



Oxidation behaviour of zirconium-doped NiAl coatings deposited on pure nickel

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ABSTRACT

Purpose: In this paper the oxidation behaviour of zirconium-doped NiAl coatings deposited on a pure nickel was investigated.

Design/methodology/approach: The zirconium-doped NiAl coatings were deposited by the chemical vapour deposition method on the pure nickel. The microstructure investigations of zirconium-doped aluminide coatings were performed by the use of an optical microscope (Nikon Epiphot 300) and a scanning electron microscope (Hitachi S-3400N) equipped with an Energy Dispersive Spectroscopy EDS (VOYAGER of NORAN INSTRUMENTS). Oxidation behaviour at 1100°C for 500 h in the air atmosphere in the furnace manufactured by Czylok company was evaluated. The phase composition of oxidized coatings were identified by the X-ray (ARL X'TRAX) diffractometer.

Findings: The microstructures of zirconium-doped aluminide coatings consist of the β -NiAl, γ' -Ni₃Al and γ -Ni(Al) phases. EDS analysis results of elements distribution indicate that zirconium is located at the distance of 13-16 μ m from the surface after 1.5 h of aluminizing and randomly distributed in the whole coating after 5 h of aluminizing. Zirconium (less than 1% at) could contribute to a faster reduction of Al vacancies through fast diffusion towards the metal/oxide interface and increases adhesion of the oxide layer to the coating and this why the oxidation resistance improves.

Research limitations/implications: The research involve microstructure, phase composition and oxidation behaviour investigation of zirconium doped aluminide coatings.

Practical implications: The zirconium-doped aluminide coatings may be used as the cheaper alternative to platinum and palladium modified aluminide coatings for turbine blades of aircraft engines.

Originality/value: The range of investigation includes microstructure, phase composition and oxidation behaviour of zirconium doped aluminide coating.

Keywords: Pure nickel; Zirconium-doped aluminide coatings; Oxidation behaviour

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

The application of diffusion coatings on nickel based superalloys have a beneficial influence on the high temperature performance of gas turbines operating at elevated temperatures. The most common type of coatings for environmental protection of superalloys are aluminide diffusion coatings, which develop aluminide (CoAl or NiAl) outer layers that enhance the oxidation resistance [1-4]. This outer layers come into being by the reaction of aluminium with nickel or cobalt in the base metal. Some research has been made of aluminides containing chromium or silicon and in recent years noble metals such as platinum, hafnium yttrium have been used to enhance the oxidation resistance of aluminides [5]. The most widespread aluminide modifier is platinum. Platinum serves several purposes: it stabilizes an aluminum-rich surface for the continued Al_2O_3 formation, it improves Al_2O_3 scale adhesion and the hot corrosion resistance of NiAl [4, 6-10]. Silicon is especially beneficial in coatings exposed to high concentrations of sulfur. Silicon modified aluminides are resistant to both high-temperature and low-temperature hot corrosion. They are also less expensive than platinum-aluminide coatings [5].

Chromized coatings provide protection against scale-fluxing attack (hot corrosion) that occurs when a molten sulfate is deposited. Such coatings are used on components in the latter stages of the turbine where the temperatures are reduced to below 900°C [5]. The adhesion of the oxide scale on the NiAl layer is an important aspect of the lifetime of turbine blades. Doping NiAl coatings with reactive elements such as Zr has been reported to improve the adhesion of thermally grown alumina scale on NiAl and could drastically reduce the cost of the process [11]. Hafnium addition has been recently proposed as to decrease the propensity for rumpling when it diffuses into the coating and to the growing aluminum oxide [12-13].

In this paper the experimental results of oxidation behaviour of zirconium doped-aluminide coatings deposited by the CVD method on pure nickel are presented.

