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Strong correlation between high temperature oxidation resistance and nitrogen mass gain during near alpha titanium alloys exposure in air

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Abstract

Nitrogen is known to play a role in the oxidation of titanium and titanium alloys in air. This paper shows the strong correlation between the high temperature oxidation kinetics of eight near-alpha titanium alloys, in the class of Ti6242S, exposed for 3000 hours in air at 650 °C. Nuclear reaction analysis (NRA) was used to quantify and locate the nitrogen inside the material. An excellent linear correlation between the total mass gain measured by gravimetry and the nitrogen mass gain measured by NRA is revealed: less the alloys oxidize, more the nitrogen is involved in the oxidation process.

Keywords

near alpha titanium alloys, high temperature oxidation, nuclear reaction analysis, nitrogen quantification

Introduction

Titanium and its alloys are increasingly used in high value parts especially in aerospace industry and in medical devices due to its interesting properties like the specific strength, good corrosion properties and excellent biocompatibility. Titanium alloys are used in the hot zones of jet engines generally up to 550°C. The extent of this temperature by 50 or 100°C could bring high advantages in terms of weight gains with strong impact on fuel consumption and manoeuvrability.

The Ti6242S, a near alpha titanium alloys with a nominal mass composition Ti-6%Al-2%Sn-4%Zr-2%Mo-0.15%Si is used in aerospace industry for its good high temperature mechanical and oxidation resistance up to 550°C. Its high temperature oxidation behaviour was widely investigated [1-6].

The titanium alloys are designed to satisfy particular requirements as high resistance at low and high temperatures, high fatigue resistance, low creep at high temperature, high resistance to oxidation or other distinctive specifications. Some alloying elements have notorious influence on the high temperature oxidation in air, like Al [7,8], Si [9–12], Nb [13–15] or Cr [16]. Kitashima and Kawamura [17] proposed a function for the prediction of the mass gain after 240 h of exposure at 700 °C in air of Ti alloys as a function of the composition.

The high temperature oxidation of titanium is known to be based on the diffusion of O²⁻ anions through the under-stoichiometric oxide and their reaction with titanium at the oxide/metal interface to produce new oxides [18]. Several authors pointed out the role involved by the nitrogen in the oxidation in air of titanium [19–22] or near-alpha titanium alloys [2–4,23] and remarked the presence of this element at the oxide/metal interface. Thus, Dupressoire et al. [2] compared the oxidation kinetics of Ti6242S alloy in synthetic air and in a mixture of 80% Ar - 20% O₂ and found that the presence of nitrogen significantly decreases the oxidation rate. Kitashima et al. [23] pointed out the role of nitrogen in the recrystallization of titanium grains at the oxide/metal interface of a near-alpha titanium alloy (TKT 41) oxidized at 750 °C in air. They showed that the nitrides are involved in the recrystallization process and found that the recrystallized grains contain less oxygen than their precursors. Abdallah et al. [4] observed discontinuous layers of nitrides and oxynitrides at the oxide/metal interface of oxidized Ti6242S alloy for 1000 h at 650°C in air.

In previous works the authors showed that mechanical surface treatment like shot-peening and laser shock peening can improve the oxidation resistance of pure Ti [20–22,24] or beta-metastable Ti alloy [25,26]. It was also remarked that the oxidation resistance improvement was always accompanied by larger quantities of nitrogen, but the nitrogen mass gains were not quantified at that time. In recent works [27] the authors succeeded to quantify the nitrogen mass gain for pure Ti oxidized at 700°C using ion beam techniques and nuclear reaction analysis.

In the present work the same procedure as described in [27] is used to quantify the nitrogen content of several nuances of near-alpha, derived from Ti6242S. The aim of this article is devoted to show the strong correlation between the high temperature oxidation resistance and the quantity of nitrogen involved in the mass gain for six different near-alpha alloys, in the family of the Ti6242S. A deeper study of the influence of each particular alloying element on the oxidation behaviour will be addressed in future papers.

