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HIGH TEMPERATURE CORROSION OF TiAlCrNb ALLOY WITH TiAl₂ OUT-OF-PACK COATING IN N₂-O₂-SO₂-HCl ENVIRONMENTS

ABSTRACT

In this article results of microstructural analysis and corrosion resistance tests of 48-2-2 alloy (TiAlCrNb) with and without protective coating were presented. The aluminide coating was deposited by out-of-pack method on the base alloy. The thickness of the coating was 10µm and it was composed of TiAl₂ phases. The corrosion resistance tests of the base alloy with and without the protective coating have been conducted at 600°C in the atmosphere containing nitrogen, with the addition of 9% of O₂, 0,08% of SO₂ and 0,20% of HCl. The tests lasted for 1250h. The aim of the conducted tests was to determine the mass gain of the samples in the given conditions and to identify the corrosion products, using X-ray phase analysis and EDS chemical content microanalysis. The detailed investigation has been done after 25, 50, 100, 150, 250, 500,750, 1000 and 1250h of testing. As clearly indicated by the results of investigations, aluminide coating improves the corrosion resistance of TiAl alloy in the conditions of the performed test. The corrosion-resistance-enhancing effect of this type of diffusion coatings was attributed to the surface layer consisting of TiAl₂.

Key words: *TiAl alloys, TiAl₂, protective coatings, corrosion in HCl, aluminides*

INTRODUCTION

Many industrial processes are characterized by the use of chlorine and compounds containing low molecular weight chlorine (e.g. HCl). As a consequence, an acute problem appears, concerning the damage of numerous parts due to the accelerated corrosion at high temperature, particularly when the chlorine is present in the atmosphere. On the other hand, the partial pressure of oxygen in the atmosphere is a significant parameter, which may decisively influence the resistance of the materials against corrosion in atmospheres containing chlorine. In high temperature corrosion conditions the main reason of protective properties of materials is related to the formation of a dense and slowly growing oxide scale. In case of oxidation at high temperature such scale can be formed from oxides such as Cr₂O₃, Al₂O₃ and SiO₂. But in case of chlorine contaminations this situation may change significantly due to formation of volatile metal chlorides [1].

The issue of the γ-TiAl alloy resistance to other aggressive environments besides oxygen and air, particularly when exposed to sulphur and chlorine, has not been

