A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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MICROSTRUCTURAL CHARACTERIZATION OF GAS PHASE ALUMINIZED TiAlCrNb INTERMETALLIC ALLOY

CHARAKTERYSTYKA MIKROSTRUKTURY STOPU TiAlCrNb PO PROCESIE ALUMINIOWANIA GAZOWEGO

This article presents a microstructure characterization of an alloy coating based on Ti-48Al-2Cr-2Nb- type $\gamma + \alpha_2$ intermetallic phases deposited via an out-of-pack aluminizing process. The goal of the aluminizing process was to obtain a coating composed of aluminum-rich $TiAl_2$ or $TiAl_3$ phases with greater oxidation resistance compared to the base alloy. The results showed that the gas-phase aluminizing process produced a coating with specific microstructural properties. The thickness of the layer obtained, including the transition zone, was approximately 20 μm. X-ray diffraction (XRD) phase composition studies demonstrated that the outer coating zone was primarily composed of a $TiAl_2$ phase, and its thickness was approximately 10 μm. Microanalysis of the chemical composition showed that, in addition to the main components, i.e. titanium and aluminum, chromium and niobium were present in the outer coating. Electron backscatter diffraction (EBSD) studies further indicated the probable presence of a $TiAl_2$ phase. The coating obtained was of good quality, and cracks or pores, which are typical of coatings obtained via powder methods, were not detected.
Keywords: coatings, microstructure characterization, titanium aluminides, EBSD

W artykule przedstawiono wyniki badań mikrostruktury warstwy wierzchniej stopu na osnowie faz międzymetalicznych $\gamma + \alpha_2$ typu Ti-48Al-2Cr-2Nb po procesie aluminiowania metodą out-of-pack. Celem procesu aluminiowania było uzyskanie warstwy zewnętrznej zbudowanej z bogatych w aluminium faz typu $TiAi_2$ lub $TiAl_3$ o wyższej odporności na utlenianie w porównaniu do stopu podłoża. Zrealizowane badania wykazały, że zastosowanie metody aluminiowania gazowego pozwoliło na wytworzenie na powierzchni stopu pokrycia o zakładanych właściwościach mikrostrukturalnych. Grubość otrzymanej warstwy, łącznie ze strefą przejściową wynosiła ok. 20μm. Mikroanaliza składu chemicznego wykazała również, że poza głównymi składnikami tj. tytanem i aluminium w obszarze tym obecne były również chrom i niob. Badania EBSD wykazały ponadto prawdopodobną obecność fazy Ti_3Al_5. Uzyskane pokrycie było dobrej jakości, nie stwierdzono pęknięć ani pustek, typowych dla warstw otrzymanych metodami proszkowymi.

1. Introduction

$\gamma-$TiAl intermetallics are characterized by a very attractive set of properties that are ideal for high-temperature applications, particularly in aircraft and automotive industries. Intermetallics feature a high elastic modulus, low density, and good creep resistance at high temperatures [1,2]. However, methods for the deposition of γ-TiAl intermetallics are limited by two factors: low plasticity at room temperature, and insufficient resistance to oxidation at temperatures exceeding 800°C [3]. Relatively poor oxidation resistance of this group of alloys is a result of the aluminum content, which prevents formation of a continuous Al_2O_3 layer. Thus, wider application of aluminides in industry demands the development of techniques that can increase oxidation resistance. Larger quantities of alloying elements, which improve oxidation resistance, may have deleterious effects on the materials mechanical properties [4,5]. Surface modification techniques provide a possible solution for improving the oxidation resistance of γ-TiAl alloys. An extensive body of literature on the subject describes development of a number of promising oxidation-resistant coatings that may be deposited onto γ-TiAl alloys. This group of coatings comprises aluminide coatings made by pack cementation [6,7] or slurry methods [8], MCrAlY-type coatings [9,10], the silicide/ceramic system of coatings [11,12], or cathodic arc physical vapor deposition (Arc-PVD) coatings [13-15]. The use of contactless gas-phase aluminizing methods,

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described here, present very interesting possibilities, as has been previously suggested [16, 17].

