

# Effect of $\text{Al}_2\text{O}_3$ and AlCrN coatings on $950^\circ\text{C}$ cyclic oxidation behaviours of $\gamma\text{-TiAl}$

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## Properties

### ABSTRACT

**Purpose:** The reason for this research is to test the intermetallic alloy with coatings  $\text{Al}_2\text{O}_3$  and AlCrN improved oxidation resistance in air at temperatures  $950^\circ\text{C}$ , typical for working conditions of highly loaded parts of gas turbine.

**Design/methodology/approach:** The objectives were achieved using several techniques including conventional metallography, SEM, BSE, EDX and precision measurements of mass loss. The oxides scales and their effects were investigated at temperatures  $950^\circ\text{C}$ .

**Findings:** This investigation confirms that the deposited AlCrN coating significantly reduces spalling processes and makes for lesser mass growth of the oxidized alloy. Heat resistance of the alloy coated with a protective film of  $\text{Al}_2\text{O}_3$  is higher than in the initial state alloy. This coating adds to reducing the oxidation rate and causes the mass growth to be smaller compared to the uncoated layer.

**Research limitations/implications:** The basic limitations concern alloys in another temperature and also, atmosphere with content of  $\text{SO}_2$  should be tested.

**Practical implications:** One of practical outcomes is to select the coatings which guarantee the reduction of oxidation behavior. It is recommended to use alloys with  $\text{Al}_2\text{O}_3$  and AlCrN coatings.

**Originality/value:** Original value of the paper is assessing of the oxidation resistance of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni-based intermetallic alloy with the  $\text{Al}_2\text{O}_3$  and AlCrN coatings. The novelty of this research deals with the mechanism of oxidation alloy with this coatings. This knowledge can support the design of parts made of the intermetallic alloy. The problem considered is currently important for aeroplane and automotive industry, especially for gas turbine manufacturers.

**Keywords:** Oxidation; Corrosion; Intermetallics; Coatings

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## 1. Introduction

Intermetallic phase based Ti-Al alloys represent very attractive structural materials for operation at elevated temperatures and in aggressive chemical environments. Gamma Ti-Al alloys with other aerospace structural materials and shown

that new capabilities become available on account of its properties. The most important pay-offs involve [1]:

- high melting point,
- low density,
- high specific strengths and modul,
- low diffusivity,

- good structural stability,
- high ignition resistance (when compared with conventional titanium alloys).

Titanium aluminide intermetallics are particularly popular as materials used in production of gas turbine components and they promise to improve reliability, lower the emission, lengthen the life and lower the cost of manufacturing [2-3].

Efficient application of these alloys is however restricted by their low plasticity at room temperature and insufficient resistance to oxidation above 700°C. During high temperature oxidation, a protective coating of Al<sub>2</sub>O<sub>3</sub> is not formed whereas the coating consisting of the mixture of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> does not possess sufficient protective properties [4-5].

Otherwise construction elements in such devices can operate not only in high temperatures, but also in conditions that require periodical activation and deactivation. Such cyclic oxidation may result in scale spalling and chipping, hence the local or total loss of the protection layer provided by intact scale. In case of reheating, places where scale spalled may be subject to accelerated oxidation. Therefore, cyclic oxidation testing has become the basis for developing specifications of materials used for operation in high temperature. It is required that formed products of oxidation of metallic substrate do not only limit the rate of layer increase, but are also resistant to mechanical defects while cooling down and withholding room temperature.

Some methods have been proposed for improving the oxidation resistance of TiAl-based materials. One of the methods of affecting the properties of these alloys is modifying their chemical composition accomplished by introducing certain alloying elements to the mass of material. As presented in papers [6-14] the addition of Nb, W, B, Cr, Mo, Si, Ta, Y and Zr may improve the oxidation resistance of Ti-Al intermetallic phase based alloys. Accordingly the protection properties of these additions depend on their concentration.

Over past decade, there has been a systematic effort to improve the strength and damage tolerance of titanium aluminides by microalloying and optimization of the microstructure. This has led to complex alloys with the general composition governing by the following percentage rule:



where:

X - contents of Cr, Mn, Ta;

Y - contents of W, Hf, Zr;

Z - contents of C, B, Si;

RE - rare earth elements.

