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The Preparation and Properties of Ni_2Al_3 Intermetallic Compound Coating

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Abstract: In this work, a Ni_2Al_3 intermetallic compound coating was prepared on 45 # steel by combining methods of low-pressure cold spray and heat treatment. Firstly, powders mixed with Ni powders, Al powders, and Al_2O_3 powders as a mass ratio of 20:6:4 were sprayed on surface of 45 # steel by low-pressure cold spraying technology to prepare a Ni-Al pre-coating. Subsequently, the pre-coating was annealed at 570 °C in an argon atmosphere for 12 h to obtain the Ni_2Al_3 intermetallic compound coating. The composite coating was characterized using TEM, SEM, and XRD. High temperature oxidation performance of the composite coating was analyzed by isothermal oxidation tests conducted at 600 °C in air atmosphere for 96 h. The results show that the composite coating is composed of Ni_2Al_3 phase. Under a high-temperature oxidation environment, a protective oxide film composed by Al_2O_3 and NiO was formed on the coating surface, which resulting in a superior high-temperature oxidation resistance compared to 15CrMo heat-resistant steel. The mechanism of the Ni_2Al_3 coating resistance to high-temperature oxidation is that an oxide film mainly composed of Al_2O_3 and NiO formed on the surface during the high-temperature oxidation process; this oxide film can effectively resist oxidation and protect the substrate material from oxidation at a high temperature of 600 °C.

Keywords: cold spraying; heat treatment; intermetallic compound coating; high temperature oxidation performance

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1. Introduction

NiAl intermetallic compounds have low density, good oxidation resistance, and excellent high-temperature strength [1]. Under specific conditions, a series intermetallic compounds can be formed between metal Ni and Al, including $NiAl_3$, Ni_2Al_3, NiAl, and Ni_3Al [2,3]. These intermetallic compounds not only possess the toughness of metals and the high-temperature resistance of ceramics, but also have the characteristics of low density and high melting point, by which they have great application prospect in high-temperature field [4–7]. Ni_2Al_3 intermetallic compounds have good resistance to high-temperature oxidation and corrosion, and have a broad application in the field of high-temperature protection [8–10]. However, the disadvantage is that Ni_2Al_3 intermetallic compounds have high room temperature brittleness, so it is difficult to form and process the intermetallic compounds. Therefore, preparing Ni_2Al_3 coating on the surface of an alloy is a promising approach to promote its engineering application. Mohammadnezhad et al. [11] prepared a nanostructured NiAl coatings on carbon steel by mechanical alloying method. Yu et al. [12] prepared Ni_3Al intermetallic compound coatings by using laser cladding method. Moreover, Xiang et al. [13] and Zheng et al. [14] systematically prepared Ni_2Al_3 coatings on steel substrates using a two-step method. At present, the preparation methods

of Ni_2Al_3 coatings mostly use electroplating Ni first, and then infiltration Al, in order to obtain Ni_2Al_3 coatings during the infiltration Al process [15]. The electroplating Ni process, however, imposes stringent requirements, and is limited to producing coatings with a thicknesses of around 10 μm [16], rendering it unsuitable for applications that demand thicker coatings, such as the high-temperature oxidation resistance coating for cast iron, which is 30~100 μm [17]. Patel et al. prepared a high temperature oxidation-resistant coating on Ti6Al4V alloy by diffusion heat treatment after hot-dip aluminizing [18]. Relevant studies have shown that Ni and Al can form intergranular compounds at high temperatures, but the Ni_2Al_3 formed is only on the Ni/Al interface [19]. Therefore, if a mixed coating with uniform distribution of Ni and Al was formed before high temperature treatment, a full Ni_2Al_3 coating maybe formed after heat treatment. The key is how to form a mixed coating with uniform distribution of Ni and Al.

Cold spraying, also known as cold aerodynamic spraying method, is a spraying technology based on aerodynamic principles. It obtains high-speed airflow through the process of heating and pressurization, and impacts the substrate at a critical or supercritical speed, causing the sprayed powder particles to undergo thermal softening and plastic deformation, and deposit on the surface of the substrate. The raw material for cold spray is metal powers, which means that powders can be flexibly selected [20], so it is a promising way to obtain the mixed coating with uniform distribution of Ni and Al by cold spraying. In recent years, using cold spraying technology to prepare metal matrix composite coatings has attracted widespread attention from scholars both domestically and internationally.

This article used low-pressure cold spraying technology and heat treatment process to prepare a Ni-Al composite coating with Ni_2Al_3 as the main phase. The microstructure of the surface and cross-section of the composite coating was characterized, and the phase composition was analyzed. The high-temperature oxidation performance of the composite coating was tested by isothermal oxidation tests in a high-temperature air environment at 600 °C; 15CrMo heat-resistant steel was used as a comparison sample. This work would produce an enlightening significance for the high-temperature protection of Ni_2Al_3 intermetallic compound composite coating.

