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Effect of Oxygen Concentration and Distribution on the Compression Properties on Titanium Foams**

By *Louis-Philippe Lefebvre* and *Eric Baril**

It is well known that interstitial solutes such as oxygen, nitrogen, carbon and hydrogen affect the mechanical properties of titanium and titanium alloys. The effect of different interstitial on the properties of bulk titanium has been reported in the literature.^[1] These interstitials reduce significantly the ductility of titanium and increase the yield strength, the hardness and to a lesser degree the elastic modulus. For example, R. A. Wood reported that the effect of 2 atoms of oxygen on the Vickers hardness of pure titanium was equivalent to that of 1 atom of nitrogen and 4 atoms of carbon.^[2] Similar trends were also observed on other properties (yield strength, ductility), where the effect of nitrogen was generally the most important, followed by oxygen and carbon.

The introduction of solute atoms into solid solution invariably produces an alloy which is stronger than the pure metal. If the solute atom diameter is less than 59% of the solvent one, the atoms occupy interstitial positions in the solvent lattice.^[3] The effect of interstitial solid solution solute atoms on the mechanical properties was initially demonstrated in 1924.^[4] The hardening effect was mainly attributed to difference in size of the solute and solvent atoms and the resulting change in lattice parameter. It was found that the correlation between hardening and lattice parameter change was even stronger when the relative valence of the atoms of the solute and solvent atom were considered. It was also observed that the entire stress-strain curve was affected by solute atom addition which led to the conclusion that those atoms influence the frictional resistance to dislocation motion. The interaction of dislocations with solute atoms is generally considered to be of three principal types: elastic (lattice distortion and elastic moduli difference of solute and solvent atoms), chemical (stacking fault, solute clustering, and breaking of chemical

bonds) and electrical.^[1] The elastic interaction is expected to be dominant in high stacking fault energy material such as α -titanium.

In the context of titanium, which has an atomic radius of 0.147 nm, if the solute atomic radius is less than 0.088 nm (e.g. H, N, O, C), the atoms occupy interstitial sites and have substantial solubility. Table 1 presents the atomic diameter of different interstitials, the volume expansion associated with their insertion in α -titanium as well as their maximum solubility and activation energy for diffusion in α -titanium.^[5] The solubility is inversely proportional to the volume expansion caused by the difference between the solute diameter and the interstice diameter (Tab. 1 and Fig. 1). Besides, the activation energy for the diffusion of the interstitial increases from carbon, nitrogen to oxygen, with values for oxygen and nitrogen approaching those for titanium self diffusion (50–57 Kcal/mole for oxygen and nitrogen in titanium compared to 60 Kcal/mole for Ti self diffusion).^[1]

Because of the strong influence of interstitial elements on the mechanical properties of titanium, chemical requirements have been established for different applications. For bulk titanium and titanium alloys, several standards have been developed. Since porous titanium coatings are commonly used in orthopedic applications, standards have also been developed to monitor and control their chemical composition (Tab. 2). Due to the high affinity of titanium for oxygen and the inevitable presence of oxygen in thermal processes of titanium, oxygen is an important element to monitor. The ASTM standard for porous coating for orthopedic implants states that the maximum oxygen content in the starting powder must be lower than 0.4 wt%. Since the production of the porous coating is generally done at high temperature where the reactivity of titanium is important and the diffusivity of oxygen is high, the oxygen content of the final coating is inevitable higher than that of the initial powder. However, the ASTM standard does not specify the oxygen content of the final coating.

Titanium reacts with oxygen to form an inert and adherent oxide layer on its surface. The oxide layer naturally formed at room temperature has generally a thickness between 2–7 nm.^[6] The oxide layer contains primarily TiO₂ that act as a diffusion barrier that provides the biocompatibility and the good corrosion resistance to titanium. The oxygen coming from the surface oxide can be a significant contributor to the total oxygen content if the material has high specific surface area and/or if the oxide layer is thick (Fig. 2). For example, a 7 nm thick oxide film on the surface of a porous titanium ma-

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Table 1. Interstitial solute diameter, volume expansion caused by the insertion of the solute elements in the Ti lattice, maximum solubility in α -titanium at room temperature and the activation energy for diffusion in α -titanium [1].

