Study of the cyclic oxidation behaviour of Cr-modified aluminide coatings on nickel-based single crystal high temperature alloys

Dezheng Ma*, Minglu Guo, Yanwen Xu, Mengxue Guan, Haoran Chen, Hao Liu

Tianjin Key Laboratory of High Speed Cutting and Precision Machining, Tianjin University of Technology and Education, Tianjin 300222, PR China

*Dezheng Ma

Abstract

Cr-Al coatings were prepared by a two-step chemical vapour deposition (CVD) method (Cr infiltration, followed by Al infiltration) on nickel-based single crystal high temperature alloys, with a simple NiAl coating as a comparison, and the coatings were subjected to cyclic oxidation experiments in air at 1100 °C . XRD, SEM and EDS methods were used to analyse the phase structure, coating structure, composition, elemental surface distribution and coating ageing pattern of the Cr-Al coatings during cyclic oxidation at high temperature. The results showed that: the oxidation kinetics of the coating conformed to the parabolic evolution law after 160 cycles at 1100 °C. The simple NiAl coating degraded severely, the oxide film appeared multilayered, cracking and flaking occurred more seriously, and a large amount of γ' -Ni₃Al phase appeared in the coating; the oxide film of the Cr-modified aluminide coating remained intact, and the β-NiAl phase was mainly dominant in the coating. The degradation phase change process of the Cr-Al coating was investigated. The oxide film of the coating is more complete after the addition of Cr to the coating, and the β -phase within the coating is more increased. Cr doping in the NiAl coating can promote the formation of α -Al₂O₃ film, improve the surface quality of the oxide film and reduce the oxidation rate. Cr reduces the interdiffusion between the coating and the matrix elements, and the Cr-Al coating contains more β-phase in the late stage of cyclic oxidation. Therefore, Cr helps to improve the high temperature oxidation resistance of NiAl coatings.

Keywords

Cr-Al coatings; CVD chemical vapour deposition; cyclic oxidation; coating degradation.

1. Introduction

As the working temperature of the hot end of aircraft engines and gas turbines continues to increase, the working temperature of the hot end components is getting higher and higher, and the mechanical properties and resistance to high temperature oxidation of the workpieces are required more and more. It is difficult to maintain both the excellent high temperature mechanical properties and the resistance to high temperature oxidation in the same material. So coating an alloy substrate with excellent mechanical properties with a coating that has excellent resistance to high temperature oxidation is an effective way to solve this problem ^[1]. Since the 1960s, simple aluminide coatings have been widely used in Ni-based aero engines and gas turbines. Simple NiAl coatings are currently the most widely used high-temperature protective coatings and are generally prepared by encapsulated aluminisation, slurry methods or chemical vapour phase infiltration processes^[2]. The outer layer of the coating is mainly composed of the β -NiAl phase and the Al content is generally greater than 25 wt%. This is higher than the critical Al content (>19wt.%) for the selective oxidation of Al in NiAl coatings. Due to its high Al content, the simple NiAl coating can rapidly form an Al₂O₃ film during the high

ISSN: 1813-4890

temperature oxidation process, improving the high temperature oxidation resistance of the substrate. However, Al_2O_3 film and coating bonding effect is not good, especially in the process of cyclic oxidation, alumina film and coating will produce large thermal stress, alumina film flaking serious, in high temperature cyclic oxidation (≥ 1050 °C) when the performance is relatively poor. The low Cr content ($\leq 6wt.\%$) in the high generation single crystal alloy results in poor thermal corrosion resistance. High temperature oxidation and thermal corrosion phenomena are the main forms of failure in single crystal turbine blades during service.