The gas phase (or "out-of-pack") aluminizing method involves placing coated components in a container such that they do not contact the (usually granulated) powder mixture. The samples are placed in a retort or vacuum furnace and heated. Over the course of the coating deposition process, a neutral carrier gas is fed into the container, which enables the transfer of the coat-forming gases created during the process. Several types of out-of-pack methods are currently applied, the most appealing of which are the subatmospheric pressure process, pulse vapor phase aluminizing process developed by SNECMA, and a process performed on, e.g., two mixtures of varying chemical content. The main benefits of the out-of-pack process are: no contact between the coated material and powder, which notably improves coating surface; increased control during the deposition process; increased tidiness of the process (in comparison with powder technologies); as well as the fact that aluminide coatings may be modified by a number of elements to increase their heat resistance [18].

2. Materials and methods

The two-phase alloy ($\gamma + \alpha_2$) Ti-48Al-2Cr-2Nb (at.%) was chosen as a base material. Due to its material properties at high temperatures, this alloy has been used in compressor elements and airplane engine turbines: in the CF6-80C2 engine, in the low-pressure turbine in section 5 and 6, as well as in the GE90 engine compressor [19]. A two percent addition of chromium to the alloy ensures good plasticity, whereas niobium addition corrects the alloy's oxidation resistance. The coating was obtained via the out-of-pack method. Aluminizing was typically applied using an $AlCl_3$ activator at 1050°C for 4 hours. The resulting coating was characterized by X-ray diffraction (XRD) analysis to yield the phase composition of the aluminized surface (JEOL JDX-7S diffractometer) and energy dispersive X-ray (EDX) spectrometry microanalysis to determine the chemical composition (Hitachi 3400N scanning microscope with the Noran System Six software). Electron backscatter diffraction (EBSD) experiments were conducted using the Hitachi 3400N microscope with the HKL Channel 5 software.

3. Results

The first stage of investigation involved characterizing the alloy coating after the aluminizing process. The physical properties of the obtained layer were assessed, and the layer's chemical and phase composition were measured. The macro- and microscopic investigations that were conducted demonstrated the coating was equally deposited on the surface. The presence of cracks or delamination of the coating were not observed. The coarse grinding of the powder evidently affected the coating's surface topography, in the form of cracks (Fig. 1). The surface of the obtained coating was fine-grained and of relatively greater coarseness with visible small concavities on the surface (Fig. 2).

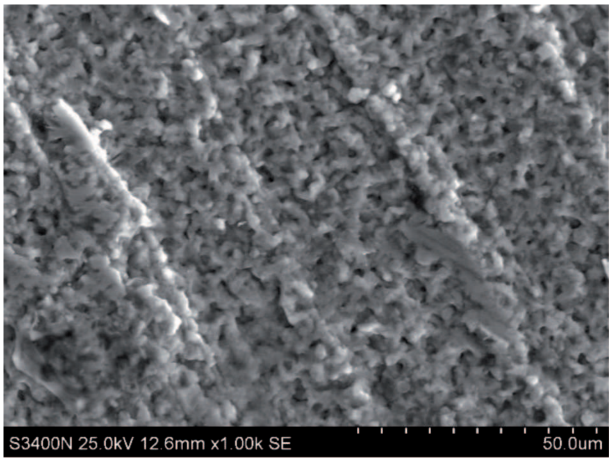


Fig. 1. Top surface microstructure of Ti-48Al-2Cr-2Nb alloy after gas phases aluminizing

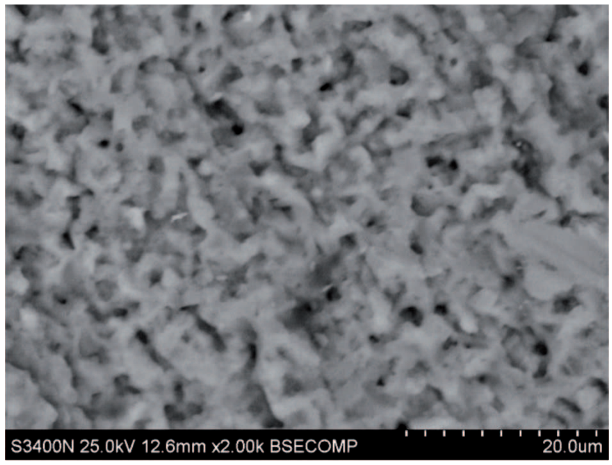


Fig. 2. Top surface microstructure of Ti-48Al-2Cr-2Nb alloy after gas phases aluminizing – other places of observations

Analysis of the surface chemical composition (Table 1) showed a significant increase in aluminum content, amounting to ~61 at.%, at the expense of a decrease in titanium content, relative to the base alloy (Fig. 3, point A). An increase in chromium content and decrease in niobium content were observed in the alloy coatings.

