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High temperature oxidation resistance and microstructure of laser-shock peened Ti-Beta-21S

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ABSTRACT

Keywords:

Mechanical surface treatments
Metastable beta-titanium
High temperature oxidation
Oxidation kinetics
Oxygen diffusion

Improving the high temperature (HT) resistance of titanium alloys is currently a technological challenge for extending their use in aerospace engines. Ti-Beta-21S is a metastable β titanium alloy specifically designed for high temperature applications up to 593 °C. We report the effect of a surface treatment by laser-shock peening (LSP) on the high temperature behavior of Ti-Beta-21S in order to increase further its maximum service temperature. The oxidation kinetics at 700 °C for duration up to 3000 h showed that the LSP treatment increases the oxidation resistance of Ti-Beta-21S. The effects of the LSP treatment on the alloy microstructure, its evolution at high temperature and the diffusion of light atmospheric elements (oxygen and nitrogen) are also reported.

1. Introduction

Aviation is currently one of the fastest-growing sources of greenhouse gas emissions. This is a huge ecological challenge for aeronautics. In order to reduce pollutant emissions, aircrafts of the future require the development of components with improved lightness, efficiency and durability. The excellent combination of lightness and good physical and chemical properties makes titanium alloys very attractive in this context [1,2]. They are especially found in compressor blades and discs and engine housings, as well as in structures. However, their use is still limited to temperatures below 550 °C because of their low resistance to oxidation above this limit [3]. Implementing Ti alloy components which could resist to higher temperatures would provide a mass gain of approximately 50% compared to nickel-based superalloys currently in use above 550 °C. Extending the use of these alloys to the turboengines of the aircraft of the future would make titanium alloys even more attractive.

Mechanical surface treatments such as shot-peening (SP) or laser-shock peening (LSP) appear as possible technological solutions to extent the service temperature range of various metals [4,5]. Those techniques are already used in the industry to improve some particular properties of metals at ambient temperature: mechanical (fatigue resistance) [6,7], tribological (resistance to wear) [8,9] and electrochemical

(resistance to pitting) [10]. The beneficial effect of SP and LSP treatments on the high temperature (HT) oxidation resistance of pure titanium at 700 °C has been reported by Kanjer et al. [11,12]. The reduction of both the mass gain and the diffusion length of oxygen in the Ti- α matrix [12], which corresponds to the so-called α -case, were remarkable in LSP treated samples. To the best of our knowledge, the possibility of using this kind of surface treatments to increase the maximum application temperature of metastable beta titanium alloys has not been studied. The improved high specific strength and cool formability of metastable β -titanium alloys are great assets in aeronautics applications.

The aim of this study is to investigate the effect of the LSP treatment on the high temperature oxidation resistance of a metastable β -titanium alloy, as well as on the microstructure and its evolution at high temperature.

The material used for this work was the Ti-Beta-21S alloy from TIMET (TIMETAL 21S), which has been specifically designed for improved oxidation resistance, elevated temperature strength, creep resistance and thermal stability [13–15]. Ti-Beta-21S is reported by TIMET as suitable for high temperature applications up to 593 °C.

The study of the oxidation kinetics of LSP treated plates at 700 °C in dry air during 3000 h showed higher oxidation resistance of LSP treated samples compared to the reference material. The structural

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characterization of LSP treated samples and the analysis of the spatial distribution of the main alloying elements (molybdenum and aluminum) and light atmospheric elements (oxygen and nitrogen) after exposure at high temperature were addressed to explain the improvement of the oxidation resistance. Electron Backscattering Diffraction (EBSD) and scanning electron microscopy coupled to electron microprobe (EDS) were used for this purpose. Moreover, ion beam microanalysis was used for mapping the distribution of light elements in the cross-section of oxidized samples. The diffusion of oxygen and the insertion of nitrogen under the oxide scale have been investigated in this way.

2. Experimental details

2.1. The material

The material used in this study was the Ti-Beta-21S metastable β titanium alloy (TIMET supplier). This alloy is used in aeronautics for its good mechanical and chemical resistance up to 600 °C. Stabilized mainly in the metastable β -Ti phase, its chemical composition (in wt%) is: Ti 78, Mo 15.13, Nb 2.65, Fe 0.26, Si 0.2, Al 3.45, C 0.013, O 0.13, N 0.02.

For LSP treatments, pieces of $25 \times 50 \text{ mm}^2$ were cut from 1.8 mm thick cold-rolled strips produced by TIMET. High temperature oxidation experiments were made on samples of $10 \times 10 \times 1.8 \text{ mm}^3$.

In order to facilitate the reading of the following results, the untreated samples will be designated here by the abbreviation US, while those treated by laser-shock peening will be called LSP. Untreated and laser treated samples oxidized 3000 h at 700 °C will be called US-3000 h and LSP-3000 h, respectively.

2.2. Surface mechanical treatments and HT oxidation experiments

Laser-shock peening was performed at the PIMM laboratory of ENSAM Paris, using a GAIA HP laser source [4]. After coating the surface of the sample with an aluminum foil tape, the samples were placed in a water container. The water media was used to confine the plasma plume produced by the laser beam. The aluminum coating absorbs the thermal effects generated by the laser irradiation and the water media amplifies both the amplitude and the duration of the shock effect within the treated material. The wavelength of the laser beam was 532 nm and the diameter of the focal spot was 4 mm. The duration of the laser shots was 7 ns and the frequency 0.5 Hz. The deposited laser irradiance was 9.1 GW/cm^2 . The laser beam scanned the sample surface on snake-shaped parallel lines with a velocity of 1.1 mm/s. The area of the overlap between two successive shots was 30%. The two faces of the sample were treated successively.

The treated and untreated samples (LSP and US) were oxidized under synthetic dry air at 700 °C during 3000 h by using a SETNAG quartz tube furnace. The samples were extracted every 160 h, weighed to evaluate their mass gain, and replaced into the furnace. Under these conditions, the material was thus cooled to room temperature and then put back to the oven after each weighing. A purge was carried out before introduction of the oxidizing gas, to avoid any presence of water vapors.

2.3. Characterization techniques

The surface topography of the samples was studied using a VEECO WYCO NT 9100 optical profilometer.

