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PREPARATION OF SIO_2 COATING BY SOL-GEL METHOD, TO IMPROVE HIGH-TEMPERATURE CORROSION RESISTANCE OF A γ-TiAl PHASE BASED ALLOY

ABSTRACT

This study presents the test results of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy isothermal oxidation with regard to a coating of SiO_2 deposited by the sol-gel method. The oxidation test was carried out in air at 900°C. The SiO_2 coating is not an effective and stable diffusive barrier, which would considerably improve oxidation resistance of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy.

Keywords: *intermetallics, high temperature corrosion, oxidation, coatings*

INTRODUCTION

Ti-Al alloys based on intermetallic phases can produce a series of valuable properties i.e. low density, good strength at high temperatures or creep resistance, however, they require a method to be found that would increase the resistance to high temperature oxidation [1÷4]. The limitation to wider application of γ-TiAl phase based alloys is its inability to produce the protective layer of Al_2O_3, whereas the combination of aluminum oxide and rutile formed during oxidation shows too weak protective properties at high temperature [5].

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. 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.

Another way that could provide a sufficient protection against oxidation may be surface treatment, and in particular applying appropriate protective coatings.

Among the present protective coatings the following can be distinguished:

- aluminide coatings Ti_3Al [6],
- modified aluminide coatings Pt [7],
- MCrAlY coatings [8],
- Al-Ti-Cr two-phase coatings [9],

- silver modified coatings Al-Ti-Ag [10],
- Si_3N_4 coatings [11],
- SiO_2 based coatings [12],
- $CaTiO_3$, $SrTiO_3$, $BaTiO_3$, $SrTiO_3$, $AlTiO_5$ coatings [13],
- plasma-deposited ZrO_2-Ni-$_{4.5}$Al coatings [14],
- aluminum and silicone coatings [15÷16],
- ceramic coatings based on Si-Al-N structure [17],
- Ti44Al28Cr, Ti55Al8,5Cr, NiCrAlY + Al_2O_3, Ti44Al28Cr, NiCrAlY/Al_2O_3, Ti55Al9Cr coatings HVOF TiAlCr, LPPS TiAlCr i HVOF CoCr(WSiC) [18],
- Al_2O_3 coatings [19].

Nevertheless, they are not always sufficient in terms of adhesion and ductility. Therefore, searching for new solutions with regard to chemical composition and methods of coatings' deposition is necessary. Sol-gel immersion method provides numerous possibilities in this field.

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 [19]. It was determined that Al_2O_3 coating deposited on γ-TiAl alloy improved its oxidation resistance.

Therefore, it was decided to present research done on SiO_2 sol-gel generated coating and its effect on oxidation.

EXPERIMENTAL

The tests were performed on multi-component alloy Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni with the content of 46%at Al, 7%at Nb, 0.7%at Cr, 0.1%at Si and 0.2%at Ni. The material in the shape of a roll with the diameter of about 69 mm was purchased from Flowserve Corporation Titanium and Reactive Metals Foundry (USA). The structure of the tested alloy was determined as duplex [20].

The tests of isothermal oxidation in air were performed at the temperature of 900°C. Mass changes due to isothermal oxidation processes were controlled by a precision scale with the accuracy of 10^{-4} g. Specimens of 20x15x2mm were cut from the purchased rod. Surface parameters of the samples after polishing with 800^{th} grade abrasive paper were determined by means of Hommel Tester 1000 profilometer with LV15 measuring head. The roughness of the surface prepared in this manner was R_a =0.06μm. A layer of SiO_2 coating was deposited on such a surface. As a result, samples with a coating of SiO_2 were received with the thickness of about 0.2 μm.

The alloy's structure and the structure of oxidation products were analyzed by a scanning electron microscope Philips XL20 equipped with EDAX analyzer.

RESULTS AND DISCUSSION

Previous research studies concerned determining the area of resistance to high temperature oxidation of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy without protective coatings. It was determined that during oxidation a multi-phase scale is formed characterized by identical

sequence of sublayers: the outer sublayer is made of rutile, the middle sublayer is rich Al_2O_3 and contains a lesser amount of TiO_2 and the sublayer containing Al_2O_3, TiO_2 and oxides of Nb, Cr, Ni [20].
The surface of the sample with the deposited coating is shown in Fig. 1. The generated coating is coherent, except for a few minor defects - white spots noticed on the surface.