Materials and methods

The alloys used in this study are near alpha titanium alloys with various composition containing 4 – 6 wt. % Al, 1 – 4 wt. % Sn, 0 – 4 wt.% Zr, 1 – 4 wt. % Mo, 0 – 2 wt. % Nb and 0 – 0.2 wt. % Si. The commercial Ti6242S alloy was used as reference. Eight alloys are compared here.

Small ingots of several alloys were synthesized by arc melting by Timet France. The compositions of these alloys, measured by the supplier by Inductively Coupled Plasma (ICP), are given in Table 1. In this paper the denomination of the alloys is made using the wt. % of the Al, Sn, Zr and Mo respectively, followed by the wt. % of Nb (if Nb is present) and the letter “S” if Silicon composition is 0.11% or “S2” if Silicon is 0.22%.

Table 1. Given name and measured composition of alloys used in this study. The at.% is indicated between parentheses.

Alloy	Al wt.% (at.%)	Sn wt.% (at%)	Zr wt.% (at%)	Mo wt.% (at%)	Nb wt.% (at.%)	Si wt.% (at.%)
Ti6242S	5.8 (10.3)	2.1 (0.8)	4 (2.1)	1.9 (0.9)	0 (0)	0.11 (0.19)
Ti5104S	4.6 (8.1)	1 (0.4)	0 (0)	3.6 (1.8)	0 (0)	0.11 (0.19)
Ti54041S	4.7 (8.4)	4.1 (1.7)	0 (0)	3.8 (1.9)	1 (0.5)	0.12 (0.21)
Ti61141S	5.9 (10.4)	1.1 (0.4)	1 (0.5)	3.8 (1.9)	1 (0.5)	0.12 (0.2)
Ti6244	5.8 (10.4)	2.1 (0.9)	4.1 (2.2)	3.8 (1.9)	0 (0)	0 (0)
Ti6244S	5.6 (10.4)	2 (0.8)	4 (2.1)	3.7 (1.9)	0 (0)	0.11 (0.19)
Ti6244S2	5.7 (10.2)	2.1 (0.9)	4.1 (2.2)	3.7 (1.9)	0 (0)	0.22 (0.38)
Ti62441	5.8 (10.4)	2.1 (0.9)	4 (2.1)	3.8 (1.9)	0.9 (0.5)	0 (0)

The ingots were β -forged, rolled and solution treated in β phase at 1015°C, followed by air cooling to room temperature, aging for 2h at 650 °C and then air-cooled to obtain a lamellar microstructure. Cylindrical rods about 12 mm diameter were machined and ~2mm thick samples were cut for oxidation tests. The samples were polished up to P600 grit, then ultrasonic cleaned in ethanol, dried, measured, weighted and oxidized.

Several samples of each alloy were oxidized in muffle furnace at 650 °C for periods up to 3000 h in laboratory (atmospheric) air. At defined durations (25 h, 100 h, 300 h, 500 h, 1000 h, 1500 h and 3000 h) one sample of each alloy was extracted, weighted. For some durations the samples were doubled in order to check the repeatability.

The oxidized samples were cross-cut, electrolytically covered with a thin layer of Cu to avoid delamination of oxide layers, embedded in resin and mirror-polished up to 30 nm colloidal silica for microscopic observations. The high-resolution scanning electron microscope images were taken using a Schottky field emission SEM JEOL JSM-7600 F with LABE detector (Low Angle Backscattered Electron). The EDS/WDS cartographies were recorded using JEOL JSM7600F SEM equipped with Oxford Instruments energy dispersive (EDS) SDD Xmax 80mm² and wavelength dispersive spectroscopy (WDS) INCA Wave 500 detectors.

