Effect of mechanical surface treatments on the high temperature oxidation of pure titanium: the role of nitrogen

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Abstract

The mechanically treated high temperature (700°C) oxidation of commercially pure titanium was studied for long exposures (3000 h). The treatments studied here are the shot-peening and the laser-shock peening. The mass gain was measured by discontinued weighing. SEM and Raman imaging revealed strong differences between laser-shock peened, shot-peened and untreated oxidized samples. The laser treatment leads to thin compact and protective oxide layer while the shot-peened and untreated samples exhibit cracked oxide layers. The distribution of light elements like carbon, oxygen and nitrogen was revealed by Ion Beam Analysis. The presence of nitrogen located at the interface between the oxide scale and the metal was revealed on laser-shock peened samples. It is supposed the nitrogen slows-down the oxygen diffusion into the metal. The extent of the oxygen-enriched metal is also smaller on LSP samples, which improves the ductility of titanium.

1. Introduction

Titanium and titanium alloys have been widely used in aerospace industry for many years as material having light weight, high strength and excellent corrosion resistance up to 500°C (1) (2). The improvement of the oxidation resistance of titanium would allow its use in components operating at higher temperatures.

At high temperatures, the growth of an oxide scale on the surface of titanium is accompanied by inward diffusion of oxygen which leads to the formation of a hard and brittle oxygen enriched layer beneath the scale, known as "α-case" (3). In the case of oxidation in air, Coddet and Chaze (4) reported that the presence of atmospheric nitrogen can reduce the penetration of oxygen into the metal compared to oxidation in pure oxygen. However, they did not demonstrate the insertion of nitrogen by analytical techniques.

Many works have been devoted to the improvement of the mechanical properties of Ti alloys by mechanical surface treatments (5) (6) (7) (8) (9), but very few works have been focused on the high temperature (HT) oxidation behaviour. In particular, shot-peening treatments by SMAT (Surface Mechanical Attrition Technique) have shown their capability to improve the high temperature oxidation behaviour of zirconium (10). For titanium, Wen and al. showed that the SMAT treatment of grade 2 Titanium increased the diffusion of light elements (O, N, C) due to the high density of the diffusion paths (11) (12). As a consequence, the degradation of mechanical properties as resilience and ductility can be observed, which represents a major issue for the industrial applications.

Laser-shock peening treatments on titanium alloy TC11 have shown a higher fatigue resistance in NaCl conditions (13). Recently, Kanjer and al. studied the influence of shot-peening and laser-shock peening treatments on the high temperature resistance of pure titanium in dry air. The decrease of both the oxide scale thickness and the oxygen diffusion depth in LSP treated titanium plates was shown (14) (15) (16).

Here, we study the role of nitrogen in the high temperature oxidation of pure titanium previously treated by shot-peening (SP) and laser-shock peening (LSP). Thin plates of SP and LSP treated titanium were exposed to long duration (3000 h) exposures at 700 °C under synthetic dry air. The in-depth distribution of both oxygen and nitrogen in the oxidized samples was studied by ion beam analyses. The results obtained in this way are correlated here with those obtained by scanning electron microscopy, and micro-Raman spectroscopy in order to explain the benefits of the LSP treatment on the high temperature oxidation resistance of titanium.

2. Experimental

2.1. Material and mechanical treatments

Commercially pure titanium (grade 1, Goodfellow) plates ($8 \times 8 \times 1 mm^3$) were used for thermo-gravimetric analyses. Two kinds of mechanical treatments were used in this work: ultrasonic shot-peening (SP) and laser-shock peening (LSP). Experimental details on both kinds of treatments are given in previous papers (14) (15). For simplicity, shot-peened samples are named here SP, while laser-shock peened samples are named LSP in the following sections. Untreated samples (named further US) are also studied for comparison.

2.2. High temperature oxidation experiments

These samples were oxidized for long oxidation periods (3000 h) at 700 °C in air, using a SETNAG furnace. Weight mass gains were measured regularly. On the following, the duration of the oxidation process will be added to the sample name. For example, SP-3000h designates shot-peened samples oxidized during 3000 hours.