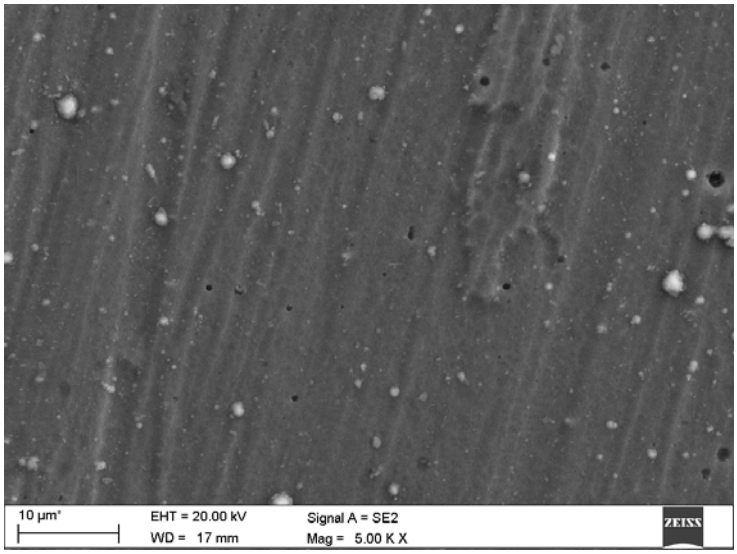

Fig. 1. SEM microphotograph for the surface of an as-deposited SiO_2 coating on a γ-TiAl specimen

Oxidation kinetics

In oxidation trials, the material destruction process includes the formation of oxides in heating cycles, chipping during cooling and holding in room temperature. The course of isothermal oxidation kinetics of the alloy with the deposited coating of SiO_2 was presented in Fig. 2. The oxidation rate in the initial period for the uncoated alloy is insignificant but along with the extension of the time of the test the mass gains are considerable.
Isothermal oxidation at 900°C during 250 hours causes mass gain, which intensifies in the case of the alloy in initial state. After 250 hours of oxidation mass gains of 3.7801 mg/cm^2 and 2.6584 mg/cm^2 were obtained for the uncoated and SiO_2-coated alloy respectively.

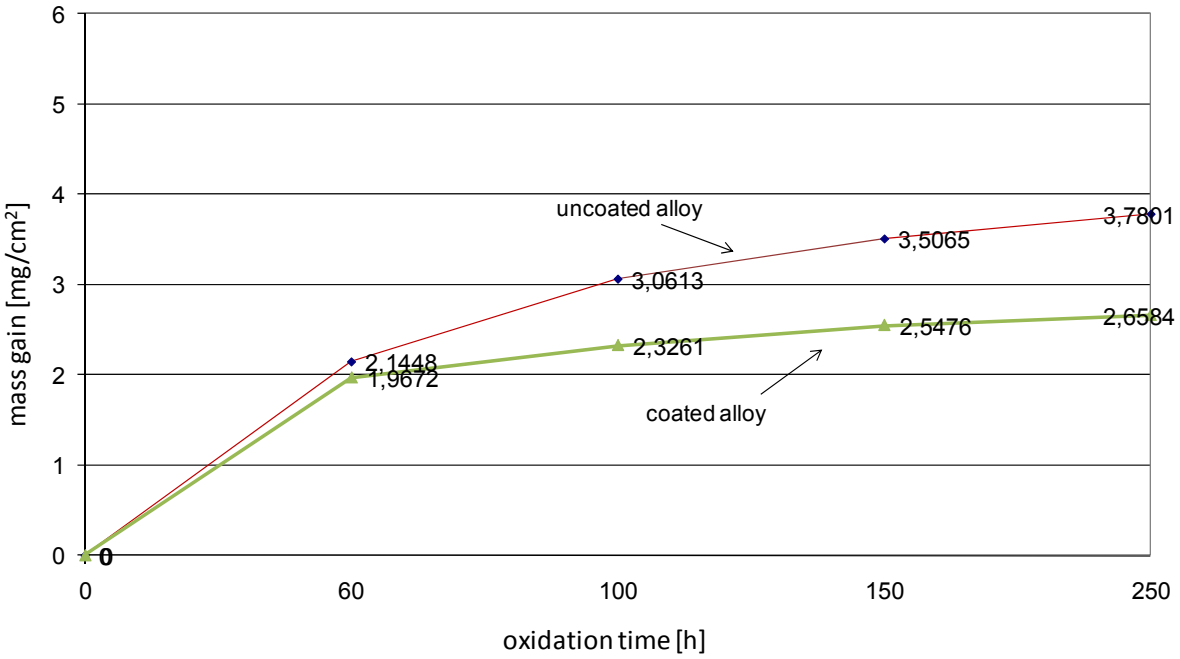

Fig. 2. The mass change of Ti–46Al–7Nb–0.7Cr–0.1Si–0.2Ni oxidized isothermally at 900°C

