

# Evolution of mechanical properties of Ti6242S alloy after oxidation in air at 560°C: influence of solid salts deposits

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## **Abstract**

Titanium alloys are widely used in aerospace applications due to their good ratio of weight versus mechanical properties. When exposed to air at 560°C, Ti6242S titanium alloy presents very good oxidation resistance: a very thin oxide layer forms at its surface and oxygen dissolution inside the metallic material is rather limited. However, in real functioning conditions of the plane, near seas or oceans, the atmosphere contains NaCl, that can crystallise at the surface of hot parts. An active corrosion mechanism is established in these conditions, with catastrophic effect on the material behaviour at high temperature: very thick and brittle oxide scales and very important damaging of the metal outer part. Another issue is the formation of Na<sub>2</sub>SO<sub>4</sub> specie by reaction of NaCl with kerosene combustion gases (SO<sub>2</sub>/SO<sub>3</sub>), leading to mixed NaCl/Na<sub>2</sub>SO<sub>4</sub> deposits. The effect of exposure conditions on the mechanical properties of titanium alloy Ti6242S was evaluated through tensile tests performed on the raw alloy and after oxidation in air at 560°C of the specimens: without any deposit, with NaCl solid deposit, with NaCl/Na<sub>2</sub>SO<sub>4</sub> solid deposit. The evolution of mechanical properties was interpreted in connexion with the microstructural modifications that occur during the high temperature ageing.

## **Introduction**

Titanium alloys are very interesting for aeronautic applications because of their high specific mechanical strength. However, recent developments demand the use of these materials at higher temperatures than those initially defined, revealing some uncertainties on their behaviour, related to increased oxidation rate. Furthermore, it is well-known that oxygen dissolution occurs during high temperature exposure in air of titanium alloys [1,2], leading to the formation of an underlying oxygen rich layer inside the base metal. This O-enriched layer is less ductile and might affect the mechanical properties of the alloy.

Apart from temperature, another parameter that can significantly influence the material behaviour is the exposure environment composition. In some conditions, NaCl solid deposits may form [3] and give catastrophic corrosion behaviour at high temperature [4,5]. Literature shows that in presence of NaCl solid deposits, titanium alloys are subject to an active corrosion mechanism, leading to very thick corrosion products and to a strongly damaged metallic substrate [6,7]. Another issue is the formation of Na<sub>2</sub>SO<sub>4</sub> specie by reaction of NaCl with kerosene combustion gases (SO<sub>2</sub>/SO<sub>3</sub>), leading to mixed NaCl/Na<sub>2</sub>SO<sub>4</sub> deposits [8]. This study aims at determining the mechanical properties of titanium alloy Ti6242S after exposure at 560°C and at evaluating the impact of solid salt deposits on their evolution.

## **Material and experiments**

Ti6242S is a near- $\alpha$  titanium alloy containing 6 wt.% Al, 2 wt.% Sn, 4 wt.% Zr, 2 wt.% Mo and 0.1 wt.% Si. Its bimodal microstructure is composed of HCP  $\alpha$ -phase and CC  $\beta$ -phase. Salt deposits were performed by pulverisation of over-saturated NaCl and NaCl/Na<sub>2</sub>SO<sub>4</sub> solutions in order to obtain fully covering deposits of 3-4 mg/cm<sup>2</sup>. Thermal oxidations were performed in laboratory air at 560°C for different periods up to 1000 hours, on both classic samples and tensile test specimens. Specimens for tensile tests were prepared with a gauge part of 35 mm length and 0.5 x 4 mm cross section. Tensile tests were carried out at room temperature on raw and aged samples by using a Shimadzu AGS-X set-up at an imposed 0.016 %/s strain rate.

All samples were characterised by SEM-EDS, XRD and micro-hardness profiling on cross-sections. The oxide surface and cross-section morphologies were analysed using a JEOL JSM-7600F scanning electron microscope. The chemical composition of the corrosion products was obtained by energy dispersive X-ray spectroscopy (EDS). Phase composition of the oxide scales was determined by X-ray diffraction with Bruker Discover diffractometer equipped with LINXEYE detector and using Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation with fixed incidence angle of 2° for samples oxidised without salt and of 8° for

samples with salt deposits. The Vickers micro-hardness of each sample was evaluated with Zwick Roell ZHμ set-up using a charge of 25 g. Measurement points were done on the whole thickness of the metallic material, each 3 μm near the surface.

