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MCrAlY Coating for High Temperature Oxidation Resistance of Engine Blade

Yan LI [1], Yue HU [2] *, Bo YU [3]

[1] *School of Mechanical and Electrical Engineering, Changchun Institute of Technology, Changchun, Jilin 130012, China*
[2] *College of Physics and Electronic Engineering, Hebei Minzu Normal University, Chengde, Hebei 067000, China*
[3] *School of Mechanical and Electrical Engineering, Changchun Institute of Technology, Changchun, Jilin 130012, China*

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With the continuous innovation of technology the requirements for the use of engines have become more stringent. In the current actual work of the engine, the import temperature has approached a thousand degrees, which makes the engine blades produce a temperature oxidation phenomenon under such harsh conditions, thus reducing their service performance. In order to improve the service life of engine blades under the current working environment, the technology MCrAlY coating with high-temperature oxidation resistance has become a hot spot for research at home and abroad, the arc ion plating coating preparation process has developed unprecedentedly and gradually become mature. Using GH4133 nickel-based high-temperature alloy material as the matrix, NiCrAlYSi coating was prepared its surface by using arc ion plating technology, and its thermal treatment was performed, and the anti-high-temperature oxid performance of the coating was tested under a high-temperature environment, and the oxidation test was carried out for 192 hours continuously under a constant temperature of 1000 °C, and the microstructure of the coating and the physical process of high-temperature oxidation were analyzed. The experiment shows: 1) the NiCrAlSi coating is smooth and flat, the cross section is clear and dense, there is no pore defect, the coating is tightly adhered with the matrix; 2) after the thermal treatment, the macrodroplets of the NiCrAlYSi coating are more densely arranged, and the coating-substrate interface become blurred due to mutual diffusion, but no obvious mutual diffusion layer is formed, through the analysis of XRD pattern, the NiCrAlYSi coating will significantly enhance its anti-high temperature oxidation performance after the thermal treatment; 3) during the anti-high temperature oxidation process of the NiCrAlYSi coating, no peeling and pores appeared on the surface of the coating within 200 h, and the diffusion of elements occurred between the coating and the matrix, and then, the peeling and pores gradually appeared on the surface of the coating, but due to the diffusion of elements, it made the coating matrix can still re-form the oxide protective layer, which prolonged the life of the high-temperature alloy.

Keywords: engine blade, coating, high temperature oxidation, GH4133.

1. INTRODUCTION

With the rapid development of science and technology, our country has made great progress in the field of industry, and the engine rose to prominence in this context.

At present, the nickel-based high-temperature alloy is widely used in the engine blade, represented by GH4133. In actual application, the engine is in a very harsh working environment, and the working temperature can be as high as 1000 °C, which makes the alloy blade of the engine prone to high-temperature oxidation behavior under this working background, resulting in the failure of blade strength and reducing the use of the engine [1].

Therefore, the study of anti-high-temperature oxidation for engine blades has become the key technology of current research.

To improve the high-temperature oxidation resistance of the nickel-based high-temperature alloy of the engine blade, the coating technology has attracted extensive attention from scholars at home and abroad, especially in the coating of the MCrAlY coating (M refers to Fe, Ni, Co, etc.) on the nickel-based high-temperature alloy of the engine blade, and the appropriate active elements are added to improve the high-temperature oxidation resistance of the material, which has become a hot spot for experts in industry to study [2, 3].

Arc ion plating (AIP) technology, known as a mature process technology for preparing MCrAlY coatings, has been used in engineering fields in recent [4, 5].

AIP in a vacuum environment, using arc evaporation as the coating ion source to achieve the process of ion plating. Its remarkable feature is that it can produce plasma composed of highly ionized evaporation target particles, with an ionization rate of 70%-80%, which is the most dense coating technology in ion plating at present [6].

