Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 58
ISSUE 1
May
2013

The surface layer degradation of γ-TiAl phase based alloy

J. Małecka*
Opole University of Technology, P.O. Box 321, 45-271 Opole, Poland
* Corresponding e-mail address: j.malecka@po.opole.pl

Received 05.03.2013; published in revised form 01.05.2013

Properties

ABSTRACT

Purpose: The aim of the present research is to describe the chemical composition and microstructure of the surface layer of Ti-46Al-7Nb-0.7Cr-0,1Si-0.2Ni alloy after the test of isothermal oxidation in 9%O_2+0.2%HCl+0.08%SO_2+N_2 during 250 h.
Design/methodology/approach: The objectives were achieved using several techniques including conventional metallography, SEM, BSE, EDX. The oxides scales and their effects were investigated at temperatures 750ºC.
Findings: This investigation confirms that the better protection of the substrate was determined using AlCrN coating.
Research limitations/implications: The basic limitations concern alloys in a higher temperature and establish the oxidation kinetics of the analysed alloy as a function of time and temperature.
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 AlCrN coating.
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 at the conditions combining high temperature and sulphur and chlorine compounds-containing atmosphere. The novelty of this research deals with the mechanism of oxidation at such boundary conditions. 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: Corrosion; Intermetallics; Oxidation; Sulfidation; Coatings

Reference to this paper should be given in the following way:
J. Małecka, The surface layer degradation of γ-TiAl phase based alloy, Journal of Achievements in Materials and Manufacturing Engineering 58/1 (2013) 31-37.

1. Introduction

Structural materials designed for such extremely thermally loaded parts, as for example turbine blades for aircraft engines, automobile parts, automotive industries, should have good mechanical properties under working conditions.

Among them, titanium-aluminide intermetallics are being considered as promising choice for high temperature applications, because of their high strength and low density [1-2]. TiAl - intermetallic based alloys are next generation structural materials, lighter than the conventional titanium alloys with the density lower than nickel-base superalloys [3]. However, the industrial applications of these materials are yet limited by their low ductility at room temperature, poor creep and oxidation resistance at elevated temperature [4]. Titanium with a low aluminum contents and Ti_3Al alloy are already widely used because of excellent mechanical properties, but at low working temperatures due to insufficient oxidation resistance. Therefore, titanium alloys with higher aluminium contents, such as TiAl and $TiAl_3$ compounds, are being developed for high temperature applications [5]. However, poor oxidation resistance limits the use of TiAl alloys above about 800ºC because the external layer formed on these compounds does not protect Al_2O layer and also TiO_2 or mixture Al_2O_3 and TiO_2 [6].

Ensuring long-term operation under high-temperature oxidation requires efficient protection against it. One of the methods to affect the properties of alloys is to modify their microstructure and chemical composition.

Extensive studies have been made to improve their oxidation resistance, for instance, by alloying and surface modification. Alloying with ternary, quaternary or more elements including Nb, Mo, Cr, Si, Ta Zr, V and W was found to be an important method to improve their mechanical and oxidation properties [4-10]. Accordingly, the protection properties of these additions depend on their concentration rates.

Over the 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 governed by the following percentage rule [11]:

$$Ti\text{-}Al_{42\text{-}46}\text{-}Nb_{4\text{-}10}\text{-}X_{0\text{-}3}\text{-}\ Y_{0\text{-}1}\text{-}Z_{0.1}\text{–}RE_{\ 0\text{-}0.5} \qquad (1)$$

X - contents of Cr, Mn, Ta;
Y - contents of W, Hf, Zr;
Z - contents of C, B, Si;
RE - rare earth elements.

However, despite widespread research by both the industrial sector and in laboratories, the current methods have not enabled such a modification of the chemical composition or microstructure that would guarantee long-term resistance to oxidation.

In order to broaden the application and heat-resistance of elements made of these materials, research is done to describe and produce protective layers or coatings on their substrates [12-30].

Among the present protective coatings the following can be distinguished:

- Al_2O_3 coatings,
- aluminide coatings Ti_3Al,
- modified aluminide coatings Pt,
- MCrAlY coatings,
- Al-Ti-Cr two-phase coatings,
- silver modified coatings Al-Ti-Ag,
- Si_3N_4 coatings,
- SiO_2 based coatings,
- CaTiO, $SrTiO_3$, $BaTiO_3$, $SrTiO_3$, $AlTiO_5$ coatings,
- plasma-deposited ZrO_2-$Ni_{-4.5}$-Al coatings,
- aluminum and silicone coatings,
- ceramic coatings based on Si-Al-N structure,
- Ti44Al28Cr, Ti55Al8,5Cr, NiCrAlY + Al_2O_3, Ti44Al28Cr, NiCrAlY/ Al_2O_3, Ti55Al9Cr coatings HVOF TiAlCr, LPPS TiAlCr i HVOF CoCr(WSiC).