2. Experimental Materials and Methods

2.1. Materials

The experiment selected 45 # steel as the matrix material, and the powder used in this experiment was Ni, Al, and Al_2O_3 produced from Beijing Xingrongyuan Technology Co., Ltd., Beijing, China. Before spraying, the three powders were uniformly mixed in a mass ratio of 20:6:4. The addition of Al_2O_3 was mainly aimed at improving the flowability of the powder during the cold spraying process and enhancing the wear resistance of the coating [21].

2.2. Preparation of Coatings

The experiment used a low-pressure cold spraying system (the Russian DYMET-423), with compressed air as the accelerating gas, at a pressure of 0.6–0.8 MPa and a temperature of 500 °C. The movement speed of the spray gun was 300 mm/min, and the nozzle was 15 mm away from the surface of the sample. The base material was 45 # steel, with a size of 20 mm × 20 mm × 3 mm. Before spraying, the 45 # steel was polished with sandpaper and ultrasonic cleaned in alcohol and acetone solution in sequence to remove oil stains attached on the surface. After drying, it was ready for use. Preparation of Ni_2Al_3 coating: Firstly, preparation of Ni-Al composite pre-coating by spraying mixed powders on 45 # steel. Then, the pre-coating was placed in a tubular furnace for heat treatment, heat at a rate of 10 °C/min in an argon environment to 570 °C for 12 h, and then cooled at a rate of 5 °C/min to room temperature.

2.3. High-Temperature Oxidation Test Method

The high-temperature oxidation experiment adopted the static isothermal oxidation method, and the weight increase method was used to evaluate the high-temperature oxidation resistance of the coating, with 15CrMo heat-resistant steel as a comparison sample. The chemical composition of 15CrMo steel was shown in Table 1. Firstly, the Ni_2Al_3 composite coating sample was cleaned with acetone and blown dry. It was placed in a crucible and heated together with the crucible in a box-type resistance furnace. The oxidation temperature was set at 600 °C, and the oxidation time was 96 h. During this period, the weight was taken out and weighed every 12 h. The sample and crucible were placed in a drying oven to cool to room temperature before weighing. After weighing, the sample was returned to the furnace to continue the next cycle of testing until all tests were completed and calculated the oxidation weight gain rate per unit area (mg/cm^2). The weighing instrument used in this work is an electronic analytical balance with an accuracy of 0.1 mg.

Table 1. Elements in15CrMo steel.

Element	C	Si	Mn	Cr	Mo	Fe
Mass%	0.16	0.21	0.52	0.98	0.48	Bal.

2.4. Characterization Methods

The microstructure of the coating was observed using field emission scanning electron microscopy (SEM, SU8010, Hitachi, Tokyo, Japan). High-resolution images of the coating were obtained using field emission transmission electron microscopy (TEM, Talos F200, FEI, Brno, Czech Republic), enabling analysis of the coating's microstructure, crystal plane spacing, and electron diffraction patterns. The chemical element composition for the coating was detected by Energy Dispersive X-ray Spectroscopy (EDS), and the phase composition of the coating was analyzed by using an Ultima IV X-ray diffractometer (XRD, D/max-γA10, Rigaku, Tokyo, Japan). The chemical state of the composite coating material was characterized using an X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific, Waltham, MA, USA). A thermogravimetric analyzer (TGA4000, PerkinElmer, Waltham, MA, USA) was used to perform thermogravimetric analysis on the coating, with an initial temperature of 25 °C and a heating rate of 10 °C/min.

3. Results and Analysis

Figure 1 shows the cross-sectional SEM morphology of the Ni_2Al_3 coating after heat treatment, and the EDS result detected along straight-line M in the marked area of the cross-section of the Ni_2Al_3 coating also displayed. As shown in Figure 1a, a compact composite coating is deposited on the substrate, and the average thickness of the coating is approximately 600 μm. In the low-pressure cold spraying process, the continuous particle acceleration and impact process cause the powder to flatten, forming a continuous coating. The collision and impact between the powder and the powder stack compact the coating, and enhance the bonding force between the coating and the 45 # steel [22–24]. As shown in Figure 1b, from the EDS result, it can be seen that the main elements of the coating are Ni and Al, and the content ratio of Ni to Al is close to 2:3; the main element of the matrix is Fe. After heat treatment, Ni and Al elements diffuse towards the substrate material, while Fe elements diffuse towards the coating. The mutual diffusion between the coating and substrate elements can improve the bonding force between the coating and substrate.