discussed in many works so far. It is essential to state that NaCl is the main component of the deposit forming on the surface of turbine blades. The oxidation resistance tests performed on the samples covered with NaCl at temperatures ranging from 350°C to 850°C have revealed that NaCl notably accelerates the oxidation of γ -TiAl due to the NaCl reacting with oxygen, Al and Ti, which leads to the formation of scale devoid of any protective properties. The scale is porous, which seems to be the result of the creation of volatile chlorides [2]. Other research suggests that the presence of NaCl deposits may increase the multiply the corrosion rate by as much as 20 times in comparison with oxidation processes. This appears to be due to the impact of NaCl on the initial stage of the oxide scale formation. Initially, the salt deposit reacts with the thin layer of rutile, and, consequently, sodium titanates, NaOH, HCl, chlorine and titanium chlorides are created. Additionally, alloy compound chlorides, mainly Al, Mo and Zr, are formed, being thermodynamically much more obtainable than titanium chlorides. The subsequent pyrohydrolysis of the said chlorides results in the formation of HCl. Consequently, inward diffusion of volatile HCl and chlorine occurs and the compounds react with the base alloy. Subsequently, a mixture of chloride deposits of a lower melting point is formed and, as a result, the liquid deposit on the surface of the alloy increases, which expands the corrosion-threatened area. The corrosion rate increases during the initial stage, and the process kinetics is logarithmic [2]. The mass gain related to the acceleration of the corrosion into NaCl increases as the amount of the salt deposit, the oxygen concentration in the atmosphere and the temperature grow [3]. The second stage of the corrosion in the molten salt environment is signalled by the appearance of aluminium oxides in the form of whiskers on the surface of the scale, the massive introduction of chlorines in the lamellar α_2 phase area and the formation of porous rutile scale in the areas rich in salt. This stage is related to HCl and chlorine outward diffusion through pores and channels in the rutile scale, formed during stage 1. It is during this stage that these gases react with the components of the alloy, forming volatile aluminium and titanium halides. The remaining halides diffuse in the same manner, but in the opposite direction – outwards, to the outer layer of the scale, where they react with oxygen or water vapour, taking the form of rutile and aluminium oxide, emitting HCl and chlorine again. This halide transfer mode, taking the shortest diffusion routes, triggers the formation of aluminium oxide whiskers due to the rapid oxidation of AlCl₃ created on the surface of the scale, which takes place on top of the gas transfer channels. The halides might also be transferred through the porous scale, which results in the formation of fine dispersion aluminium oxides. The kinetics of the second stage is logarithmic as well. The transition into the parabolic range indicates the initiation of the third stadium, which includes the covering of the alloy surface with aluminium oxides in the form of whiskers and the creation of the thin, two-layer scale. The parabolic character of the process suggests volumetric diffusion through the scale [2]. As is the case with hot corrosion, other corroding environments (e.g. oxygen-sulphur or chlorine) receive little attention. The results of the present study suggest better resistance of lamellar alloys in comparison with duplex alloys in H₂/H₂S/H₂O atmosphere at 750°C and 900°C. The tests of TiAl alloys in atmosphere containing 2%Cl₂ at 300°C revealed only low corrosion development. At 500 °C, however, rapid progress of the degradation process on the surface of the alloy could be observed. The obtained scale was remarkably thick and composed of a mixture of titanium and aluminium silicides with a minor chlorine addition. At 650 °C, chemically complicated scale, containing titanium, oxygen and chlorine, is formed. As well as this, the destruction of the scale was

confirmed to result from the formation of volatile aluminium and titanium chlorides. At 800 °C, the created scale was also thick, but devoid of chlorine [1,5].

METHODOLOGY AND MATERIALS

The methodology of the research concerning high-temperature corrosion tests is based upon the experience gained during the research projects realised in the Institute of Materials Science at The Silesian University of Technology and follows the Testcorr regulations. The cubicoidal samples, coated and uncoated, measuring 15x10x4 mm, were used in the study. They were ultrasound-cleaned in trichloroethylene and air-dried. Afterwards the samples were measured, their area was calculated, and finally they were weighed on an analytical balance with an accuracy of 10^{-4} g. The stand for high temperature corrosion testing consists of the cylinder containing the gases included in the simulation mixture, single-stage panel regulators, gas connection, rotameters with integral regulation valves, three-way ball valves, check valves, tubulation, pipe furnaces, quartz or ceramic pipes (depending on the testing temperature) and a neutralising system. Having passed the chamber, the mixture of gases reaches the scrubber, and, after its harmful part is removed, it is released to the atmosphere. The testing procedure involves three stages:

- Heating the furnace charge in argon atmosphere to the given temperature in order to avoid sample oxidation;
- The actual test in the corroding atmosphere containing a specified concentration of the selected gases, at the given temperature and gas flow, enabling a single atmosphere exchange in four hours;
- Cooling the furnace charge in the atmosphere of argon to ambient temperature.

During the tests, the corrosion resistance was checked in the following conditions:

- In the reaction atmosphere containing $N_2 + 9\%O_2 + 0,2\%HCl + 0,08\% SO_2$, at 600°C;
- The test lasted for 1250h.

Ti48Al2Cr2Nb commercial alloy was used as the base material for the study, uncoated and covered with a protective aluminide $TiAl_2$ -phase-based coating deposited with out-of-pack method.

RESULTS AND DISCUSION

The results of the investigation indicate that $TiAl_2$ -coated base alloy exhibits better corrosion resistance in chlorine-containing atmosphere for the total exposure time in comparison to bare basic 48-2-2 alloy samples. The mass gain ratio is stable and amounts for ca. 2.5 both in the initial stage of the test and after 1250h of exposition (Fig.1). After 1000h of testing, the bare alloy exhibited a tendency to oxide spallation, which might be due to the generation of high stress, resulting from the growth of the oxide layer and/or the cooling of the sample. The results have been verified by the macroscopic analysis of the top surface of bare samples (Fig.2).