However, a significant and yet unsolved problem is, apart from low flow, insufficient resistance to oxidation in the atmosphere containing sulphur and chlorine. This is due to the fact that components operating in high temperatures are subject to adverse changes in mechanical properties caused by corrosion damages and this negative process is more pronounced when corrosion is intensified by sulphurous environment.

In many industrial applications Ti-Al alloys are subject of researches connected with high temperature corrosion in the atmosphere with sulphur content. Sulphur considerably accelerates the damaging process in comparison to oxidation in air. In fact, the melting point of sulphides is low and, therefore, the liquid phase in the scale may appear very fast. Another important issue is corrosion pits triggered by high sulphide pressure which contributes to intercrystalline corrosion. The result of sulphurous corrosion is a great loss of material, and its prevention still poses a considerable technical problem.

The corrosion induced by oxidizing atmosphere in the presence of chlorine is a significant operational issue directly linked to the combustion of fuels in the power industry. Additionally, the high temperature of the dry steam contributes to corrosive processes. The corrosion threatens mainly the materials of evaporators and superheaters [31]. The degradation of the surface layer under corrosion in elevated temperature results from the interaction of its multiple elements [31-32] The chemical composition of emissions is an important factor during corrosion. Gaseous ingredients of emissions exhibit particularly high corrosive activity i.e. O_2, SO_2, H_2S, Cl_2,HCl and CO. During combustion, sulfur compounds undergo oxidation mainly to SO_2 and SO_3. In the case of oxygen deficit, however, H_2S [33] also appears. Chlorine shows particularly high corrosive activity at high temperature. It causes active oxidation which destroys the protective layer of oxides. The source of chlorine (Cl_2) near the surface may be the hydrogen chloride (HCl) [34] present in the emissions.

The presence of sulfur and chlorine in the fuel enables two mechanisms of high temperature corrosion:

- sulfate-sulfuric,
- chloride [35].

The kinetics of corrosion employing the mentioned mechanisms is of two orders higher than the oxidation of these materials in air [31] and depends mainly on the material the evaporator pipes are made of.

The paper presents the results of own research regarding the impact of high-temperature oxidizing atmosphere ($9\%O_2+0{,}2\%HCl+0{,}08\%SO_2+N_2$) on the condition of the coating generated on γ-TiAl phase based alloy.

2. Material and research methodology

The tests were performed on γ-TiAl phase based titanium alloy composed of 46%at Ti, 46%at Al, 7%at Nb, 0.7%at Cr, 0.1%at Si and 0.2%at Ni. The alloys has a duplex microstructure (Fig. 1), made of lamellar grains of γ-phase and α_2 and granular γ-phase grains. Colonies of α_2-Ti_3Al precipitates were also found.

The fracture of the tested alloy occurring in granular and lamellar area is presented in Fig. 2

The substrate surfaces were polished and degreased in acetone before depositing the coating. Two types of coatings were deposited: AlCrN deposited by PVD method and SiO_2-Al_2O_3 by the sol-gel method.

The tests of the samples' resistance to high temperature and aggressive environment were carried out during isothermal experiments in the model reactive atmosphere containing $9\%O_2+0.2\%HCl+0.08\%SO_2+N_2$ in a Carbolite resistance furnace heated to 750°C at a research station (Fig. 3) allowing maintaining the model atmosphere throughout the entire test. The samples of initial state alloy and samples of coated alloy were put in the furnace. The samples were heated up with the furnace, then annealed in 750°C during 250 hours, and subsequently cooled down to the room temperature.

Before and after the test, the samples were assessed macroscopically by the observation with a naked eye of the samples' surface and determining the nature of the changes and analysed with SEM

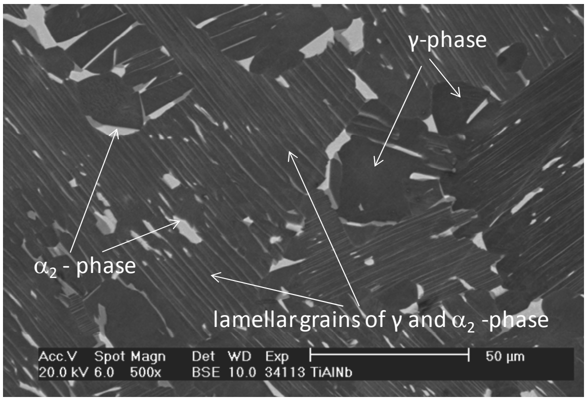

Fig. 1. SEM images (BSE detector) of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni

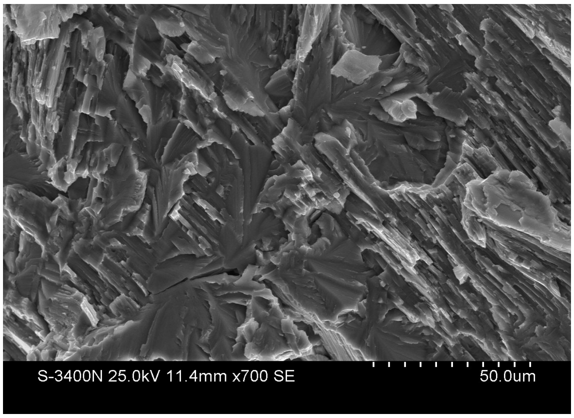

Fig. 2. SEM images (SE detector) of fracture of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy in granular and lamellar area

3. Test result and analysis

During the oxidation of Ti-Al phase equilibrium titanium alloys in air, TiO_2+Al_2O_3 oxide layer forms on their surface. TiO_2-rutile forms on the surface at the initial stages of oxidation as titanium's activity is much higher than aluminum's activity. Columnar crystallites TiO_2 growing in various directions can be observed on the oxidized surface (Fig. 4). The content of Al_2O_3 in the oxide layer is considerably lower. [36]. The lack of propensity to form protective layer of Al_2O_3 by these alloys is the main reason for their little resistance to high-temperature corrosion.

Columnar crystallites TiO_2 growing in various directions can be observed on the oxidized surface. Microanalysis of this surface shows the dominance of Ti with a much lower share of Al (Fig. 5).

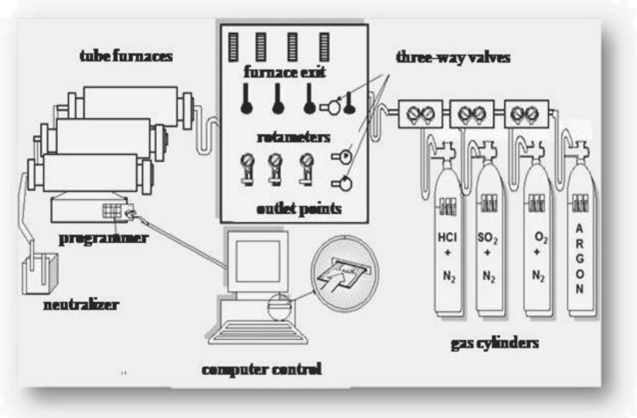

Fig. 3. Scheme of research station for testing high-temperature oxidation in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere

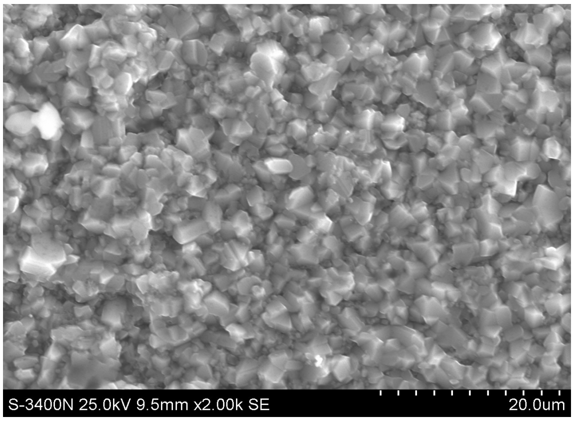

Fig. 4. SEM images morphology of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni without protective coating after the test in air atmosphere

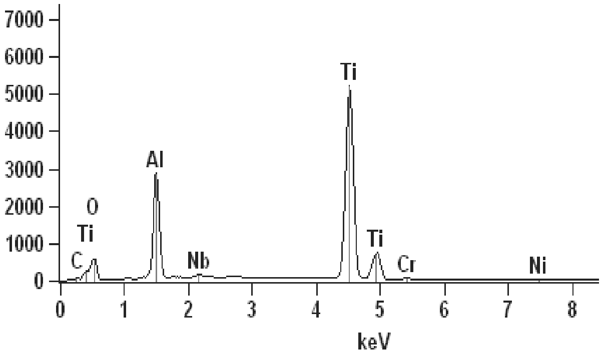

Fig. 5. EDX analysis results of the surface as per Fig. 4

The aim of the present research is to describe the chemical composition and microstructure of the surface layer of Ti-46Al-7Nb-0.7Cr-0,1Si-0.2Ni alloy after the test of isothermal oxidation in 9%O_2+0.2%HCl+0.08%SO_2+N_2 during 250 h. The microscopic analyses and microanalyses of the chemical composition was carried out by means of Scanning Electron Microscopy (SEM) equipped with EDS add-on. The formed layers are characterized by a high stability at the temperature up to 750°C. No chipping or degradation in form of cracks or loss was determined.