## **Results and discussion**

### *Raw material*

Tensile test performed on raw Ti6242S shows a ductile behaviour (table 1), with an elastic domain that reaches 0.8% elongation and an ultimate elongation of 8.3%. The estimated Young's modulus is of 110 GPa and the 0.2% offset yield strength is of 1021 MPa. The ultimate tensile strength is of 1086 MPa. These latter values are slightly higher than those already reported in literature for Ti6242S alloy [9]. Indeed, it is known that the mechanical properties of Ti alloys are strongly dependant on the thermal treatments that they have undergone during the fabrication process, as well as on their resulting microstructure [10].

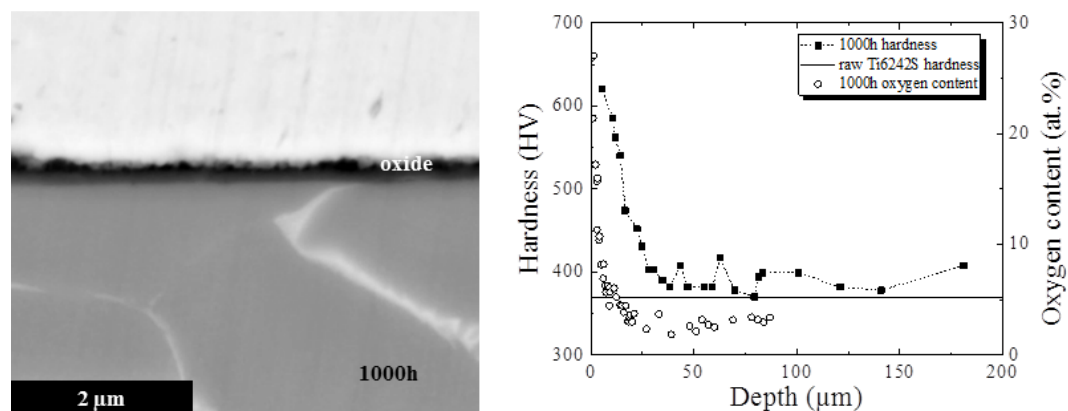
<b>Mechanical property</b>	<b>Value</b>
Young's modulus <b>E (GPa)</b>	128
0.2% Yield strength <b>Rp0.2% (MPa)</b>	1021
Ultimate tensile strength <b>Rm (MPa)</b>	1086
Elastic domain elongation (%)	0.8
Ultimate elongation <b>Ar (%)</b>	8.3

**Table 1. Mechanical properties of Ti6242S raw alloy**

### *Oxidation in air without deposit*

The oxide layer grown after exposure at 560°C in laboratory air is very thin (50 nm after 100 hours and 130 nm after 1000 hours), continuous and adherent to the substrate (as shown in figure 1 by cross-section SEM analysis after 1000 hours of exposure). DRX analysis showed that the scale is mainly composed of TiO<sub>2</sub> rutile; some TiO<sub>2</sub> anatase was equally detected after 1000 hours of oxidation. SEM-

EDX analyses of oxygen concentration at the outer part of the metal and micro-hardness profiles in the same region allow determining the depth affected by oxygen dissolution. Oxygen dissolution phenomenon was evidenced on 4  $\mu\text{m}$  and respectively 25  $\mu\text{m}$  depth in the metallic substrate after 100 and 1000 hours of exposure.



**Figure 1.** SEM image, EDX oxygen content and micro-harness profiles of Ti6242S alloy oxidised in air for 1000 hours at 560°C

Ageing at 560°C leads to an important change of Ti6242S mechanical properties (table 2). A small increase of the Young's modulus and of the yield strength occurs with the ageing time. At the same time, the ductility of the samples strongly decreases with the oxidation time, showing that the dissolution of oxygen into the metallic matrix leads to the embrittlement of the material. Indeed, the tensile test fracture occurs in the plastic domain for 3.1 % elongation after 100 hours ageing and at the limit of the elastic domain for 0.8% elongation after 1000 hours ageing.