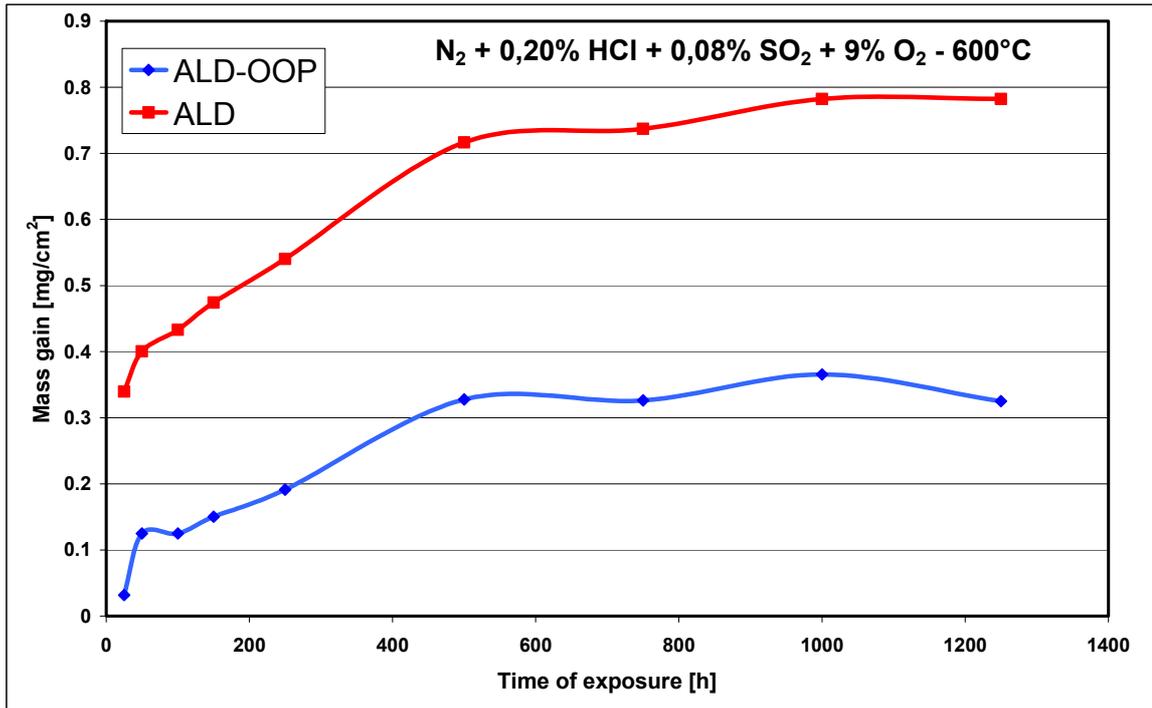


Fig. 1. Mass gain of 48-2-2 alloy with and without TiAl₂ coating during the corrosion test at 600°C