Alloys of such a chemical composition (1) deserve a special industrial attention. They can be used as a new generation construction material for combustion engines, gas turbine blades, turbo compressor rotators, or even components of supersonic constructions.

Nevertheless, the addition of such elements may result in increasing the density of the initial material and deterioration of mechanical properties of the alloys.

To improve high temperature oxidation resistance of Ti-Al based alloys many investigation have been carried out. Therefore, the best way of improving Ti-Al alloy oxidation resistance is the

application of appropriate protective coatings. The current literature widely presents achievements concerning the protective coatings that improve high temperature resistance of Ti-Al intermetallic alloys [15-25].

This article presents the results of research on resistance to cyclic oxidation of Ti-46Al-7Nb-0,7Cr-0,1Si-0,2Ni alloy with Al<sub>2</sub>O<sub>3</sub> and AlCrN layer applied. Previously, the problem of the oxidation corrosion of the uncoated TiAl alloy was discussed in Ref. [13,25].

## 2. Experimentation

### 2.1. Materials

The study has been done on cast Ti-46Al-7Nb complex alloy containing 46%at Al, 7%at Nb, 0,7%at Cr, 0,1%at Si and 0,2%at Ni. The material in the form of a cylinder of ca. 69 mm in diameter was fabricated by Flowserve Corporation Titanium and Reactive Metals Foundry company (USA).

### 2.2. The test device and procedure

The samples of alloy with dimensions of 20×15×2 mm were polished with 800 grade abrasive paper and subsequently degreased in acetone. The surface roughness was measured using a Hommel Tester 1000 profilometer with a LV15 measuring head. The values of the average roughness Ra measured on the machined surface of specimens were obtained to be about Ra = 0.06 μm.

The Al<sub>2</sub>O<sub>3</sub> layer was obtained by means of magnetron method, AlCrN coating obtained in PVD process. The thickness of the Al<sub>2</sub>O<sub>3</sub> coating was circa 3 μm and the AlCrN coating was 30 μm.

Investigations of the material structure and chemical constitution in the micro-areas of the specimens were performed using a Philips XL20 microscope equipped with an EDAX analyzer and a Hitachi S-4200 microscope furnished with a Therm NORAN and System Six attachment. To obtain better compositional contrast BSE detector was used.

Cyclic oxidation tests under air were conducted in 950°C. Each cycle consisted of sample heating to a certain temperature, holding the samples in the temperature for 1 hour and then cooling down and withstanding the room temperature for 15 minutes. The mass variation resulting from the cyclic oxidation process was specified on scales with accuracy to 10<sup>-4</sup> g. During tests, the corrosion intensity and oxidation wear mechanisms occurring were studied.

After the test was finished, surfaces and cross-section of the oxidized specimen were studied by scanning electron microscopy (SEM) and subsequently subjected to energy-dispersive X-ray microanalysis. Cross-section was prepared by conventional metallographical techniques. On the other hand, specimens were etched with reagent to provide structure investigation, as follows:

- 30 ml C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>,
- 15 ml HNO<sub>3</sub>,
- 5 ml HF.

Phase identification of the oxide scale was performed by X-ray diffraction (XRD).

### 3. Results and discussion

The structure of the tested alloy (duplex) is presented in Fig. 1. Results of EDX analysis are presented in Fig. 2. According to the microstructure classification of Ti-Al alloys on intermetallic phase matrix  $\gamma$ -TiAl suggested by Clemens et al. [26], such a structure type can be specified as duplex.