The surface of the uncoated alloy after 250 hours of isothermal oxidation in the atmosphere of 9%O_2+0.2%HCl+0.08%SO_2+N_2 was shown in Figs. 6-8. The chemical composition analysis showed the presence of elements which diffused out of the metallic alloy substrate (Ti, Al, Nb, Cr) covering the surface with specific precipitates (Fig. 9).

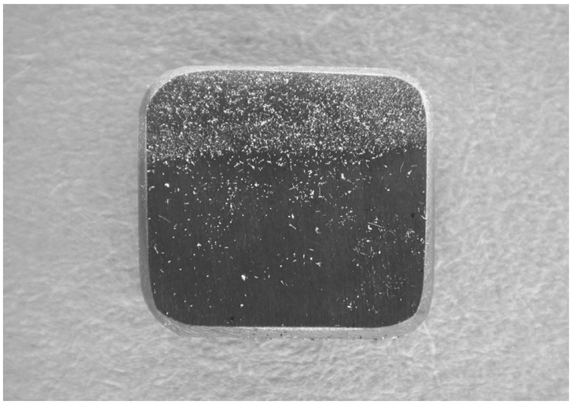

Fig. 6. The macroscopic image of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni without protective coating after 250 h of the test in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere

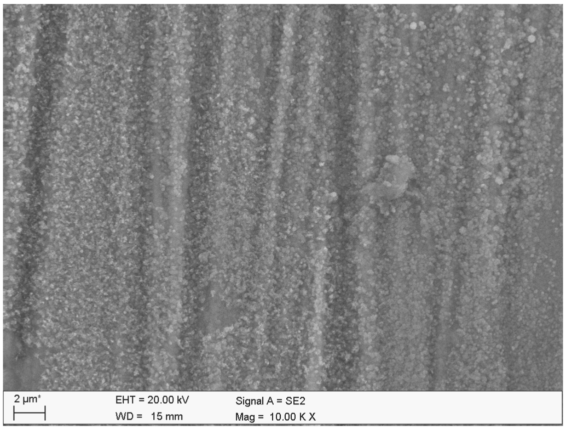

Fig. 7. SEM images morphology of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni without protective coating after 250 h of the test in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere (at low magnification)

However, the domination of Ti indicates that the product formed on the outer surface is rutile crystallites TiO_2, generated as a result of out-core diffusion of titanium (Figs. 7-8).

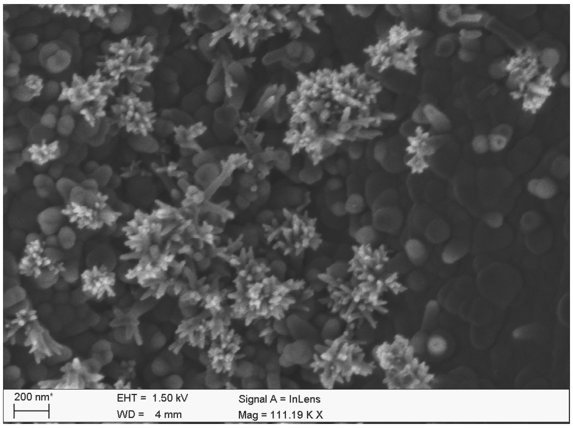

Fig. 8. SEM images morphology of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni without protective coating after 250 h of the test in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere (at high magnification)

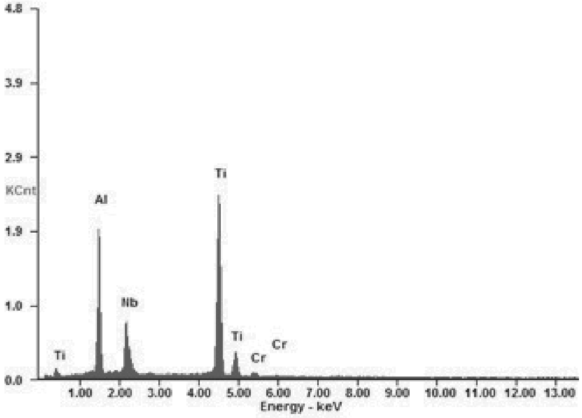

Fig. 9. EDX analysis results of the surface as per Fig. 7

Among oxide ceramics the diffusion of oxygen is the lowest in SiO_2 and Al_2O_3 so the coatings based on these compounds may be promising. Own research showed satisfactory results for Al_2O_3 based coating [12].