The quantification and localization of nitrogen under the oxide scale was performed at CEA Saclay using ion beam analysis. A high energy deuteron beam (d^+) accelerated at 1.9 MeV was directed perpendicularly to the oxidized surface of the samples. Given the high energy of the beam, the deuterons penetrate the material on depths much larger than the oxide thickness, investigating the oxide, the oxide/metal interface as well as part of the metal under the oxide. A surface of 200 × 200 μm^2 on each sample is irradiated with $\sim 7.5 \cdot 10^{15}$ ions/cm² during about 2 hours and the emitted particles are detected with an annular detector. Some deuterons passing close enough to the nuclei of light elements can provoke nuclear reactions, reactions that occur with very low probabilities because of the small size of light elements nuclei Here we investigate the reaction $^{14}\text{N}(d,\alpha_1)^{12}\text{C}$, when an atom of ^{14}N reacts with a deuteron to produce a ^{12}C atom on the first excited state and emit an alpha particle. The emitted alpha particle has an energy that depends on the incident particle energy and of the nature of the reaction. If the reaction occur at the surface of the material, the ions energy is the nominal energy (here 1.9 MeV) and the corresponding energy for the emitted alpha particle is 6788 keV [28]. The incident deuteron loses also energy when it penetrates the material. As well, the alpha emitted particle loses energy too in its way out from the material to the detector. Thus, by measuring the energy of the emitted alpha particle one can deduce the depth at which the nuclear reaction occurred. The software Pyrole developed at CEA Saclay France [29] is used to find the conversion between the energy of the particle and the depth at which the reaction occurred. By measuring the number of reactions that occur at a certain energy

and using the probability of the reaction to occur (called the cross-section of the reaction) one can deduce the concentration of the target atoms at a specific depth. Standard samples with known stoichiometries are used to calibrate the electronic stage of the measurement chain. This technique allows then to measure the concentration and the spatial distribution of light elements (here the nitrogen). More details about the facility, the technique and the cross-section of the particular nuclear reaction used here for quantification can be found here [27,28,30].

Results and discussion

After oxidation the samples were analysed by various techniques. In this article we will present the results about the gravimetry, oxide morphology and nitrogen quantification.

Mass gain measurements

The samples were weighted before and after the oxidation. The mass gain per unit of area after 3000 h of oxidation at 650°C is given in the second column of the Table 2. Details and a deeper analysis of the kinetics of oxidation will be given in a future paper. After 3000 h of oxidation one can remark big differences between the mass gain values for these alloys, despite the small differences in composition. The most resistant alloy exhibits a mass gain less than half compared to the less resistant one. Thus, relatively subtle changes in the compositions bring noticeable differences in high temperature oxidation behaviour.

SEM investigations

The cross-section SEM images allow to reveal the morphology of the oxides. The Figure 1 gives an example of the structure of the oxide scales as well the EDS cartographies for Ti, Al, O and N chemical elements for two different alloys. The third column of the Table 2 shows the measured oxide scale thicknesses of all the alloys studied here. Again, despite the very close compositions of these alloys the oxide scales thicknesses are very different. One can remark that the oxide layers are stratified but remain adherent. An aluminium rich layer can be seen in the top of the rutile layer, which is probably alumina, as detected by other authors [2,5,6]. Other thinner aluminium-rich layers can be also seen between the rutile layers. The oxide layer is mainly constituted from the outer scale to the inner scale of: a thin rutile layer (of about ~200 nm), followed by a thin alumina layer (of about ~200 nm) and a thicker rutile that constitutes the internal part of the oxide scale (up to several microns). These morphologies were already described in the literature [2,5,6]. The nitrogen is difficult to quantify by EDS in presence of titanium since the $K\alpha$ emission ray of nitrogen is close to the $K\beta$ ray of titanium. Thus, EDS cartography of nitrogen can be used to highlight the presence of this element, but its quantification is influenced by the presence of titanium; this is why for quantification purposes the nuclear reaction analysis will be used further in this article.