Element	Atomic Diameter	Volume expansion	Maximum solubility		Activation energy for diffusion
	nm		nm ³ per at.%	Atomic%	
O	0.12	0.00013	30	12.5	50
N	0.142	0.00018	19	6.4	57
C	0.154	0.00049	2	0.25	46

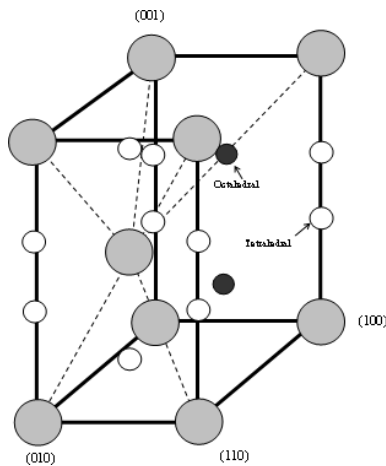


Fig. 1. Octahedral (0.122 nm) and tetrahedral sites (0.066 nm) in α -titanium.

terial having a specific surface area of 0.05 m²/g represents a 0.06 wt%O contribution to the total oxygen content of the material.

Due to the high solubility of oxygen in titanium, the oxide layer is generally dissolved at high temperature. Using high temperature microscopy, S.Malinov et al. presented the *in situ* formation of the oxide and its dissolution when titanium alloy specimens were treated at high temperature.^[7] After its dissolution, an oxide layer is re-formed on the titanium surface when exposed to oxygen at lower temperature, where oxygen diffusivity is low. Accordingly, the cycling between

Table 2. ASTM chemical requirement for titanium powder for coatings of surgical implants [6].

Element	Maximum Concentration wt.%
O	0.4
C	0.1
N	0.05
H	0.05

high and low temperature or between dissolution and reformation of the oxide layer inevitably lead to an increase of the total amount of oxygen in the material. This contribution can be particularly important with materials having high specific surface areas.

Beside the total amount of oxygen, its distribution has also a very important impact on the properties of the material. Indeed, the effect of oxygen in solution is very different from that of the oxygen coming from the oxide film on the surface of titanium. As state before, the oxygen in solution will have important effects on the mechanical properties (yield strength, ductility, fatigue, hardness, etc.), while the oxide layer will mostly affect the surface properties of the material (corrosion resistance, biocompatibility, surface energy, wetting, etc...). The effects of oxygen and surface oxidation on the properties of titanium foams are not well documented. This comes from the fact that titanium foams are relatively new materials and it remains difficult to precisely discriminate the amount of oxygen coming from the oxide from that in solution in the titanium matrix.

Analytical techniques generally used to determine the oxygen concentration (LECO analyzers, plasma ICP, fluorescence) do not allow the discrimination of the amount of oxygen coming from the solid solution and the surface oxide in foams. Accordingly, those techniques can only be used to determine the global oxygen concentration in the material. Besides, it is difficult to measure with good spatial resolution small concentrations of oxygen (smaller than 0.5 wt.%) using techniques such as X-Ray energy dispersive spectrometry (EDS) or wavelength dispersive spectroscopy (WDS) in microprobe. Hardness and X-Ray diffraction (i.e. lattice parameters calculation) can be used to determine the amount oxygen in solution. These techniques have been used with success on bulk titanium.^[8,9,10,11] For example, Brown et al. correlated the