Therefore SiO_2-Al_2O_3 based coating can be acknowledged to be an alternative diffusion barrier blocking the oxidation process. Therefore, the formation of SiO_2-Al_2O_3 layer on the surface could add to improving the oxidation resistance of the analyzed alloy. This is the reason for focusing this paper on the issue of improving the resistance of intermetallic Ti-Al alloy to high-temperature oxidation by means of inducing SiO_2-Al_2O_3 layer using the sol-gel method.

However, the morphology of the surface oxide layer coated with SiO_2-Al_2O_3 (Fig. 10) is characterized by the occurrence of TiO_2 and Al_2O_3 (Fig. 13) oxides in form of needles (Figs. 11-12). The formation of discontinuous oxide layer of such morphology at the initial stage of corrosion is insufficient to block the out-core diffusion of elements. For it is impossible for a continuous layer made of Al_2O_3 to be formed and contribute to slowing down the process.

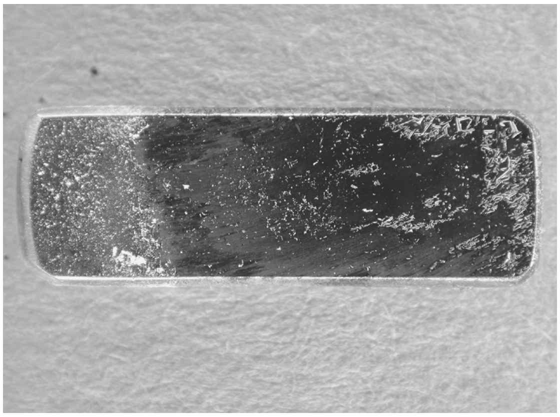

Fig. 10. The macroscopic image of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni with SiO_2-Al_2O_3 protective coating after 250 h of the test in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere

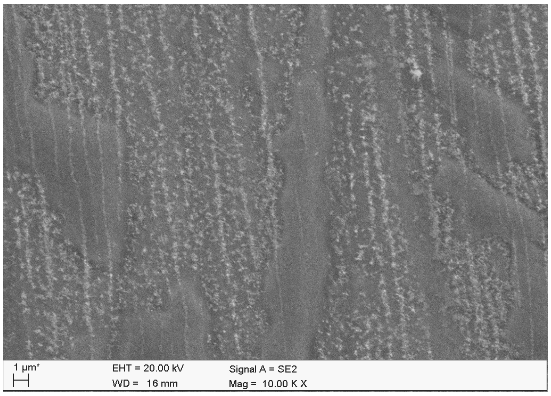

Fig. 11. SEM images morphology of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0,2Ni with SiO_2-Al_2O_3 protective coating after 250 h of the test in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere (at low magnification)

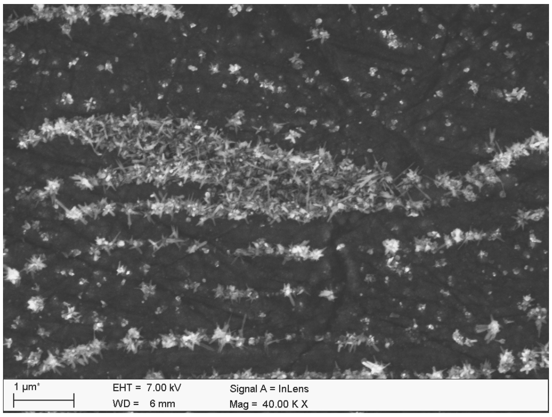

Fig. 12. SEM images morphology of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni with SiO_2–Al_2O_3 protective coating after 250 h of the test in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere (at high magnification)