2.3. Characterization techniques

The cross-sections of oxidized samples were observed by SEM using a Tescan Vega 3 microscope in back-scattering electrons (BSE) mode. Moreover, the insertion of light elements (oxygen, nitrogen and carbon) in the metal was investigated by Ion Beam Analysis (IBA). In particular, nuclear reaction analysis (NRA) was used in scanning mode to obtain the spatial distribution of oxygen, nitrogen and carbon. The beam used here was deuterons with an energy of 0.92 MeV.

Raman spectra were obtained with an InVia Renishaw set-up working in backscattering configuration. The wavelength was 532 nm and the excitation power was about 0.5 mW to avoid heating the samples.

3. Results and discussion

3.1. Characterizations before high temperature oxidation

Cross-sections of US, SP and LSP samples were studied by SEM (Figure 1) before high temperatures oxidation experiments. In the case of the SP treatment, a huge density of twins appears under the sample surface. The mean grain size is difficult to be estimated since the grains are very fragmented. After the LSP treatment, the SEM images reveal the formation of quite a lower number of twins. The grain size distribution remains similar to that of the US sample.

Previous studies showed that the SP treatment induces contamination with WC particles coming from the shot-peening balls (14), whereas the LSP treatment preserves the surface chemically clean (15).
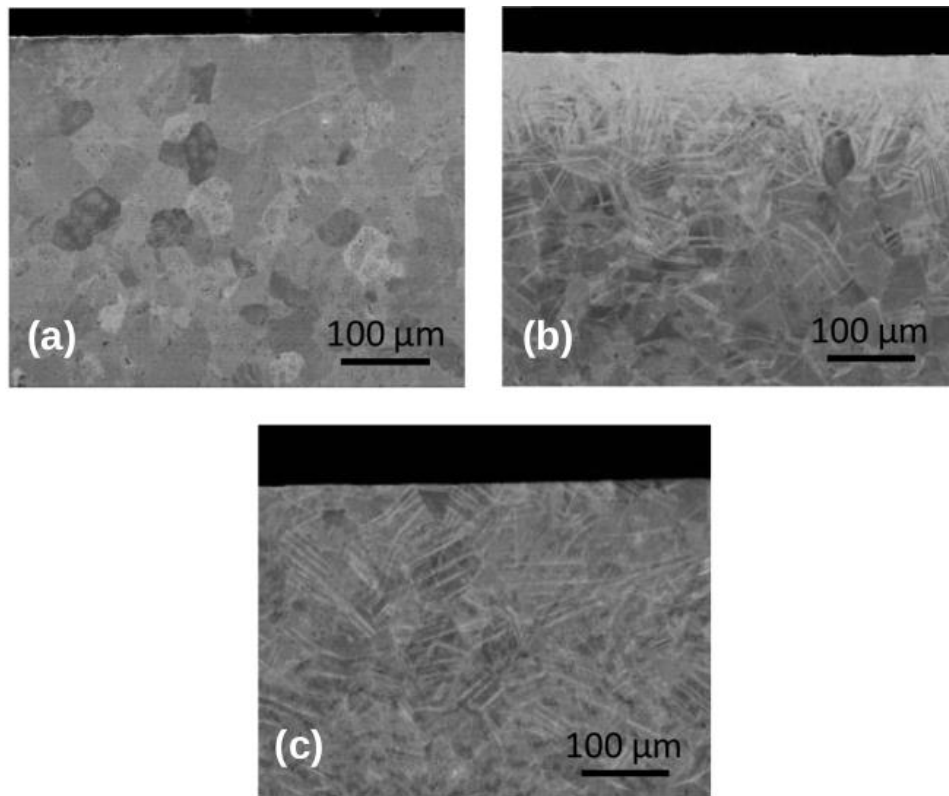
Figure 1 - Cross-section SEM images of (a) US, (b) SP and (c) LSP samples before exposition to high temperature.