Morphology observation

In Fig. 3 the surface morphology of the coated alloy after the oxidation trials was presented. The analysis of the chemical composition of the surface shows mainly occurrence of Al, Si and Ti. Specific whisker-like efflorescences of irregular shape can be observed. The outer inspection of the sample do not reveal destruction processes of the surface layer. The surface morphology of the oxidized uncoated alloy was shown in Fig. 4. A scale with the outer layer made of columnar crystallites was observed. The performed chemical analysis shows the dominance of Ti and Al, Nb i Cr.

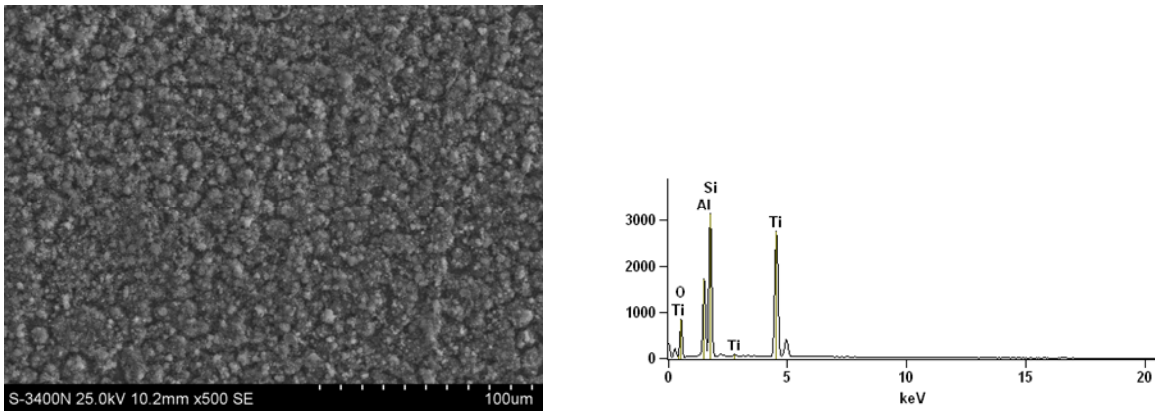

Fig. 3. SEM microphotograph for the surface of a SiO_2-coated TiAl specimen after isothermal oxidation at 900°C in air and EDX analysis results of the surface

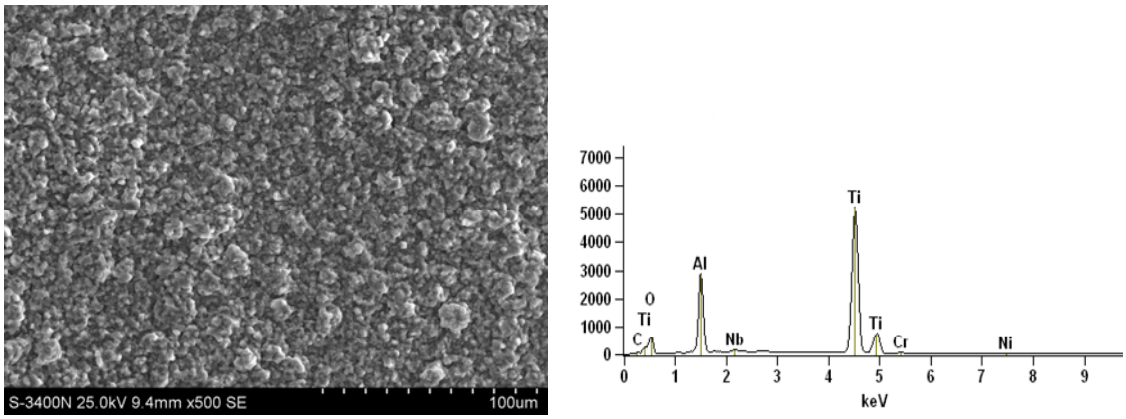

Fig. 4. SEM microphotograph for the surface of a uncoated TiAl specimen after isothermal oxidation at 900°C in air and EDX analysis results of the surface

The cross section through the oxidized sample is shown in Fig. 5. The scale has a multilayered nature. Internal and external layer were distinguished. The internal layer is coherent (contains aluminium and titanium) and mostly made of mixture of TiO_2 and Al_2O_3 (Fig. 5a). Above it, a much thicker layer with porous structure, which of Si, Al, and Ti can be fund (Fig. 5b).