2. Experimental procedure

The nickel of 99.95% wt purity was used in this study. The cylindrical samples of 20 mm diameter and 4 mm high were cut and grounded up to SiC No 1000, degreased in ethanol, ultrasonically cleaned and zirconium-aluminized. The zirconium-doped aluminide coatings were made using the CVD equipment BPXPR0325S manufactured by IonBond company. The aluminizing by the chemical vapour deposition method was performed two times, for 1.5 h and for 5 h. Aluminium chloride vapour AlCl_3 was produced in an external generator at 330°C according to the reaction: $2\text{Al}+6\text{HCl}\rightarrow 2\text{AlCl}_3+3\text{H}_2$. Zirconium chloride ZrCl_3 vapour was produced in a separated external generator at 440°C according to the reaction: $2\text{Zr}+6\text{HCl}\rightarrow 2\text{ZrCl}_3+3\text{H}_2$. The aluminium and zirconium chlorides were transported in the hydrogen gas into the reactor. The AlCl_3 and ZrCl_3 vapour reacted with nickel samples at 1020°C and an intermetallic phase NiAl(Zr) was formed according to the reaction: $\text{AlCl}_3+\text{ZrCl}_3+\text{Ni}+3\text{H}_2\rightarrow \text{NiAl}(\text{Zr})+6\text{HCl}$

The microstructure of the cross-section of the coatings was investigated by an optical microscope Nikon Epiphot 300, scanning electron microscope (SEM) Hitachi S-3400N and energy dispersive spectroscope (EDS) [14]. Phase composition of the coatings was investigated using the ARL X'TRA X-ray diffractometer, equipped with a filtered copper lamp with the voltage of 45 kV. Oxidation resistance was investigated at 1100°C for 500 h in the air atmosphere. The samples were annealed isothermally for 20 h and then cooled to the room temperature. Twenty five cycles of heating and cooling were carried out. The mass change was measured after each cycle.

3. Results and discussion

The SEM investigation and the EDS analysis of the zirconium-doped aluminide coatings obtained during 1.5 h CVD process on the pure nickel revealed the presence of a triple zone microstructure (Fig. 1). The chemical composition of the top layer indicates the presence of the β -NiAl phase. The layer below the β -NiAl phase corresponds to the γ' - Ni_3Al phase. The third inner zone corresponds to γ -Ni(Al) phase. The microstructure analysis of the top layer of zirconium-doped aluminide coatings revealed that the γ' intermetallic phases is distributed along the grain boundaries of β -NiAl phase.

Zirconium was found between the β -NiAl and the γ' - Ni_3Al layers 13-16 μm from the surface. Zirconium content on the boundary of β -NiAl/ γ' - Ni_3Al phases was 1.48%wt (0.79% at).

The microstructure of the zirconium-doped aluminide coating deposited for 5 h consists of the same three zones, that is β -NiAl, γ' - Ni_3Al and γ -Ni(Al) phases (Fig. 2), but there was no γ' inclusions along the grain boundaries of β -NiAl phase.

The phase composition of both types of coatings was the same, but the total coating thickness was different (Fig. 3). EDS results of elements distribution indicate that zirconium is situated at the distance of 13-16 μm from the surface after 1.5 h aluminizing process and randomly distributed in the whole coating after 5 h aluminizing process (Fig. 4. a-b).

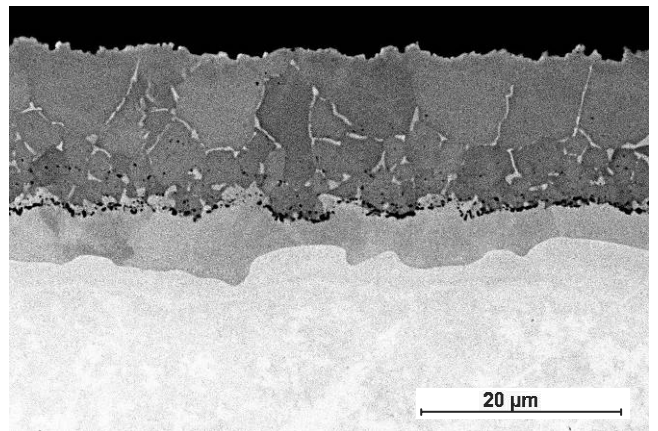


Fig. 1. Microstructure of the cross-section of zirconium doped-aluminide coating deposited by CVD method during 1.5 h

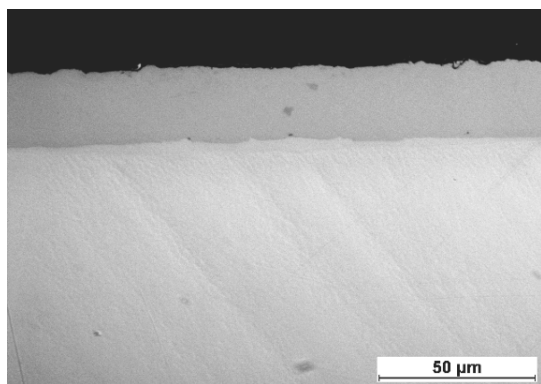


Fig. 2. Microstructure of the cross-section of zirconium doped-aluminide coating deposited by CVD method during 5 h