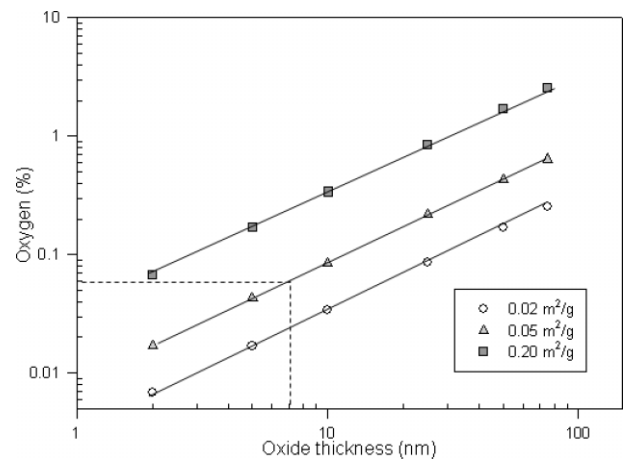


Fig. 2. Effect of oxide film thickness on the oxygen contribution for materials with different specific surface areas.

Brinnell hardness with the composition of 152 grades of titanium sponges.^[2] They obtained the following relationship:

$$\text{BHN} = 57 + 196\sqrt{\%N} + 158\sqrt{\%O} + \sqrt{\%C} + \sqrt{\%Fe} \quad (1)$$

The small cross section of the titanium phase (the cell walls or struts) in foams makes the measurement of the hardness more difficult and sensitive to factors such as the grain orientation, oxygen distribution, proximity to grain boundaries or to the metallographic mounting media. Accordingly, to be able to measure the hardness of the titanium matrix in the foams, small charges must be used to get indentations significantly smaller than the cell wall or strut thickness (few tens of microns). These factors reduce the precision of the measurements and the ability to correlate the hardness with the oxygen content.

It is difficult to determine statistically representative thickness of the oxide film on foams using standard analyzing techniques such as metallography (i.e. polished cross sections), transmission electron microscopy (TEM), Auger spectroscopy, X-ray photoelectron spectroscopy (XPS) or secondary ion mass spectroscopy (SIMS). Indeed, the oxide is very thin (generally much smaller than 100 nm), does not have a uniform thickness and covers irregular surfaces. Thus, the methods cited above do not have the spatial resolution, are too local to be statistically relevant or simply cannot be used on irregular surfaces.

Surface color can give an indication of the oxide thickness. However, this evaluation method is not precise and authors have reported different colors for oxide films having similar thicknesses.^[12,13] This is because the color of oxide films does not only depend on their thickness but also on their refraction index that is affected by their composition and structure.

This paper presents a simple method to discriminate the amount of oxygen coming from the oxide and from the solid solution in titanium foams. The effect of oxygen concentration and distribution on the mechanical properties (hardness, compression modulus, yield strength and ductility) is also presented and discussed.

Experimental

Small cylinders (diameter: 6.8 mm, length between 9 mm and 15 mm) of titanium foams were produced using the process described in Figure 3 and further described in.^[14] Plasma atomized CpTi spherical powder (−180 μm, 0.12 wt.% oxygen) was admixed with a polyethylene wax powder and a chemical foaming agent (*p,p'*-oxybis[benzenesulfonyl hydrazide]). The resulting powder mixture was transferred into a mold and foamed at 210 °C in air. The resulting material was debinded at 450 °C in Ar and sintered 1 h at 1400 °C under vacuum (10^{−5}–10^{−6} Torr range).

Foams containing different oxygen content were produced by heat treating the specimens in an Ar-20%O₂ atmosphere

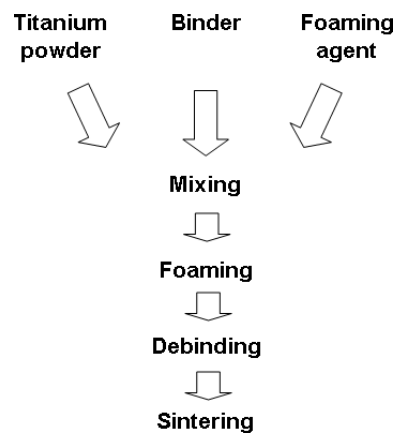


Fig. 3. Schematic description of the process (further described in [15]).

for 1 h at different temperatures (300 to 450 °C). Some of the oxidized foams obtained were solutionized at 1000 °C under vacuum (10^{−5}–10^{−6} Torr range) to dissolve the oxide layer and increase the oxygen content in solution in the titanium matrix.