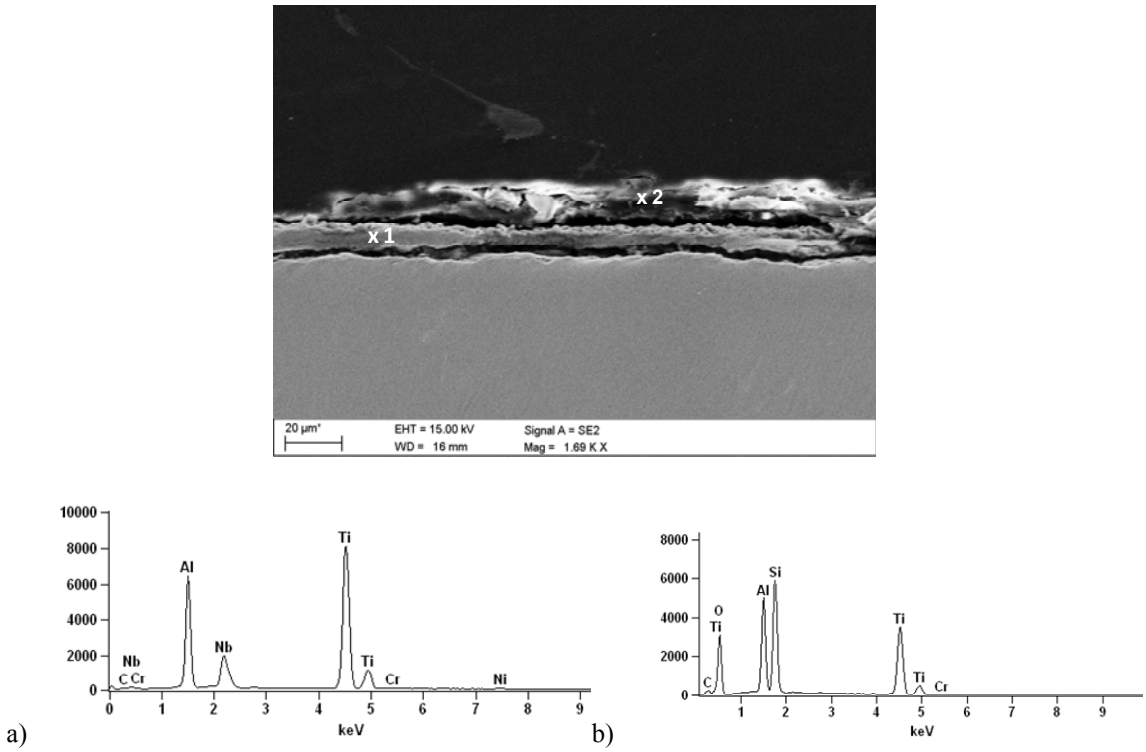

Fig. 5. Cross-section of the SiO_2 coated specimen of TiAl alloy after isothermal oxidation and EDX analysis results (a) in point #1, (b) in point #2

For comparative purposes, Fig. 6 shows the cross section through the uncoated sample. In this case, the forming layer has a multilayered nature. Underneath the outer layer (Fig. 6a) consisting of rutile crystallites, a layer mainly made of Al_2O_3 is forming (Fig. 6b) which is heterogeneous as it also contains (although in lesser amounts) TiO_2. Due to the in-core diffusion of oxygen through the defective anionic subnetwork of rutile in this layer a third sublayer forms consisting of TiO_2 and Al_2O_3 (Fig. 6c). The presence of C in the results of X-ray microanalysis is caused by organic pollutions occurring on the surface of the sample.