Cr-Al coatings were prepared by adding Cr elements to simple NiAl coatings to modify the coatings. Some studies have shown that the addition of Cr elements to simple NiAl coatings will improve the resistance to high temperature oxidation^[3]and reduce the degradation efficiency of the coatings. Li Jing^[4] Cr elements can reduce the critical Al content of Al required for Al selective oxidation. In recent years aero-engine turbine blades are basically hollow-based and need to be coated with a protective coating in the inner cavity of the blade to enhance the blade's resistance to high temperature oxidation and corrosion. The shape of the inner cavity of the blade is becoming more and more complex, the traditional embedding method, the slurry method is no longer suitable for the inner cavity coated with Cr-Al coating situation.

In this paper, Cr-Al coatings are prepared by a two-step process using chemical vapour deposition technology on nickel-based single crystal high temperature alloys, and the phase structure, microstructure and composition of Cr-Al coatings are investigated under high temperature cyclic oxidation conditions at 1100° C. The oxidation kinetics of the entire cyclic oxidation process is analysed to explore the high temperature cyclic oxidation behaviour of Cr-Al coatings. The phase structure, microstructure and composition of the Cr-Al coating were investigated during the oxidation process.

2. Coating preparation and experimental methods

2.1. Coating preparation

The experimental substrate was a nickel-based high-temperature single crystal alloy (10.1Co-4.3Cr-9.6W-6.2Al-1.4Mo-4.6Ta-4.6Re-0.15C-BalNi wt.%), which was machined into a specimen of Φ 15mm×2mm by wire cutting. The specimens are then ground with 150#, 400# and 600# sandpaper and rounded. After blasting with a sand blasting machine with deionised water, anhydrous ethanol and acetone in turn ultrasonically cleaned and dried.

The Cr layer was firstly deposited on the substrate by chemical vapour deposition at 1050°C for 2 h. The Al layer was secondly deposited on the surface of the Cr layer at 1050°C for 4 h.

2.2. Experimental method

Oxidation experiments were carried out in a muffle furnace at a temperature of 1100 $^{\circ}$ C. One cycle consisted of 50 min holding at 1100 $^{\circ}$ C and 10 min of air cooling. The number of cycles of oxidation at 1100 $^{\circ}$ C was 140, with cycles of 1C, 3C, 5C, 10C and 20C, and a sample was taken every 20 cycles after 20C. The weighing balance has a sensitivity of 1 x 10⁻⁵ g. Oxide film flaking during the thermal cycling process due to factors such as thermal stress can cause fluctuations in the test data. The cyclic oxidation kinetic curve therefore reflects the combined process of oxide film growth, flaking and regrowth.

The phase structure of the coating was analysed using X-ray diffractometry, and the relevant areas were examined for coating composition using scanning electron microscopy (SEM) and an electron microscope with its own energy spectrometer (EDS).

3. Experimental results and discussion

3.1. 1100°C cyclic oxidation kinetic curves

The oxidation weight gain curves for the four coatings oxidised for 160 cycles at 1100°C are shown in Figure 1(a)(b), with the coatings gaining weight rapidly in the first 10 cycles and then entering a plateau oxidation phase. The simple NiAl coating and the Cr-NiAl coating showed similar weight gain trends and behaved similarly during the cyclic oxidation process. During the first 10 cycles of oxidation, the simple NiAl coating maintained the maximum oxidation weight gain of 0.49 mg·cm⁻², while the Cr-NiAl coating gained 0.45 mg·cm⁻². The Cr-NiAl coating had the lowest weight gain of 0.36 mg·cm⁻². The simple NiAl coating gained about 1.3 times more weight than the Cr-NiAl coating. Throughout the oxidation cycle, the simple NiAl coating maintains the maximum weight gain, with a weight gain of 0.91 mg-cm-2 in 160 cycles, while the Cr-NiAl coating has the lowest weight gain of 0.63 mg·cm⁻². The simple NiAl coating has a weight gain of 1.44 times that of the Cr-NiAl coating. The simple NiAl coating showed weight loss at 120 cycles.