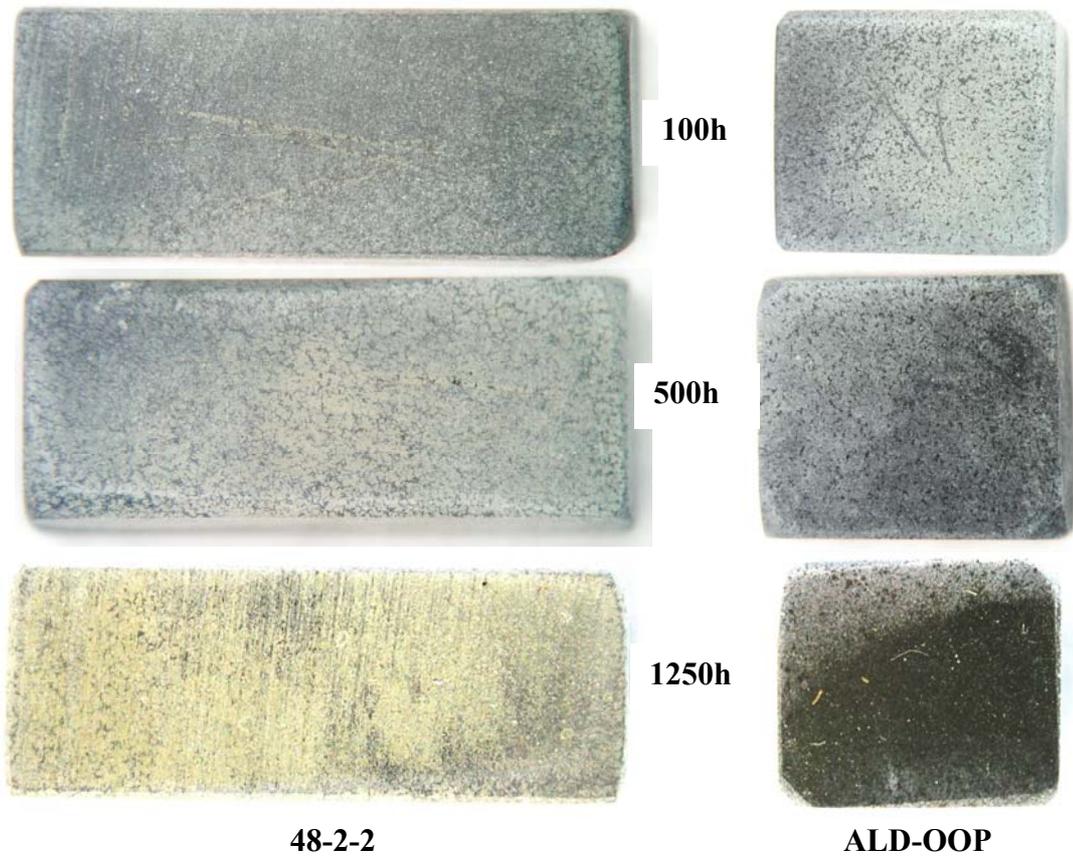


Fig. 2. The macroscopic view of investigated specimens after 100, 500 and 1250h of testing

After 500h of the test, the process of covering the sample of 48-2-2 base alloy with a thin oxide layer became apparent. Nevertheless, the majority of the sample surface was still free from the corrosion product. A more significant effect of the corrosion process was observed after the next 250h of exposure. And in case of 1250h of testing the entire sample surface was covered with the bright grey layer of oxides. The top surface SEM analysis and EDS chemical content analysis as well as the phase analysis have confirmed TiO_2 to be the dominant oxide after the longest base alloy exposure time (Fig.3). In case of 48-2-2 alloys, the effect of oxide spallation was observed and the inner alumina oxide layer was uncovered. In case of the coated samples, the top surface was covered with a mixed oxide layer of alumina and titania, but the dominant peaks of XRD phases analysis are from aluminide TiAl_2 type phase.