X-ray diffraction phase analysis was carried out by using a BRUKER D8-A25 DISCOVER diffractometer. A Cu anticathode was used with beam incidence fixed at 2°.

The chemical state of the samples before HT oxidation experiments was analyzed by XPS (PHI Versaprobe 5000). In order to clean the sample surface, the very first superficial layers of the material were

removed by bombardment with a 5 keV argon ion beam (Ar^+) for 1 min.

After LSP treatment and oxidation for different durations of exposure to HT, the samples were cross-sectioned, resin-embedded and mechanically polished up to 50 nm colloidal silica suspension. Cross-sections of US and LSP samples were analyzed by SEM coupled to an electron microprobe in order to investigate the distribution of the alloying elements (Mo, Al, ...). Two microscopes coupled to energy-dispersive spectroscopy (EDS) probes were used here, a TESCAN VEGA 3 and a field-emission microscope JEOL JSM-7600F.

The grain orientation was analyzed by Electron Backscattering Diffraction (EBSD) using a TSL EDAX OIM X4M EBSD system coupled with a JEOL-7600F microscope. The working distance was 20 mm, the tension 20 kV, the magnification $\times 70$ and the step of scanning 1 μm . Cross-sections of US-3000 h and LSP-3000 h samples were prepared as follows for EBSD analysis. The specimens were embedded in a cold-cure resin with rapid polymerisation and small shrinkage. They were mechanically polished with P600 and P1200 grit SiC papers. Then they were mirror-finished and slightly chemically etched using a 70:30 mixture of a colloidal silica suspension and H_2O_2 on a polishing cloth (Presi, Supra).

Ion beam microanalysis was mainly used for mapping the distribution of light elements (oxygen and nitrogen) in the cross-section of oxidized samples. The operating principle of these techniques is summarized in Fig. S1 (Supplementary Material). The nuclear microprobe of CEA-Saclay was used for this study. Depending on the implemented technique, the experimental beam conditions were as follows:

- Proton Induced X-ray Emission (PIXE) and Proton Induced Gamma-Ray Emission (PIGE) spectra were recorded with a 3 MeV proton beam (spot size $4.5 \mu\text{m} \times 3.5 \mu\text{m}$) for Ti (K_α and K_β lines) and ^{27}Al (1013 keV line), respectively.
- Nuclear Reaction Analysis (NRA) and Deuteron Induced Gamma-ray Emission (DIGE) spectra were recorded with a 1.9 MeV deuteron beam (spot size: $4.5 \mu\text{m} \times 3.5 \mu\text{m}$) for the reactions of ^{14}N ($^{14}\text{N}(d,p)^{15}\text{N}$ and $^{14}\text{N}(d,\alpha)^{12}\text{C}$), and ^{16}O (871 keV line), respectively.

3. Results

3.1. Consequences of LSP treatments on the raw material

Fig. 1 presents a 3D reconstruction of the surface topography of the US and LSP samples of Ti-Beta-21S before and after the LSP surface treatment. The roller marks are clearly visible on the US sample, whereas they have practically disappeared after the laser treatment. The total roughness, R_t , slightly decreased from 6.4 μm for US sample to 6.2 μm for LSP sample. The average roughness, R_a , remained unchanged and equal to 0.4 μm for both US and LSP samples.

The hardness profiles along the thickness (Fig. S2) were measured on the cross-section of samples before and after LSP treatment. The variation of hardness along the thickness was negligible for both kinds of samples, and the mean value was around 330 HV. The absence of strain hardening leads to the conclusion that the LSP treatment does not induce plastic deformation. The same result was obtained for the LSP treatment of pure α -Ti [12].

The cross-sections of US and LSP samples were observed by SEM in back-scattering electrons mode (BSE) (Fig. 2). The size distribution and the shape of the grains are similar for both US and LSP samples. However, only the images of LSP samples show in many areas a network of parallel straight lines (bright lines in Fig. 2b) which cross the grains and which can extend into neighboring grains. High magnification views given in Fig. 2c and d show these bright lines near the grain boundaries. The in-depth hardness profile has shown that the plastic deformation of the treated samples is negligible, so these lines cannot be explained as dislocations induced by the LSP treatment. Similar lines were also observed in the cross-section SEM images of LSP treated pure

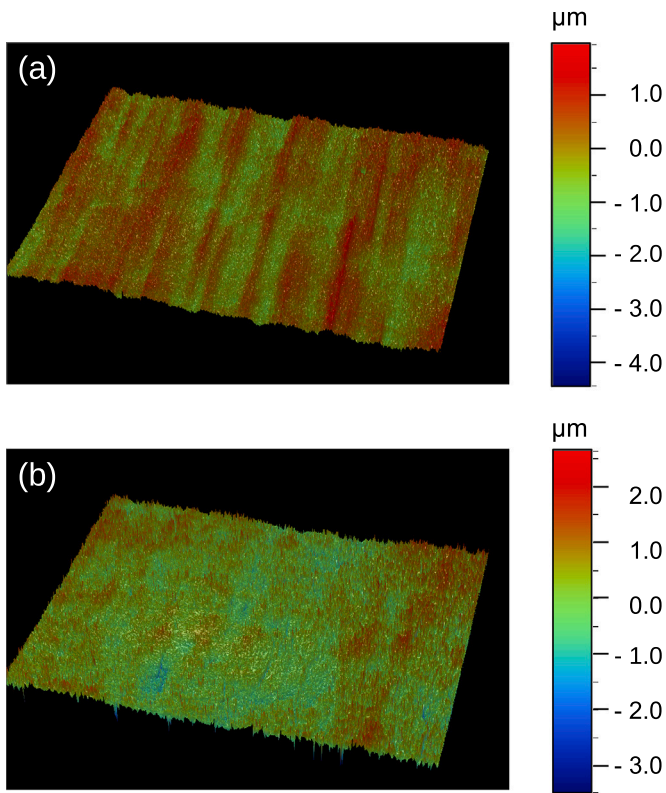


Fig. 1. Surface optical profilometry of Ti-Beta-21S samples before (a) and after (b) the LSP treatment.