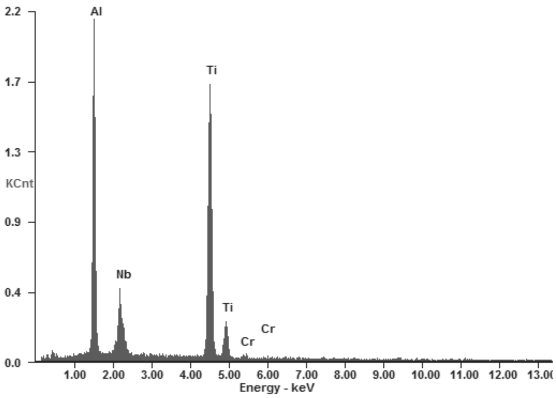

Fig. 13. EDX analysis results of the surface as per Fig. 11

The alloy coated with AlCrN looks completely different (Figs. 14-16). Whereas on the surface of AlCrN coating on the tested alloy's surface, a layer of aluminum oxides and chromium (most probably originating from the coating) and silicone are formed. No titanium presence was determined (Fig. 17). It proves good resistance of AlCrN coating against oxidation. The coating is an effective barrier to out-core diffusion of titanium. If the formed oxide layer consisted of Al_2O_3, then the rutile formation could be limited, adding to minimizing the degree of corrosion.

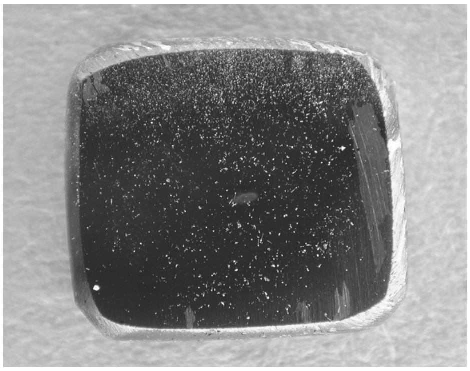

Fig. 14. The macroscopic image of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy samples coated with AlCrN after 250 hours in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere

The high temperature of oxygen affecting the AlCrN layer causes the formation of scale, presumably consisting of Cr_2O_3 and Al_2O_3 (that presumption is supported by the performed microanalyses of chemical composition). Chromium as the basic ingredient of the deposited coating is an element which reacts with air, undergoes passivation, so the obtained chromium oxide (III) becomes a protective coating. Besides that, it creates Laves' phases - Ti(Cr) with low permeability of oxygen. As a consequence of oxidation, aluminium activity intensifies and the resulting increase in tendency for its selective oxidation takes place. The dominating ingredient of the formed scale is Al and Cr as expected, which has a positive impact of the applied coating on increasing the heat resistance of the alloy.

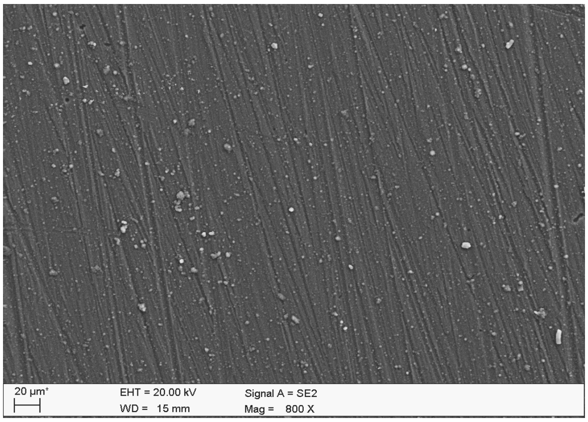

Fig. 15. SEM images morphology of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy samples coated with AlCrN after 250 hours in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere (at low magnification)

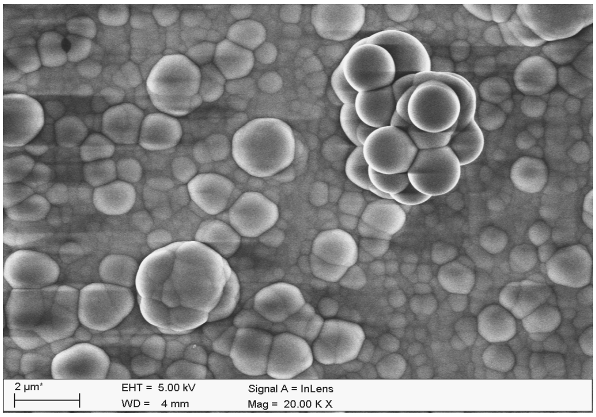

Fig. 16. SEM images morphology of the surface layer of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy samples coated with AlCrN after 250 hours in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere (at high magnification)