The density of the specimens was evaluated using the weight (Ohaus, Explorer, 210 g ± 0.1 mg) and physical dimensions of the cylinders. Specimens were observed using JEOL 6300 scanning electron microscope (SEM) and Hitachi S-4700 field-emission gun scanning electron microscope (FEG-SEM) and a X-Tek HMXST 225 X-ray microtomograph (μCT). The specific surface area was evaluated by gas adsorption (BET) using a Micrometrics ASAP 2010 system with krypton as adsorbate. The oxygen was evaluated by inert gas fusion techniques using a LECO TCH-600 analyzer. Microhardness were measured with a Buehler Micromet II microhardness tester (10 gf for 15 sec) equipped with a Clemex CMT image analysis system. Compression tests were done on a MTS 100 kN testing machine using a crosshead speed of 1.25 mm/min. Unloadings were done to monitor the evolution of the elastic modulus during compression.

To evaluate the thickness of the oxide layer and the amount of oxygen coming from the oxide, the sintered specimens were exposed to a series of cycles between dissolution and oxide formation. The samples were exposed to a heat treatment (1 h at 1000 °C under vacuum) to dissolve the oxide film and bring the oxygen into solution in titanium. This heat treatment will be further called solutionizing treatment. Then, the samples were exposed to air at room temperature. The amount of oxygen coming from the formation of the new oxide film from the exposure to air was measured using the sample weight and oxygen content increase after each cycle. The weights were measured on all specimens after all cycles, starting with 6 specimens for the 1st cycle and ending with one after the 6th cycle. The composition was evaluated on only one specimen after the different cycles (3 measurements per specimen). Knowing the surface area of the foam, it was possible to determine the thickness of the oxide film formed after each cycle.

Results

Characterization of the As-Produced Foams

The structure of the as-produced titanium foam (i.e. after the sintering and before oxidation treatment) is presented in Figure 4. The porosity is 49% and the pores are typically between 50 and 400 μm . The porosity is open and the material is permeable. The foam has high specific surface area (evaluated to 0.05 m^2/g by BET). The high surface area is associated with the powder metallurgy process used. During sintering at high temperature under vacuum, thermal etching occurs and reveals the crystallographic planes of the titanium crystals. This thermal etching generates the fine submicronic features observed on the surface of the titanium foam (Fig. 5(c)) and also contributes to the high surface area of the material.

Evaluation of the Oxide Thickness

Figure 6 presents the oxygen content increase as a function of the number of solutionizing treatment cycles. The correlation between the weight pick-up and the number of cycles is

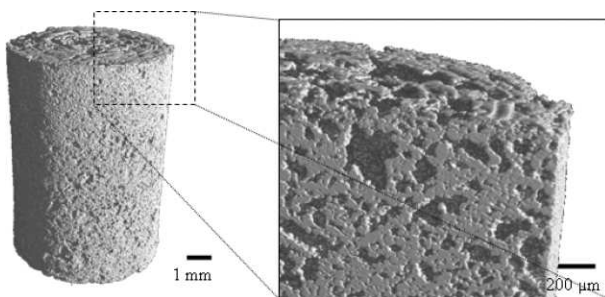


Fig. 4. μCT scan of the titanium foam.