α -Ti [12], and they were assigned to mainly compressive twins.

Fig. 3 displays the XRD patterns obtained with the beam incidence fixed at 2° for untreated and laser treated samples. The depth of the analyzed area was estimated around $1 \mu\text{m}$. The patterns of untreated samples show only the peaks of the β -Ti phase (ICSD: 0773482). For

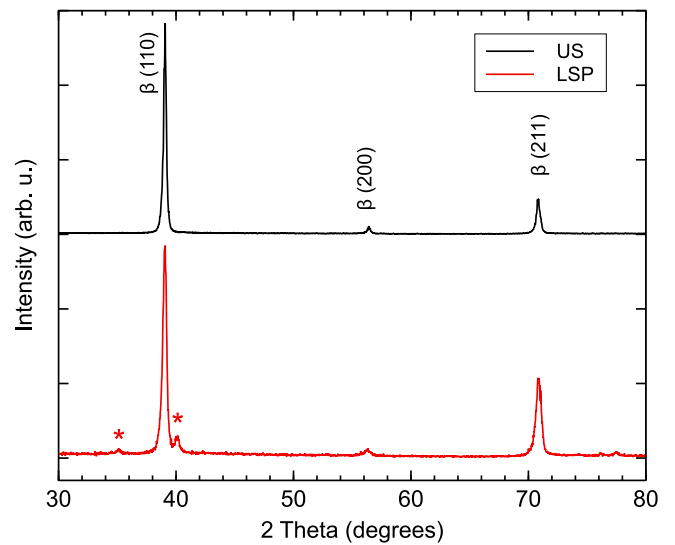


Fig. 3. Grazing incidence X-ray diffraction patterns (incidence angle: 2°) of untreated (US) and LSP treated samples. The peaks assigned to the β -Ti phase (ICSD: 0773482) are indicated. The intensity has been normalized to that of the β -Ti(100) reflection. The peaks tagged by stars (*) have been tentatively assigned to the martensitic α'' -Ti phase.

laser treated samples, the same diffraction peaks of the β -Ti phase are observed, but their absolute intensity is smaller, and they are slightly broader. These effects can be mainly attributed to the disorder induced by the treatment and/or a refinement of crystallites on the surface. Nonetheless, the relative intensity between matching peaks of the β -Ti phase is quite similar in the patterns of both samples. This means that the laser treatment does not result in a different texturing than that produced after rolling.

The XRD patterns of LSP samples display also two additional small peaks at 35.1 and 40.1° , which reveal the presence of a second phase formed as a consequence of the LSP treatment. The position of these

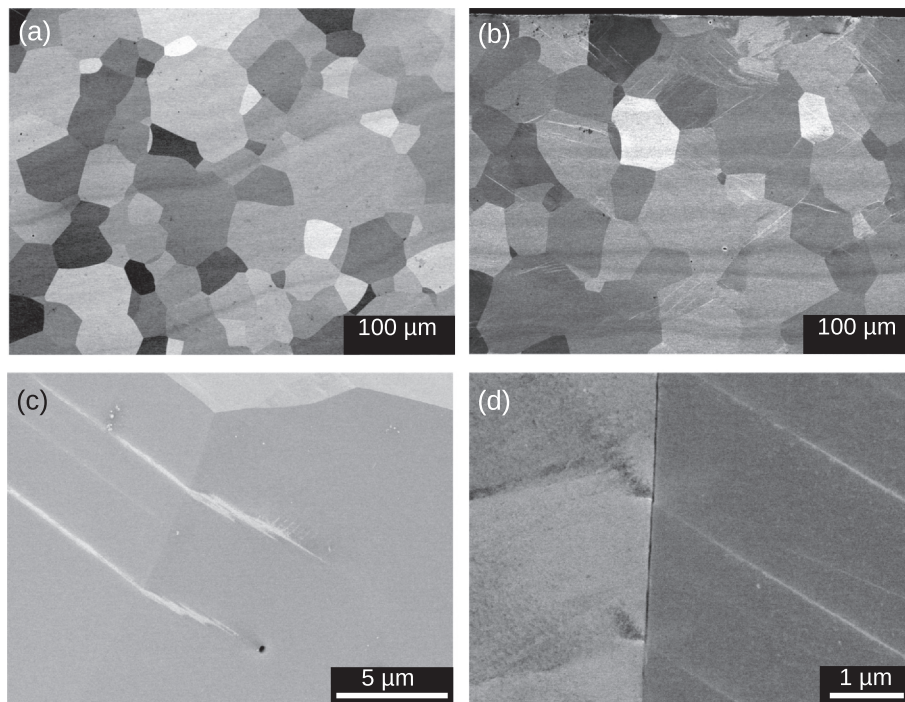


Fig. 2. Cross-section SEM views of (a) US and (b) LSP samples. The surface of the cross-sectioned sample is at the top of both images. (c, d) High magnification views of the grain boundaries taken in the cross section of the LSP sample.

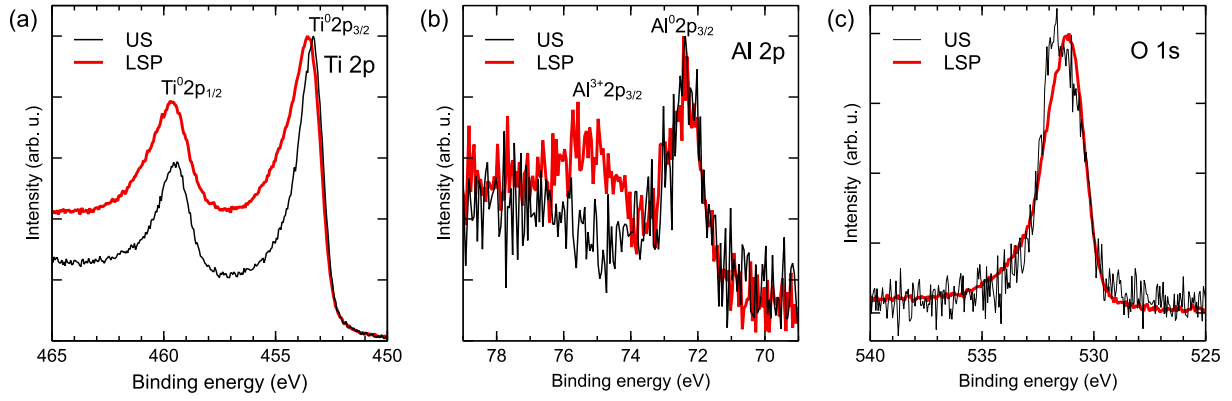


Fig. 4. XPS spectra of untreated (US) and laser treated samples (LSP) in the spectral ranges corresponding to the following XPS lines: (a) Ti2p, (b) Al2p and (c) O1s.

