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High temperature corrosion of Ti-46AI-7Nb-0.7Cr-0.1Si-0.2Ni intermetalics—based alloys in N₂-O₂-SO₂ environments

J. Małecka, W. Grzesik*

Opole University of Technology, P.O. Box 321, 45-271 Opole, Poland * Corresponding author: E-mail address: w.grzesik@po.opole.pl

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<u>ABSTRACT</u>

Purpose: The reason for this research is to test the intermetalic alloy with improved oxidation and sulfidation resistance to air and a N_2 - O_2 -SO₂ gas mixture at temperatures higher than 900 °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 and compared for two test temperatures, i.e. 900 °C and 950 °C.

Findings: This investigation confirms that oxidation in $9\%O_2+0.3\%SO_2+N_2$ atmosphere causes an increase in the rate of oxidation in comparison to the pure oxidation in air. The main conclusion is that combined oxidation and sulfidation at temperature between 900 °C and 950 °C results in the formation of specific phases at the product-substrate and product-oxide boundaries.

Research limitations/implications: The basic limitations concern alloys with different chemical composition, especially with different percentage of niobium (between 4-10 at %), not only with 7 at % as in the present investigation. Also, atmosphere with higher content of SO_2 should be tested. Another problem is to optimize the surface integrity including surface roughness and sublayer properties.

Practical implications: One of practical outcomes is to select the thermal conditions and surface preparation technology which guarantee the reduction of oxidation in $9\%O_2+0.3\%SO_2+N_2$ atmosphere. It is recommended to use alloys with higher content of niobium.

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-containing atmosphere. The novelty of this research deals with the mechanism of oxidation at such boundary conditions and its quantification. This knowledge can support the design of parts made of the intermetalic alloy. The problem considered is currently important for aeroplane and automotive industry, especially for gas turbine manufacturers. **Keywords:** Corrosion; Intermetallics; Oxidation; Sulfidation

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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 [2-3]. TiAl intermetallic based alloys are next generation structural materials, lighter than the conventional titanium alloys with the density lower than nickel-base superalloys [4]. 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 [1, 5]. Titanium with a low aluminum contents and Ti₃Al 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 TiAl₃ compounds, are being developed for high temperature applications [6]. However, poor oxidation resistance limits the use of TiAl alloys above about 800 °C because the external layer formed on these compounds does not protect Al₂O layer and also TiO_2 or mixture Al_2O_3 and TiO_2 [7].

Some methods have been proposed for improving the oxidation resistance of TiAl-based materials. Extensive studies have been made to improve their oxidation resistance [8-10], 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 [5-6, 11-16]. 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 [17]:

$$Ti-Al_{42-46}-Nb_{4-10}-X_{0-3}-Y_{0-1}-Z_{0,1}-RE_{0-0.5}$$
(1)

X - contents of Cr, Mn, Ta; Y - contents of W, Hf, Zr;

- Z contents of C, B, Si;
- RE rare earth elements.

Alloys with such 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 aircraft constructions.

These alloys are an attractive alternative for nickel superalloys, especially in the backmost sections of turbines, in which replacing nickel alloy blades results in lowering the mass of the rotator. However, a significant and yet unsolved problem is, apart form low flow, insufficient resistance to oxidation in the atmosphere containing sulphur. 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 aims of the research is to quantify the oxidation rates and reveal physical mechanisms or characteristic corrosion products under these working conditions.

2. Experimentation

2.1. Materials

The study has been done on cast Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni (at%) type alloy. 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

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.

Oxidation tests were carried out on rectangular coupons of 20x15x2 mm. The surfaces were finished using abrasive paper of 800F-grade. 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.

Isothermal oxidation experiments were performed at two temperatures: 900 °C and 950 °C. Oxidation processes were carried out in air and $9\%O_2+0.3\%SO+N_2$ atmosphere during 250 hours. After the test exposure, samples were weighed with a accuracy of $\pm 10^{-4}$ 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 C₃H₆O₃,
- 15 ml HNO₃,
- 5 ml HF.

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



Tested Ti-46Al-7Nb alloy, observed within the range of magnifications has characteristic cast structure. Therefore, a dendritic structure with clear contrasts between dendrite axes and interdendritic spaces and phases is visible in Fig. 1.

a)





b)

Fig. 1. SEM images (BSE detector) of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy for magnifications 200×(a) and 1000×(b)

According to the microstructure classification of Ti-Al alloys [18] on intermetallic phase matrix γ -TiAl suggested by Clemens et al. [17], such a structure type can be specified as duplex. Both γ -TiAl and α_2 -Ti₃Al phases form a lamellar system and g-phase presented in the granular form (Fig. 1a). Moreover, irregular concentration of α_2 -Ti₃Al phase occurs on the border of the plate-grain system, as shown in Fig. 1b. Results of EDX analysis are presented in Fig. 2.