Phase  $\gamma$  and  $\alpha_2$  form lamellar structure, and phase  $\gamma$  locally appears in granular form. On the boundaries in lamella-grain structure irregular concentrations of the phase  $\alpha_2$ -Ti<sub>3</sub>Al were observed. The microanalysis of these clusters points out that not only do they have a higher titanium content but also a higher concentration of chromium and niobium (Fig. 2b). On the other hand, grains of  $\gamma$  phase contain almost 48% at Al and 7% at Nb (Fig. 2a)

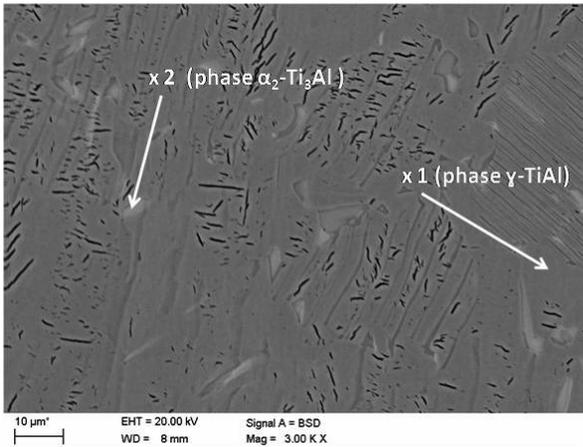


Fig. 1. SEM images (BSE detector) of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni

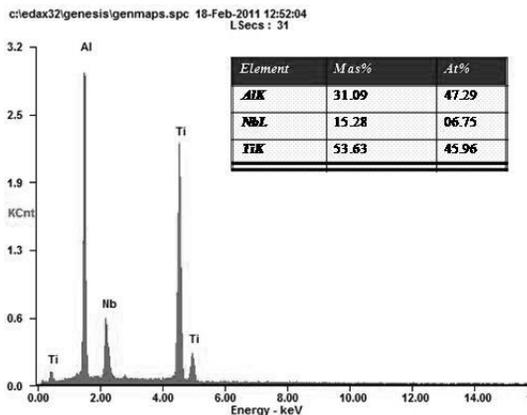


Fig. 2a. EDX analysis results in place 1 according to Fig. 1

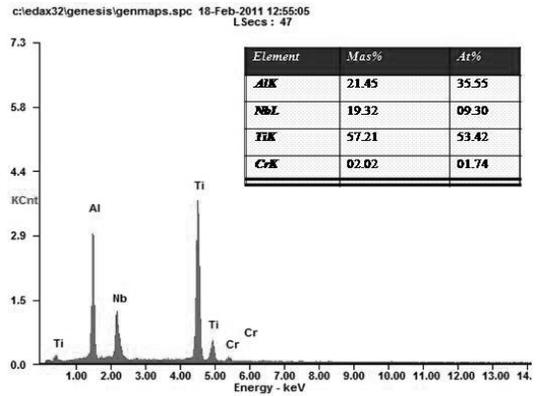


Fig. 2b. EDX analysis results in place 2 according to Fig. 1

#### 3.1. Cyclic oxidation behaviour of the alloy

The course of oxidation of the oxidized alloy was presented in Fig. 3. Cyclic oxidation at 950°C during 60 cycles of uncoated alloy and for samples with the coating of Al<sub>2</sub>O<sub>3</sub> results in mass increment only in initial cycles and then mass decrement dominates caused by chipping in the cooling cycle. For uncoated alloy, this happens after ca. 30 oxidation cycles, whereas for alloy with Al<sub>2</sub>O<sub>3</sub> coating - after 40 oxidation cycles. In further cycles, only mass decrement occurs. However, smaller mass gains were observed for the alloy with Al<sub>2</sub>O<sub>3</sub> coating in the function of time.

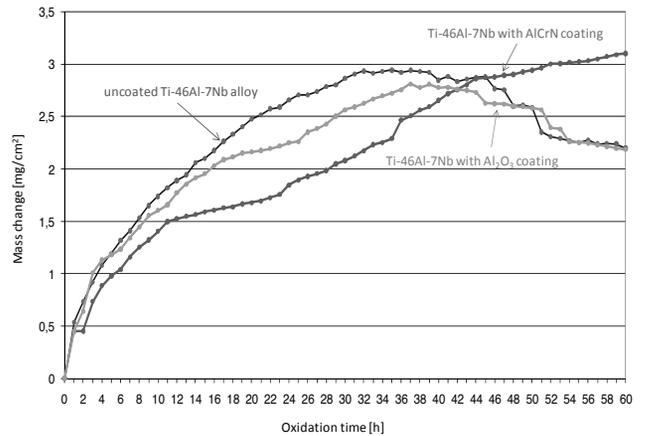


Fig. 3. Course of cyclic oxidation of Ti-46Al-7Nb alloy at 950°C (uncoated and with Al<sub>2</sub>O<sub>3</sub> and AlCrN coated)

Oxidation of alloy with AlCrN coating results only in mass increment. Forming oxidation products showed good adherence to the metallic substrate.