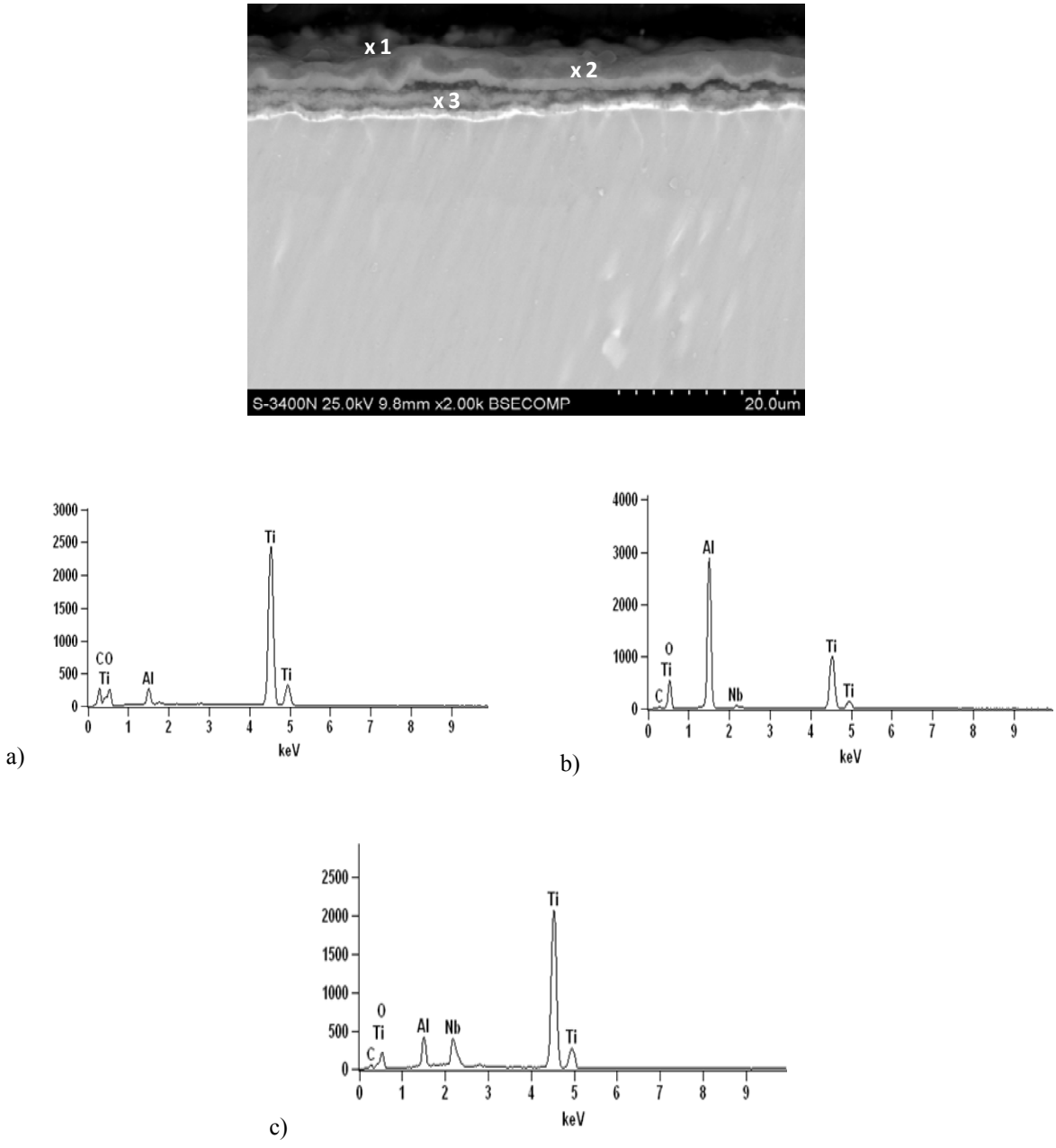

Fig. 6. Cross-section of the uncoated specimen of TiAl alloy after isothermal oxidation and EDX analysis results (a) in point #1, (b) in point #2, (c) in point #3

The oxide layer forming on the uncoated alloy provides insufficient protection, which contributes to the high rate of oxidation in the pure TiAl alloys. As previously mentioned (Fig. 2), the oxidation rate in the initial period for the uncoated alloy is insignificant but along with the extension of the time of the test the mass gains are considerable. It can be explained by oxygen diffusion, which increases along with the extension of oxidation time and adds to the progress of the layer's destruction, which may be caused by the formation nitric oxide. The uncoated samples observed immediately after the completion of isothermal oxidation were characterized by good adhesion of products to the metallic substrate up to 100 hours of oxidation. After 250 hours, chipping of scale fragments was observed during cooling down to room temperature.