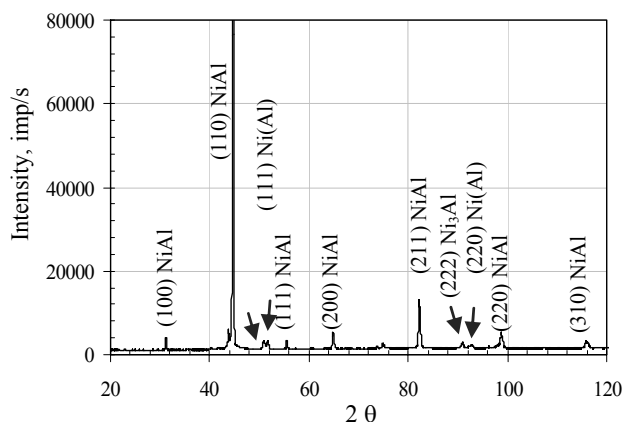


Fig. 3. The X-ray diffraction results of zirconium doped aluminide coating deposited by CVD method on the pure nickel

The chemical composition on the cross-section indicates of the total coating thickness of zirconium doped aluminide coating deposited for 1.5 h is about 30 μm. The increase of aluminizing time from 1.5 h to 5 h lead to obtain the aluminide coating of the total thickness of about 45 μm (Figs. 5-6).

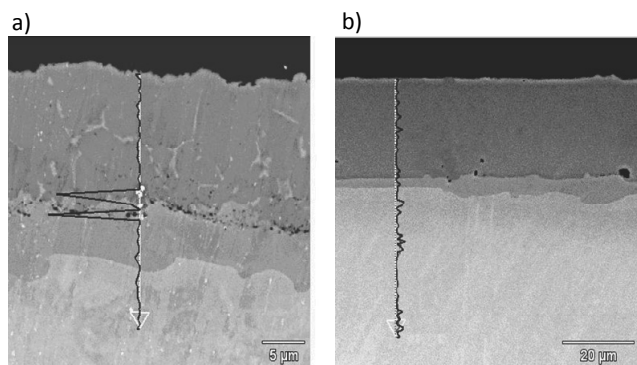


Fig. 4. The analysis of the zirconium distribution on the cross-section of the aluminide coatings deposited for a) 1.5 h aluminizing; b) 5 h aluminizing

The analysis of the concentration profiles and the phase diagram of the Ni-Al system [2] confirms the existence of the above mentioned phases: β-NiAl, γ'-Ni₃Al and γ-Ni(Al) (Figs. 5-6).

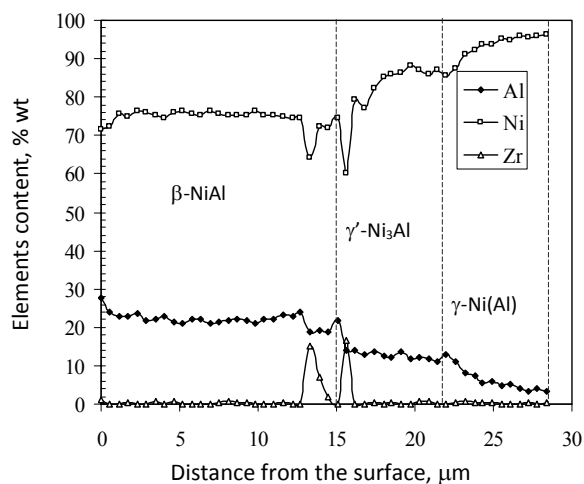


Fig. 5. Concentration profiles of Ni, Al and Zr across the coating deposited for 1.5 h by the CVD method