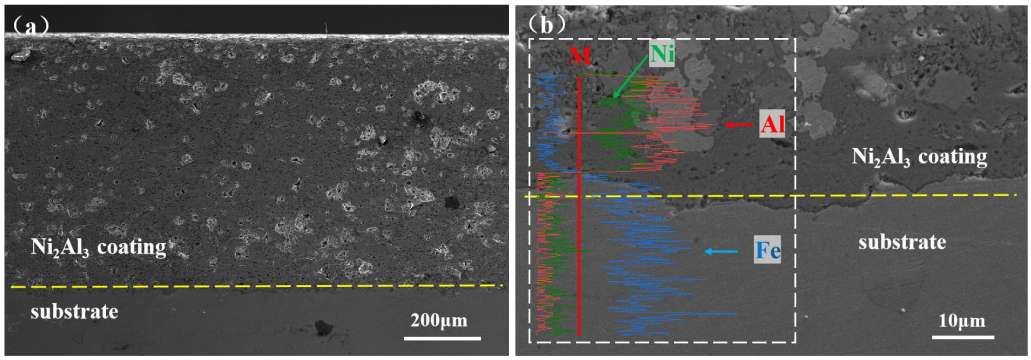


Figure 1. SEM images of cross-sectional of the coating (**a**) and EDS analysis of cross-sectional of the coating (**b**).

Figure 2 shows the XRD of the pre-coating before and after heat treatment. As shown in Figure 2a, the pre-coating before heat treatment is mainly composed of Ni (JCPDS: 04-0850), Al (JCPDS: 04-0787), and Al_2O_3 (JCPDS: 82-1399) phases. As shown in Figure 2b, it can be seen that the coating is mainly composed of Ni_2Al_3 (JCPDS: 14-0648) and also contains a small amount of NiAl (JCPDS: 44-1188), Ni_3Al (JCPDS: 09-0097), Ni (JCPDS: 04-0850), and Al_2O_3 (JCPDS: 82-1399) phases, while a small amount of elemental Ni phase is left by an incomplete solid-state reaction. Cold-sprayed Ni-Al alloy coatings can obtain coatings with Ni_2Al_3 as the main phase under high-temperature conditions for insulation [25]. It found that the order of the solid-state reaction products of Ni-Al metal is $NiAl_3$, Ni_2Al_3, NiAl, and Ni_3Al [26]. In Ni-Al pre-coating, due to the combined effect of thermal energy and deformation energy, Al will diffuse towards the Ni-rich region and react with Ni to generate $NiAl_3$. This reaction will release a large amount of heat, which will further promote the diffusion of $NiAl_3$ into the Ni-rich region and react with Ni atoms to generate Ni_2Al_3. Under the heat treatment conditions of this experiment, the phase transition from $NiAl_3$ to Ni_2Al_3 mainly occurred, resulting in the formation of the Ni_2Al_3 phase. Although Ni_2Al_3 has a tendency to diffuse towards areas rich in Ni and generate NiAl, the process is limited due to the solid-state phase transition reaction rate of the metal being much lower than the liquid reaction rate, illustrating in a lower content of NiAl phase in the coating [27,28].

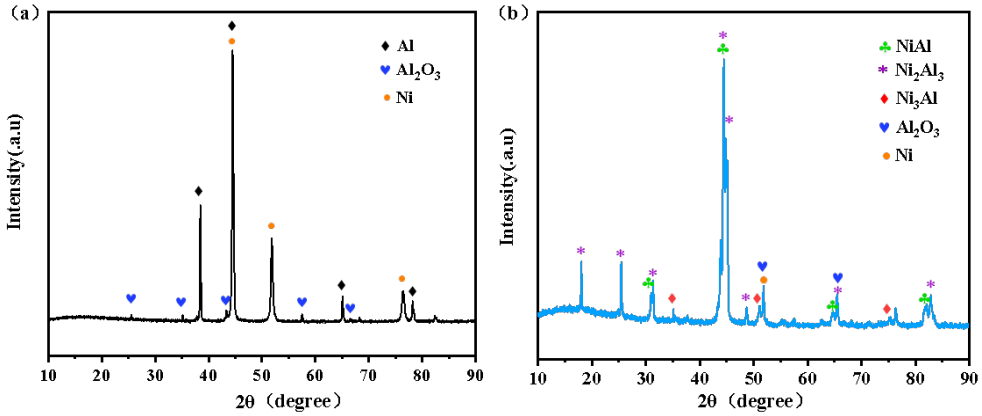


Figure 2. The XRD of the pre-coating ((**a**) before heat treatment; (**b**) after heat treatment).

Figure 3a is a TEM image of the coating surface. The different contrasts represent different microstructures or grain orientations of the same structure. According to the energy spectrum analysis of Region 1 in Figure 3a, the main elements in this region are Ni and Al. Table 2 shows the proportion of atomic content in Region 1. The proportion of Ni and Al atoms in Region 1 is 35.21% and 52.97%, respectively. According to the results of the energy spectrum analysis, the composition of the coating Region 1 is relatively close to Ni_2Al_3.