3.2 High temperature oxidations

Figure 2 shows the mass gain for long oxidation tests, up to 3000 hours. Both SP-3000h and US-3000h show spallation of the oxide layer after 1700 hours. The SP treatment reduces the mass gain compared to untreated samples, but it does not provide enough oxidation protection. On the contrary, no spallation is observed for LSP samples Moreover, the mass gain can be fitted by a parabolic law, which can indicates that the oxide layer is dense and provides a protection to the metal.
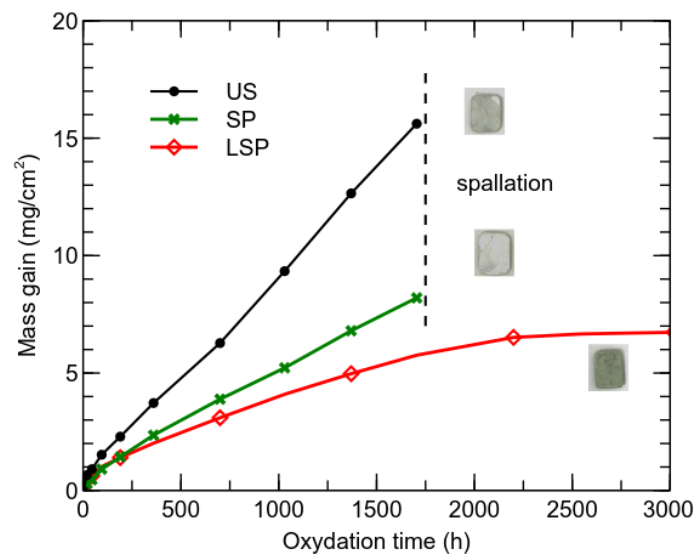
Figure 2- Mass gain as a function of the time up to 3000 h for US, SP and LSP samples at 700 °C under dry air.

Figure 3(a,b,c) displays cross-section SEM images of the three samples recorded in back-scattering electrons mode (BSE). The different effect of the SP and LSP treatments is clearly shown. Only the LSP-3000h sample displays a continuous, unstratified and adherent oxide layer about 40 μm thick. The other samples show stratification and spallation of the oxide scale.

Cross-section of US-3000h, SP-3000h and LSP-3000h samples were also analysed by Raman spectroscopy, which showed in the oxide scale only the peaks corresponding to the rutile phase of titanium dioxide. Figure 3(d,e,f) shows Raman maps of the three samples displaying the intensity of the peaks of rutile. For the US-3000h sample, the intensity of the rutile Raman peaks varies through the thickness of the oxide scale. It is lower in the outer part of the scale compared to that in the inner part, near to the substrate. The lower Raman intensity can be explained by a lower compactness of the outer part of the scale.

For the SP-3000h sample, the cross-section Raman image shows mainly the stratification and cracks of the oxide scale. This fact exhibits a lower adhesion of the oxide scale to the metal. On the contrary, the LSP-3000h displays homogeneous Raman intensity of rutile throughout the whole oxide scale.

The cross-sections of the three samples were also analysed by nuclear reaction analysis (NRA) in scanning mode in order to investigate the diffusion of oxygen and also nitrogen in the metal under the oxide layer. The energy of the deuteron beam was fixed at 0.92 MeV, which allows detecting the nuclear reactions of the ^{16}O isotope (17), but also those of the isotopes ^{14}N and ^{12}C. However, the cross-section of the nitrogen nuclear reactions is low within these experimental conditions. Figure 4 shows the NRA maps (300 x 400 μm^2) obtained for the isotopes ^{16}O, ^{12}C and ^{14}N in the cross-section of the samples US-3000h, SP-3000h and LSP-3000h. In these maps, the oxidation layer is in the top of the analysed area. So, only its lower part, near to the oxide/metal interface, is analysed. The signal of the nuclear reactions of oxygen is very high in this layer.

Under the oxide layer, Figure 4 shows the diffusion of oxygen in the metal for all the samples over several hundreds of micrometres in-depth. The LSP-3000h sample displays both the lowest quantity of oxygen dissolved in the metal and the lowest diffusion depth, while the SP-3000h shows the highest oxygen concentration and the highest diffusion depth. The insertion of oxygen into the metal core can be detrimental for the mechanical properties of titanium due to the decrease of its ductility.

At the interface between the oxide and the metal a narrow strip of carbon is visible mainly for US and SP samples. It can be due to contamination during the polishing process.