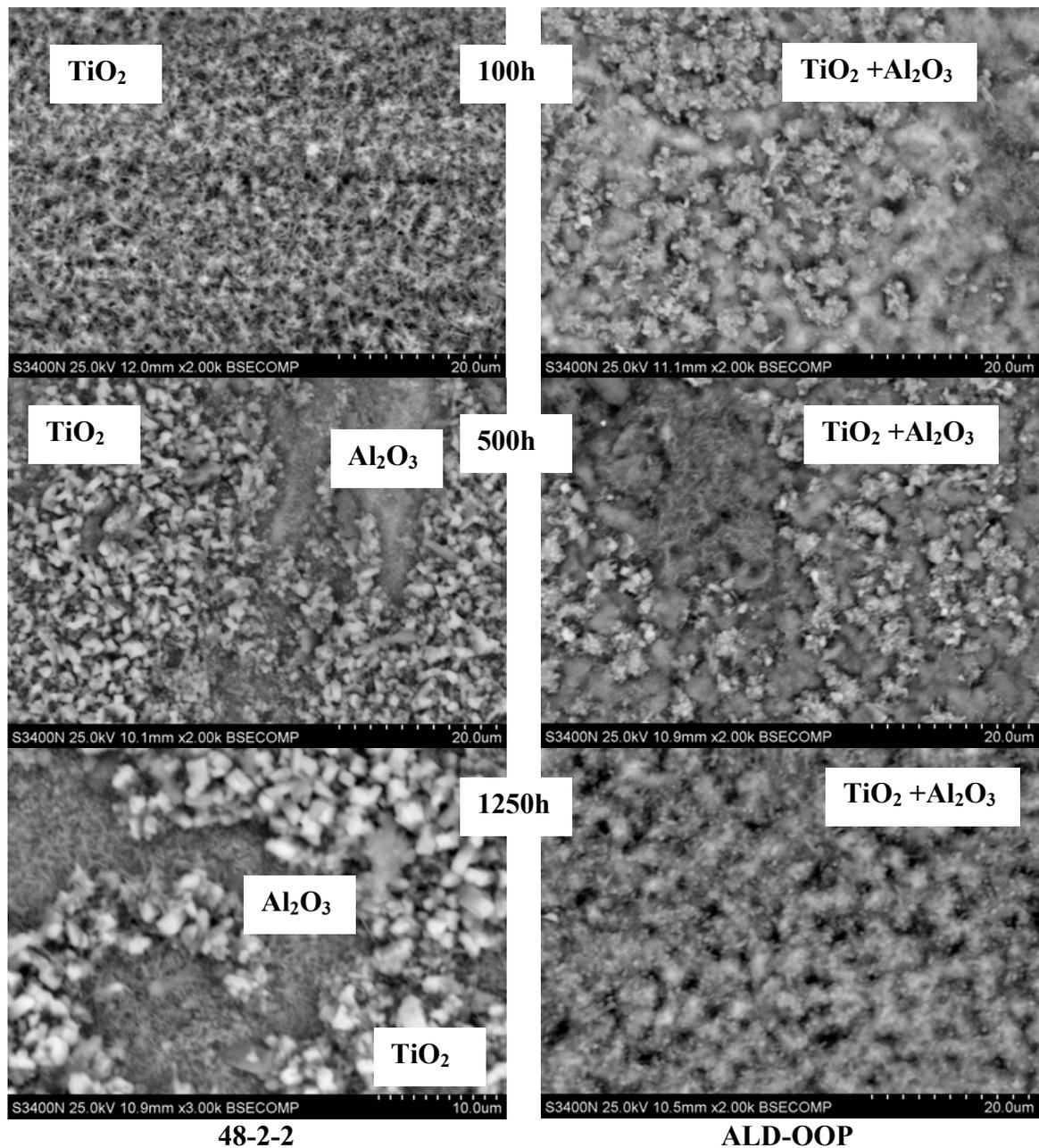


Fig. 3. SEM microstructure of top surface of investigated specimens after 100, 500 and 1250h of test

To improve the corrosion resistance, type TiAl₂ coating has been employed. The coating was circa 10µm thick, and its chemical composition was as follows (Fig.4). Results of cross section SEM investigations are presented in Fig.5 and 6.