This research is based on the arc ion plating technology, where the GH4133 nickel-based superalloy is used as the matrix material and its surface is coated with NiCrAlYSi coating. The anti-high temperature oxidation performance test is carried out, and the analysis methods such as SEM, XRD and EDS are used to investigate the influence of heat treatment on NiCrAlYSi coating, the influence of high temperature on the microstructure of NiCrAlYSi coating and the influence of high temperature on the phase composition of NiCrAlYSi coating. The high temperature constant temperature oxidation kinetics characteristics are studied to provide a new experimental basis for the alloy leaf anti-high temperature oxidation selection.

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*Corresponding author: Y. Hu
E-mail address: *jdhy@hbun.edu.cn*

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Base material selection

At present, the engine blade is mainly made of nickel-based superalloy material, and GH4133 nickel-based superalloy is used the matrix material. The test sample size is selected as 30 mm × 30 mm × 5 mm according to the test standard HB 5258-2000 [7], 2000# sandpaper is used for surface grinding, and 240# white corundum is used for surface wet spray treatment, so that the test sample $Ra \leq 1.6$ μm. Table 1 shows the composition of the GH4133.

Table 1. Nominal composition of GH4133

Num	Element	Ratio
1	Al	0.98 %
2	Ti	2.90 %
3	Nb	1.35 %
4	Cr	20.23 %
5	C	0.035 %
6	B	0.003 %
7	Ni	other

2.2. Coating preparation

Ion-assisted vacuum arc coating equipment was used to coat the NiCrAlYSi coating on the surface of the test piece respectively. The arc current was 110 A, the bias voltage was –50 V, the gas pressure was 1 Pa. During the coating preparation, the argon ions that were highly ionized were deposited on the substrate surface in a non-continuous manner under the action of pulse bias voltage. Table 2 shows the composition of the prepared coating.

Table 2. Nominal composition of prepared NiCrAlYSi

Num	Element	Ratio
1	Al	10 – 14 %
2	Cr	20 – 25 %
3	Y	0.5 – 1.0 %
4	Si	0.5 – 1.0 %
5	Ni	Other

2.3. Heat treatment

Thermal treatment of MCrAlY coating can effectively achieve the optimization of coating structure and interface strengthening, specifically: (1) it can effectively eliminate micro-pores and interlayer unmelted particles formed by high-temperature diffusion bonding of thermal spraying, so as to improve its density; (2) it can effectively the mutual diffusion of elements, so that Al/Cr is fully diffused to the surface of the coating, pre-form a continuous Al_2O_3 protective film, and enhance metallurgical bond of the coating-substrate interface, and relieve the thermal mismatch stress; (3) regulate the β-NiAl phase, long-term annealing promotes theolution of brittle phase and precipitates fine and uniform β phase, so as to balance the oxidation resistance and toughness, and ensure the continuous supply of aluminum in service.

Before the heat treatment, the coated test pieces were placed in a high-temperature resistant alumina crucible, and then placed in a vacuum heat treatment furnace, that each test piece was kept in a consistent heat treatment state. The thermal diffusion was carried out at 1080 °C for 4 h, followed by aging treatment at 870 °C for 32 h, and then phased cooled to 100 °C with N_2 as the protective gas, and finally to room temperature.

2.4. High-temperature oxidation experiment

According to the standard of HB5258-2000, the test sample surface is polished with 2000# sandpaper to a test sample $Ra \approx 0.8 \sim 1.6$ μm, and the test sample of the alloy NiCrAlYSi coating after heat treatment is put into a 30 ml corundum crucible. High-temperature oxidation test at 1000 °C is carried out in a box-type resistance furnace, with a continuous time of 192 h, and the discontinuous weighing method is used for weighing, sorting out the corresponding data, and drawing the oxidation kinet curve [8]. Table 3 shows the specific instrument details used in the experiment. The XRD parameters used in the experiment are as follows: (1) cathode: voltage 40 kV, current 40 mA; (2) scan: step size 0.02° – 0.05°, speed 2 – 5°/min, 2θ range 20° – 0°.