As expected, the intensity was very low, no significant signal of nitrogen is observed for US and SP samples. By contrast, a slightly strip of nitrogen can be observed at the interface oxide/metal for the LSP treated sample. This confirms the significant role of nitrogen in the high temperature oxidation process. The reasons explaining the formation of this nitrogen-enriched layer can be related to both the higher diffusion rate of nitrogen through the rutile phase of TiO$_2$ compared to oxygen and the lower diffusion rate of nitrogen in metallic titanium (4). At 700°C, the solubility of nitrogen in titanium is only about 8 % at. As a consequence, nitrogen atoms diffused through the oxide layer are retained on top of the metal which gives rise to a nitrogen-enriched layer. This layer could also reduce the mechanical stress generated by the growth of the oxide which leads to the spallation of the scale.

The absence of a similar insertion of nitrogen at the interface for US and SP samples can be explained by the stratification and the cracks of the oxide layer shown in Figure 3 for these samples. The formation of cracks allows a direct contact of the ambient air with the deepest parts of the oxide layer. So, they are exposed to large flow of oxygen. This promotes the diffusion of oxygen and can be a reason explaining the disappearance of nitrogen at the oxide-layer interface. Titanium monoxide and dioxide are thermodynamically more stable than titanium nitride at room temperatures, but also at 700 °C. The Gibbs free energy of formation is -780 kJ/mol for the rutile phase of TiO$_2$, -510 kJ/mol for TiO and -308 kJ/mol for TiN. This makes possible for oxygen to progressively replace nitrogen in a nitrogen-enriched layer that would be located at the metal-oxide interface. In the case of shot-peening treatment, as soon as cracks appear in the oxide layer, the presence of nitrogen in the scale decreases. Further work is in progress to study this behaviour.
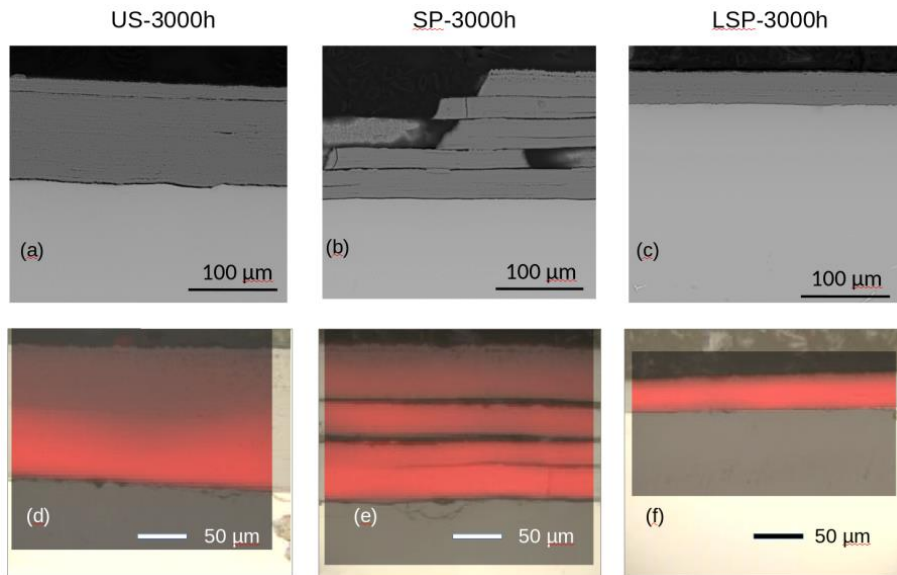
Figure 3 - Cross-section views of US, SP and LSP samples after oxidation at 700 °C during 3000 h. (a,b,c) SEM views obtained in BSE mode; (d,e,f) Optical micrographs (in the background) and Raman maps (darker areas in the foreground) displaying (in red) the integrated intensity of the bands of the rutile phase of TiO$_2$.
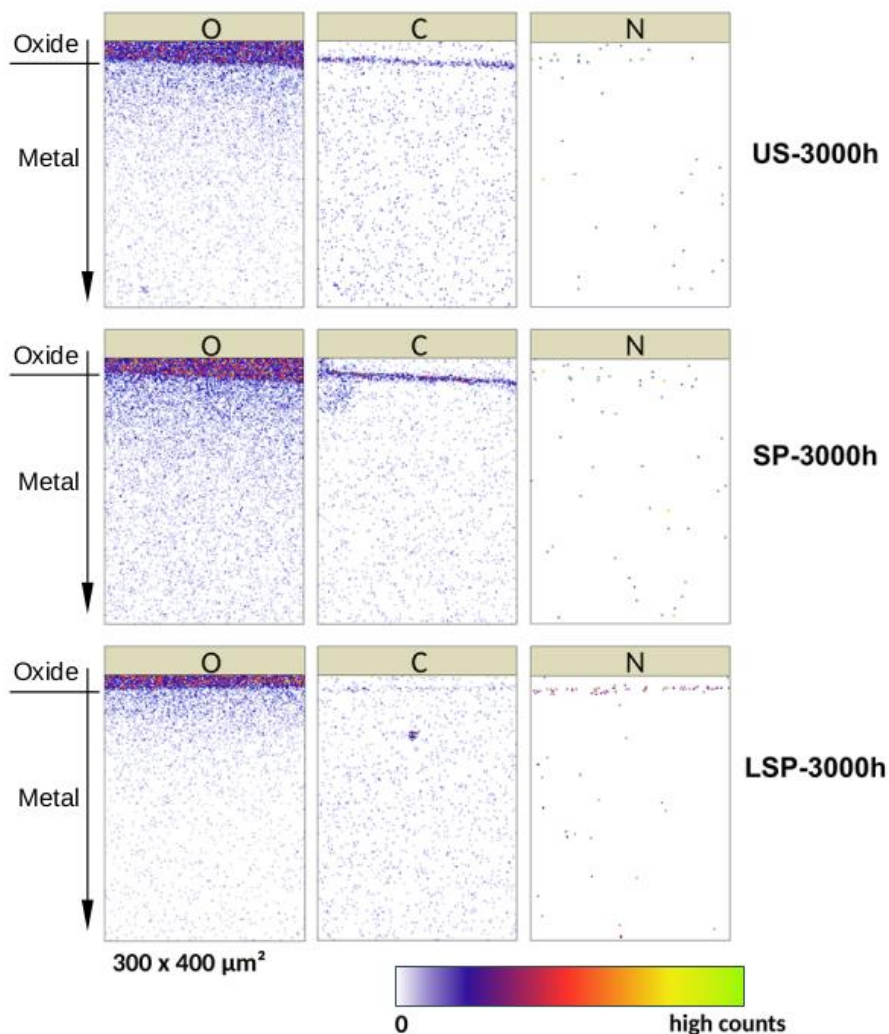
Figure 4: NRA maps (300 x 400 µm^2) displaying the spatial distribution of the isotopes ^{16}O, ^{12}C and ^{14}N in the cross-section of the samples US-3000h, SP-3000h and LSP-3000h.