The distance between α_2 plates in a plate mixture $\alpha_2+\gamma$ is from ca. 0.5 mm to ca. 1.5 mm, whereas the thickness of γ phase plates is 4 to 10 times higher than α_2 phase. The fracture of the tested alloy occurring in granular and lamellar area is presented in Figs. 3a and b respectively.

3.1. Oxidation and sulfidation behaviour of the alloy

It is obviously known that the intensity of high temperature oxidation is markedly influenced by oxidizing environment. In many industrial applications, among ordinary atmospheres, various gaseous mixtures can be found.



Fig. 2. EDX analysis results: (a) in area inside the rectangle number 1 marked in Fig. 1 and (b) in area inside the rectangle number 2 marked in Fig. 1

a)







Fig. 3. SEM images (SE detector) of fracture of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy: (a) in granular area and (b) in lamellar area

Therefore, oxidizing atmosphere with a content of sulphur compounds $(9\%O_2+0.3\%SO_2+N_2)$ is proposed for controlled oxidation. Concurrent tests of isothermal oxidation in air and isothermal oxidation in the modelled sulphurous atmosphere showed that sulphur content consequently increases the rate of oxidation. After 250 hours of oxidation, the mass growth of the alloy was observed to be higher when oxidized in the atmosphere containing $9\%O_2+0.3\%SO_2+N_2$ (Fig. 4).

In the heat resistance test performed by means of isothermal oxidation in both atmospheres the mass growth was established to occur. Nevertheless, with the extension of oxidation period, the process of fragmentary scale chipping took place at the stage of cooling down to the ambient temperature. Oxidation products formed during heating are subject to fragmentary chipping, which becomes massive with the increase of time and temperature.



Fig. 4. Course of isothermal oxidation of Ti-46Al-7Nb alloy for the two atmospheres: $9\%O_2+0.3\%SO_2+N_2$ (continuous curves) and air (dot curves)

Specimens observed instantly after isothermal oxidation tests in both oxidizing atmospheres at 900 °C were characterized by good adhesion of products to their metallic substrate within 100 hours of oxidation. After 250 hours chipping of scale's parts could be observed during cooling down to room temperature. At a higher oxidation temperature of 950 °C, chipping in the room temperature was noticeable after shorter periods and with increasing the oxidation time chipping of basic reaction products becomes more intensive (Figs. 5a and 5b) and another sublayer is uncovered. Despite sticking to the surface, which occurs immediately after the tests, most products chipped afterwards, leaving behind only "micro-islands" and exposing the metallic substrate entirely. Diffusion processes, which contribute to the loss of cohesion between the scale and the substrate, are activated along with the rise of temperature and 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 oxidized in air

Regardless of the temperature of isothermal oxidation process, a scale with identical sequence of sublayers is formed.

Columnar crystallites TiO_2 (Fig. 6b) growing in various directions can be observed on the oxidized surface (point 1 in Fig. 6a). Beneath columnar crystallites of rutile another sublayer exists, which gives a grey-black heterogeneous contrast in BSE scanned images (point 2 in Fig. 6). Microanalysis of this sublayer shows the dominance of Al with a much lower share of Ti (Fig. 7b). 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. 7c.



a)

b)



Fig. 5. Fragmentary chipping of products resulting from a fracture of a sample subjected to isothermal oxidation at 950 °C after 250 hours: (a) specimen surface after isothermal oxidation in air, (b) specimen surface after isothermal oxidation in $9\%O_2+0.3\%SO_2+N_2$

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 N₂ and O₂.

XRD diffraction results of products of isothermal oxidation in air at 900 °C were shown in Fig. 8. The highest peaks in the diffraction pattern come from rutile TiO₂, and next in order from Al₂O₃. The diffraction analysis of the oxide layer, which broke off from the metallic substrate after oxidation in 950 °C, showed that the main component of the chipped scale was rutile. Little amount of Al₂O₃ was also found, but in this case the peak intensity in the diffraction spectrum was considerably lower as shown in Fig. 9. a)



Fig. 6. Fracture surface (a) and topography (b) of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni after isothermal oxidation in air at 900 °C

3.3. Structure and morphology of the product layer oxidized in 9%0₂+0.3%SO₂+N₂ atmosphere

A situation similar to that described in Section 3.2 occurs when testing the surface of the specimen in the corrosive environment with sulphur compounds content. Oxidation of Ti-46Al-7Nb alloy in $9\%O_2+0.3\%SO_2+N_2$ atmosphere results in forming a multiphase scale which consists of contrasting sublayers. Chemical composition of the generated layer of oxidation products points out to aluminium oxide growth and rutile growth on the surface. However, whisker morphology of oxides makes it impossible for them to protect the alloy against corrosive environment in the further stages of the oxidation test.

Oxidation under these process conditions results in formation of rutile blooms on the external surface (Figs. 10 and 11) beneath which another layer is uncovered. It is worth noticing that no sulphides were found on the oxidized surface. On the other hand, growing oxides expand when temperature and the time of process increase.