These results are in agreement with the literature, as the oxygen dissolution is well-known to lead to an important embrittlement of Ti alloys [11,12,13]. The loss of ductility occurs for short oxidation times (12 hours at 650°C, as shown by Shenoy et al. [12]), but also for low oxygen concentrations (less than 1% as observed by Liu et al. [8]). If the exposure time increases, the quantity of dissolved oxygen equally increases, leading to a complete loss of ductility as observed for the tensile test exposed for 1000 hours. This result can be correlated with our previous study [14] showing that the maximum limit of oxygen solubility in  $\alpha$ -phase of Ti is reached in the outer part of the metallic material after 1000 hours of oxidation. These observations are also in agreement with those of Chan et al. [15], which report the formation of cracks perpendicular to the surface of titanium alloy TA6V after oxidation

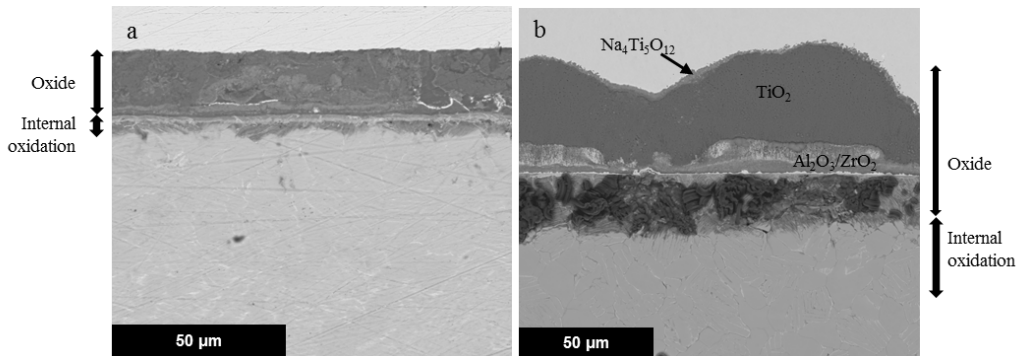
in air, of depth similar to the thickness of oxygen dissolution area. In the present work, the brittle behaviour observed after 1000 hours of oxidation might be issued from cracks formation in the oxygen dissolution area (representing 10% of the specimen cross-section) that would propagate deeper in the metallic substrate.

Mechanical property	Raw	Oxidation in air	
		100 h	1000 h
<b>E (GPa)</b>	128	135	146
<b>Rp<sub>0.2%</sub> (MPa)</b>	1021	1103	1075
<b>Rm (MPa)</b>	1086	1137	1075
<b>Ar (%)</b>	8.3	3.1	0.8

**Table 2. Mechanical properties of Ti 6242S alloy oxidized in air for 100 hours and 1000 hours compared to the mechanical properties of raw alloy**

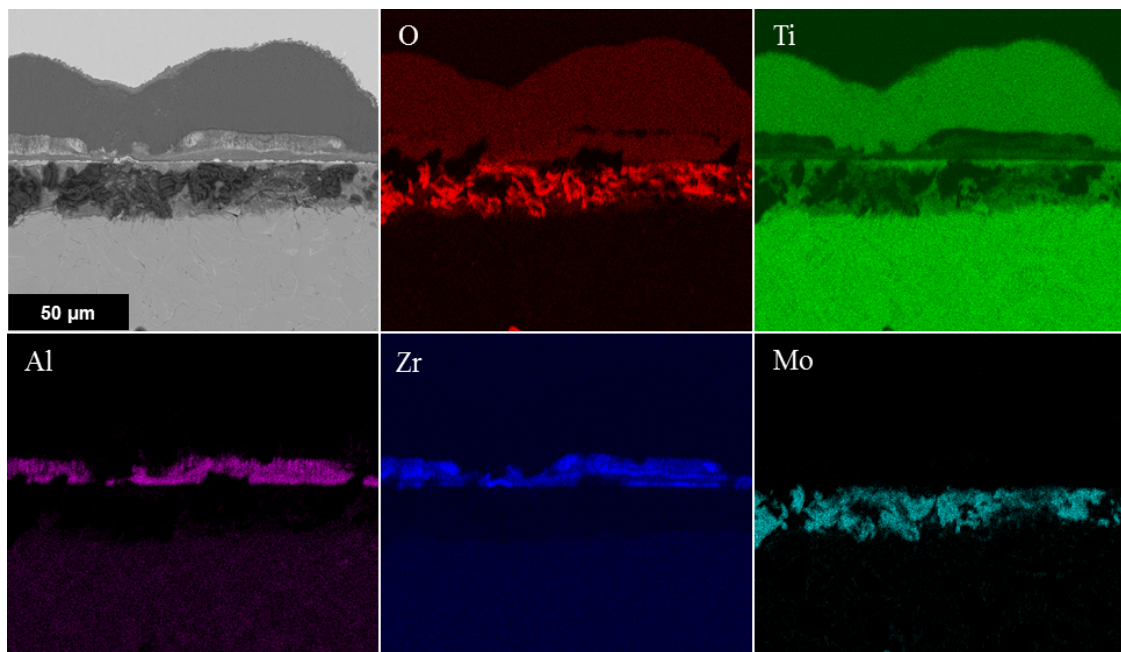
*Oxidation in presence of NaCl solid deposit*