peaks is close to that given in Ref. [16] for the α -Ti phase formed in Ti-Beta-21S by oxidation at 650 °C during 50 h. However, the heating induced by the LSP treatment is too low to induce the $\beta \rightarrow \alpha$ phase transition. These small peaks at 35.1 and 40.1° could correspond to the martensitic α' -Ti phase which in general can be formed by deformation of β -Ti at room temperature [17–20]. Here, the formation of α' -Ti would be induced by the recoiled pressure of the laser-shock wave.

In order to investigate the chemical composition at the extreme surface, XPS analyses were conducted for US and LSP samples. The results are shown in Fig. 4 in the spectral ranges corresponding to the XPS lines Ti2p, Al2p and O1s. The spectra showing the XPS lines Mo3d, Mo3p and Nb3d are given in Fig. S3 (Supplementary Material).

For the US sample, Fig. 4a displays the characteristic spectrum of metallic titanium which shows the Ti $^{2+}$ 2p $_{3/2}$ and Ti $^{2+}$ 2p $_{1/2}$ lines at 453.7 and 459.8 eV, respectively [21]. The slight broadening of both peaks towards higher binding energies observed for LSP samples can be interpreted as due to a slight oxidation of the surface. As a reference, Ti $^{4+}$ 2p $_{3/2}$ line is given at 458.5 eV and Ti $^{4+}$ 2p $_{1/2}$ at 464.2 eV for TiO $_2$ [21].

For the Al2p line (Fig. 4b), the main peak corresponds for both samples to metallic aluminum, Al 0 2p $_{3/2}$ at 72.7 eV [22]. For the LSP sample, a small component at about 75.2 eV can be attributed to Al $^{3+}$ 2p $_{3/2}$ [22]. The XPS lines of molybdenum and niobium (Fig. S3) suggest also a slight surface oxidation of the LSP sample.

As regards oxygen, the shape of the O1s line (Fig. 4c) is slightly different for US and LSP samples. The O1s line corresponding to O–Ti bonds has been reported at about 530 eV, while that corresponding to O–Al bonds is at about 532 eV and that for O–Ti bonds at about 530 eV [22,23]. Compared to the US sample, the relative intensity of the contribution associated to Ti–O bonds is higher in the spectrum of LSP samples. This shows that the surface oxidation of LSP samples is slightly higher compared to US samples.

3.2. Kinetics of the high temperature oxidation

Fig. 5 shows the variation of the mass gain reported to the surface of the sample, $\Delta m/S$, in US and LSP samples for non-isothermal oxidation at 700 °C. The mass gain of LSP treated samples after exposure to high temperature for 3000 h is about 2.5 times smaller for laser-shock treated samples compared to untreated ones. So, the mass gain is about 60% smaller for laser-shock treated Ti-Beta-21S. This clearly demonstrates the benefits of the LSP treatment to increase the oxidation resistance of Ti-Beta-21S at 700 °C.

The analysis of the oxidation kinetics was done on the basis of the most-general expression of parabolic kinetics as proposed by Monceau and Pieraggi [24]:

$$t = a_0 + a_1(\Delta m/S) + a_2(\Delta m/S)^2 \quad (1)$$

where t is the time, Δm the mass intake, S the sample surface, and a_i

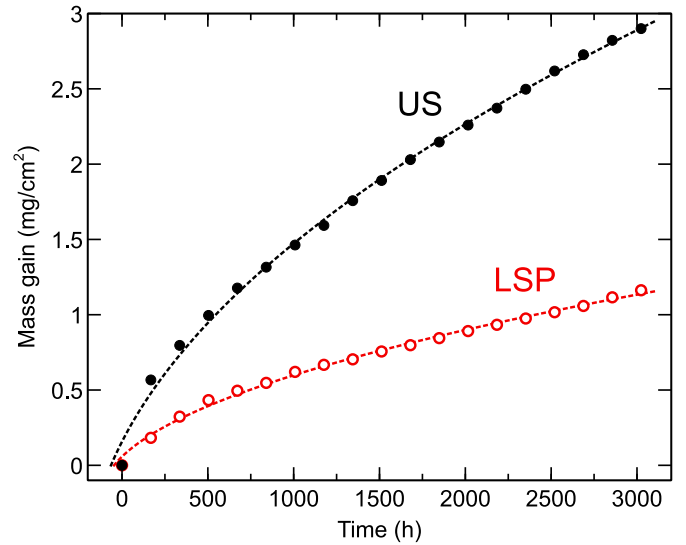


Fig. 5. Mass gain curves of US and LSP samples during oxidation at 700 °C under synthetic dry air. Dotted lines correspond to the fitting of the experimental data to Eq. (1) with the parameters given in Table 1.

($i=0,1,2$) the fitting coefficients. The reciprocal of a_2 is equal to the parabolic rate constant, k_p , which describes the effect of the diffusion processes on the mass intake. A parabolic law is associated to an effective protection of the metal against the oxidation provided by the oxidation scale, which grows with a continuing decreasing rate [25]. The reciprocal of a_1 is the linear rate constant, k_l , which together with the coefficient a_0 depends on the initial thickness of the oxide and the oxidation mechanisms involved in a transient period.

The experimental data were fitted to Eq. (1) in the 0–3000 h range. The fitting parameters are given in Table 1, together with the corresponding linear and the parabolic rate constants. The linear rate constant, k_l , is almost 2 times higher for the untreated Ti-Beta-21S compared to the laser treated alloy. The parabolic rate constant, k_p , is about 7 times higher for the US sample than for the LSP one.