The aluminum content of the surface coating (~61 at.%) corresponded, in a Ti-Al phase system, to the two-phase γ-TiAl-Ti_3Al_5 (Fig. 3, point B). However, phase composition studies, using surface XRD methods clearly indicated the presence of a $TiAl_2$ phase (Fig. 4).

TABLE 1

Results of chemical compositions analysis from top surfaces in microareas of basic alloy in initial conditions and after gas phases aluminizing

48-2-2	Al-K	Ti-K	Cr-K	Nb-L
Weight %	33.0±1.5	60.0±2.5	5.2±0.4	1.8±0.1
Atom %	47.7±2.0	48.8±2.0	2.2±0.3	1.3±0.1

Coating	Al-K	Ti-K	Cr-K	Nb-L
Weight %	46.3±2.0	49.8±2.0	1.8±0.1	2.6±0.2
Atom %	61.1±2.5	36.7±1.5	1.3±0.1	1.0±0.1

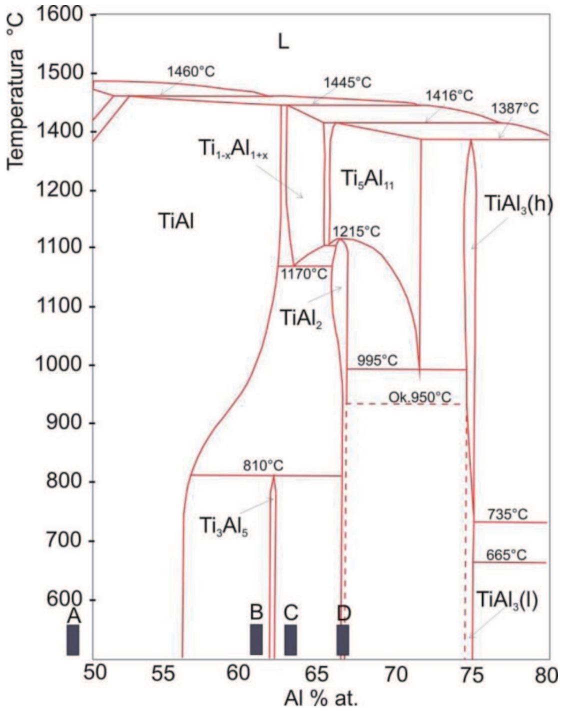


Fig. 3. Ti-Al binary system [20] with marked areas meeting results of chemical and phases compositions analysis