The presence of NaCl solid deposit at the surface of the alloy leads to catastrophic behaviour, with a mass gain that increases by a factor of 15 after 100 and 1000 hours ageing at 560°C as compared to samples oxidised without any deposit. Corrosion scales are very thick: 18 µm after 100 hours and 55-75 µm after 1000 hours ageing (figure 2). Moreover, they are very brittle, affected by cracks or pores and present very low adherence to the metallic substrate. Cross-section SEM-EDX elementary mapping (figure 3) and surface XRD analysis show that the oxide scale is composed by several phases: Na<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> in its outer part, TiO<sub>2</sub> as intermediate layer and majority phase, as well as Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> at the interface with the metallic material.



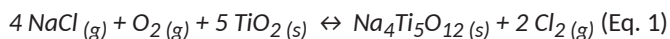
**Figure 2. Cross-section SEM images of Ti6242S alloy oxidised in air for (a) 100 and (b) 1000 hours at 560°C with NaCl solid deposit**

The outer part of the metallic substrate is extremely damaged. An important depletion in metallic elements was shown by SEM-EDX analyses (figure 3) leading to an important loss of metallic grains cohesion. Consequently, an internal oxidation process takes place. Indeed, the oxygen content found in this region, of around 60%, largely overcomes the oxygen dissolution limit of 33%. Moreover, micro-hardness measurements performed on cross-section showed values close to the raw material hardness all over the thickness of the sample. The thickness affected by internal oxidation is of 6 µm after 100 hours and of 40 µm after 1000 hours of oxidation.



**Figure 3. Cross-section SEM-EDX elementary mapping of Ti6242S alloy oxidised in air for 1000 hours at 560°C with NaCl solid deposit**

The enhancement of the oxidation phenomenon in presence of a solid NaCl deposit is attributed to an “active oxidation” mechanism [16]. Thermodynamic calculations performed with Factsage 6.4<sup>TM</sup> software showed that the mechanism is initiated by a reaction between Ti contained in the metallic substrate and gaseous NaCl, that is present in the system at an important vapour pressure of  $3.10^{-7}$  mbar [6]. In agreement with the composition of the oxide scale, the first reaction of the active oxidation mechanism can be written as follows:



The as-released chlorine can migrate toward the metal/oxide interface and react with metallic Ti in order to form a gaseous Ti chloride, in agreement with the important depletion of Ti at the outer part of the metallic substrate and with the very high porosity observed near the metal/oxide interface



The volatile  $TiCl_4$  can be partially released, but can equally react with the oxygen than can easily arrive through the important cracks that formed inside the oxide layer. This reaction leads to the formation of rutile and production of gaseous chlorine:



Chlorine that forms during reaction (3) can then feed reaction (2): an active corrosion mechanism [16] is established, these two reactions can take place indefinitely, as long as Ti can be provided, i.e. until the complete consumption of the alloy.

The specimen oxidised for 1000 hours in presence of NaCl solid deposit broke during its storage, showing the catastrophic effect of NaCl presence on the mechanical behaviour of the alloy after oxidation. This behaviour is in agreement with SEM observations (figure 2) showing that the very thick oxide scale is not adherent to the metallic substrate. Moreover, the active oxidation process highly impacts on the cohesion of metallic grains. The section of the tensile test bearing the load is than diminished by a factor that increases with the oxidation time, allowing to explain the behaviour after 1000 hours oxidation.

The mechanical properties of Ti6242S alloy oxidised for 100 hours in presence of NaCl solid salt are presented in table 3. The tensile test evidenced a brittle behaviour: the fracture occurs at the limit of the elastic domain for 0.9 % elongation. The apparent elastic modulus and the ultimate tensile strength present a slight decrease as compared to the raw material. The detrimental effect of the solid salts is once more highlighted: ageing for 100 hours in presence of NaCl deposit has the same negative effect on the ductility of the material as the exposure for 1000 hours without any deposit.