3.3. Effects of high temperature exposure on the microstructure and the diffusion of alloying and light atmospheric elements

Fig. 6 shows the XRD patterns of US and LSP samples oxidized for 3000 h at 700 °C in dry air. The main phase observed for both samples is TiO $_2$ -Rutile. A small contribution of Al $_2$ O $_3$ -corundum can also be identified, mainly for the US-3000 h sample. This is in agreement with the results reported by Wallace et al. [26] and by Behera et al. [16] showing the formation of an alumina layer on the top of the rutile scale. Stringer et al. [27] also showed the formation of a small amount of

Table 1

Results of fitting the experimental oxidation curves (Fig. 5) to a complete parabola (Eq. (1)). The linear rate constant, k_l is the reciprocal of a_1 , and the parabolic rate constant, k_p is the reciprocal of a_2 .

Sample	a_0 (h^{-1})	a_1 ($\text{h} \cdot \text{g}^{-1} \cdot \text{cm}^2$)	a_2 ($\text{h} \cdot \text{g}^{-2} \cdot \text{cm}^4$)	k_l ($\text{s}^{-1} \cdot \text{g} \cdot \text{cm}^{-2}$)	k_p ($\text{s}^{-1} \cdot \text{g}^2 \cdot \text{cm}^{-4}$)
US	-64.3	371.7	238.3	7.47×10^{-10}	1.17×10^{-12}
LSP	-46.5	703.0	1751.1	3.9×10^{-10}	1.59×10^{-13}

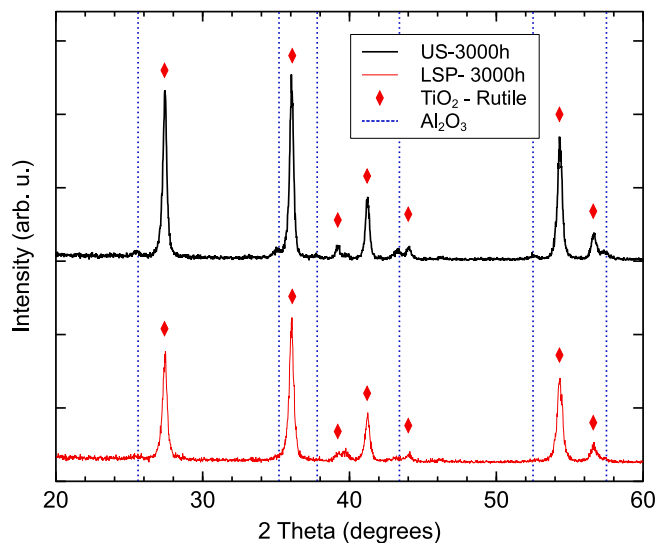


Fig. 6. Grazing incidence XRD patterns of untreated (US) and laser treated samples (LSP) after oxidation at 700 °C during 3000 h. ICDS number of the compounds and phases identified in the pattern: TiO₂-rutile: 070-7347, Al₂O₃ (corundum): 070-5679.

molybdenum oxide in the scale in the high temperature oxidation of a Ti-15% Mo alloy. However, the volatilization process of molybdenum oxide, MoO₃, at high temperature is well known [28]. Here, no diffraction peaks of MoO₃ or mixed oxides could be clearly identified.

Fig. 7 displays cross-section maps of oxidized US-3000 h and LSP-3000 h samples showing the spatial distribution of β -Ti (in green) and α -Ti (in red) phases obtained by EBSD study of both samples.

For the US-3000 h sample, the β -Ti phase is found in about 60% of the cross-section image, while 40% corresponds to α -Ti phase. For the LSP-3000 h sample, the percentage of β -Ti phase is higher, about 68%, while 32% corresponds to α -Ti phase. The ratio β -Ti/ α -Ti increases from 1.5 for US-3000 to 2.1 for LSP-3000 h, which shows that the LSP treatment acts to inhibit the $\beta \rightarrow \alpha$ phase transition.

Moreover, the distribution of the α -Ti phase is different in both samples. For the untreated sample, the α -Ti phase is mainly found in the grain boundaries which are broadened. For the LSP-3000 h sample, the α -Ti is not mainly formed in the grain boundaries, but inside the grains. For both samples, the percentage of α -Ti phase is higher near the surface (on top of both images in Fig. 7). In a range going from the surface to 30 μm in-depth, the percentage of α -Ti phase increases to about 53% for the SP-3000 h sample, while it is about 39% for the LSP-3000 h sample.

In order to investigate the segregation of the alloying elements due to high temperature exposure, SEM observations were coupled to EDS mapping of different elements. Cross-section SEM views and EDS maps showing the spatial distribution of Ti, Al and Mo are given in Fig. 8 for US and LSP samples.

After 3000 h at 700 °C, the thickness of the oxide scale has increased in both samples, but it is clearly thinner in the LSP sample than in the US one. For the US sample the thickness of the oxide scale is not homogeneous, it can vary from about 10 to 35 μm thick. In these latter zones the scale is stratified and then provides little protection against

