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THE KINETICS OF SCALE GROWTH ON Ti-25Al-12.5Nb ALLOY DURING HIGH TEMPERATURE OXIDATION IN 9%O₂+0.2%HCL+0.08%SO₂+N₂ ATMOSPHERE

ABSTRACT

The paper presents research results of isothermal oxidation of Ti-25Al-12.5Nb alloy. Oxidation was carried out in $9\%O_2+0,2\%HCl+0,08\%SO_2+N_2$ atmosphere at the temperature of 700 and 750 °C.

Keywords: high temperature corrosion, oxidation, sulphidation

INTRODUCTION

Alloys based on titanium have properties similar to the properties of traditional heat resistant materials. They can be used in a wide range of temperatures, which makes them materials with great perspectives for evolution. Up to the present, the broad research work focused mainly on titanium alloys based on γ -TiAl [1÷5]. In late eighties of 20th century a new phase was discovered, so called orthorhombic phase: O-Ti₂AlNb [6]. Substituting α 2-Ti₃Al phase for Ti₂AlNb in Ti-Al alloys caused the increase in their density, which was, however, offset by the improvement of other properties i.e. increasing the flow. In the oxidation research there are a few methodologically important factors. An important

In the oxidation research there are a few methodologically important factors. An important role besides the temperature may be played by: the cooling rate, the frequency of the cycle, the temperature of final cooling and the method of preparing specimens (surface roughness). The intensity of high-temperature corrosion clearly depends on the atmosphere of the oxidizing environment [7]. The chemical composition of emissions is an important factor during corrosion. Gaseous ingredients of emissions exhibit particularly high corrosive activity i.e. O₂, SO₂, H₂S, Cl₂,HCl and CO. Corrosion triggered by aggressive impact of elementary sulphur and its compounds is a major problem in many branches of modern industry. Environments with a content of sulphur or its compounds are usually more aggressive than oxygen containing environments [8].

The fast development of contemporary technology sets ever growing demands with respect to metallic construction materials designed for operation in elevated and high temperatures. High-temperature corrosion is particularly present in extreme forms in chemical industry where many structural elements are exposed to the aggressive impact of hot vapours and gases. Also power industry records considerable losses caused by the oxidation of construction elements of high-pressure boiler and gas and vapour turbines [9]. Further development depends to a great extent on the research progress in the area of resistance of special alloys designed to work in a very high temperature with the exposure to oxidising impact of gas jet at the same time.

This paper presents the results of research on high temperature corrosion of the alloy based on O-Ti₂AlNb in aggressive environments containing $9\%O_2+0,2\%HCl+0,08\%SO_2+N_2$.

EXPERIMENTAL PROCEDURE

The tests were performed on O-Ti₂AlNb based alloy Ti-25Al-12.5Nb (at. %) with β -stabilising elements content: Mo (6.01 at%) and V (0.48 at.%). Isothermal oxidation experiments were performed at the temperature 700 °C and 750 °C in the atmosphere with the content of 9%O₂+0,2%HCl+0,08%SO2+N₂. Specimens (20x15x2mm) were abraded on abrasive paper of 800 grade paper and subsequently degreased in acetone.

The oxidation behaviours of the specimens were studied in $9\%O_2+0.2\%$ HCl+ $0.08\%SO_2+N_2$ atmosphere at 700 and 750 °C during 50, 100, 300 and 500 hours, and subsequently cooled down to the room temperature. After cooling, it was weighed using a balance with an accuracy of 10^{-4} g to characterize the oxidation rate. Surface morphology and microstructure before and after oxidation were performed using a scanning electron microscope (SEM) with energy-dispersive (EDS) and wavelength-dispersive (WDS) X-ray spectrometer.

RESULTS AND DISCUSSION

The chemical composition of gas during the oxidation has a considerable effect on the course of reaction. Sulphur and chlorine present in the modelled atmosphere promote the increase of the oxidation rate as compared to oxidation in air, additionally causing a change in the type and composition of oxidation products and their morphology [10].



Fig. 1. The mass change of Ti-25Al-12.5Nb oxidized isothermally in $9\%O_2+0.2\%HCl+0.08\%SO_2+N_2$ atmosphere at 700 °C and 750 °C

The mass change obtained during oxidation at 700 and 750 °C in the atmosphere of $9\%O_2+0.2\%$ HCl+0.08%SO₂+N₂ are presented in Fig. 1. At the temperature 750 °C, the alloy was characterized by an exceptionally big mass gain during the oxidation test. The mass change is progressively increased, reaching about 0.8059 mg/cm² after 500 hour. At the temperature 700 °C, the mass change was characterized by an subsequent slow-down represented. As can be see after 500 hour the mass gain of alloy is by far smaller and the mass change did not exceed 0.4 mg/cm².

Samples of the alloy oxidised in the atmosphere of $9\%O_2+0.2\%$ HCl+ $0.08\%SO_2+N_2$ examined directly after the ending of the experiment at the temperature of 700 °C were characterised by a good adhesion of the scale to the metallic substrate. No chipping of the scale was observed during cooling down to room temperature. For the higher temperature of 750 °C, as the oxidation time increases, the chipping of oxide layer intensifies After short isothermal oxidation in the atmosphere of $9\%O_2+0.2\%$ HCl+0.08%SO₂+N₂, the scale is thin and adheres well to the metallic substrate. However, as the oxidation time passes, internal stresses and forming microcracks cause the spallation and chipping of some of the products. The surface of the specimens oxidised at 750 °C during 50, 100 and 300 hours does not display signs of devastation. Further increasing the oxidation time, however, adversely affects this situation and the adhesion of the scale becomes insufficient. After 500 hours of oxidation and subsequent cooling down to ambient temperature it is characterized by fragmentary chipping of considerable part of reaction products. Despite the fact that the products stuck to the surface of specimens directly following the experiment already after 24 hours most of the scale chips away.