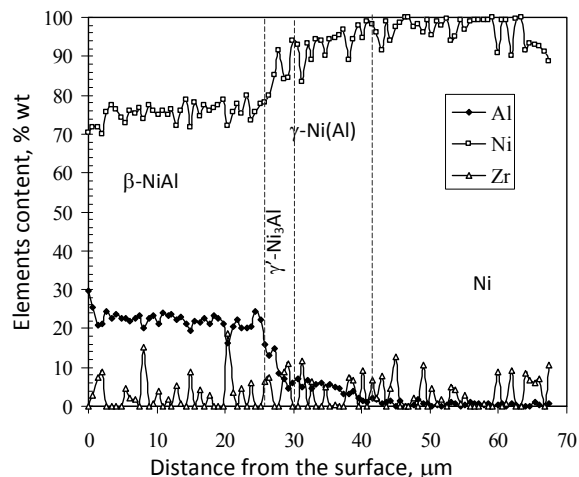


Fig. 6. Concentration profiles of Ni, Al and Zr across the coating deposited for 5 h by the CVD method

The investigation of the oxidation kinetics proved that the weight of zirconium doped aluminide coating deposited for 5 h begins to decrease after 200 h of oxidation (Fig. 7). The weight decrease is due to the spallation of the oxide layer. The mass of the zirconium doped aluminide coating deposited for 1.5 h rises for about 500 h of oxidation (Fig. 7).

The oxidation resistance depends on the zirconium content in the coating [11-13,15]. According to [11,15] the zirconium-doped aluminide coatings (0.4% at Zr) have better oxidation resistance in comparison to platinum modified aluminides. The worse oxidation resistance of zirconium-doped aluminide coatings deposited by 5 h may be due to higher zirconium content (1.17% at in the γ'-Ni₃Al phase) in comparison to coatings

deposited by 1.5 h aluminizing where zirconium content was less than 1% at.

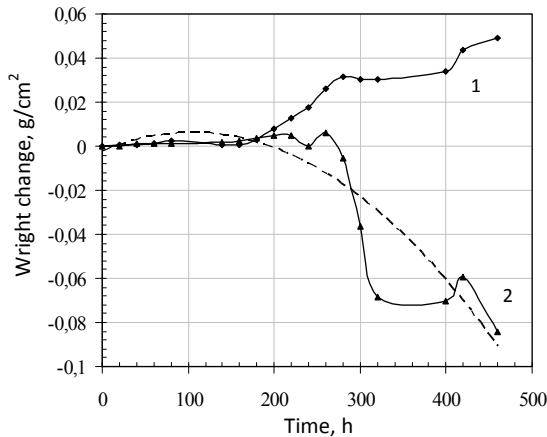


Fig. 7. Oxidation kinetic of zirconium doped aluminide coatings deposited by CVD method: 1 - 1.5 h aluminizing; 2 - 5 h aluminizing

According to Hamadi [11] zirconium initially distributed at the depth of 13-16 μm below the coating surface during oxidation migrates towards the surface and is distributed uniformly in the whole oxide layer. Some authors [16] claim that zirconium may migrate via NiAl grain boundaries to the coating surface. Zirconium delays the oxide scale spallation and inhibits cavities formation at the metal/oxide interface. The absence of cavities in the presence of Zr improves thermally grown oxides adhesion on nickel aluminide. Authors [17] allege that there are two main mechanisms of interfacial cavities formation. The first one is a Kirkendall effect mechanism. According to Kirkendall mechanism the depleted zone near metal/oxide is a result of opposite fluxes of Ni atoms towards the substrate and Al atoms toward the depletion zone. As a result of higher nickel atoms diffusion in comparison to aluminum atoms diffusion voids are formed [11]. The second mechanism is related to the injection of aluminum vacancies in the coating. Two mechanism lead to coalescence of vacancies and cavities formation. Zirconium (less than 1% at) could contribute to a faster reduction of the Al vacancies through fast diffusion towards the metal/oxide interface [11]. As a result of this phenomena the adhesion of the oxide layer to the coating increases and oxidation resistance improves.

It seems, that zirconium-doped aluminide coating deposited for 1.5 h, of lower Zr content (below 1% at) followed this pattern. Zirconium initially distributed at the depth of 13-16 μm below the coating surface during oxidation migrated towards the surface, and distributed uniformly in the whole oxide layer and the oxidation resistance improved (Fig. 7)

Examination of coatings after a long time oxidation (500 h) performed by XRD methods revealed, that the phase composition of both types of coatings is the same. There were observed bilayer oxides. The green color inner oxide layer consists of only NiO phase but outer one black color consists of NiAl₂O₄ and NiO phases (Figs. 8-9). This observation agrees with the phenomena described by [18], that NiO and NiAl₂O₄ oxides are formed the pure nickel after a long time oxidation (500 h).