Figure (b) Oxidation rate, Kp for the simple NiAl coating was 3.54×10^{-2} mg²·cm⁻⁴·h⁻¹ for the first 10 cycles of oxidation, the Cr-NiAl coating had the smallest oxidation rate with Kp of 1.87×10^{-2} mg²·cm⁻⁴·h⁻¹, the oxidation rate for the simple NiAl coating was about 1.9 times that of the Cr-NiAl coating. During the 10-160 cycles, the simple NiAl coating still has the maximum oxidation rate with Kp of 3.90×10^{-3} mg²·cm⁻⁴·h⁻¹ and the Cr-NiAl coating has the minimum oxidation rate with Kp of 1.58×10^{-3} mg²·cm⁻⁴·h⁻¹. The oxidation rate of the simple NiAl coating is about 2.5 times that of the Cr-NiAl coating.



Figure 1: Simple NiAl and Cr-NiAl coatings at 1100°C cyclic oxidation 160C mass gain curves (a) mg/cm2 vs time (b) cm2/cm4 vs time.

3.2. Phase structure analysis during constant temperature oxidation at 1100°C Figure 2(a)(b) shows the XRD diffraction spectra of the simple NiAl coating and the Cr-NiAl

Figure 2(a)(b) shows the XRD diffraction spectra of the simple NiAl coating and the Cr-NiAl coating oxidised at 1100°C for 5 and 160 cycles. After five cycles of oxidation, the surface oxidation products were mainly Al_2O_3 , indicating that a pure Al_2O_3 film was produced in the first stage of cyclic oxidation. β -phase dominated the diffraction peaks. After 160 cycles of oxidation, the main oxide in the simple NiAl coating is still Al_2O_3 , followed by mixed oxides of NiO and NiAl₂O₄. Inside the coating the γ' -Ni₃Al phase dominates the diffraction peaks, while the β -NiAl phase diffraction peaks are weaker and γ -Ni is also present. 160 cycles of oxidation of the simple NiAl coating resulted in a high depletion of Al. The oxide film of the Cr-modified

aluminide coating is dominated by Al_2O_3 , while large amounts of Cr_2O_3 and $Ni(Al,Cr)_2O_4$ spinel are also detected. A large amount of spalling of the coating occurred during the long oxidation process, and the Cr elements in the coating diffused into the oxide film to participate in the reaction and generate oxides. The coating is still dominated by the β -NiAl phase, and the intensity of the diffraction peak of the aluminium-poor phase γ' -Ni₃Al is enhanced, indicating that more Al was consumed in the coating to generate the Ni₃Al phase.



Figure. 2 XRD diffraction spectra of simple NiAl coating and Cr-NiAl coating oxidised by cycling at 1100°C, (a) coating cycled 5 times (b) coating cycled 160C

3.3. Tissue characterisation of 1100°C cyclic oxidation products

Figure 3 shows the surface morphology of the simple NiAl coating and the Cr-NiAl coating after five cycles of oxidation at 1100°C. In the cyclic oxidation experiments, the samples were tested in alternating hot and cold cycles, resulting in very high thermal stresses in the oxide films. As a whole, the oxide films of both coatings flaked, with the simple NiAl coating flaking more severely, with more flaking locations and new oxide films generated at the flakes. the Cr-NiAl coating also showed a small amount of oxide film cracking and flaking after 5 cycles of oxidation, but generally maintained the surface morphology before oxidation, with no significant flaking found.