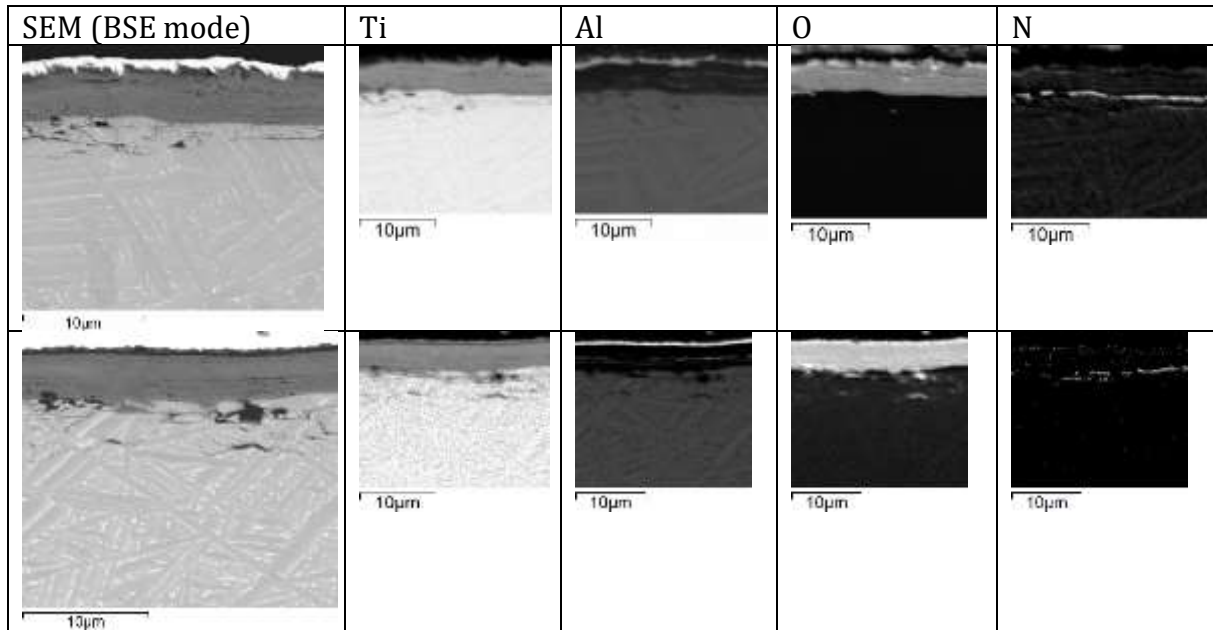


Figure 1. Cross-section SEM images and corresponding EDS cartographies for Al, O and N for two alloys (top – Ti6242S; bottom – Ti6244) after oxidation at 650°C for 3000 h under air.

Nitrogen quantification

The spectra of the emitted α particles produced by the nuclear reaction $^{14}\text{N}(d,\alpha_1)^{12}\text{C}$ are recorded for each sample during about 2h of irradiations with deuterons (d^+). Spectra of three samples are given Figure 2 along with the TiN standard spectrum. As mentioned, if the nuclear reaction that we consider here occurs at the surface of the material, the energy of the emitted alpha particle is 6788 keV. The standard TiN sample used for calibration purposes shows the particle detection up to this energy value. On the contrary, for all the Ti alloys samples the spectra do not extend more than 6500 keV, which shows that the nitrogen is located under the surface of the oxides. The reactions occurring deeper into the material produce lower energy particles. Thus, one can easily remark that for all the titanium alloys samples the reaction does not occur at the surface of the material but inside it. This is not surprising, since several authors showed that the nitrogen is located mainly at the oxide/metal interface. We must notice that there is a small peak centred on 6600 keV which is not given by the nitrogen nuclear reaction but by two reactions of Al: $^{27}\text{Al}(d,p_0)^{28}\text{Al}$ and $^{27}\text{Al}(d,p_1)^{28}\text{Al}$ that can be detected at 6678 and 6649 keV, respectively (when the Al is located at the surface of the material). These reactions are not very energetic, but they will however be eliminated from the spectra for nitrogen quantification purposes to improve the quantification accuracy.