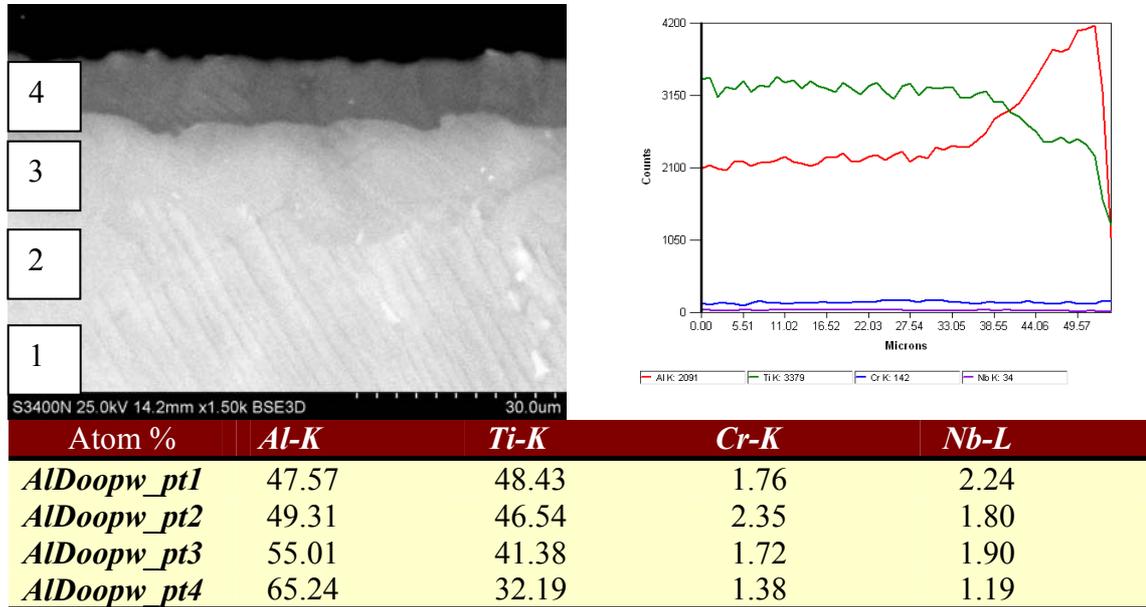


Fig. 4. SEM microstructure and chemical composition of 48-2-2 alloys with aluminide coating