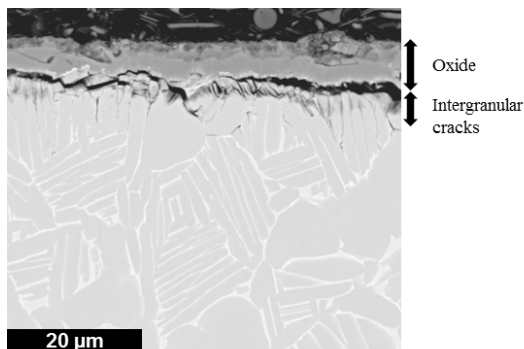
Mechanical property	Raw	Oxidation in air 100 h	
		Without NaCl	With NaCl
<b>E (GPa)</b>	128	146	118
<b>Rp0.2% (MPa)</b>	1021	1103	961
<b>Rm (MPa)</b>	1086	1075	961
<b>Ar (%)</b>	8.3	0.8	0.9

**Table 3. Mechanic properties of Ti6242S alloy oxidized in air for 100 hours with NaCl solid deposit compared to the raw alloy and to the alloy oxidised for 100 hours without deposit**

*Oxidation in presence of equimolar NaCl/Na<sub>2</sub>SO<sub>4</sub> solid deposit*

The disastrous effect of NaCl appears significantly lowered in presence of Na<sub>2</sub>SO<sub>4</sub> (figure 4). Indeed, the oxide layer grown after 100 hours of oxidation with equimolar NaCl/Na<sub>2</sub>SO<sub>4</sub> solid deposit is thinner, of 12 μm thick, but still not adherent to the metal. The oxygen dissolution is avoided, but the internal oxidation takes place on 2-3 μm within the substrate. The metallic material is affected by cracks on 5-6 μm, corresponding to 4% of the tensile test section.

Na<sub>2</sub>SO<sub>4</sub> presence in the solid salt deposit slows down the active corrosion mechanism. The better behaviour can be related to the fact that, at 560°C, Na<sub>2</sub>SO<sub>4</sub> is solid: it cannot cause hot corrosion [13], but acts as protection barrier, preventing or slowing down Cl<sub>2</sub> diffusion to the metal. A second explanation for the positive impact of Na<sub>2</sub>SO<sub>4</sub> presence might be related to the formation of a protective metallic sulphide layer at the metal/oxide interface. Already observed for the oxidation of steels in presence of NaCl/Na<sub>2</sub>SO<sub>4</sub> [17], the sulphide layer isolates the metallic matrix from the chlorine attack [18,19]. Nevertheless, such sulphide layer was not observed in the present study.



**Figure 4.** SEM image of Ti6242S alloy oxidised in air for 100 h at 560°C with NaCl/Na<sub>2</sub>SO<sub>4</sub> solid deposit

The mechanical behaviour of the tensile test aged in presence of NaCl/Na<sub>2</sub>SO<sub>4</sub> is very similar to that of the raw alloy, as shown in table 4. The Young's modulus and the yield strength are the same as for the raw alloy. However, an important loss of ductility is still observed, the break occurring at the beginning of the plastic domain for 1.4 % elongation.

Mechanical property	Raw	Oxidation in air 100 h	

		<b>Without deposit</b>	<b>With NaCl</b>	<b>With NaCl/Na<sub>2</sub>SO<sub>4</sub></b>
<b>E (GPa)</b>	128	146	118	128
<b>Rp<sub>0.2%</sub> (MPa)</b>	1021	1103	961	1000
<b>Rm (MPa)</b>	1086	1075	961	1021
<b>Ar (%)</b>	8.3	0.8	0.9	1.4

**Table 4. Mechanical properties of Ti6242S alloy after oxidation in air for 100 hours in presence of NaCl/Na<sub>2</sub>SO<sub>4</sub> solid deposit. Comparison with the raw alloy and the alloy oxidised in the same condition without any deposit and with NaCl solid deposit**

## **Conclusion**

The evolution of mechanical properties of Ti6242S alloys after exposure in air at 560°C in presence of solid salts was tested and related to microstructural changes. Oxidation in air without any deposit leads to a decrease of the material ductility that is completely lost after 1000 hours of exposure. NaCl solid deposit leads to catastrophic effect in relation to active corrosion phenomena. Exposure for 100 hours in presence of NaCl has the same negative effect on the mechanical properties of Ti6242S as 1000 hours exposure without any deposit. The disastrous effect of NaCl is decreased in presence of NaCl/Na<sub>2</sub>SO<sub>4</sub> mixed deposit, probably in relation to the formation of a sulphide layer that protects the metal from chlorine attack.

## **Acknowledgements**

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