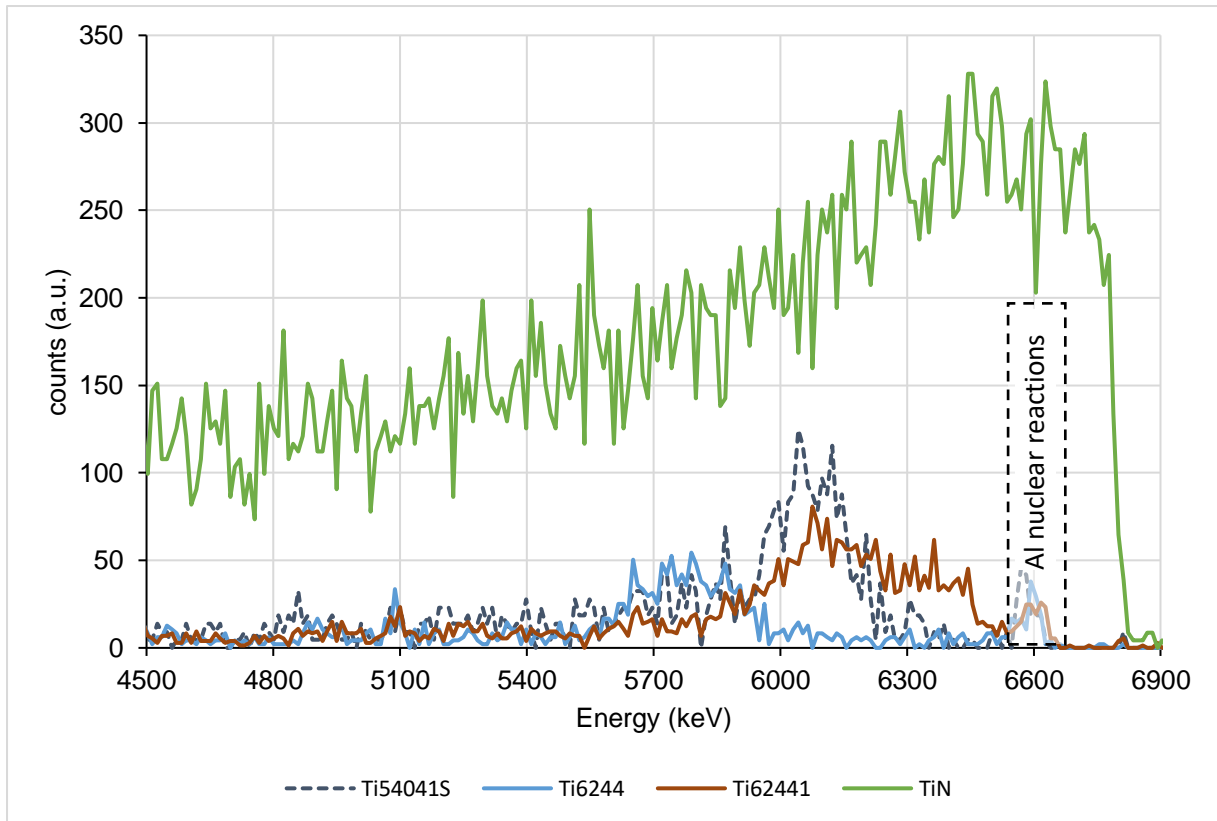


Figure 2. The spectra given by the reaction $^{14}\text{N}(d,\alpha_1)^{12}\text{C}$ for all the alloys studied here (oxidized for 3000 h at 650°C in air) and for the TiN standard. The main interfering peak given by the reaction $^{27}\text{Al}(d,p)^{28}\text{Al}$ around 6600 keV is eliminated for the quantification procedure.

The processing of the spectra shown Figure 2 allows to obtain the nitrogen concentration profiles with respect to the depth. Three profiles of nitrogen concentration are presented in Figure 3 only for three alloys for better readability. One can observe for each alloy a large peak of nitrogen detected at various depths, with various intensities. This main peak covers a range of about 2-2.5 μm and its in-depth location is roughly centred on the position of the oxide/metal interface, where the nitrogen is located, as previously shown by several studies [3-6,23].