Specimens with AlCrN coating observed instantly after cyclic oxidation tests at 950°C were characterized by good adhesion of products to their metallic substrate.

The chipping of scale's parts could be observed during cooling down to room temperature for uncoated alloy and also for alloy with Al<sub>2</sub>O<sub>3</sub> coating.

The chipping in the room temperature was noticeable with increasing the oxidation time chipping of basic reaction products becomes more intensive and another sublayer is uncovered.

Diffusion processes, which contribute to the loss of cohesion between the scale and the substrate, are activated along with the oxidation time. Thus, ex-core ionic diffusion is accompanied by an increase in the concentration of vacancies at the product-substrate boundary up to the point of cohesion breach. Compressive stresses generated upon oxidation and cooling of the sample down to the room temperature cause the buckling of the layer and its removal from the substrate.

### 3.2. Structure and morphology of the product layer of uncoated alloy

The oxidation Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy not only includes scale formation, but also alterations in the substrate caused by ex-core diffusion of alloying elements and by forming phases and solid solutions due to in-core diffusion of oxygen and nitrogen.

During oxidation of initial state Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy, columnar crystallites  $\text{TiO}_2$  growing in various directions can be observed on the oxidized surface (Fig. 4).

The analysis of the structure and composition of the isothermal air oxidation products allows concluding that the product covering the surface contains more titanium compared to aluminium content (Fig. 5a), which indicates that the product formed on the outer surface is rutile crystallites  $\text{TiO}_2$ , generated as a result of ex-core diffusion of titanium. Beneath columnar crystallites of rutile another sublayer exists, which gives a grey-black heterogeneous contrast in BSE scanned images. Microanalysis of this sublayer shows the dominance of Al with a much lower share of Ti (Fig. 5b). The third sublayer extends as far as the metallic substrate boundary. Aluminium oxides occur in this sublayer but Ti oxides are dominant. It is confirmed by the inner analysis of the sublayer in point 3 in Fig. 5c. On the metallic substrates side a light band occurs. It is a region rich in Nb (Fig. 5d).

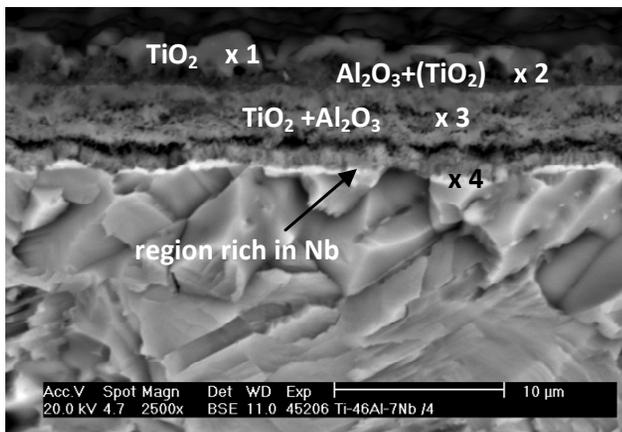


Fig. 4. Fracture surface of uncoated Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy after cyclic oxidation in air at 950°C