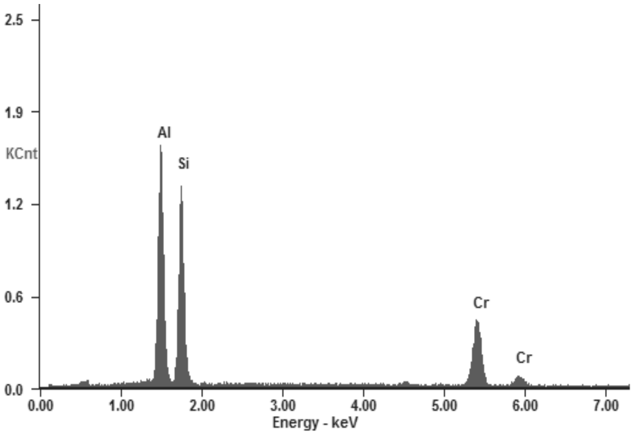

Fig. 17. EDX analysis results of the surface as per Fig. 15

4. Conclusions

The process of high temperature corrosion of TiAl(γ)-phase based titanium alloy is linked to intensive formation of titanium and aluminum oxides on the surface. The analysis of the corrosion resistance tests results showed their sufficient resistance in the applied atmosphere. Substrate degradation effects were not observed. However, a better protection of the substrate was determined using AlCrN coating. No signs of corrosion were observed after oxidation test at 750°C during 250 h in 9%O_2+0.2%HCl+0.08%SO_2+N_2 atmosphere.

Titanium was not noticed on the surface - the formed coating is a barrier to out-core diffusion of this element. However, in order to verify the performed research and determine the impact of the coating on corrosion in the tested atmosphere, it seems necessary to carry out tests in a higher temperature and establish the oxidation kinetics of the analysed alloy as a function of time and temperature.

Acknowledgements

The research study was financed from the funds for science in 2012-2013 as research project no. 2011 033371.

References

[1] E.A. Loria, Gamma titanium aluminides as prospective structural materials, Intermetallics 8 (2000) 1339-1345.

[2] C.M. Ward-Close, R. Minor, P.J. Doobar, Intermetallic-matrix composites-a review, Intermetallics 4 (1996) 217-229.

[3] F. Appel, M. Oehring, R. Wagner, Novel design concepts for gamma-base titanium aluminide alloys, Intermetallics 8 (2000) 1283-1312.

[4] Y. Wu, K. Hagihara, Y. Umakoshi, Improvement of cyclic oxidation resistance of Y-containing TiAl-based alloys with equiaxial gamma microstructures, Intermetallics 13 (2005) 879-884.

[5] B.G. Kim, G.M. Kim, C.J. Kim, Oxidation behaviour of TiAl-X (X=Cr, V, Si, Mo or Nb) intermetallics at elevated temperature, Scripta Metallurgica et Materialia 3/7 (1995) 1117-1125.

[6] M. Yoshihara, Y.W. Kim, Oxidation behaviour of gamma alloys designed for high temperature oxidation, Intermetallics 13 (2005) 952-958.

[7] V. Shmet, M. Yurechko, A.K. Tyagi, W.J. Quadakkers, L. Singheiser, The influence of Nb and Zr additions on the high temperature oxidation mechanism of γ-TiAl alloys in Ar/O_2, Metals and Materials Society (1999) 783-790.

[8] S. Król, Cyclic oxidation of γ-TiAl based multicomponent alloys with addition of Ta, Protection Against Corosion 11A (2005) 194-198 (in Polish).

[9] L. Huang, P.K. Liaw, C.T. Liu, Microstructural evolution of TiAl -intermetallic alloys containing tungsten and boron, Oak Ridge National Laboratory, Managed by UT Battelle for the Department of Energy, Proceedings paper 2, 2005.

[10] N. Toshio, I. Takeshi, M. Yatagai, T. Yoshioka, Sulfidation processing and Cr addition to improve oxidation resistance of TiAl intermetallics in air at 1173K, Intermetallics 8 (2000) 371-379.

[11] H. Clemens, H. Kestler, Processing and applications of intermetallic γ-TiAl-based alloys, Advanced Engineering Materials 9 (2000) 551-570.

[12] J. Małecka, Effect of an Al_2O_3 coating on the oxidation process of a γ-TiAl phase based alloy, Corrosion Science 63 (2012) 287-292.

[13] J. Małecka, Effect of Al_2O_3 and AlCrN coatings on 950°C cyclic oxidation behaviours of γ-TiAl, Journal of Achievements in Materials and Manufacturing Engineering 50/1 (2012) 40-46.

[14] M. Góral, G. Moskal, L. Swadźba, Gas phase aluminising of TiAl intermetallics, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 443-446.

[15] G. Moskal, Microstructure and oxidation behaviour of TiAlSi coatings on TiAlCrNb alloy, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 263-266.