4. Conclusion

The effect of two mechanical treatments, ultrasonic shot-peening and laser-shock peening, on the high temperature (700 °C) oxidation resistance in air of commercially pure titanium plates was studied here for long exposures (3000 h). The goal was to investigate the role of nitrogen in the high temperature oxidation process and how it explains the different oxidation behaviour depending on the mechanical treatment applied to the titanium plates.

Both mechanical treatments induced changes in the microstructure of titanium, mainly a huge density of twins in SP treated samples, while LSP treated samples display less twinning.

At 700 °C in air, untreated and SP treated samples showed the spallation of the oxide layer after about 1700 h. This was not observed in LSP samples for 3000 h exposure. The LSP treatment induced the formation of a dense, compact and adherent oxide scale, and subsequently it reduced the α-case extent, compared to shot-peening. This is a great advantage since the oxygen enrichment of the titanium is one of the most undesirable features when the ductility is an important parameter to be preserved.

Nuclear reaction analysis was used to investigate the insertion of oxygen, nitrogen and carbon in the metal under the oxidation layer. It was found that, in LSP treated samples, nitrogen is located in a thin layer at the interface between the oxide and the metal which is not observed in untreated and SP treated samples. This confirms the role of nitrogen in the slow-down of the oxidation process in LSP treated samples.

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