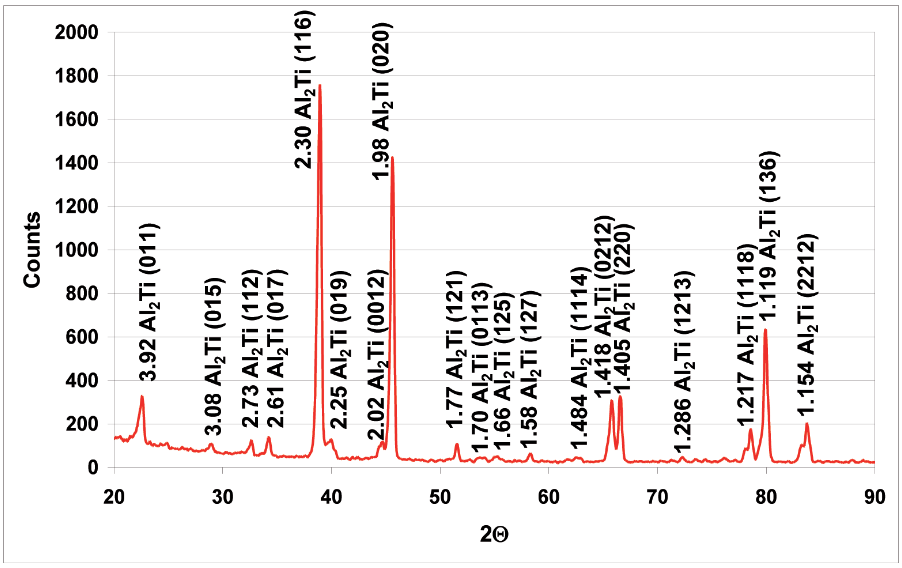
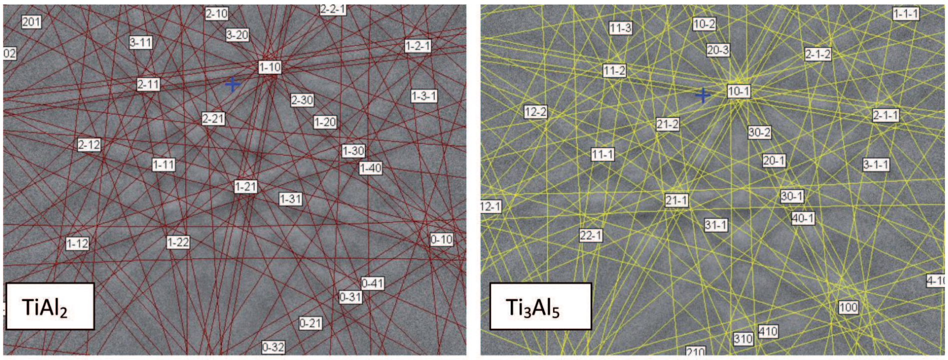


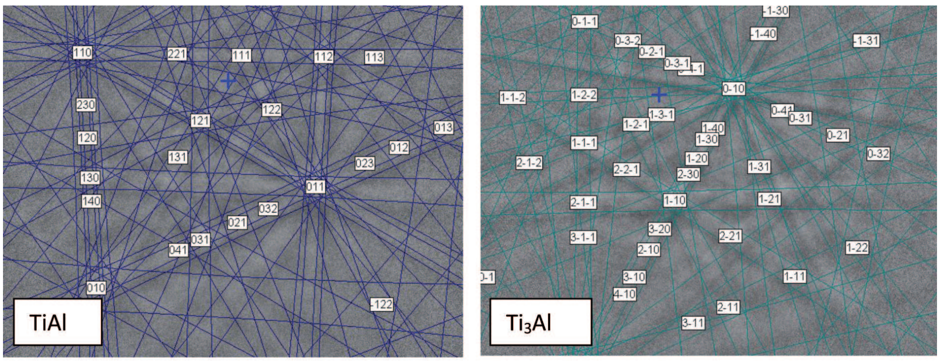
Fig. 4. Results of phases compositions analysis of Ti-48Al-2Cr-2Nb alloy after gas phases aluminizing by XRD method

The $TiAl_2$ phase was characterized as a $HfGa_2$-type tetragonal structure with a c/a ratio of >6, containing 24 atoms in the unit cell. This phase was characterized by an aluminum content of 66–67 at.% at 1100°C and was stable for temperatures up to 1215°C (Fig. 3, point D) [20]. This result suggested the presence of a secondary type of solid solution, $Ti(Al,Cr,Nb)_2$ containing ~63 at.% Al, Cr, and Nb, which situated the area under study in the two-phase Ti_3Al_5–$TiAl_2$ zone. Considering the measurement errors and the results from XRD analysis, the analysis was assumed to have been performed on a $TiAl_2$ phase sample area (Fig. 3, point C). EBSD analysis of selected points in the coating zone for both the basic alloy and the coating prepared by gas phase aluminizing methods, is shown in Figs. 5 and 6. The multiwavelength anomalous diffraction (MAD) value indicated a high probability for the presence of $TiAl_2$ and $TiAl_5$ phases, and a relatively lower probability for the presence of a $TiAl_3$ phase.