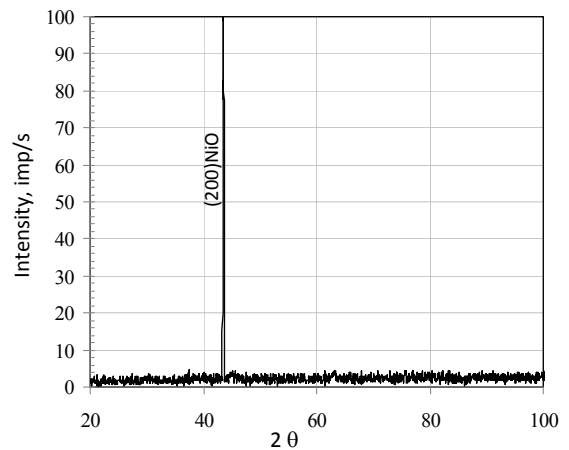


Fig. 8. X-ray diffraction results of inner oxide layer of zirconium doped aluminide coating deposited by the CVD method on pure nickel after 500 h oxidation at 1100°C temperature

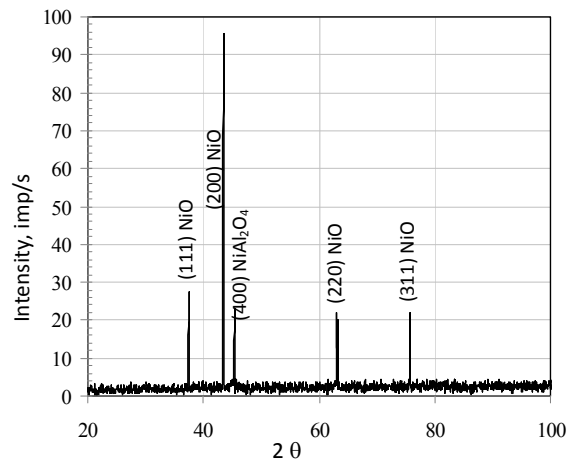


Fig. 9. X-ray diffraction results of outer oxide layer of zirconium doped aluminide coating deposited by the CVD method on pure nickel after 500 h oxidation at 1100°C temperature

The outer oxide layer is formed as a result by outward diffusion of ions and electrons of nickel and aluminium. The inner oxide layer is formed by inward oxygen diffusion (Fig. 10) [18].

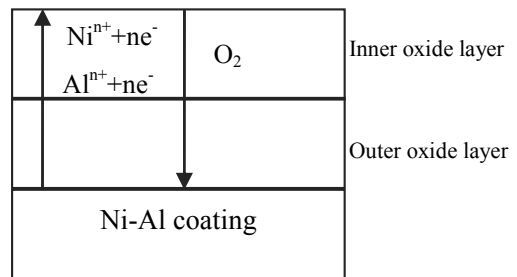


Fig. 10. Mechanism of bilayer oxides formation on Ni-Al coating after 500 h oxidation at 1100°C temperature [18]

4. Conclusions

Two kinds of zirconium-doped aluminide coatings were obtained by the CVD method on the pure nickel. The triple zone structure of the both kind of coatings was observed. It consists of β -NiAl, γ' -Ni₃Al and γ -Ni(Al) phases. Zirconium-doped aluminizing process carried out by 1.5 h lead to obtain 'inclusion' of the NiAl(Zr) phase at the distance of 13-16 μ m from the surface. The zirconium content in this inclusion was about 0.8% at. The random zirconium distribution in the coating obtained by 5 h CVD aluminizing was observed. The zirconium content in the second kind of coating was above 1% at. The better oxidation resistance has the coating where zirconium content is lower than 1% at. Zirconium (less than 1% at) in the aluminides delays the oxide scale spallation and inhibits cavities formation at the metal/oxide interface. Zr improves thermally grown oxides adhesion on nickel aluminide. The oxidation of zirconium-doped aluminide coatings at the 1100°C during 500 h led to obtain bilayers oxides. The formation of these oxides is the result of aluminum depletion during oxidation.

Acknowledgements

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