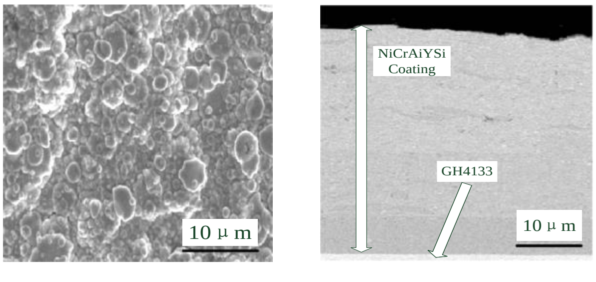
Table 3. List of instruments required for experiment

No.	Detection	Instrument details
1	Physical characterization of materials	Rigaku D/max-II B X-ray diffractometer
2	X-ray photoelectron spectroscopy	ESCALABMKII spectrometer
3	Morphology of materials	JEOL JSM 4800F Scanning electron microscope
4	Morphology of materials	JEOL-2100F Transmission electron microscope

3. DISCUSSION AND ANALYSIS

3.1. Analysis before and after coating thermal treatment

The surface and cross-section morphology of the NiCrAlYSi coating before thermal treatment are shown in Fig. 1. As shown in Fig. 1 a, there are some unmelted particles and liquid drops on the coating surface, which is an inherent characteristic of thermal spraying process. Except for the unmelted particles liquid drops, the coating is still flat and dense, and no holes appear. As shown in Fig. 1 b, the cross-section of the coating is very uniform and dense, without obvious defects such as small holes, and the coating is closely combined with the substrate material, with a very clear interface.



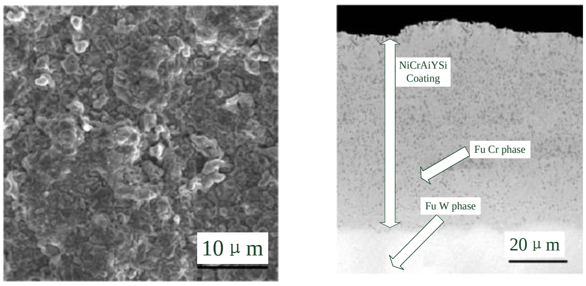
a b

Fig. 1. Morphology of surface and cross section of NiCrAlY coating before thermal treatment: a – surface; b – section

The surface and cross-section morphology of the

NiCrAlYSi coating after heat treatment are shown in Fig. 2. As shown in Fig. 2 a, after heat treatment, the particles on the surface of the coating become more compact. As shown in Fig. 2 b, after heat treatment, the boundary between the coating and the substrate material becomes blurred, indicating that the elements in the coating and the substrate have occurred mutual diffusion, but no obvious mutual diffusion layer is formed. The element precipitates to form the α-Cr phase and is uniformly distributed in the coating with good uniformity.

The XRD patterns of NiCrAlYSi coating before and after heat treatment are shown in Fig. 3. The main phases of the deposited coating are γ'-Ni_3Al/γ-Ni phases, and a small amount of β-NiAl phase is generated at the same time. After heat treatment, α-Cr is formed, and the peak of β-NiAl phase decreases, and the peak of γ'-Ni_3Al phase increases, indicating that the process of β-Ni phase transforming to γ'-Ni_3Al phase has occurred. γ'-Ni_3Al is a strengthening phase, which can significantly improve the anti-high temperature oxidation resistance of the coating [9].



a b

Fig. 2. Surface and cross-section morphology of NiCrAlY coating after heat treatment: a – surface; b – section