	$TiAl_2$	Ti_3Al_5
Name	Al_2Ti	Al_5Ti_3
Composition	62,5\37,5	62,5\37,5
Laue and space group no.	5, 4mmm, 123	5, mmm, 47
Unit cell lengths	4,03; 4,03; 3,95 Å	4,03; 3,96; 4,03 Å
Unit cell angles	90,0, 90,0 90,0 °	90,0, 90,0 90,0 °
MAD	0,215°	0,305°
Orientation	(134,4; 85,1; 62,2)°	(29,9; 155,6; 93,3)°
Spec plane ~	(6-3-1)	(10-2)

Fig. 5. Results of phases compositions analysis of Ti-48Al-2Cr-2Nb alloy after gas phases aluminizing by EBSD method



	TiAl	Ti_3Al
Name	AlTi	$AlTi_3$
Composition	50\50	25\75
Laue and space group no.	5, 4mmm, 123	9, 6mmm, 194
Unit cell lengths	4,00; 4,00; 4,07 Å	5,78; 5,78; 4,65 Å
Unit cell angles	90,0, 90,0 90,0 °	90,0, 90,0 120,0 °
MAD	0,181°	1,049°
Orientation	(80,1; 58,2; 61,1)°	(69,0; 113,2; 10,2)°
Spec plane ~	(634)	(4.-117)

Fig. 6. Results of phases compositions analysis of Ti-48Al-2Cr-2Nb alloy by EBSD method

The phase composition of microspaces, determined by EBSD, confirmed that the phase of the main compound in the coating under investigation was a $TiAl_2$ phase. Although the presence of both $TiAl_5$ and $TiAl_3$ phases were also found, they were not detected in conventional diffraction studies. These results indicated the presence of local heterogeneity in the chemical composition, particularly variable aluminum content, and suggested a need for additional heat treatment processes to homogenize the structure.

The diffusion coating's microstructure was examined by optical and scanning microscopies, indicating the presence of a dual-layer coating structure that resulted from the diffusion deposition process.

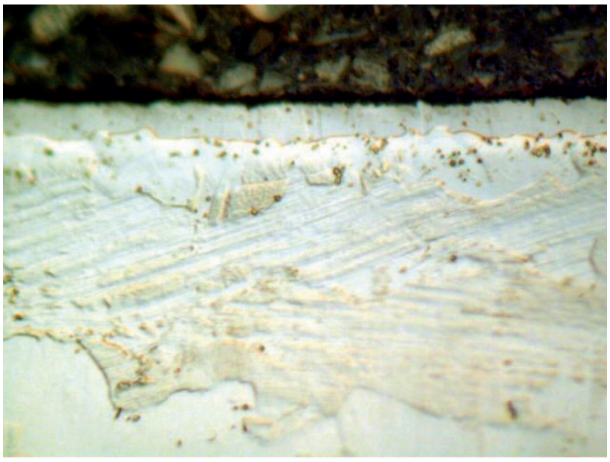


Fig. 7. Microstructure of gas phases aluminized layer – LM DIC mag.400x

The coating was characterized by a thickness of 10 μm with a high degree of uniformity across the length of sample analyzed. Differential interference contrast (DIC) microscopy showed that the grain boundaries in the coating were oriented perpendicularly to the base surface (Fig. 7). The separation front between the growing layer and the diffuse interface zone was likewise clearly visible. The thickness of the diffuse interface zone was also on the order of 10 μm. Similar to the results from optical microscopy, scanning microscopy (SEM) indicated the disappearance of the lamellar structure in the diffusion zone (Fig. 8).