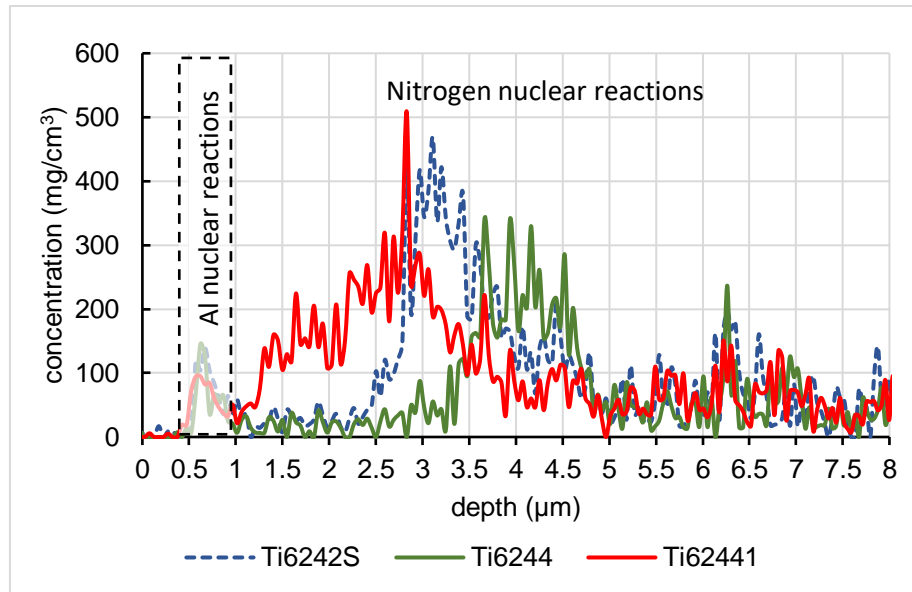


Figure 3. Nitrogen concentration profiles for three different alloys after 3000 h of oxidation at 650°C in air.

From the nitrogen concentration profiles one can easily calculate by integration the total quantity of nitrogen inserted into the material, for each alloy. The NRA signal corresponding to the reactions $^{27}\text{Al}(d,p)^{28}\text{Al}$ is eliminated from the quantification. The nitrogen mass intake (in mg/cm^2) is presented in the fourth column of the Table 2. A comparison of the nitrogen mass gain and the total mass gain can then be realized. Then, a plot of the nitrogen mass gain as a function of the total mass gain measured by gravimetry can be drawn, as shown Figure 4. The graphic shows that more the nitrogen is present, less the alloy oxidize (lower is the mass gain during oxidation). A linear regression show a coefficient of determination $R^2 = 0.98$, which suggest that the nitrogen is a first order element in the resistance to oxidation in air of near alpha titanium alloys. This suggests that the alloying elements have an indirect influence on the oxidation resistance of these alloys by stabilizing the nitrides and possibly by modifying the solubility of the nitrogen and probably also of the oxygen into the metal. The role of the alloying elements on the stability of nitrides will be addressed in a future article. One can also point-out that at this temperature the nitrogen mass gain can represent up to more than 6% of the total mass gain, as shown in the fifth column of the Table 2.

Table 2. Oxidation at 650°C for 3000h under air: mass gain per unit area deduced from gravimetry, measured oxide thicknesses, nitrogen mass gain deduced from NRA quantifications, percentage of nitrogen from the total mass gain, percentage of oxygen involved in the oxide formation from the total mass gain (1 μm of TiO_2 represents 0.169 mg/cm^2 of oxygen)