Oxidation in such conditions causes the formation on the surface of specific eruptions underneath which another sublayer is exposed. The surface of alloy specimens after oxidation in $9\%O_2+0.2\%HCl+0.08\%SO_2+N_2$ at the temperature of 700 °C was presented in Fig. 2a-d, whereas that in 750 °C in Fig. 3a-d. Fig. 4 presents the X-ray spectrum of Energy Dispersive Spectrometry of the alloy surface after the oxidation in atmosphere of $9\%O_2+0.2\%HCl+0.08\%SO_2+N_2$.



Fig. 2. Surface of Ti-25Al-12.5Nb alloy after isothermal oxidation in 9%O₂+0.2%HCl+0.08%SO₂+N₂ atmosphere at 700 °C after (a) 50 hours, (b) 100 hours, (c) 300 hours, (d) 500 hours



Fig. 3. Surface of Ti-25Al-12.5Nb alloy after isothermal oxidation in 9%O₂+0.2%HCl+0.08%SO₂+N₂ atmosphere at 750 °C after (a) 50 hours, (b) 100 hours, (c) 300 hours, (d) 500 hours



The analysis of the outer layer of the alloy after the oxidation in the atmosphere of $9\%O_2+0.2\%HCl+0.08\%SO_2+N_2$ proved that the forming outer layer is composed mainly of the mixture of oxides Al and Ti (Fig. 4). Furthermore, the occurrence of Nb and traces of S were observed on the oxidised surface. It was noticed that the forming oxides grow with the rise of temperature and time of the process, and the increase of the temperature causes the formation of a scale with particularly a whisker-like morphology of the oxides, which

effectively hinders the protection of the alloy against the impact of the corrosive environment at the next stages of the test.

The examination of cross-sectional metallographic specimens after experiments in the atmosphere of $9\%O_2+0.2\%HCl+0.08\%SO_2+N_2$ allowed revealing the multi-layered nature of the scale (Fig. 5-6). Based on the chemical composition analysis of the layers it was determined that, directly under the outer layer (I) containing mainly Ti and Al, a sublayer is formed with a dominance of Al (II), and another mixed sublayer rich in titanium oxides, aluminium and alloying elements (III) with a dominance of Ti. The presence of S was also confirmed in this layer; most probably TiS compound forms here. The detailed chemical composition of respective layers was presented in Tab. 1-2.



Fig. 5. Cross-section of products and metallic sublayer of the oxidized Ti-25Al-12.5Nb alloy after oxidation in 9%O₂+0.2%HCl+0.08%SO₂+N₂ atmosphere at 700 °C



Fig. 6. Cross-section of products and metallic sublayer of the oxidized Ti-25Al-12.5Nb alloy after oxidation in 9%O₂+0.2%HCl+0.08%SO₂+N₂ atmosphere at 750 ° C

Table 1. WDS-analysis (at.%) of locations labelled on Fig. 5

Location	N	0	S	Al	Nb	Ti	Mo	V
#1	0.00	49.99	3.21	14.31	5.78	26.71	0.00	0.00
#2	0.00	55.74	0.00	36.17	0.97	6.29	0.71	0.12
#3	0.00	44.61	7.91	18.92	1.93	24.76	1.02	0.85

Table 2. WDS-analysis (at.%) of locations labelled on Fig. 6

Location	N	0	S	AI	Nb	Ti	Mo	V
#1	0.00	56.01	4.57	10.07	4.21	25.14	0.00	0.00
#2	0.00	54.35	0.00	37.86	1.19	5.64	0.51	0.45
#3	0.00	43.47	6.27	21.53	2.04	25.37	0.72	0.60

It is noteworthy that the layer of corrosion products formed in the atmosphere of $9\%O_2+0.2\%HCl+0.08\%SO_2+N_2$ is characterised by porous structure, which is well pronounced in Fig. 5 and 6. Therefore, it does not provide sufficient protection against the destructive impact of corrosive environment. Lower cohesion of the scale facilitates the bidirectional transport of metal ions and oxidants (O, N and S), causing the product to grow faster on both phase interfaces i.e. product-substrate interface and product-oxidant interface, and the inner layer is characterised by a large number of pores. Most likely such course of reaction is caused by reactivity of sulphur vapours which belong to the most aggressive ones as regards corrosion due to the fact that sulphur reacts with almost all metallic elements

SUMMARY

The course of corrosion of Ti-25Al-12.5Nb-3Mo-0.48V alloy in the atmosphere of $9\%O_2+0.2\%$ HCl+0.08%SO₂+N₂ may be compared to corrosion occurring in air. However, in the environment containing even such small amounts of sulphur, metallic materials resistant to high temperature oxygen corrosion may undergo degradation, which can lead to breakaway corrosion.

Research results confirm that multi-layered scales are formed on the surface of the alloy during the process, however, in the presence of sulphur in the oxidising atmosphere they show poor protective properties due to their structure (cracks, voids at the interface between scale and metallic substrate, chipping), therefore they do not protect the material against further corrosion.

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