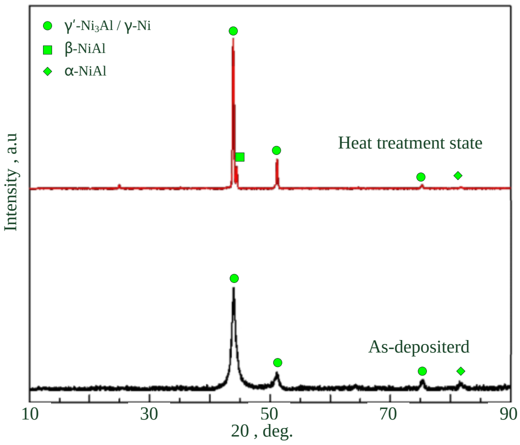


Fig. 3. The XRD patterns of NiCrAlY coating before and after heat treatment

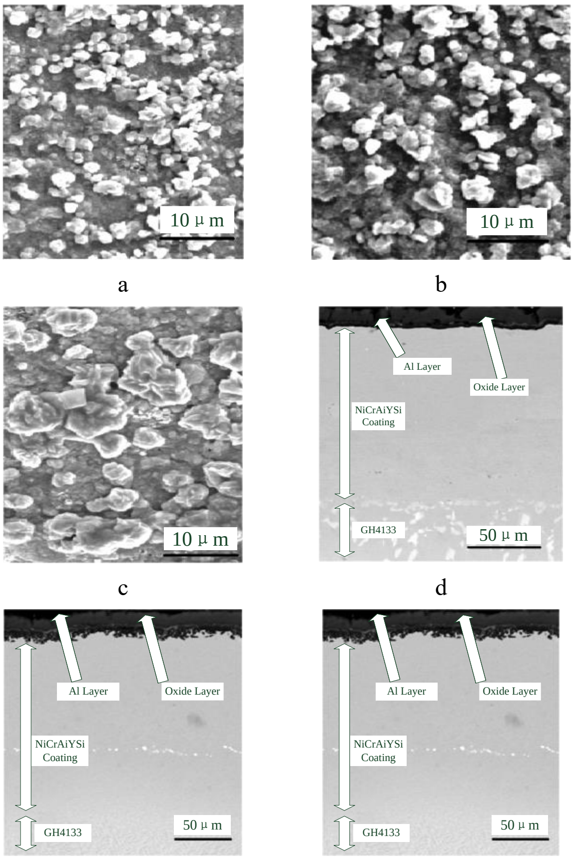
3.2. Influence of high temperature oxidation on the microstructure of the coating

The surface and cross-sectional morphologies of the NiCrAlYSi coating oxidized for different times are shown in Fig. 4. As shown in Fig. 4 a, after 48 h of oxidation, a large number of fine oxides are formed on the surface, which are evenly distributed. According to the EDS analysis, the atomic percentage of O and Al is 49.64 % and 31.26 % respectively, which is approximately 3:2. Combined with its morphological characteristics and XRD phase analysis, it can be seen that it is mainly α-Al_2O_3.

As shown in Fig. 4 b, after oxidation for 96 h, some coral-like aggregations formed on the surface, and the EDS spectrum analysis, it was composed mainly of Al, Cr and O, which could be a mixture of oxides of Cr and oxides of Al.

As shown in Fig. 4 c, after oxidation for 192 h, some parts of the coating surface fall off and some small pores.

As shown in Fig. 4 d, it can be found from the cross-sectional morphology that a very dense and uniform oxide film with a of about 3.5 µm was formed when the coating was oxidized for 48 h. At the interface between the coating and the substrate, an obvious interdiffusion layer formed, which was due to the uneven distribution of alloy elements in the coating and substrate, and the interdiffusion phenomenon occurred at high temperature, thus forming an interdiffusion layer the interface between the coating and the substrate.



a b

c d

e f

Fig. 4. Surface and cross-sectional morphologies of the coated oxidized at different times: a – 48 h surface; b – 96 h surface; c – 192 h surface; d – 48 h section; e – 96 h section; f – 192 h section

As shown in Fig. 4 e, after oxidation for 96 h, the oxide film thickness increases by about 6 µm, the interface between the oxide scale and the coating begins to become uneven, and the oxide grows unevenly in various regions of the coating. Combined with its surface morphology, it can infer that due to the gradual thickening of the oxide scale and the appearance of spallation, the fresh surface area is more conducive to the dynamic infiltration of O so the coating is more likely to be oxidized, resulting in uneven oxide growth. In addition, the interdiffusion area between the coating and the substrate becomes unclear, indicating the alloying elements in the coating and the substrate have diffused relatively uniformly. From the high-temperature oxidation behavior of the coating, it can be seen that the oxide film effectively prevents the diffusion of external gases into the metal, and prolongs the service life of high-temperature alloys [10].

As shown in Fig. 4 f, when oxidized for 192 h, the oxide growth layer is somewhat thickened, and oxygen permeates into the coating along the holes to oxidize the interior of the coating, resulting in a less uniform oxide layer than that of 96 h, but it still exhibits good effect.