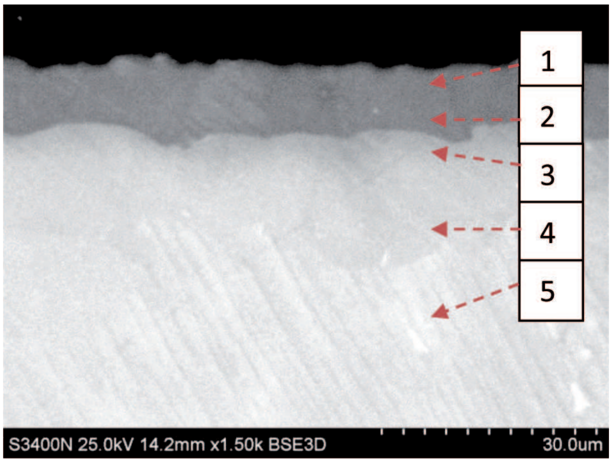


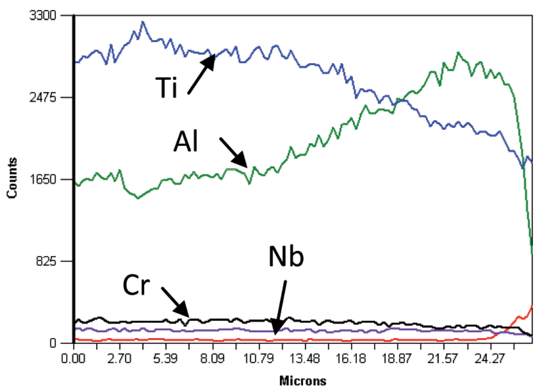
Fig. 8. Microstructure of gas phases aluminized layer – SEM

The EDX study (Fig. 9) of microsections indicated that the aluminum content of the outer surface of the coating was consistent with the value give in Table 1.

On the other hand, the Al, Cr, and Nb contents were measured to be 66 at.%, which undoubtedly corresponded to a $TiAl_2$ phase. The distribution of the aluminum and titanium content was indicative of the typically diffuse nature of the coating. Alloy components were consistently present in both the coating and the base material for the duration of the study.

4. Summary

The fundamental problem of unsatisfactory oxidation resistance of the $(\gamma + \alpha_2)$ TiAl phase alloys, which limits the alloys maximum working temperature, is described in this article. A limit on the maximum working temperature narrows the range of uses for this group of



% at.	*Al-K*	*Ti-K*	*Cr-K*	*Nb-L*
pt1	62.2 ± 2.5	34.2 ± 1.5	1.5 ± 0.2	2.1 ± 0.2
pt2	61.3 ± 2.5	35.4 ± 1.5	1.7 ± 0.2	1.7 ± 0.2
pt3	57.6 ± 2.0	38.1 ± 1.5	2.0 ± 0.2	2.3 ± 0.2
pt4	53.5 ± 2.0	42.9 ± 1.5	1.6 ± 0.2	2.0 ± 0.2
pt5	45.3 ± 1.5	50.4 ± 1.5	2.0 ± 0.2	2.3 ± 0.2

Fig. 9. Results of chemical compositions analysis in microareas of aluminized diffusion layer and base materials

materials, particularly for components that may be exposed to large stresses, aggressive environments, and high temperatures. It was described the preparation of a heat-resistant aluminide coating for the surfaces of a Ti-48Al-2Cr-2Nb alloy, on the basis of a $TiAl_3$ or $TiAl_2$ phase via the "out-of-pack" gas phase aluminizing method, with the goal of increasing the base alloy's working temperature.

The material coating method described here produced a diffuse protective aluminide layer of a suitable– but above all, controllable– thickness, free from the cracks and pores characteristic of powder-based technologies.

The beneficial impacts of the coatings, which improved the base alloy's oxidation resistance, relied on the presence of an aluminum-rich $TiAl_2$ phase, which enabled decidedly improved oxidation resistance relative to the γ-TiAl phase. This phase was characterized by an aluminum content that was high relative to the titanium content, which allowed for the selective oxidation of aluminum, yielding a more thermodynamically stable oxide, Al_2O_3.

The obtained coating layer was characterized by good metallurgical qualities. No concavities, pores, delaminations, or cracks that are typical of other diffusion methods of preparation were detected. The obtained aluminide coating was characterized by a dual-layer structure with a thickness on the order of 20 m. The outer layer, roughly 10 μm thick, was created by a dominant $TiAl_2$ phase, as well as a less frequently occurring Ti_3Al_5 phase. The presence of a $TiAl_3$ phase was also possible. The demonstrated phases were created by secondary solid solutions combined with alloy additions (i.e., chromium and niobium), which were present in quantities of ~3% in total. The interface layer constituted another zone of thickness ~10 μm; this zone most likely formed between equidistant γ-TiAl phase grains upon the addition of chromium and niobium (in quantities totaling ~4%). The interface zone was characterized by the disappearance of the lamellar areas, typical of the base alloy. This effect resulted from the oxidation of aluminum and a shift toward a single phase γ-TiAl.

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