[16] M. Góral, G. Moskal, L. Swadźba, The influence of Si on oxidation resistance of aluminide coatings on TiAl alloy, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 459-462.

[17] M. Góral, G. Moskal, L. Swadźba, T. Tetsui, Structure and oxidation of Si modified aluminide coating deposited on TiAlNb alloy by slurry method, Journal of Achievements in Materials and Manufacturing Engineering 21 (2007) 75-78.

[18] Z.D. Xiang, S. Ros, P.K. Datta, Pack deposition of coherent aluminide coatings on γ-TiAl for enhancing its high temperature oxidation resistance, Surface and Coating Technology 161 (2002) 286-292.

[19] D.F. Bettridge, R. Wing, S.R.J. Saunders, The exploration of protective coating and deposition processes for nickelbase alloys and gamma titanium aluminides, Materials for Advanced Power Engineering 2 (1998) 961-976.

[20] Z. Tang, F. Wang, W. Wu, Effect of MCrAlY overlay coatings on oxidation resistance of TiAl intermetallics, Surface and Coating Technology 99 (1998) 248-252.

[21] Z. Tang, L. Niewolak, V. Shemet, L. Singheiser, W.J. Quadakkers, F. Wang, W. Wu, A. Gil , Development of oxidation resistant coatings for γ-TiAl based alloys, Materials Science and Engineering A 328 (2002) 297-301.

[22] Z. Liu, T. Narita, The effect of water vapor on the oxidation behavior of γ-TiAl-Ag coatings at 1073K in air, Intermetallics 11 (2003) 795-805.

[23] S. Taniguchi, T. Shibata, T. Yamada, X. Liu, S. Zou, High temperature oxidation resistance of TiAl improved be IBEDSi3N4 coating, The Iron and Steel Institute of Japan International 33 (1993) 869-876.

[24] Y.C. Zhu, Y. Zhang, X.Y. Li, K. Fujita, N. Iwamoto, The influence of magnetron-sputtered SiO_2 coatings on the cyclic oxidation behavior of γ-TiAl alloys, Materials Transactions 41 (2000) 1118-1120.

[25] M. Yoshimura, W. Urushihara, M. Yashima, M. Kakihana, $CaTiO_3$ coating on TiAl by hydrothermal-electrochemical technique, Intermetallics 3 (1995) 125-128.

[26] I.C. Hsu, S.K. Wu, Oxidation improvement of Ti-48Al-2Cr-2Nb intermetallics by air plasma sprayed ZrO2-Ni-4.5wt.%Al coatings, Surface and Coating Technology 90 (1997) 6-13.

[27] Z.D. Xiang, S. Rose, J.S. Burnell-Gray, P.K. Datta, Co-deposition of aluminide and silicide coatings on γ-TiAl by pack cementation process, Journal of Materials Science 38 (2003) 19-28.

[28] Z.D. Xiang, S. Rose, P.K. Datta, Vapour phase codeposition of Al and Si to form diffusion coatings on γ-TiAl, Materials Science and Engineering A 356 (2003) 181-189.

[29] E. Lugscheider, C.W. Siry, S.R.J. Saunders, The behaviour of PVD SiAlN type coatings deposited on TiAl, Materials for Advanced Power Engineering 2 (1998) 1319-1327.

[30] J.C. Scheaffer, R.L. McCarron, High Temperature coatings for titanium aluminides, WL-TR-95-4108, General Electric Co Cincinnati OH aircraft Engine Technical Div, Final Report, 1994.

[31] A. Hernas, J. Dobrzański, Durability and destruction of the elements of boilers and turbines, Silesian University of Gliwice, 2003 (in Polish).

[32] S.C. Srivastava, K.M. Godiwalla, M.K. Banerjee, Fuel ash corrosion of boiler and superheater tubes, Journal of Material Science 32 (1997) 835-849.

[33] M. Pronobis, The modernization of power boilers, Publishing House WNT, Warsaw, 2002,

[34] H.J. Grabke, E. Reese, M. Spiegel, The effects of chlorides, hydrogen chloride, and sulfur dioxide in the oxidation of steels below deposits, Corrosion Science 37 (1995) 1023-1043.

[35] J.N. Harb, E.E. Smith, Fireside corrosion in pc-fired boilers, Progress in Energy and Combustion Science 16 (1990) 169-190.

[36] J. Małecka, W. Grzesik, A. Hernas, An investigation on oxidation wear mechanisms of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni intermetallic-based alloys, Corrosion Science 52 (2010) 263-272.