



# Nanoparticles in zirconium-doped aluminide coatings



Maryana Zagula-Yavorska, Jerzy Morgiel\*, Jolanta Romanowska, Jan Sieniawski

Institute of Metallurgy and Materials Sciences, PAS, 25 Reymonta st., 30-059 Kraków, Poland

## ARTICLE INFO

### Article history:

Received 4 July 2014

Accepted 20 September 2014

Available online 22 October 2014

### Keywords:

Zirconium

TEM analysis

Aluminide coating

Nanoparticles

## ABSTRACT

The microstructure of the zirconium doped aluminide coating deposited on the nickel substrate by the CVD method is presented. TEM analysis proved that the  $\beta$ -NiAl and the  $\gamma'$ -Ni<sub>3</sub>Al are the main phases of the deposited coating. Some dislocations in the nickel substrate and in the coating were observed. The cross section chemical composition examination revealed, that the coating was formed via the inward aluminum diffusion and the outward nickel diffusion. SEM analysis revealed small zirconium content (0.2–0.4 at%) on the cross-section of the aluminide coating. Such zirconium content leads to zirconium dissolution in the aluminide coating. Long time of zirconizing (4 h) caused the appearance of zirconium nano particles at the surface of the coating. TEM investigations confirmed that zirconium formed inclusions on the coating's surface.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Research conducted by aircraft engines' manufacturers are aimed at the increase of engines efficiency. It can be achieved by the increase of the volume of the air flowing through the turbine as well as by the increase of the temperature at its hot stage. The increase of the temperature of gases at the turbine inlet in modern engines depends on the efficient cooling systems of turbine blades and the usage of nickel or cobalt superalloys with protective thermal barrier coatings (TBC) [1–6]. The improvement of engine efficiency by the increase of turbine inlet temperature implicates the use of different types of protecting coatings including aluminide and MeCrAlY multicomponent ones. The NiAl phase present in coatings improves hot corrosion resistance of protected superalloys. The NiAl phase is the most stable of all phases in the Ni–Al system. It is both creep resistant and assures good adhesion to the substrate [7]. Incorporation of noble metals, particularly platinum, to aluminide coatings improves resistance to oxidation and hot corrosion [8–11]. The search for bond coat to replace platinum modified aluminide coatings is aimed at:

- increasing the adherence of the thermally grown protective alumina oxides,
- reducing interdiffusion phenomena between the bond coating and the substrate,
- avoiding phase transitions such as martensite formation,

- increasing creep resistance in order to minimize surface rumpling and consequently extend the system lifetime,
- reducing the cost.

Previous experiments [12] proved that the addition of small amounts of reactive elements such as Zr, Hf, Y or Ce to the NiAl coatings has beneficial effects on oxidation resistance of superalloys. Zirconium modification of the NiAl phase improves adhesion of thermally grown alumina oxides to the NiAl coating and could drastically reduce the processing cost [13–16]. Zirconium present in the oxide lowers the stress and simultaneously reduces the oxide creep rate. Therefore, zirconium both delays the oxide-scale spalling and inhibits formation of cavities at the metal/oxide interface. Moreover, there are no voids at the metal/oxide interface, unlike in Pt-modified NiAl coatings. The absence of voids at the interface of Zr-doped coating and the substrate is expected to improve alumina adhesion on the nickel aluminide. Li et al. [13] proved, that small Zr addition (about 0.1 at%) improves oxidation resistance of the coating due to the reduction and cracking of the spalling scale. In order to improve the oxidation resistance of the coating, only a small zirconium content in the coating (0.2–0.3 at%) is required. Such small overall content makes it difficult to find and identify the zirconium enriched phases in aluminide coatings, what results in lack of the knowledge on the distribution of the latter.

In the present paper the microstructure of zirconium-doped aluminide coating deposited on the nickel substrate by the CVD method was analyzed using the transmission electron microscopy (TEM) method. The presence of Zr-bearing phases in the aluminide coatings was backed with the TEM/EDS measurements.

\* Correspondence to: Department of Materials Science, Rzeszow University of Technology, W. Pola 2 st., 35-959 Rzeszow, Poland.

E-mail address: [yavorska@prz.edu.pl](mailto:yavorska@prz.edu.pl) (J. Morgiel).

## 2. Experimental procedure

The aluminide coating was deposited using the CVD equipment BPXPR0325S manufactured by IonBond company [1,2,8,11,12,17]. The aluminizing process consisted of the following stages:

- I—heating from the room temperature up to 900 °C;
- II—aluminizing at 900 °C for 20 min;
- III—heating from 900 °C to 1020 °C;
- IV—aluminizing at 1020 °C for 5 min;
- V—aluminizing and zirconizing at 1020 °C for 4 min;
- VI—aluminizing at 1020 °C for 10 min;
- VII—cooling samples with the furnace.

The commercial nickel of 99.95 wt% purity was used in this study.

A Tecnai G2 STWIN FEG (200 kV) transmission-scanning electron microscope equipped with High Angle Annular Dark Field (HAADF) detector was used for microstructure examination. Thin foils were cut perpendicularly to the surface with the Quanta Dual Beam Focused Ion Beam (FIB) equipped with Omniprobe lift-out system.