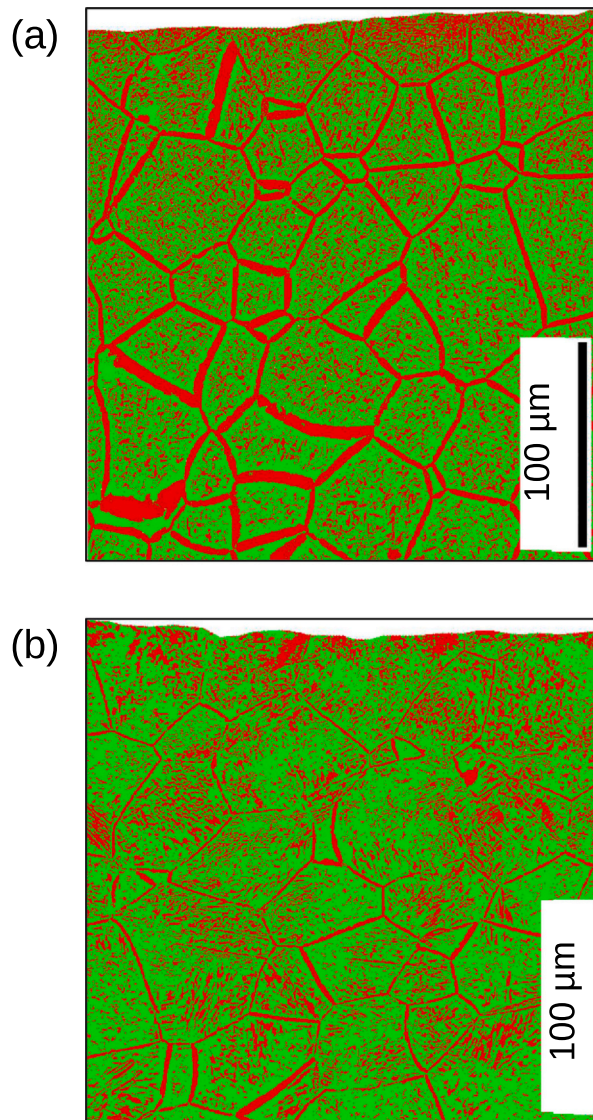


Fig. 7. EBSD results showing the spatial distribution of β -Ti (in green) and α -Ti (in red) phases in the cross section of (a) US-3000 h and (b) LSP-3000 h samples. The surface of the cross-sectioned sample is at the top of both images. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

oxidation. For the LSP sample, the oxide scale is quite homogeneous and only about 6 μm thick. It can provide an effective protection to the metal. Aluminum is clearly observed in a layer at the extreme outer surface of US and LSP samples. This agrees with XRD results, and supports the existence of a thin layer of alumina on top of the scale [16,26].

Underneath the oxide scale, Fig. 8 shows also a clear difference in the grain boundaries, which are quite broader for the US sample (about 2–5 μm thick) than for the LSP sample (about 1–2 μm thick). The spatial resolution of EDS is barely sufficient for the analysis of the grain

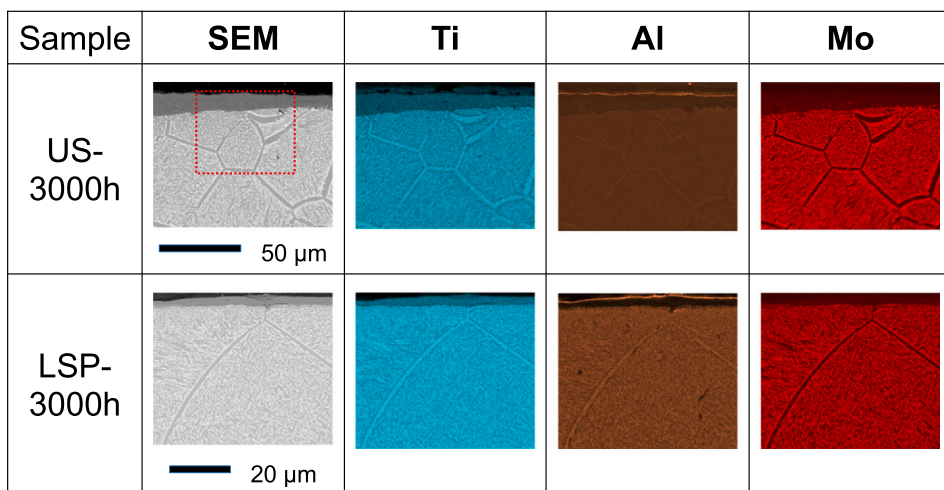


Fig. 8. Cross-section SEM views of US-3000 h and LSP-3000 h samples recorded in back-scattering electrons (BSE) configuration, and elemental EDS maps corresponding to the spatial distribution of titanium, aluminum and molybdenum. The surface of the cross-sectioned sample is at the top of the images. A higher magnification was used for the observations of the LSP-3000 h sample. For easier comparison, a dotted red rectangle of $60 \times 50 \mu\text{m}^2$ displays the size of the area analyzed for the LSP-3000 h sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

boundaries in LSP-3000 h, but it is suitable for their analysis in US-3000 h. The segregation between α - and β -stabilizing elements in the metal is clearly observed. At the grain boundaries, the concentration of aluminum is higher, whereas that of molybdenum is lower. This segregation of α - and β -stabilizing elements is also observed inside the grains.

The spatial distribution of light elements (oxygen and nitrogen) in the cross-section of these samples was also studied by EDS, but the overlap between the K_{α} lines of nitrogen and oxygen with the L_{α} and K_1 lines of titanium penalizes the accuracy of the results. Fig. S4 (Supplementary Material) displays the concentration profiles obtained for both metallic and non-metallic elements in this way.

To overcome this problem, ion-beam analysis techniques were used here to study the distribution of light elements in oxidized samples. Fig. 9 displays cross-section maps showing the spatial distribution of light elements (O and N) over $200 \times 200 \mu\text{m}$, as well as the distribution of metallic elements (Ti, Al and Mo) over $300 \times 300 \mu\text{m}$.

The spatial distribution of oxygen clearly shows the oxidation scale at the top of the images for both US-3000 h and LSP-3000 h samples, but its thickness is quite bigger for the untreated sample. Moreover, the spatial distribution of titanium shows the stratification of the oxidation layer in some areas (on the left in Fig. 9). Between two sublayers of the oxidation scale the Al-maps shows a higher concentration of aluminum, which reveals the formation of alumine Al_2O_3 on the top of the sublayers. A similar effect is not observed for molybdenum.

Under the oxide scale, the spatial distribution of Ti shows in Fig. 9 the grain boundaries in the metal, as it was previously observed in EDS maps (Fig. 8). Unfortunately, the low signal-to-noise ratio in aluminum and molybdenum maps prevents observing the segregation of these elements in the grain boundaries.

As regards the distribution of light elements under the oxide scale, Fig. 9 shows the diffusion of oxygen in the metal, which seems to be smaller in LSP treated samples than in untreated samples. To better study this effect, the variation in depth of the DIGE signal of oxygen has been plotted in Fig. 10 by using the experimental data of Fig. 9 for oxygen. For both US and LSP samples, the highest signal corresponds to the oxide scale. However, the low thickness of the scale (similar to the step in IBA maps) for the LSP-3000 h prevents obtaining the high intensity measured for the US-3000 h sample. Under the oxide scale, the signal of oxygen drastically falls down for both samples, but there are significant differences between both samples. For the treated sample, the signal of oxygen is very low and nearly constant in the analyzed range. For the untreated sample, the oxygen signal far deep from the oxide is slightly higher than for the treated sample, moreover, it is higher in a $20 \mu\text{m}$ thick strip under the oxide scale. It is worth to note the large thickness and the stratification of the oxide above this area.