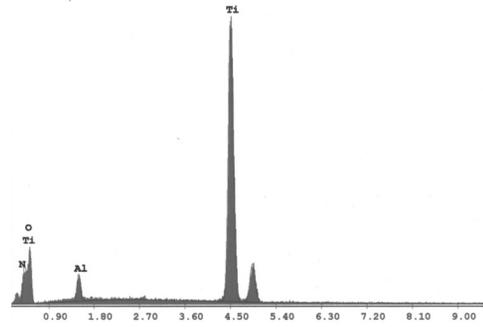


Fig. 5a. EDX analysis results in point # 1 marked in Fig. 4

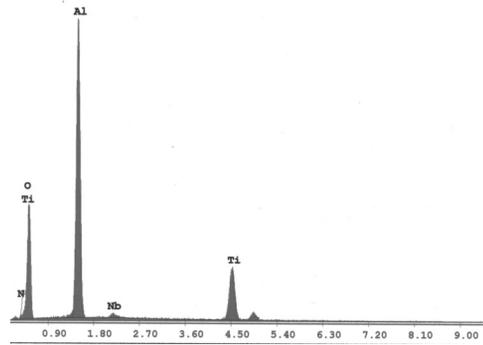


Fig. 5b. EDX analysis results in point # 2 marked in Fig. 4

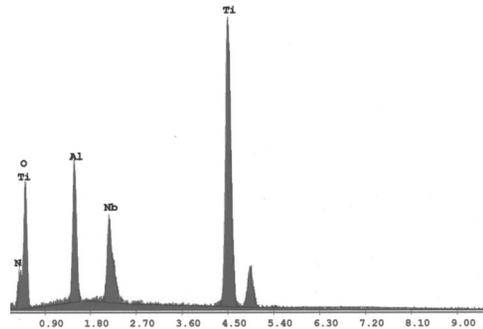


Fig. 5c. EDX analysis results in point # 3 marked in Fig. 4

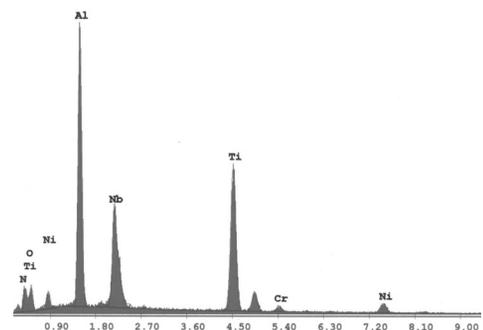


Fig. 5d. EDX analysis results in point #4 marked in Fig. 4

Oxidation of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni results not only in forming products of reaction with hot air but also additional changes in the metallic substrate take place in the occurrence of various diffusion processes at the phase boundary. These changes are caused by the ex-core diffusion of alloy-forming elements and formation of phases and solid solutions resulting from the in-core diffusion of N<sub>2</sub> and O<sub>2</sub>.

### 3.3. Structure and morphology of the product layer on coating alloy

The cross-section of the scale formed on Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni coated with Al<sub>2</sub>O<sub>3</sub> is shown in Fig. 6.

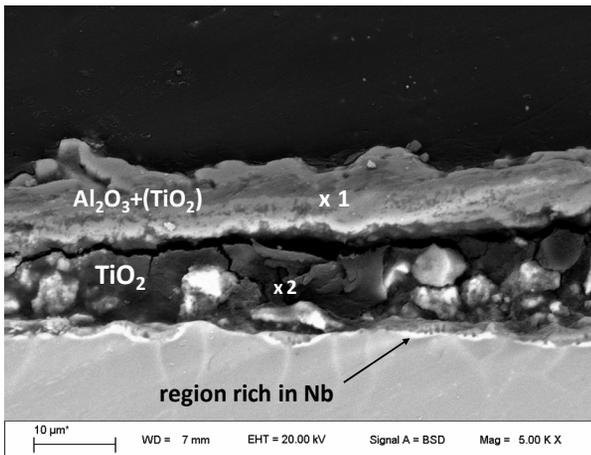


Fig. 6. Cross-section of the scale formed on Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni coated with Al<sub>2</sub>O<sub>3</sub> after cyclic oxidation in air at 950°C

The produced scale was characterized by a two-layer structure. Two layers were distinguished, an inner and an outer one. The chemical composition of the marked spots was shown in Fig. 7(a-b). Directly above the substrate of  $\gamma$ -TiAl alloy, the layer of TiO<sub>2</sub> (spot x2 according to Fig. 6) can be seen. Above Al<sub>2</sub>O<sub>3</sub> layer a scale containing Al and Ti forms. X-ray microanalysis performed in the spot x1 according to Fig. 6 (Fig. 7a), however, shows a clear dominance of aluminium in this layer. Micro-voids were also noticed, which can be seen in BSE as the black fields between these two sublayers.