## 3. Results and discussion

The TEM observations of the cross-section of the zirconium-doped aluminide coating showed that it consisted of the  $\gamma'$ -Ni<sub>3</sub>Al and the  $\beta$ -NiAl phases, as confirmed by the electron diffraction analysis (Fig. 1). Moreover, the nickel substrate/ $\gamma'$ -Ni<sub>3</sub>Al as well as the  $\gamma'$ -Ni<sub>3</sub>Al/ $\beta$ -NiAl interfaces are relatively flat. All involved phases were significantly dislocated, but the nickel substrate was definitely the most defected one. Additionally, within the  $\beta$ -NiAl and along the interface with the  $\gamma'$ -Ni<sub>3</sub>Al phase a layer of Kirkendall-like porosity was observed (Fig. 1). The maps of local chemical composition generally confirm the shifts in aluminium content in the  $\gamma'$ -Ni<sub>3</sub>Al and the  $\beta$ -NiAl phases and indicated the presence of oxygen at the mentioned previously voids (Fig. 2). The

signal from Zr was generally very weak and falling within the background noise.

The detailed examination of the near surface areas showed that occasionally, at the exit points of the boundaries of the  $\beta$ -NiAl crystallites, small nanoparticles of  $\sim 70$  nm diameter can be found (Fig. 3a). The chemical analysis of such particles performed using the EDS attachment indicates that they are built predominantly of zirconium (Fig. 3b).

The maps presenting local chemical composition confirm that zirconium is located exclusively within the discussed nanoparticle (Fig. 4). The analysis of the map of the oxygen distribution revealed the presence of small amount of aluminium oxide in the neighboring area. The electron diffraction patterns obtained from the particle (Fig. 5) matched with those calculated for the  $\alpha$ -Zr phase (hexagonal structure;  $a=3.232$  nm and  $c=5.147$  nm).

The performed research confirmed, that zirconium was incorporated into the aluminide coating during the chemical vapor deposition process, i.e. that the planned co-deposition of zirconium and aluminum through-out the procedure described in the experimental part succeeded. However, the problem of zirconium solubility in the NiAl phase is still open. Nash et al. [18] showed that solubility of zirconium in the Ni<sub>3</sub>Al phase at 1100 °C is up to 2.7 at%. Thus, one may presume that as small as 0.2–0.4 at% zirconium should dissolve in the coating. The Ni–Al–Zr ternary phase diagram near the NiAl side at the elevated temperature has not been evaluated yet, but there are some data on Ni–Al–Hf phase diagram [19,20]. Hafnium and zirconium have similar physical and chemical characteristics and similar intermetallic phases are formed in both systems. Li et al. [20] allege that the Ni<sub>2</sub>AlHf phase precipitates at 1277 °C and below this temperature. The Ni<sub>2</sub>AlZr phase exists, as shown in the Ni–Al–Zr ternary phase diagram, at 800 and 1100 °C. Despite the fact that the Ni<sub>2</sub>AlZr phase (called Heusler phase) exists at 800 °C, it was not observed in the investigated aluminide coating.

In the presented research, the zirconium particles were observed at the top surface of the  $\beta$ -NiAl layer. It indicates, that both the  $\beta$ -NiAl and the  $\gamma'$ -Ni<sub>3</sub>Al phases, formed in the coating at 1020 °C, are fully saturated with zirconium. As the diameter of

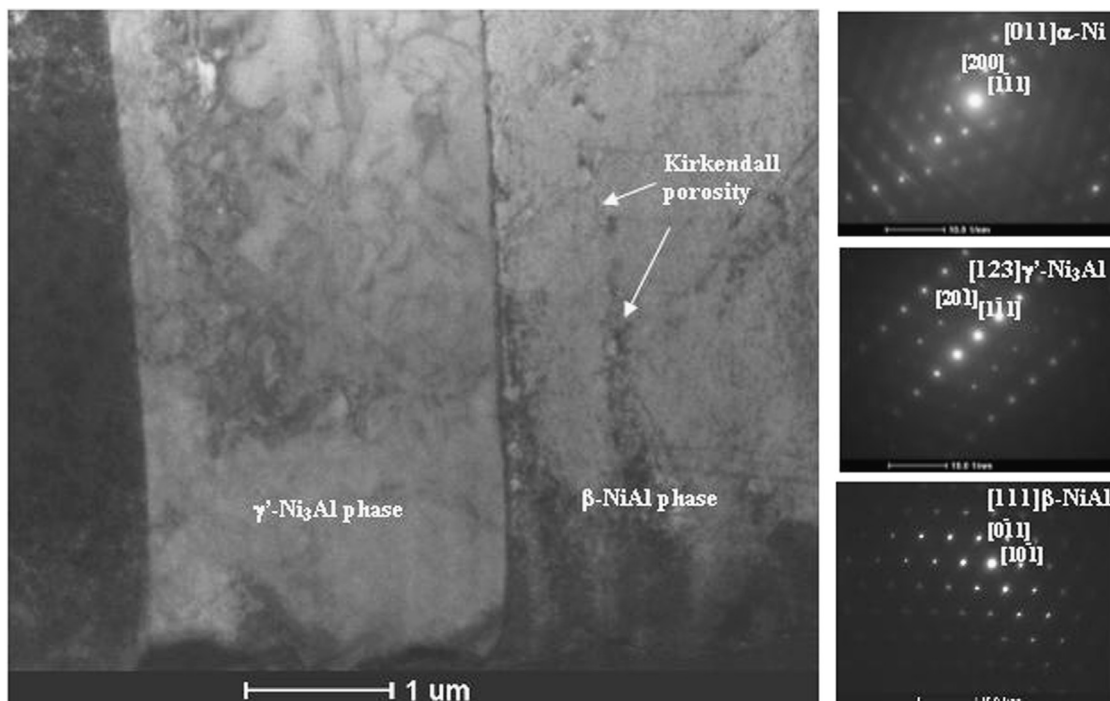


Fig. 1. TEM image of the cross-section of the zirconium-doped aluminide coatings.

Download English Version:

<https://daneshyari.com/en/article/1643515>

Download Persian Version:

<https://daneshyari.com/article/1643515>

[Daneshyari.com](https://daneshyari.com)