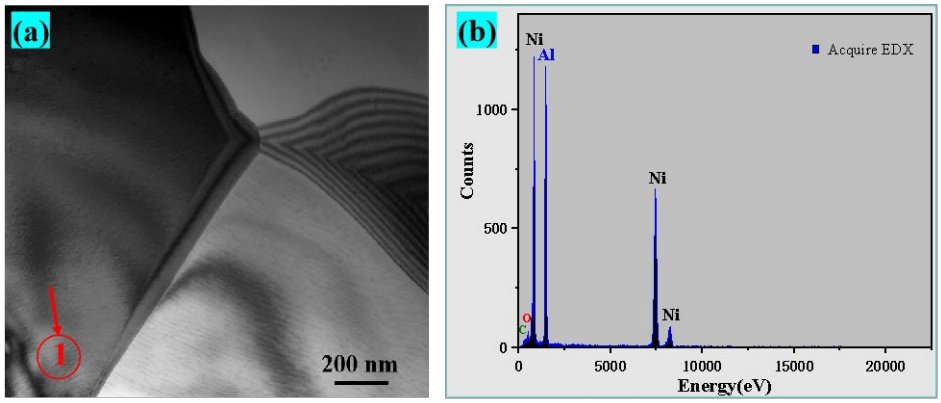


Figure 3. (**a**) TEM image of the Ni_2Al_3 coating surface; (**b**) EDX analysis of Region 1 in (**a**).

Table 2. Proportion of atomic content of Region 1 in Figure 3a.

Test Points	Ni	Al	C	O
1	35.21	52.97	5.14	6.65

To confirm the inference, selective electron diffraction (TEM) analysis was performed on Region 1 to reveal the phase composition of the coating further. Figure 4a is the TEM image near the Ni_2Al_3 coating; Figure 4b is an enlarged view of Figure 4a, which provides a clearer view of the interface between the coatings. Figure 4c shows the corresponding inverse fast Fourier transform image, with a crystal plane spacing of approximately 0.49 nm. Figure 4d shows an electron diffraction pattern; the lattice parameters were analyzed and calibrated by comparing with PDF card and. The sample is considered to be a rhombic crystal system, and can be labeled as Ni_2Al_3.

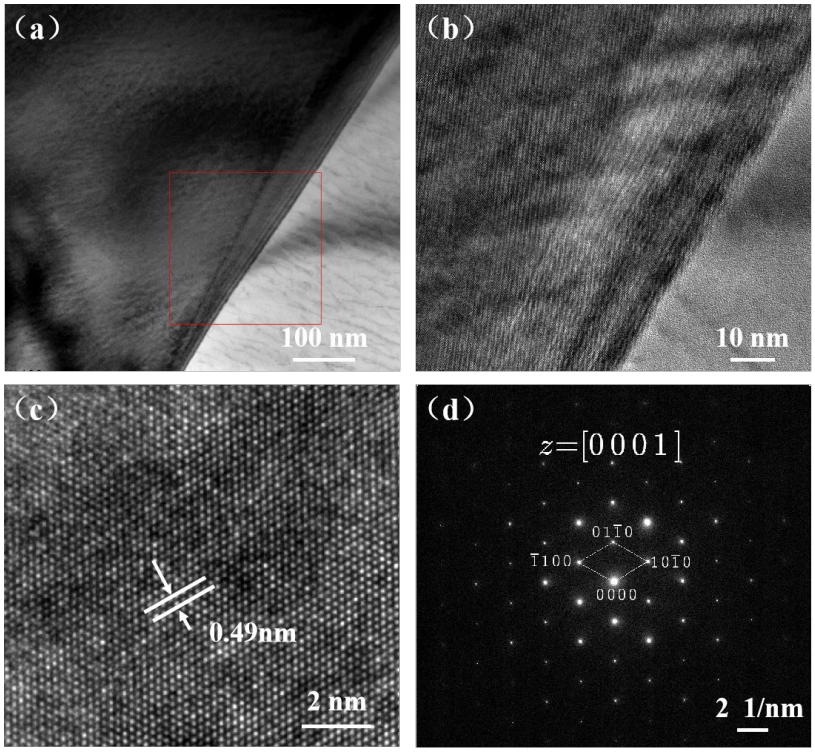


Figure 4. TEM analysis of the Ni_2Al_3 intermetallic compound coating. (**a**,**b**) HRTEM images of the intermetallic compound coating, (**c**) the corresponding IFFT image, (**d**) the SAED image of the intermetallic compound coating.

Ni_2Al_3 intermetallic compound coating was prepared on the surface of 45 # steel by using low-pressure cold spray technology, and then the thermal oxidation performance of the coating was tested by using TAG. Figure 5 shows the TAG analysis results of 15CrMo steel and Ni_2Al_3 intermetallic compound coating. As shown in Figure 5, as the temperature increases, the increase in weight of 15CrMo steel is significantly higher than that of Ni_2Al_3 intermetallic compound coating. The weight gain curves of both have a significant stable period at 500 °C and enter a rapid growth period after exceeding 500 °C.