The layer of products formed on Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy coated with AlCrN has a completely different structure. The structure of the scale surface formed upon oxidation of the alloy coated with AlCrN (Fig. 8) has a totally different appearance than that of the alloy in initial state. It was noticed that the alloy's surface after oxidation is mostly coherent, non-chipping layer containing Al and Cr. The structure of the sublayer proves that they have a multi-phase nature.

Diffusion processes activate along with the oxidation time, which is shown by higher mass growths. It was also observed that for the alloy coated with AlCrN, the formed oxide layers are well adhesive to the metallic substrate throughout the entire time of the test in this temperature range.

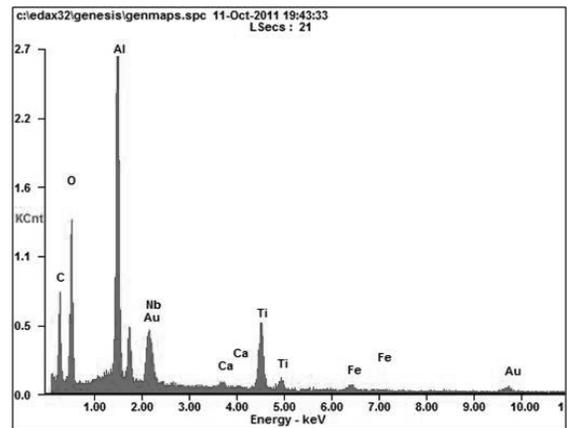


Fig. 7a. EDX analysis results in point # 1 marked in Fig. 6

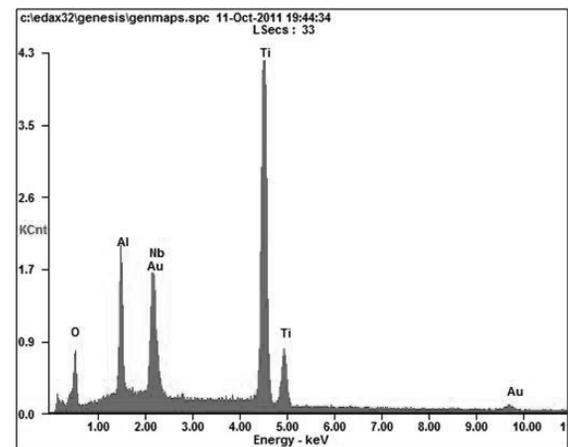


Fig. 7b. EDX analysis results in point # 2 marked in Fig. 6

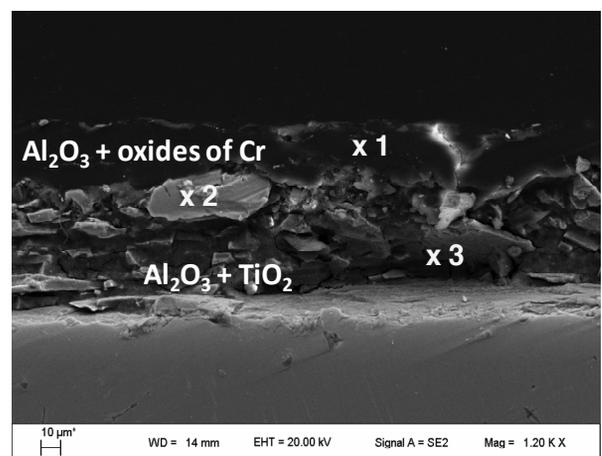


Fig. 8. Cross-section of the scale formed on Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni coated with AlCrN after cyclic oxidation in air at 950°C

The band contrast of products layer and metallic substrate calls for examining the chemical composition of individual sublayers. For this purpose microanalyses were carried out in many points of the layer. The chemical composition of the marked spots was shown in Fig. 9(a-c).

This layer was composed of alternating bright and dark grains. Detailed analysis of the chemical composition proved the presence of the scale on the coating made mainly of protective layer of oxides rich in aluminium and chromium and amount of titanium (Fig. 8). In the area of the coating the presence of voids was also established. In the transitional zone between the substrate and the coating, numerous fine-disperse secretions rich in titanium, aluminium, and chromium were revealed (point x2 marked in Fig. 8).