The atomic concentration of oxygen as a function of the oxygen signal has been calculated by using the signal of the oxide scale as a reference corresponding to TiO_2 . The difference in the slowing of the incident beam of deuterons as a function of the TiO_x stoichiometry was

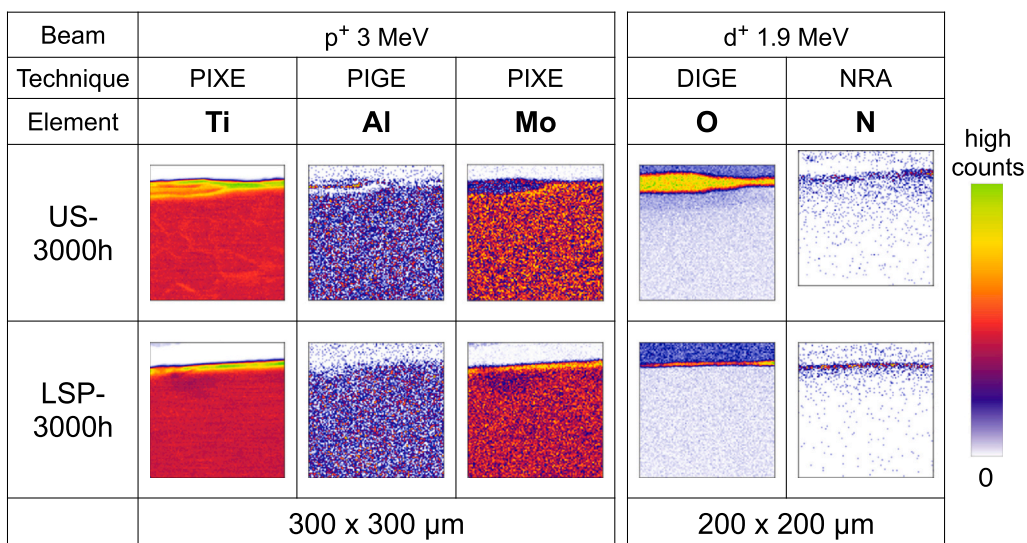


Fig. 9. Spatial distribution of different elements (Ti, Al, Mo, O and N) in the cross-section of US-3000 h and LSP-3000 h samples obtained by different ion-beam microanalysis techniques (see Section 2.3). The surface of the cross-sectioned sample is at the top of the images. The characteristics of the ion beam and the IBA technique used for detecting each element are also indicated.

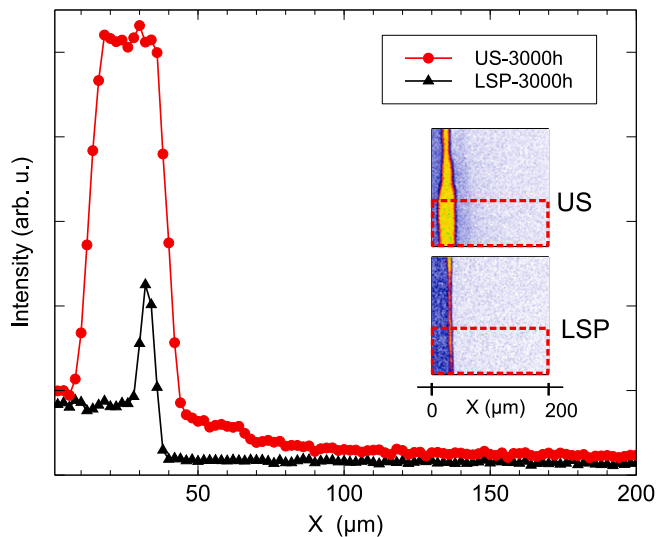


Fig. 10. Oxygen depth profile in the US-3000 h and LSP-3000 h samples. The intensity of the oxygen signal in the DIGE maps of Fig. 9 was summed at each depth X in the 40 μm large rectangles (red delimited domains in the image) to increase the S/N ratio, and plotted as a function of depth (X). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

addressed by using the Pyrole software [29]. Further details are given as Supplementary Material (Fig. S5). For the US-3000 h sample, the stoichiometry is about $\text{TiO}_{0.092}$ (8.4 at.% O) in a 20 μm thick strip under the oxide scale, but it decreases to $\text{TiO}_{0.012}$ (1.2 at.% O) 150 μm far in depth from the oxide scale. For the LSP-3000 h sample, the concentration of oxygen in the metal is smaller compared to US-300. It is negligible far in-depth in the metal, and it slightly increases up to about 0.5 at.% just under the oxide scale.

IBA experiments revealed the presence of nitrogen in the oxidized samples (Fig. 9). Nitrogen was clearly detected in both untreated and treated samples under the oxide scale, but its distribution is different. For the laser treated sample, nitrogen is located in a thin layer just under the oxide scale, while it spreads more in the metal for the untreated sample without forming a continuous layer under the oxide scale. The narrow in-depth spatial distribution of nitrogen and the low intensity of the NRA signal do not allow extracting an in-depth profile as done for the oxygen.

4. Discussion

The study of the HT oxidation resistance of untreated and laser treated Ti-Beta-21S at 700 °C during 3000 h has shown the beneficial effects of the laser treatment. They can be summarized as follows:

- The mass gain is reduced about 60% for non-isothermal oxidation during 3000 h.
- The oxidation scale is homogeneous and unstratified.
- The in-depth diffusion of oxygen in the alloy under the oxide scale is also reduced.
- The insertion of nitrogen in a thin and continuous layer at the interface between the oxide scale and the metal.
- The $\beta \rightarrow \alpha$ phase transition at high temperature is partially inhibited, even 200 μm under the sample surface.