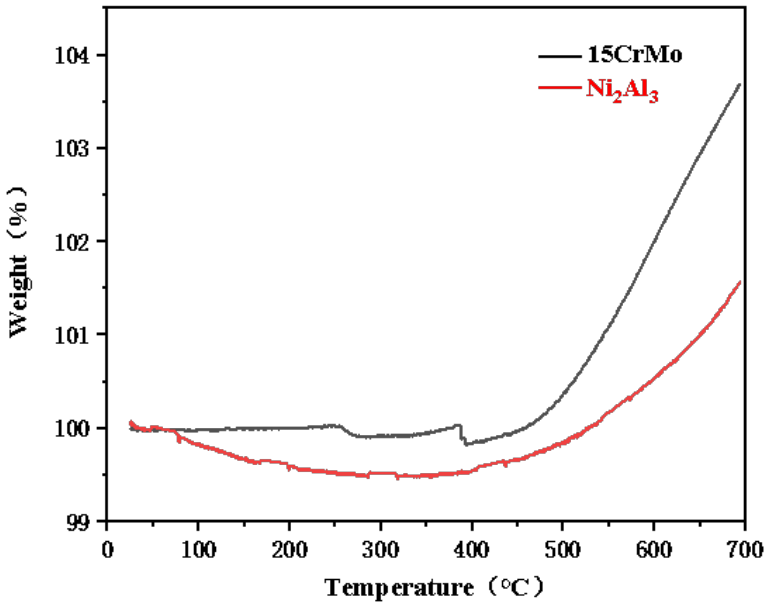


Figure 5. TAG analysis of 15CrMo steel and Ni_2Al_3 intermetallic compound coating.

When the temperature of 15CrMo steel is below 500 °C, the oxide film will be formed on the surface, which has a slower oxidation rate and slower mass growth. When the temperature continues to rise, the oxide film is destroyed and cannot prevent the iron in the inner layer from continuing to react with oxygen, resulting in a rapid increase in the mass of the sample. So, in high-temperature environments above 500 °C, the oxidation resistance of 15CrMo steel decreases.

Compared with the TAG curves of 15CrMo steel samples, the weight gain rate of Ni_2Al_3 coating is significantly lower than that of 15CrMo steel. At 0–300 °C, the weight slightly decreases, which may be caused by gas desorption adsorbed at defects such as pores in the coating during the heating process. This is because during the heating process of the coating, as the temperature increases, the oxidation products continue to increase, resulting in an increase in the weight of the sample. The thermogravimetric analysis results indicate that the Ni_2Al_3 intermetallic compound coating has better thermal stability than 15CrMo steel.

From the above thermogravimetric analysis results, it can be seen that the weight of 15CrMo steel, and Ni_2Al_3 coating only begins to increase when the temperature at 500 °C. Therefore, static oxidation tests were conducted in an air environment of 600 °C. Figure 6 shows the oxidation kinetics curves of Ni_2Al_3 coating and 15CrMo heat-resistant steel in an air atmosphere at 600 °C. Figure 6 shows that the oxidation weight gain of the Ni_2Al_3 infiltration layer is very small at 3.36 mg/cm^2, and the oxidation weight gain of 15CrMo steel is 5.68 mg/cm^2. The oxidation kinetics curves of Ni_2Al_3 coating and 15CrMo heat-resistant steel both follow a parabolic law.

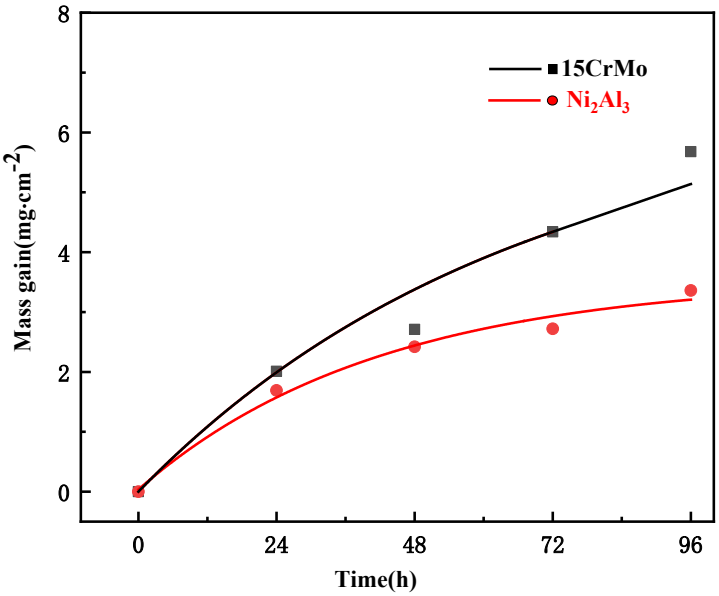


Figure 6. The oxidation kinetics curves of the Ni_2Al_3 coating and 15CrMo acquired at 600 °C.