3.3. High-temperature oxidation for phase composition analysis of the coating

Fig. 5 shows the XRD patterns of the NiCrAlYSi coating oxidized for different times at a constant temperature of 1000 °C. As shown in the figure, when the coating is oxidized for 48 h, the main phases are γ′-Ni_3Al/γ- and α-Al_2O_3 phases, and no Cr_2O_3 phase is detected.

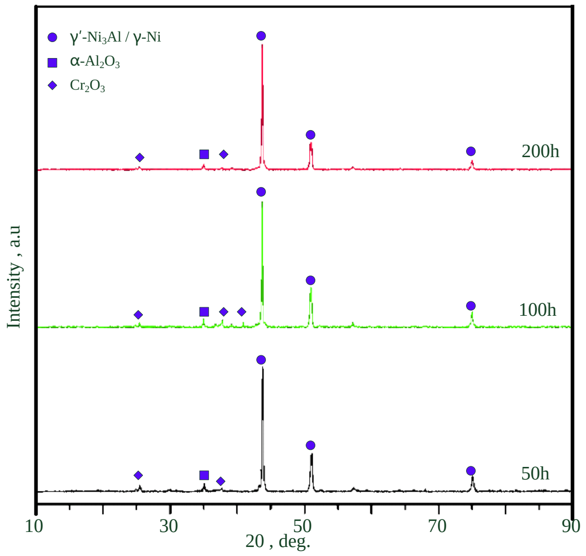


Fig. 5. XRD patterns of the coating at different oxidation times at 1000 °C

This is because a uniform and dense Al_2O_3 oxide film is formed on the of the coating at the beginning of oxidation, which prevents the infiltration of O_2 and plays an effective protective role to prevent the Cr element in the coating from being oxidized. When the oxidation time is 96 h, several characteristic peaks with small peaks of Cr_2O_3 phase appear, which is because with the increase of the oxidation, Al element is consumed in large quantities, and the formed protective layer is no longer dense and uniform, which can not prevent the diffusion of O_2 to the inside of the coating resulting in the oxidation of Cr element and the formation of oxide Cr_2O_3. When the oxidation time is 192 h, only the characteristic peaks of γ′-Ni_3Al/γ-Ni and α-Al_2O_3 phases are detected, and no Cr_2O_3 phase is detected. This is probably because part of Al in the coating diffuses to the surface of the coating, and the activity of Al to combine with O at high temperature is greater than that of Cr. When the coating is peeled, the exposed fresh surface quickly forms a dense α-Al_2O_3 protective layer, which prevents the diffusion process of oxygen to the inside of the coating and prevents the Cr element in the coating from reacting with O to form oxides. α-Al_2O_3 has good anti-high-temperature oxidation performance, which plays an effective protective role for the coating [11].

3.4. High-temperature isothermal oxidation kinetics curve analysis

In order to study the high-temperature oxidation kinetics behavior of the coating, the samples were placed in a constant temperature oxidation furnace at a temperature 1000 °C for 192 h of oxidation in a static air environment. To reduce the experimental error, two parallel samples with and without coating were placed in the furnace at the same time for a comparative study. The corresponding constant temperature oxidation kinetics curve was obtained by the weight gain method, and the kinetics curve of substrate material at constant temperature for 192 h was given at the same time.

Fig. 6 is the kinetic curve of the substrate and the substrate with the NiCrAlYSi coating at 1000 °C 192 h of isothermal oxidation.