Figure. 3 Surface morphology of the coating after cyclic oxidation at 1100°C for 5C, (a) simple NiAl (b) Cr-NiAl

Figure 4 shows the cross-sectional morphology of the simple NiAl coating and the Cr-NiAl coating after five cycles of oxidation at 1100°C. The coating has a complete oxide film after five cycles of hot and cold oxidation, and the elements in the outer layer of the coating have been inter-diffused during the cyclic oxidation process, resulting in a uniform distribution of elements. The coating consists of three parts: the outer layer, the interdiffusion zone and the

secondary reaction zone. The oxide film of the simple NiAl coating appears to flake off, and as the oxide film flakes off and consumes the Al in the coating, an obvious Al-poor γ' -Ni₃Al phase appears in the coating and below the oxide film. A new oxide film was generated at the peeled area. This indicates that only localised oxide flaking of the coating has occurred. The black particles between the outer layer of the coating and the interdiffusion zone were proved by EDS data to be aluminium oxide particles adhered to the substrate during the Cr infiltration process and the generated AlN. the interdiffusion zone is basically the same as before oxidation and is divided into two distinct upper and lower layers, the upper layer is basically the same as the simple NiAl interdiffusion zone and the lower layer is distributed in a short rod-like vertical state, which is mainly the Cr(W) precipitation phase.



Figure 4: Cross-sectional morphology of the coating after cyclic oxidation at 1100°C for 5C, (a) simple NiAl (b) Cr-NiAl.

The surface morphology of the simple NiAl coating and the Cr-NiAl coating after 160 cycles of oxidation at 1100°C is shown in Figure 5. As the number of cycles increased, the oxide films on both the substrate and coating surfaces flaked off to varying degrees, and new oxide films were generated at the locations where the oxide films had flaked off. After 160 cycles of oxidation, all four coatings showed a multilayer surface oxide film structure. Combined with the EDS spectroscopy and XRD results, it is assumed that after 160 cycles of oxidation, the oxide film of the simple NiAl coating is mainly composed of α -Al₂O₃, with the formation of loose NiAl₂O₄ and the formation of NiO in the form of a "tumour" after the oxide film peels off. The loose oxide film increases the flux of O₂ diffusion along the oxide film into the coating, increasing the O partial pressure within the coating. The new oxide film consumes the Al in the coating and when the β $\rightarrow \gamma'$ phase change occurs in the coating, volume shrinkage occurs and the coating collapses at some locations forming a "valley ridge" shape. The oxide film is subjected to tensile stresses at the ridges, leading to cracking and flaking of the oxide film. The Cr-modified aluminides also form a multilayer oxide film after 160 cycles of oxidation. Combined with EDS data analysis and XRD physical examination, the oxide film of the coating is mainly Al_2O_3 , with loose Ni(Al,Cr)₂O₄ and Cr₂O₃ mixed oxides detected in the surface layer. The loose oxide film will crack and spall due to thermal stresses under the alternating action of heat and cold. The oxide film is concave and undulating, which can lead to tensile stresses perpendicular to the interface where the oxide film is raised on the inside, accelerating cracking^[5].

The cross-sectional morphology of the simple NiAl coating and the Cr-NiAl coating after 160 cycles of oxidation at 1100°C is shown in Figure 6. The oxide film of the simple NiAl coating is discontinuous and dense, with a multilayer phenomenon, indicating that the oxide film has undergone multiple spalling and that a "tumour-like" oxide film, NiO, is also appearing. a large amount of Al-poor γ' -Ni₃Al phase is generated in the outer layer of the coating, cutting off the outer β phase of the coating, and in the XRD phase, the γ' -Ni₃Al phase The γ' -Ni₃Al phase occupies the main peak position in the XRD phase. A large number of black inclusions appear

within the coating, which were confirmed to be aluminium oxide by EDS spectroscopy and EPMA surface scan. This is because the oxide film is broken due to the presence of a large amount of γ' phase in the coating can not generate a complete and dense oxide film in time, resulting in a relatively high oxygen partial pressure at the coating location, in the high temperature cyclic oxidation process, part of the O into the inner layer of the coating to generate internal oxidation phenomenon. The other part is the use of alumina particles in the substrate before the gas phase aluminising sandblasting treatment, the gas phase aluminising residue in the coating internal, in the 160 cycle oxidation process, the coating occurred in a large number of elements diffusion, alumina particles gradually gathered to produce the phenomenon.