Alloy	Total mass gain (mg/cm^2)	Oxide thickness (μm)	Nitrogen mass gain ($\times 10^{-2} \text{mg}/\text{cm}^2$)	% of nitrogen from total mass gain	% of oxygen in the oxide from the total mass gain
Ti6242S	2.0	3.6 \pm 0.4	7.38	3.7 %	30%
Ti5104S	3.13	13.1 \pm 0.3	2.71	0.9 %	71%
Ti54041S	1.51	3.7 \pm 0.6	9.66	6.4 %	41%
Ti61141S	1.8	2.8 \pm 0.6	7.58	4.2 %	26%
Ti6244	2.46	4.7 \pm 0.4	5.17	2.1 %	32%
Ti6244S	1.78	3.4 \pm 0.3	7.67	4.3 %	32%
Ti6244S2	1.76	3.5 \pm 0.5	8.26	4.7 %	34%
Ti62441	1.82	2.5 \pm 0.7	7.87	4.2 %	23%

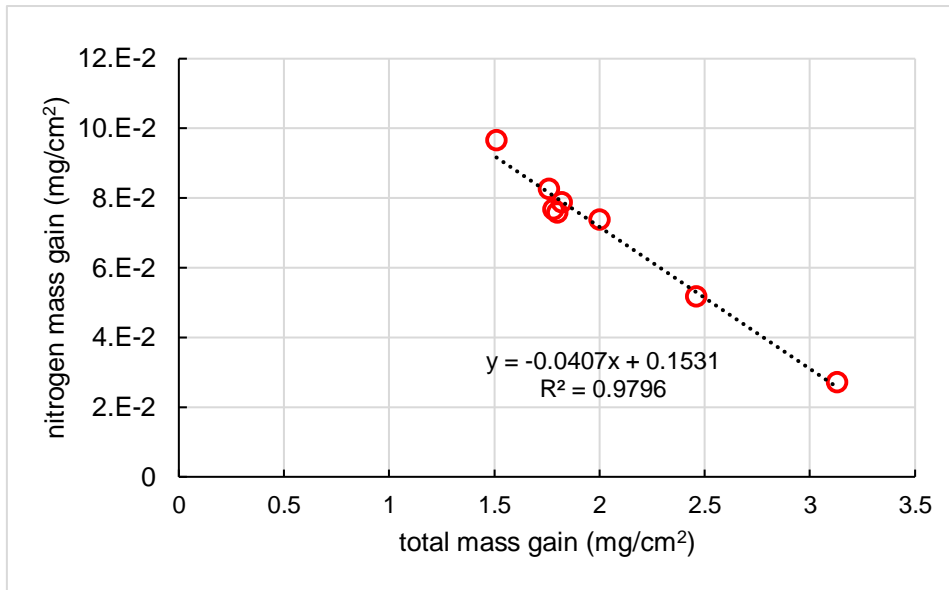


Figure 4. Nitrogen mass gain (NRA) vs total mass gain (gravimetry) for several alloys after 3000 h of oxidation at 650°C in air.

One can wonder if the nitrogen quantity is not strictly related to the oxide thickness. A graph showing the nitrogen quantity versus the oxide thickness (see Figure 5) show that there is no close correlation between these two parameters, which means that a bigger quantity of nitrogen is not a consequence of a thinner oxide layer. Thus, this suggests that the nitrogen acts directly on the diffusion of oxygen as a retarding barrier to the oxygen diffusion and, consequently, to the oxide formation.

The sixth column of the Table 2 shows the percentage of oxygen involved into the oxide formation from the total mass gain with the hypothesis that the oxide is dense ($\rho = 4.23 \text{ g/cm}^3$, which represents 0.1692 mg/cm^2 for $1 \text{ }\mu\text{m}$ of oxide). The values presented here are compatible with the ones found in the literature. The last column of the Table 2 present the proportion of oxygen present in the oxide layer from the total mass gain. This percentage is relatively small, as already remarked by Berthaud et al. [5] on Ti6242S.