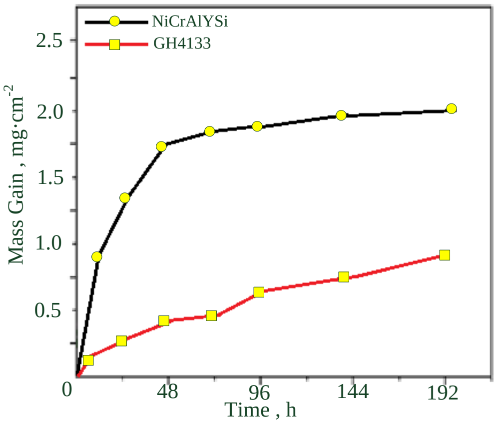


Fig. 6. Coating kinetics curve

It can be seen from the figure that the kinetic curve of the substrate is approximately parabolic, and the oxidation weight gain is greater than that of the substrate with the NiCrAlYSi coating. The oxidation weight gain rate of the substrate and the coating is relatively large within the first 9 of oxidation. Subsequently, the oxidation weight gain rate of the coating is much smaller than that of the substrate, because a layer of Al_2O_3 oxide film is formed on the surface of the coating at the beginning of oxidation, which plays an effective antioxidant role and slows down the oxidation process. At 72 h of oxidation, the oxidation weight gain rate of the coating increases significantly. This is because the oxide layer becomes thicker with the extension of the oxidation time and cracks and peels under the thermal stress. The exposed surface is re-oxidized, so there will be a phenomenon of increasing oxidation weight gain rate. During the oxidation process, peeling and oxidation are always repeated, and finally lead to the failure of the coating. After 96 h of oxidation, the oxidation weight gain rate gradually decreases again, mainly because the active elements (Y/Si)play an active role in the high-temperature oxidation process of the coating, enhancing the adhesion of the oxide growth layer and making it difficult for the oxide scale fall off. Therefore, the addition of active element Si indirectly reduces the loss of Al and prolongs the service life of the oxide film, thereby enhancing the anti-high-temperature performance of the coating, and its anti-high-temperature oxidation performance is more excellent [12].

It can also be analyzed from the figure that the actual performance of the substrate alloy is not as good as that of the coating, and the specific reasons analyzed as follows: (1) the coating can quickly form a dense Al_2O_3 film, and the high Al content in the coating can generate a continuous α-Al_2O_3 layer at the beginning of oxidation, which can effectively block the diffusion of oxygen, while the substrate alloy can not quickly form a complete protective film; (2) the dynamic-repair mechanism, the β-NiAl phase in the coating acts as a "storage pool" of aluminum, continuously decomposes to supply Al, and even if the local film falls off, a new Al_2O_3 film can be regenerated through elemental diffusion; (3) the strengthening effect of active elements, the active elements Y/Si (0.5 – 1.0 %) purify the grain boundary, anchor the interface of the oxide film, significantly improve the adhesion of the Al_2O_3 film, and effectively inhibit the peeling, while the substrate has no such component.

4. CONCLUSIONS

1. NiCrAlYSi coating was successfully prepared on the surface of GH4133 nickel-based superalloy by arc ion plating technology. The-deposited coating surface was smooth and dense, the cross section was uniform and closely combined with the substrate, and the thickness was about 65 – 70 μm. After heat treatment, the arrangement of coating particles was further densified, and XRD confirmed that the β-NiAl phase was partially transformed into the strengthening γ'-Ni_3Al phase, significantly improving the initial protective performance of the coating.
2. The coating formed an α-Al_2O_3 film at the beginning of oxidation at 1000 °C, which effectively blocked oxygen diffusion without pe or holes. With prolonged oxidation time, the consumption of Al led to the thickening and cracking of the local oxide film, but the active elements Si and Y delayed peeling enhancing the adhesion of the oxide film. More importantly, the β-NiAl phase in the coating continued to decompose to provide an Al source, dynamically repairing the oxide through elemental diffusion, achieving self-healing protection, and greatly prolonging the life of the substrate.
3. The oxidation kinetics curve of NiCrAlYSi coating exhibits a phased feature: slow weight gain due to the formation of Al_2O_3 within the first 72 h, accelerated weight gain due to film cracking in the middle stage, and a stable stage due to the inhibition of spallation by active elements in the later stage. Its core advantage lies in the combination of an optimized coating structure, elemental interdiffusion capability, and dynamic self-healing mechanism from heat treatment, the oxidation resistance of the substrate far exceed that of uncoated alloys. This research provides crucial theoretical and technical support for the design of high-temperature protective coatings forero-engine blades.

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