Figure 5: Cross-sectional morphology of the coating after cyclic oxidation of 160C at 1100°C, (a)simpleNiAl(b)Cr-NiAl.



Figure 6: Cross-sectional morphology of the coating after cyclic oxidation of 160C at 1100°C, (a) simple NiAl (b) Cr-NiAl.

3.4. 1100°C cyclic oxidation analysis

The presence of Cr in the Cr-modified aluminide coating reduces the critical Al content for the formation of a continuous Al oxide film on the one hand; on the other hand, the Cr-rich diffusion barrier in the coating reduces the diffusion of Al into the substrate to a certain extent, and the Al-rich diffusion barrier consists of α -Cr and CrW phases to block the diffusion of Al elements, thus reducing the consumption of Al elements in the coating. The chromium in the Cr-modified aluminide coating can be considered to act as an oxygen absorber, preventing the internal oxidation of aluminium. During the initial and over-oxidation phase of oxidation, all three oxides, Cr₂O₃, A12O3 and NiO, are formed, however, if the coating contains sufficient amounts of chromium, the initially formed NiO is reduced by chromium through a displacement reaction i.e.

$$3NiO + 2Cr \rightarrow 3Ni + Cr_2O_3 \tag{1}$$

The chromium oxide formed reduces the activity of the oxide film, the oxygen at the alloy interface, so that the aluminium in the alloy can be selectively oxidised at low concentrations to produce a continuous aluminium oxide film. At high temperatures, Cr_2O_3 will gradually evaporate as Cr_2O_3 , leaving a continuous and well-protected Al_2O_3 film. In addition, the addition of a suitable amount of Cr to the aluminide coating improves the adhesion between the alumina film and the coating, and it can be seen that in high temperature cyclic oxidation experiments, the alumina film on the surface of the Cr-modified aluminide coating is more dense and complete, with less peeling than in the simple aluminide coating.

4. Conclusion

(1) Under the same experimental conditions, the oxidation weight gain of the simple NiAl coating was 1.9 times that of the Cr-NiAl coating during 160 cycles of oxidation, and the oxidation weight gain of the simple NiAl coating was 2.5 times that of the Cr-NiAl coating by fitting.

(2) The γ' -Ni₃Al phase appeared in the simple NiAl coating after 5 cycles of oxidation. After 160 cycles of oxidation, the γ' -Ni₃Al phase dominates in the simple NiAl coating, while the γ -Ni phase also appears in the coating. β -NiAl phase still dominates in the Cr-NiAl coating after 160 cycles of oxidation.

(3) After160 cycles of oxidation at 1100°C, both coatings showed severe oxide film breakage and flaking. the oxide film of the simple NiAl coating was distributed in multiple layers, and Al_2O_3 , $NiAl_2O_4$ and NiO were detected in the surface layer of the oxide film, and the oxide film was incomplete and discontinuous. the oxide film of the Cr-NiAl coating remained continuous and dense, but also showed the presence of $(Al,Cr)_2O_3$ and Ni $(Al,Cr)_2O_4$.

References

- [1] LIU F, CAI Y, GUO X F, et al. Structure evolution in undercooled DD3 single crystal superalloy [J]. Materials Science and Engineering: A, 2000, 291(1): 9-16.
- [2] GOWARD G W. Progress in coatings for gas turbine airfoils [J]. Surface and Coatings Technology, 1998, 108-109: 73-9.
- [3] Zhankao W.,Zhenhua X.,Hong Z., et al. High temperature oxidation behaviour of chromium modified aluminide coatings on single crystal high temperature alloys[J]. Vacuum, 2015, 52(03): 1-5.
- [4] Jing L. Preparation and performance study of chromium modified aluminide diffusion coatings[D]; University of Sciences and Academy of Chinese, 2016.
- [5] YANG J C, SCHUMANN E, LEVIN I, et al. Transient oxidation of NiAl [J]. Acta Materialia, 1998, 46(6): 2195-201.