In the case of the coated alloy, the oxidation of the substrate was notably hindered by the desposited coating of SiO_2. However, the deposited coating cannot be considered a diffusion barrier that would block the transport of reagents in the oxide scale.

The visible voids and bucklings between the oxide layer and the alloy indicate a very poor adhesion of the scale to the metallic substrate. The protective properties of the coating are therefore insufficient.

An important aspect is a big difference in thermal expansion coefficients of SiO_2 layer and the metallic substrate as well as the generation of compressive stresses in the coating. Therefore it is probable that the coating lost its coherence immediately after heating the sample up to a high temperature. Figure 5 confirms these assumptions.

The observed lesser mass gain of the coated alloy may result from chipping of scale's fragments (which can be seen in Fig. 5).

CONCLUSIONS

In the present study, SiO_2 coating was applied by sol-gel method on γ-TiAl alloy. Subsequently, its effect on rising the high-temperature oxidation resistance was analyzed. The obtained results can be summarised as follows:

1. For SiO_2-coated alloy small mass gains were observed during isothermal oxidation in 900°C.
2. However SiO_2 coating is not an effective and stable diffusive barrier, which would considerably improve oxidation resistance of the studied Ti-46Al-7Nb as it lost its coherence upon heating to a high temperature. Therefore such a coating is unfit for the protection of TiAl alloys during long term heat exposure.

REFERENCES

1. Kakare S.A., Toney J.B., Aswath P.B.: Oxidation of ductile particle reinforced Ti-48Al composite. Metallurgical and Materials Transactions 26A (1995), 1835-1845.
2. Chan K.S.: Developing Hydrogen Tolerant Microstructures for an Alpha-2 Titanium Aluminide Alloy. Metallurgical and Materials Transactions 23A (1992), 497-507.
3. Takasaki A., Furuya Y., Taneda Y.: Hydrogen uptake in titanium aluminides covered with oxide layers. Metallurgical and Materials Transactions 29 (1998), 307-314.

4. Qu L.H., Zhou L., Wei Y.G., Zhao Y.Q.: 10th World Conference on Tutanium, Hamburg 2003, in Ti-2003 Science and Technology, edited by G. Luetjerung and J.Albrecht, IV (2004), 2449-2454.

5. Yoshihara M., Kim Y.W.: Oxidation behaviour of gamma alloys designed for high temperature oxidation. Intermetallics 13 (2005), 952–958.

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

7. Bettridge D.F., Wing R., Saunders S.R.J.: The exploration of protective coating and deposition processes for nickelbase alloys and gamma titanium aluminides. J.Lecomte-Beelceis, F. Schubert and P.J. Ennis [eds.], Materials for Advanced Power Engineering, Procedings Part II, (1998), 961-976

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

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

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

11. Taniguchi S., Shibata T., Yamada T., Liu X., Zou S.: High temperature oxidation resistance of TiAl improved be IBEDSi_3N_4 coating. ISIJ International, 33 (1993), 869-876.

12. [12]. Zhu Y.-C., Zhang Y., Li X. Y., Fujita K., Iwamoto N.: The Influence of Magnetron-sputtered SiO_2 Coatings on the Cyclic Oxidation Behavior of γ-TiAl Alloys. Materials Transactions 41 (2000), 1118-1120.

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

14. Hsu I.C., Wu S.K.: Oxidation improvement of Ti-48Al-2Cr-2Nb intermetallics by air plasma sprayed ZrO_2-Ni-$_{4.5}$wt.%Al coatings. Surface and Coating Technology 90 (1997), 6-13.

15. [15]. Xiang Z.D., Rose S., Burnell-Gray J.S., Datta P.K.: Co-deposition of aluminide and silicide coatings on γ-TiAl by pack cementation process. Journal of Materials Science 38 (2003), 19-28.

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

17. Lugscheider E., Siry C.W., Saunders S.R.J.: The behaviour of PVD SiAlN type coatings deposited on TiAl. J.Lecomte-Beelceis, F. Schubert and P.J. Ennis [eds.], Materials for Advanced Power Engineering 1998, Proceedings Part II, 1319-1327.

18. Scheaffer J.C., McCarron R.L.: High Temperature Coatings for Titanium Aluminides, WL-TR-95-4108, General Electric Co Cincinnati OH aircraft Engine Technical Div Final Report for 22 Jan.1991 -13Dec.1994.

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

20. Małecka J., Grzesik W., Hernas A.: 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.