Chemical composition microanalyses of the alloy show traces of Au (visible reflections in Au Figs. 7 and 9). It is not, however, a product of corrosion but external factor whose elimination was impossible. The presence of Au reflections on the radiation spectrum is a consequence of the methodology of the preparation of samples for microscopic examination. In order to secure proper electrical conductivity of the alloy, the samples were sputtered with gold, therefore the presence of Au is omitted in the results analysis. The presence of carbon (C) and ferryt (Fe) in the results of X-ray microanalysis is caused by organic pollutions occurring on the surface of the sample and taken into consideration in quantitative microanalysis.

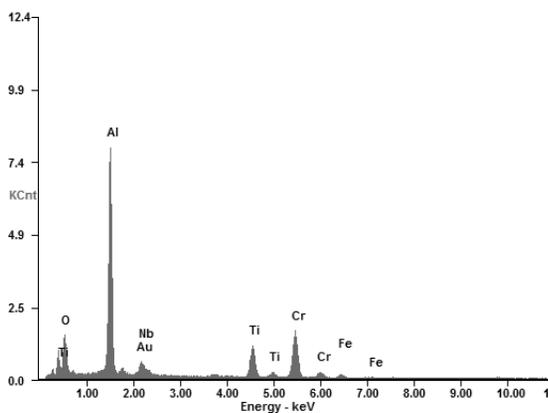


Fig. 9a. EDX analysis results in point # 1 marked in Fig. 8

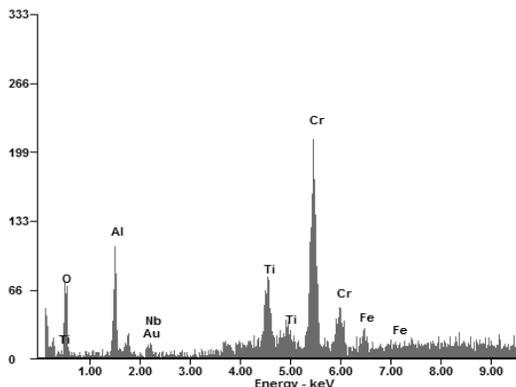


Fig. 9b. EDX analysis results in point # 2 marked in Fig. 8

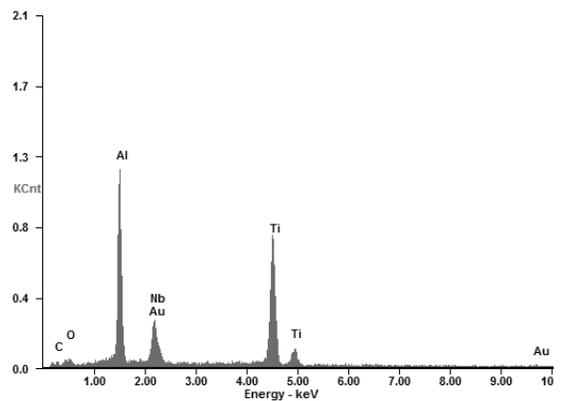


Fig. 9c. EDX analysis results in point # 3 marked in Fig. 8

## 4. Conclusions

The technology of magnetron sputtering used in this study allowed the deposition of a coating that ensured the improvement of high temperature oxidation resistance without interference in mechanical properties of the alloy.

Heat resistance of the alloy coated with a protective film of  $Al_2O_3$  and AlCrN is higher than in the initial state alloy. These coatings adds to reducing the oxidation rate and causes the mass growth to be smaller compared to the uncoated alloy. The dominating ingredient of the formed scale is  $Al_2O_3$  as expected, which has a positive impact on increasing heat resistance of the alloy. Despite high oxidation resistance of AlCrN coating, trace elements of rutile can be detected in the scale, which is generated due to ex-core diffusion of titanium.

Taking into consideration the presented results it can be concluded that the coating of AlCrN caused the heat resistance of the substrate alloy to increase without interference in its mechanical properties, which can be a foundation for its prospective application.

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