The relationship between oxidation weight gain ΔG and time t can be obtained from reference as follows [29,30]:

$$(\Delta G)^2 = K_p t + C \quad (1)$$

In the formula, C is a constant, and K_p is the oxidation rate coefficient. The K_p value is closely related to factors such as metal surface structure, temperature, and oxide film properties and can be used to evaluate the high-temperature oxidation resistance of metals. A larger K_p value indicates poor high-temperature oxidation resistance of the metal, while a smaller K_p value indicates better high-temperature oxidation resistance. Based on experimental data, it can be calculated that the K_p of Ni_2Al_3 coating and 15CrMo heat-resistant steel after oxidation at 600 °C and 96 h is: 3.267×10^{-11} $g^2 \cdot cm^{-4} \cdot s^{-1}$ and 9.335×10^{-11} $g^2 \cdot cm^{-4}$ s^{-1}. The K_p value of Ni_2Al_3 coating is significantly lower than that of 15CrMo steel, indicating that Ni_2Al_3 coating has stronger high-temperature oxidation resistance than 15CrMo heat-resistant steel, which is consistent with the results obtained from thermogravimetric analysis.

The oxidation process of metal materials includes initial oxidation, oxygen molecule adsorption, oxide film formation, and diffusion of metal and oxygen atoms. The K_p values of the oxidation kinetics curves of Ni_2Al_3 intermetallic compound coating and 15CrMo steel are different, reflecting specific differences in the above processes between the two materials.

In order to analyze its antioxidant mechanism, the surface characteristic of the Ni_2Al_3 intermetallic compound coating was analyzed after different oxidation times.

XRD analysis was also performed on the oxidized coating, and the results are shown in Figure 7a. Figure 7a shows the comparison of XRD on the surface of Ni_2Al_3 coating after different oxidation times, Figure 7b shows the partial comparison of XRD after 72 and 96 h of Ni_2Al_3 coating oxidation, and Figure 7c shows the comparison of XRD before and after high-temperature oxidation of 15CrMo. Figure 7b shows that the Ni_2Al_3 coating exhibits a NiO peak after being insulated at 600 °C for 72 h, and the Al_2O_3 peak is also significantly enhanced compared to before insulation. It indicates that during long-term insulation under 600 °C air conditions, Al and Ni elements in the coating undergo oxidation reactions with oxygen elements in the air, producing Al_2O_3 and NiO. As shown in Figure 7c, after 96 h of insulation, the main phase on the surface of the 15CrMo steel sample is Fe_2O_3, an n-type semiconductor structure. Oxygen atoms can reach the matrix through their lattice gaps and continue oxidizing the matrix's Fe atoms.

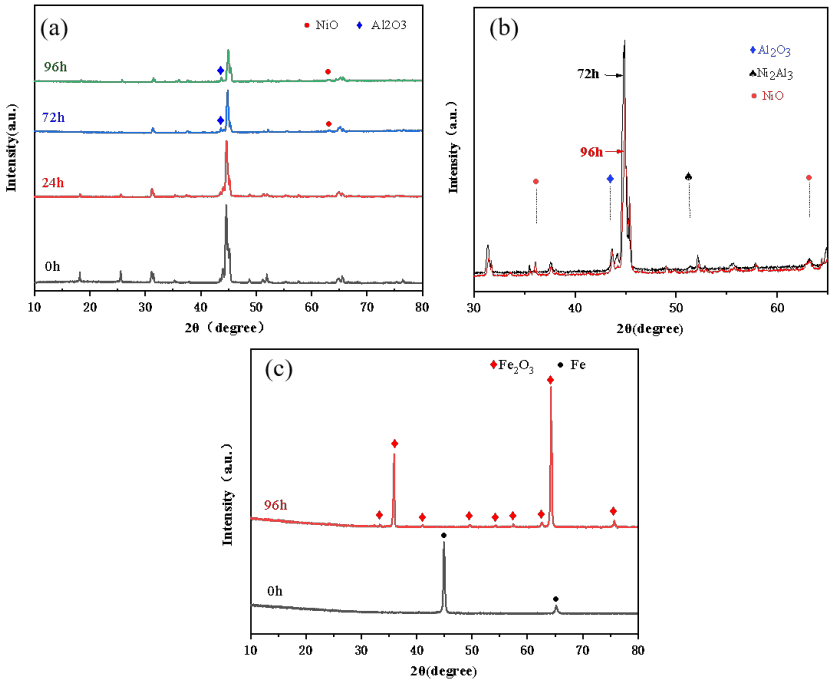


Figure 7. XRD comparison of the Ni_2Al_3 intermetallic compound coating (**a**,**b**) and 15CrMo steel (**c**) at different oxidation times.

Figure 8 shows the XPS spectrum of the Ni_2Al_3 coating surface after 96 h of oxidation. As shown in Figure 8a, there are four peaks in the high-resolution spectrum of Ni1s of the coating, with binding energies located near 878 eV, 872 eV, 861 eV, and 855 eV, respectively. It can be inferred that the peak with the second highest binding energy (approximately 872 eV) may correspond to the chemical bond formed between nickel and oxygen, namely the Ni–O bond. The peak with the lowest binding energy (approximately 855 eV) may correspond to the chemical bond formed between nickel and other metal elements, namely the Ni–Al bond. Figure 8b shows two peaks in the high-resolution spectrum of Al1s in the composite coating, with binding energies located near 74 eV and 67 eV, respectively. The binding energies of Al1s peaks are approximately 73–75 eV, which can be used as an indicator range to characterize the binding energy of Al–O bonds.