The reasons explaining these changes in the HT oxidation behavior of laser treated Ti-Beta-21S should be sought in the changes induced by the laser treatment in the sample surface and also in-depth in the alloy. The changes at the sample surface concern mainly the topography of the sample. The LSP treatment flattens the roller marks due to the

lamination process of Ti-Beta-21S and slightly reduces the total roughness. It induces also a slight oxidation of the surface. The induced hardening is negligible. The surface modified in this way can promote the growth at high temperature of a more compact oxide scale compared to untreated samples. However, the changes induced in the surface cannot explain all the effects summarized above.

The in-depth effects induced by the LSP treatment must be related to the propagation of the shock-wave in the sample. The analysis of laser treated samples has shown a partial transformation of the β -Ti phase into the martensitic α' -Ti phase. We have related this effect with the observation in SEM cross-section observations of laser treated samples of a network of lines crossing the grains of β -Ti. Taking into account that the hardening induced by the treatment is negligible, these lines cannot be assigned to dislocations. The experimental conditions used here for the laser treatment lead to the formation of a plasma over the surface sample which extends over about 10 μs for each shot [10]. This plasma induces a pressure smaller than the yield strength of Ti-Beta-21S. The shock-wave propagates in-depth in the sample at around 5000 m/s and it can be reflected on the bottom sample surface 1.8 mm below. The interference between incident and reflected waves can induce shearing strains which can promote twinning. The lines observed in the cross section of LSP samples can be due to this effect. This explanation is supported by the presence of peaks assigned to the α' -Ti phase in the XRD pattern recorded for LSP samples before the oxidation experiments.

Different works [20,30–32] have studied the stress-induced martensitic transition (SIMT) of β -Ti alloys during deformation at room temperature. They have shown that in metastable β -Ti alloys with a low molybdenum equivalency (about 8.1 wt%), SIMT is the primary deformation mode. The start of yielding can correspond to the triggering of SIMT eventually followed by dislocation slip at a higher stress, but both effects can also operate simultaneously [30]. α' -Ti plates have been observed by SEM and TEM [30]. α' -Ti is mechanically twinned, and its substructure can influence the twinning in the β -Ti phase.

For Ti-Beta-21S, the molybdenum equivalency about 13 wt% is quite higher than the stability limit α -Ti + β -Ti / β -Ti about 10 wt%. The aluminum equivalency is low, about 5 wt%. The shock-laser treatment induces fast mechanical stress with very low heating. In these conditions, SIMT can appear without dislocation slip. The presence of α' -Ti could modify the β -Ti \rightarrow α -Ti phase transition at high temperature by reducing the diffusion of alpha-stabilizing aluminum towards the grain boundaries where the β -Ti \rightarrow α -Ti transition is mainly observed in untreated Ti-Beta-21S.

Oxygen is also an alpha-stabilizing element. As regards its in-depth diffusion from the sample surface and its spatial distribution in the cross-section maps, the results do not show a significant increase of the concentration in oxygen at the grain boundaries of oxidized untreated (US) samples, where the α -Ti phase is formed at high temperature. This suggests that the diffusion of oxygen does not occur preferentially following the grain boundaries, but it takes place in the grains. The in-depth diffusion of oxygen in the alloy is also reduced by the laser treatment. This could be explained by the insertion of nitrogen in a thin and continuous layer at the interface between the oxide scale and the metal shown by IBA experiments. This layer of nitrogen would reduce the diffusion of oxygen towards the metal. This effect has been previously reported for α -Ti [12].

5. Conclusions

This work shows the beneficial effect of a laser-shock peening (LSP) treatment on the high temperature oxidation resistance of the metastable β titanium alloy Ti-Beta-21S which has been studied for a long exposure time at 700 °C in dry air. After 3000 h, the mass gain in LSP treated samples is reduced by about 60% compared to untreated Ti-Beta-21S. The oxidation scale is thinner and more homogeneous for LSP treated samples compared to untreated specimens that present stratified

oxide scales. In both cases, the oxidation layer is mainly composed of rutile with a thin layer of alumina on top of the scale. Below the oxide, we have detected the insertion of nitrogen in a narrow strip. The concentration of nitrogen is higher in laser treated samples.

The LSP treatment modifies the topography of the surface of the samples by flattening the roller marks. It also induces a slight oxidation of the surface while the induced hardening is negligible. Beyond the surface, the impact of the LSP treatment on the microstructure was revealed in SEM cross-section views by the apparition of a network of lines crossing the grains of laser treated samples. This effect was assigned to a partial transformation of the β -phase into the martensitic α'' -phase detected by XRD.

The analysis of oxidized untreated and laser treated samples under the oxidation scale has shown that the LSP treatment partially inhibits the $\beta \rightarrow \alpha$ phase transition at the grain boundaries. It is mainly found for untreated samples together with the segregation of molybdenum and aluminum. For laser treated samples, the α -phase is formed mainly inside the grains. The following explanation has been proposed based on the martensitic transformation induced by the laser treatment: at high temperature the α'' phase transforms into the α which reduces the diffusion of aluminum towards the grain boundaries and of molybdenum towards the grains core.

The diffusion of oxygen in the metal is also smaller in laser treated samples. This is noteworthy to preserve the properties of Ti-Beta-21S under high temperature exposure. The compactness of the oxide scale and the insertion of nitrogen in a thin layer under the oxide scale, acting as a break to oxygen diffusion, could explain this behavior.

In summary, the surface treatment of Ti-Beta-21S alloy by laser-shock peening is a suitable method for extending its maximum application temperature in dry air.

CRediT authorship contribution statement

L. Lavisse: Conceptualization, Methodology, Investigation, Validation, Writing - review & editing, Project administration. **A. Kanjer:** Investigation, Formal analysis, Visualization. **P. Berger:** Investigation, Methodology, Formal analysis, Writing - review & editing. **V. Optasanu:** Conceptualization, Methodology, Validation, Writing - review & editing. **C. Gorny:** Resources, Investigation. **P. Peyre:** Resources, Validation, Supervision. **T. Montesin:** Validation, Supervision. **M.C. Marco de Lucas:** Conceptualization, Methodology, Investigation, Validation, Writing - review & editing, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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