Microscopic observations of the scale after oxidation in $9\%O_2+0.3\%SO_2+N_2$ atmosphere displayed scales with pronounced division boundaries between each layer (Fig. 12). Under the layer of rutile blooms, there is a grey contrast layer in BSE image, which contains Al and lesser quantities of Ti (Fig. 13a). The middle layer of considerable thickness is a mixed sublayer containing Ti oxides and Al as well as other alloying elements (Fig. 13b).



Fig. 7. EDX analysis results: (a) in point # 1 marked in Fig. 6a; (b) in point # 2 marked in Fig. 6a; (c) in point # 3 marked in Fig. 6a; (d) in point #4 marked in Fig. 6a

b)

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Fig. 8. XRD diffraction result of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy after isothermal oxidation in air at 900 $^{\circ}$ C



Fig. 9. XRD diffraction result of the oxide layer, which broke off from the metallic substrate after oxidation in air at 950 $^{\circ}$ C

Chemical composition analysis did not show sulphur compounds in the oxidation products. Microanalyses of chemical composition of the oxidized alloy surface show that Si can also be found there. However, it cannot be regarded as a corrosion product but an external factor whose elimination was impossible. Due to the lack of tightness of the high temperature testing station, the furnace was sealed with silicone and Si entered into reaction, hence its presence in chemical composition microanalyses. As a results, Si is neglected in the analysis of experimental results.

Phase analysis of the alloy's surface after oxidation in $9\%O_2+0.3\%SO_2+N_2$ atmosphere showed that regardless of the oxidation time, the same phases are formed on the surface, namely, TiO₂, Al₂O₃, Ti₃Al₂N₂, Ti₂N, TiN and initially both γ -TiAl and α_2 -Ti₃Al. These tests did not confirm sulphides in the scale (Fig. 14).

a)



b)



Fig. 10. SEM images of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy after isothermal oxidation in $9\%O_2+0.3\%SO_2+N_2$ at 950 °C: (a) specimen surface showing rutile blooms- magnification 2000x, (b) specimen surface showing rutile blooms- magnification 5000x



Fig. 11. EDX analysis results in point # 1 marked in Fig. 10b



Fig. 12. SEM images of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni after isothermal oxidation in $9\%O_2+0.3\%SO_2+N_2$ atmosphere at 950 °C



Fig. 13. EDX analysis results: (a) in point # 1 marked in Fig. 12; (b) in point # 2 marked in Fig. 12; (c) in point # 3 marked in Fig. 12



Fig. 14. XRD diffraction result of Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni alloy after isothermal oxidation in 9%O₂+0.3%SO₂+N₂ at 900 °C

4. Conclusions

The oxidation behaviour of the Ti-46Al-7Nb-0.7Cr-0.1Si-0.2Ni has been investigated in air and $9\%O_2+0.3\%SO_2+N_2$ atmospheres at 900 and 950 °C under isothermal exposure conditions. Results are summarized as follows:

- Oxidation in 9%O₂+0.3%SO₂+N₂ atmosphere causes an increase in the rate of oxidation in comparison to the oxidation in air, however, the sequence of sublayers is not particularly different from this controlled only by air.
- 2. Corrosion resistance is higher in air, which manifests itself in a lower mass growth. It is caused by the increment of a rough scale with whisker morphology from the beginning of corrosion test in O₂-SO₂-N₂ atmosphere, which does not provide a sufficient protection against corrosive environment effects. A more rapid mass growth of the alloy in the controlled sulphur dioxide (SO₂) atmosphere is also caused by the increment of a much thicker, multilayered scale than it is in the case of tests performed in air. This allows to conclude that the bidirectional transfer of metal and oxide ions (O₂ and N₂) is facilitated as a result of a lower tightness of the scale, which is formed in 9%O2+0.3%SO2+N2 atmosphere. Therefore, the product growth rate is much higher at both the phase boundaries, that is, at product-substrate and productoxide boundaries.
- 3. Short period of isothermal oxidation contributes to the growth of a thin scale characterized by a good adhesion to the metallic substrate. With the longer oxidation time, internal stresses and micro-cracks trigger the spallation of the layer and chipping of the products both in 9%O₂+0.3%SO₂+N₂ atmosphere and in air.
- 4. X-ray phase analysis revealed the existence of sulphide-free scale, probably resulting from a low content of SO_2 in the modeled atmosphere. However, other phases ($Ti_3Al_2N_2$ and Ti_2N) appeared in comparison to oxidation in air. It is noteworthy that sulphurous atmosphere is richer in N₂ than the air atmosphere. Many experts confirm that nitrogen considerably increases the rate of oxidation [19] so it can be claimed that the higher content of N₂ in oxidizing atmosphere modifies the formation $Ti_3Al_2N_2$ and Ti_2N phases and, in turn,

contributes to the higher oxidation rate of the tested alloy in $9\%O_2+0.3\%SO_2+N_2$ aggressive environment.

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