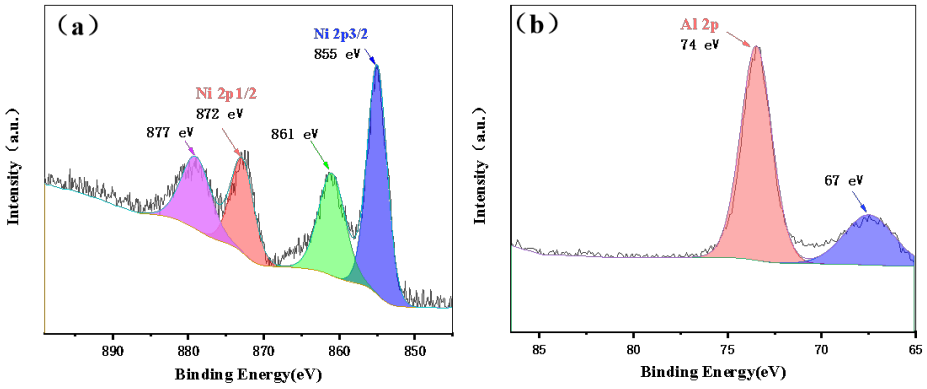


Figure 8. XPS analysis of the Ni_2Al_3 composite coating surface after 96 h of oxidation. (**a**) High-resolution XPS spectrum of Ni1s in the coating, (**b**) high-resolution XPS spectrum of Al1s in the coating.

Figure 9 is the SEM and EDS results for the cross-sections of Ni_2Al_3 coating after oxidation treatment at 600 °C for 96 h. As shown in Figure 9a,b, it can be observed that a thin oxide layer was generated on the surface of Ni_2Al_3 coating. There were some tiny

hole distributed on the oxide layer. EDS test for the oxide layer was conducted and the results were exhibited in Figure 9c–e. Atomic content ratio of corresponding element was also presented in Figure 9f. As can be seen from Figure 9f, the atoms proportion of Ni, Al, and O in this region is 38.05%, 40.09%, and 21.06%, respectively. And the content of oxygen atoms in the oxide layers is visibly enhanced compared with O content in Ni_2Al_3 coating (as displayed in Table 2), which is resulted by the oxidation occurred during the high-temperature process. Combined with the results of XRD and XPS, it is safe to infer that the main phase composition of oxide layer generated on Ni_2Al_3 coating after oxidation treatment is Ni_2Al_3, NiO, and Al_2O_3.

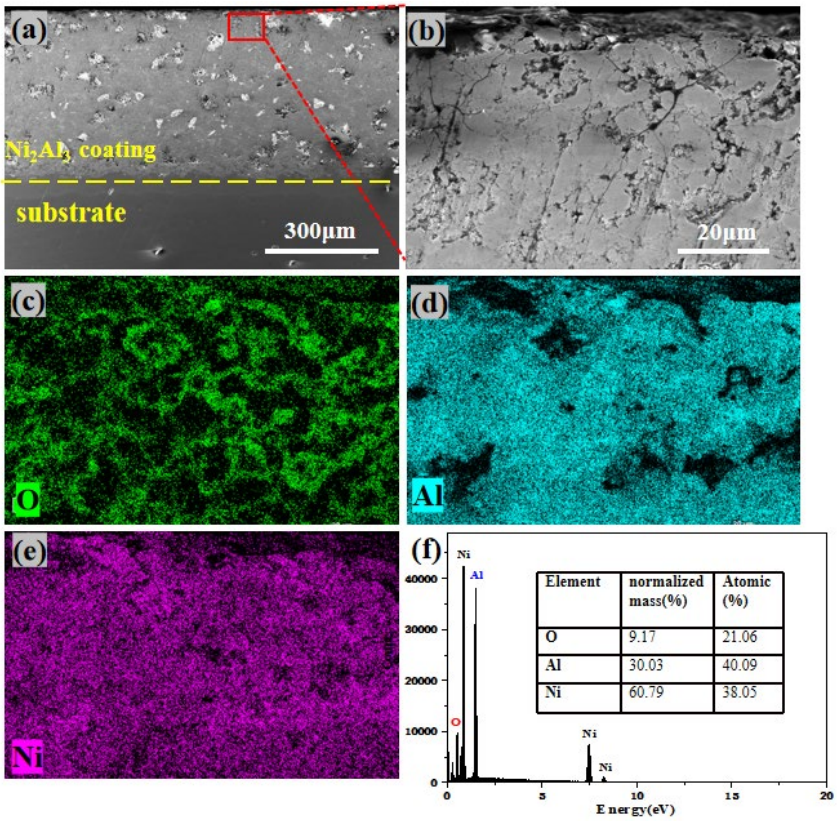


Figure 9. SEM and EDS for the cross-sections of the materials after oxidation.

