cr solid solution, and $\text{FeO}\cdot\text{Al}_2\text{O}_3$ spinel, exhibiting a very high hardness up to Hv 2400.

(3) The use of an appropriate transition layer with an optimum thickness can improve the bonding quality of the coating and the steel substrate. Under these conditions, the resulting SHS coating exhibited metallurgical bonding with the steel substrate and had an excellent thermal shock resistance.

(4) The addition of 5wt% SiO_2 was beneficial in terms of the reduction of the coating porosity and the improvement of the coating surface.

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