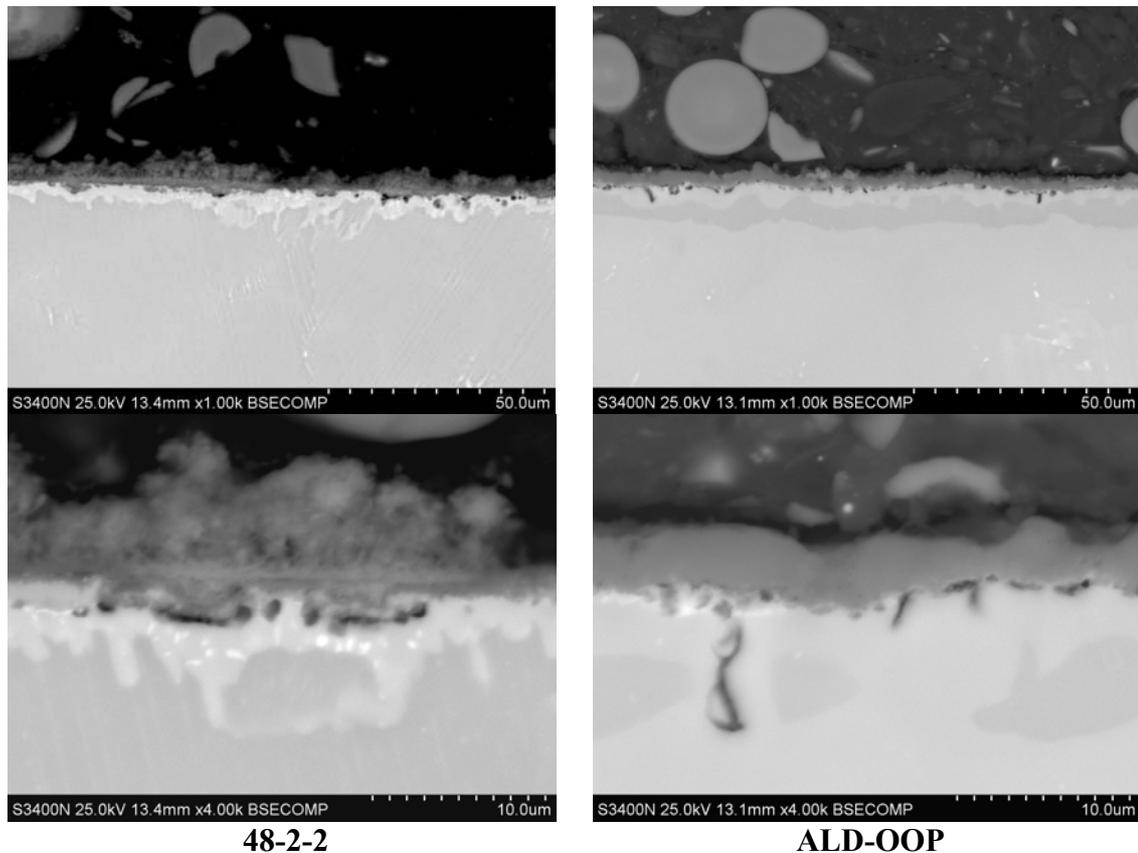


Fig. 5. SEM microstructure of 48-2-2 basic alloys without and with aluminide coating after 1250h exposure