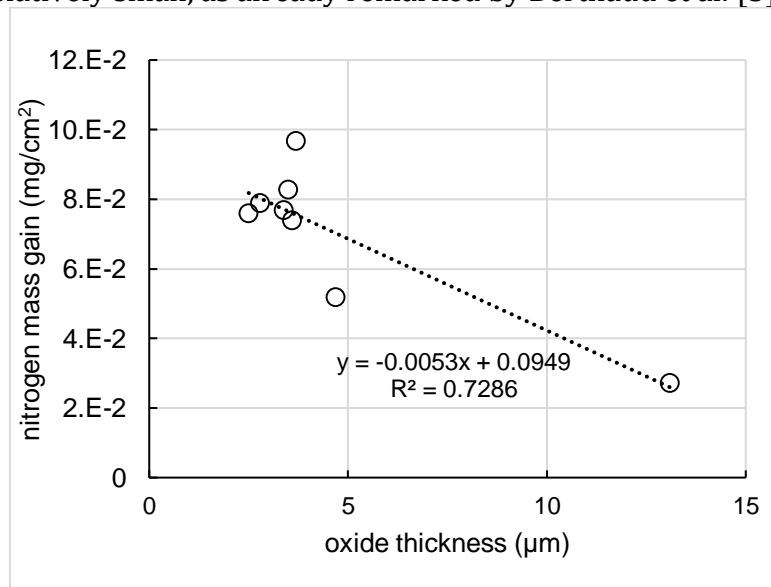


Figure 5. Nitrogen mass gain (NRA) vs oxide thickness for several alloys after 3000 h of oxidation at 650°C in air.

The influence of the nitrogen on the oxidation in air can be explained by the following features. The nitrogen atom is bigger than the oxygen. Nitrogen and oxygen occupy the same octahedral sites within the close-packed hexagonal lattice of titanium while they are in solid solution [18]. Thus, the presence of nitrogen in solid solution [4] in titanium represents a brake to the diffusion of oxygen to the core of material and then slows down the oxidation rate. Moreover, the presence of nitrides, revealed by several authors at the oxide/metal interface of pure titanium or titanium alloys [3,4,23,27] represent a slowing barrier for the formation of new oxides at this interface, as well for the diffusion of oxygen into the titanium. At the same time, it seems that the presence of these nitrides at the interface can have an influence as a mechanical adaptation layer between the oxide scale and the metal, retarding the cracking and spallation of the oxide [22].

Conclusion

The nitrogen mass gain of several near-alpha titanium alloys from the Ti6242S family was quantified after oxidation for 3000 h in air at 650°C. The method for quantification is based on the nuclear reaction analyses during irradiation with high energy deuterons beam. This method allows as well to find the in-depth distribution of nitrogen.

It was found that, for eight different near-alpha alloys close to Ti6242S, more the nitrogen is involved in the oxidation process, less the alloys oxidize. An excellent linear correlation ($R^2 = 0.98$) between the total mass gain measured by gravimetry and the nitrogen quantity inserted into the material during the oxidation shows that the nitrogen is probably the key factor in the oxidation resistance of near-alpha titanium alloys. It also suggests that the influence of the alloying elements on the oxidation resistance in air of these class of titanium alloys can be directly related to the synergy between these elements and the stability of the nitrides as well the solubility of nitrogen into the metal. At our knowledge this is the first time the nitrogen was quantified in titanium alloys oxidized in air. This is also the first proof that the quantity of nitrogen is strongly related to the total mass gain during the oxidation, and more important, that these results are obtained for different near-alpha alloys of titanium.

This work highlights the essential role of the nitrogen into the oxidation of near-alpha titanium alloys and suggest that the alloying elements can play an important role on the oxidation behaviour via the stabilization of the nitrides located at the oxide/metal interface and via the modification of the solubility of nitrogen and oxygen into the metal. This opens a new direction for the optimisation of high temperature oxidation resistance of near-alpha titanium alloys.

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Credit authorship contribution statement

V. Optasanu: Conceptualization, Methodology, Experimental setup, Investigation, Validation, Formal analysis, Data curation, Visualization, Writing – review & editing. P. Berger: Investigation, Methodology, Formal analysis, Writing – review. M.C. Marco de Lucas: Validation, Writing – review, F. Herbst: Investigation. T. Montesin: Validation, Project administration. L. Lavisse: Conceptualization, Validation, Formal analysis, Writing – review.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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