4. Discussion

From the above Analysis, it can be seen that after 96 h of high-temperature oxidation, the oxygen molecules on the coating surface form Al_2O_3 with aluminum atoms and NiO with nickel atoms. These oxides form a uniform oxide film on the substrate surface.

Figure 10 is the sketch of formation process for oxide layer. The high temperature oxidation of the coating includes four processes: initial oxidation, adsorption of oxygen molecules, formation of oxide films and diffusion of nickel and aluminum atoms. During the initial oxidation process, oxygen molecules gather on the surface of the composite coating to form an oxygen atmosphere. Because there are voids and holes on the surface of the cold sprayed metal-based coating, the oxygen molecules adsorbed in the voids and holes, forming the oxygen molecular adsorption process. With the increasing of temperature, the oxygen molecules on the surface of the coating interact with nickel and aluminum atoms, which leads to the initial oxidation of the surface form an oxide film. The oxidation resistance of the oxide film prevents the intrusion of oxygen and other substances into the matrix, and at high temperatures, the nickel atoms and aluminum atoms inside the coating migrate from the inside of the material to the surface through lattice diffusion or void diffusion, constantly forming an oxide protective layer on the surface.

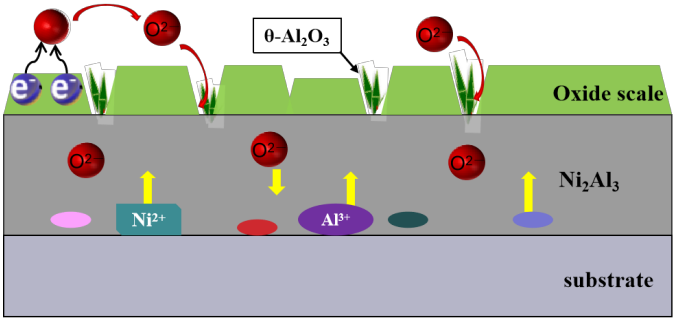


Figure 10. Sketch of formation process for oxide layer on Ni_2Al_3 coating.

As is well known, Al_2O_3 has excellent antioxidant properties. The literature indicates that the most significant advantage of NiO is that it has a similar coefficient of expansion to metal Ni and has good plasticity. Even in thermal shock environments, it can firmly adhere to the surface of the nickel. Therefore, it also has relatively good antioxidant performance. In addition, nickel and aluminum atoms migrate from the material's interior to the surface through lattice diffusion or interstitial diffusion. This diffusion process can promote the formation of a dense oxide film with protective properties, and once the oxide film is formed, it will protect the layer from further oxidation [16,26].

When high-temperature oxidation occurs, oxygen molecules adsorb on the surface of Ni_2Al_3 and interact with nickel and aluminum atoms to cause surface oxidation, forming a layer of oxide film. The Ni_2Al_3 composite coating has strong high-temperature oxidation resistance, which means it can effectively resist the oxidation process at high temperatures, delay the formation of oxide films, and slow down further oxidation of the substrate material. During the high-temperature oxidation process, the initial stage of oxidation from 0 to 24 h, and oxygen fully contacts the surface of the coating. The increase in oxide mass is controlled by interfacial reactions. Therefore, the interface reaction speed accelerates, and the mass increases rapidly. During the test time prolonged from 24 to 72 h, the rate of mass increase decreased, and the generated oxide formed a relatively intact protective oxide film on the coating surface. It effectively preventing the diffusion of external oxygen to the substrate. The increase in oxide mass was controlled by the diffusion rate of oxygen in the continuous oxide film, and its reaction rate became relatively slow.

Heat-resistant steel 15CrMo as a high-temperature structural material with good heat resistance is commonly used. Under high-temperature conditions, the surface of 15CrMo undergoes an oxidation reaction, forming a dense layer of Cr oxide film to protect the substrate material from further oxidation erosion. However, at higher temperatures, especially after exceeding 600 °C, the Cr-containing oxide film causes cracks and detachment due to the significant difference in expansion coefficient between the film and the substrate, losing its protective effect on the substrate [27].

5. Conclusions

(1) A Ni-Al intermetallic compound coating with Ni_2Al_3 as the main phase can be prepared by combining low-pressure cold spraying and heat treatment;

(2) The high-temperature oxidation kinetics curve of Ni_2Al_3 coating at 600 °C follows a parabolic law, exhibiting a stronger high-temperature oxidation resistance than 15CrMo heat-resistant steel. The mechanism of coating resistance to high-temperature oxidation is that during the high-temperature oxidation process, Ni_2Al_3 forms an oxide film mainly composed of Al_2O_3 and NiO on the surface. This oxide film can effectively resist oxidation and protect the substrate material from oxidation at a high temperature of 600 °C;

(3) Considering the Ni_2Al_3 coating on 45 # steel is designed for high-temperature service occasions, the high-temperature strength for the coating and binding performance between Ni_2Al_3 coating and 45 # steel is very important. But the mechanical property

and binding strength were not studied in this work, and those should be further investigated in our future work.

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