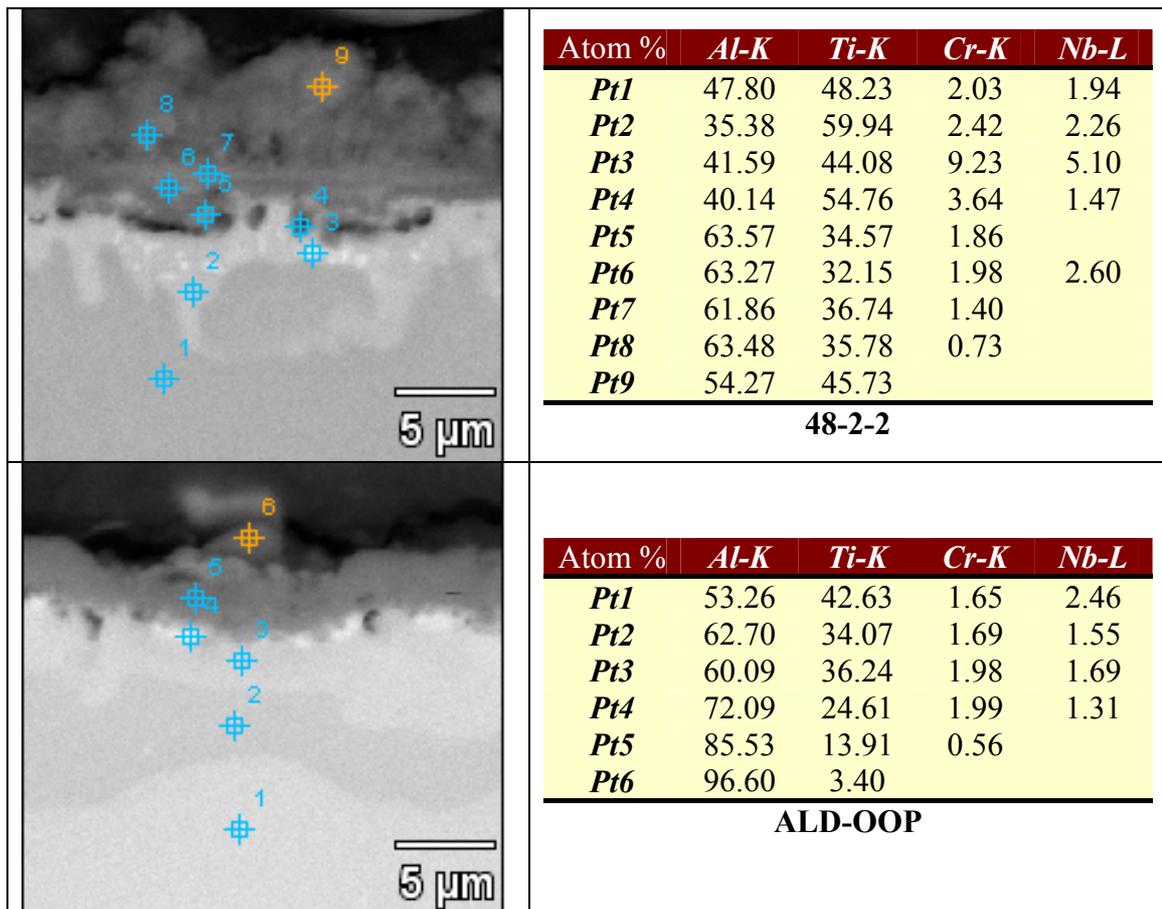


Fig. 6. EDS results of 48-2-2 basic alloys without and with aluminide coating after 1250h of exposure

Microstructural investigation of the base alloy showed the presence of mixed oxide layer made up of corrosion products, whose thickness locally reached 10 μ m. The pitting effect was detected as well. In the area beneath the pit, the concentration of titanium was much higher and white particles rich in Cr and Nb were observed (point 2 and 3). In case of the base alloy protected by TiAl₂, no important effect of top surface degradation was visible. The coating thickness was still ca. 10 μ m, and it was covered with a 5 μ m thick oxide layer. EDS results showed TiAl₂ to be the prevailing phase in the coating, although there were areas constructed of TiAl₃. The investigations of the oxide layer confirmed that alumina was the dominant corrosion product.

SUMMARY

The corrosion tests performed on Ti-48Al-2Cr-2Nb base alloy in the atmosphere of chlorine and sulphur confirmed that at 600 $^{\circ}$ C the said alloy did not possess sufficient resistance to this operating environment. This appears to be related to the intensive titanium and aluminium formation on the surface, which did not provide sufficient protection. As a result, a layer of scale, exhibiting strong flaking tendencies, was formed on the surface of the base alloy. Consequently, the base material, which had not been

exposed to the corroding environment so far, is uncovered and the corrosion processes are intensified. Such reaction of the base material could be attributed to the inclination for volatile aluminium and titanium chloride formation, which increases the porosity of the scale. The application of protective hi-aluminium TiAl₂-based coating significantly increased the resistance of the base alloy. The thickness of the formed scale did not exceed 5µm, and it was chiefly comprised of the desirable Al₂O₃ oxide. The presence of TiO₂ was detected as well. This phenomenon may be explained in terms of high aluminium concentration and high partial oxygen pressure in the corroding atmosphere in comparison with partial chlorine and sulphur pressures. Aluminium reacts with chlorine rapidly, forming volatile type AlCl₃ halides. Therefore, the claim that the increase in its concentration in the outer layer results in abrupt acceleration of corrosion seems justified. Owing to the primarily oxidizing character of the atmosphere, however, initially the protective Al₂O₃ layer is formed, which resists chloride corrosion up to 1200°C, at which point it reacts with it, creating AlOCl₂. In case of the present study, the testing temperature was two times lower; therefore intensifying the inclination of the alloy towards selective aluminium oxidation and aluminium oxide formation considerably improves resistance to corrosion in the presence of sulphur and chloride. As indicated by the diagrams of Al-O-Cl as a function of oxygen and chlorine partial pressures, aluminium oxide is the most probable corrosion product for the majority of corroding environments containing up to 1%Cl. The formation of destructive volatile halides will be impossible unless the atmosphere penetrates directly to the surface of the alloy through the scale and the conditions for the stability of the aluminium halides appear (high chloride partial pressure, lower temperature). The presented relations explain the remarkable corrosion resistance improvement, following hi-aluminium TiAl₂ coating. This is because the increase in the aluminium concentration supports selective oxidation in the oxidizing atmosphere (high partial oxygen pressure) and promotes the formation of Al₂O₃ barrier owing to the oxidation of AlCl to Al₂O₃. In case of the bare base alloy, however, titanium and aluminium oxide scale formation seems to prevail, which is detrimental even in oxidizing atmosphere, while in the presence of chlorine it may cause a high gradient of partial pressure of oxide, chlorine and sulphur to appear, which could initiate the creation of volatile aluminium and titanium chlorides.

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