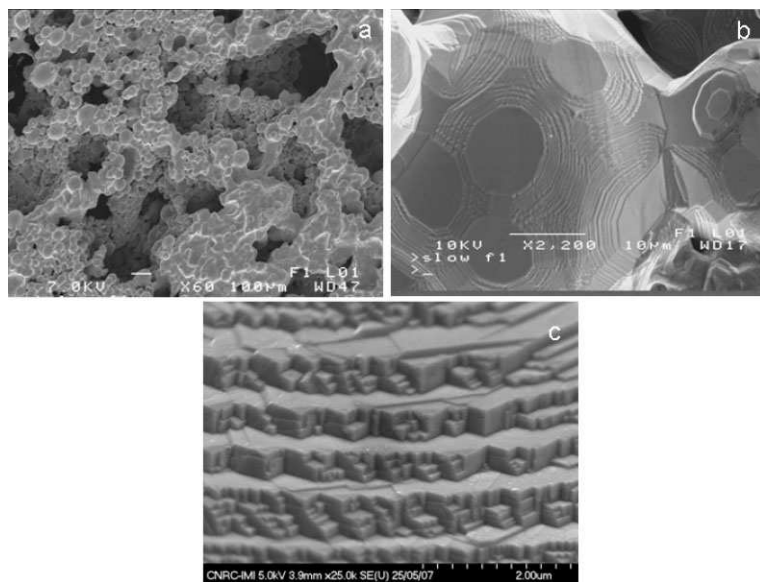


Fig. 5. SEM micrographs of the surface of the titanium foam at a) low b) medium and c) high magnifications.

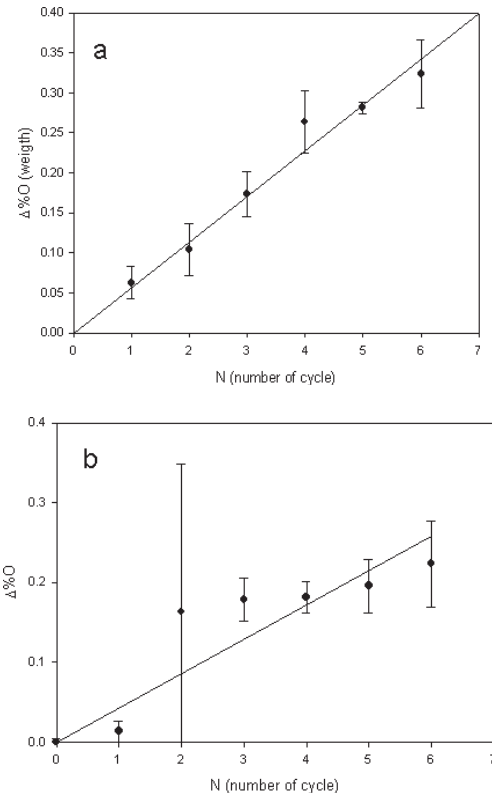


Fig. 6. Oxygen pick-up measured using a) weigh gain and b) total oxygen content measured with LECO instrument as a function of the number of solutionizing treatments at 1000 °C under vacuum (10^{-5} – 10^{-6} Torr range).

excellent and the weight pick-up is constant at each cycle. This suggests that the thickness of the oxide layer film formed in a reproducible way at the end of the solutionizing treatment and the associated oxygen pick-up is constant for each cycle. A similar trend is observed with the oxygen analysis (Fig. 6(b)). However, the later correlation is not as good due to statistical reasons and some analytical bias related to the calibration standards. Improved calibration procedure and more oxygen analysis per cycle would be required to improve these measurements.

To evaluate the amount of oxygen pick-up from the furnace atmosphere during the solutionizing treatment, a specimen was exposed at 1000 °C for 8 h. The oxygen pick-up was similar to that of the specimens treated only 1 h at 1000 °C. This indicates that the oxygen pick-up at 1000 °C was minimal and the weight pick-up mostly came from the formation of the new oxide film on the fresh titanium surface when exposed to air, at room temperature, after the solutionizing treatment. Based on these observations, we can conclude that under the conditions used in the present study, the oxygen pick-up during the solutionizing treatments only came from the formation of the new oxide film at the end of the solutionizing treatments and the weight increase measured represents the amount of oxygen in the

newly formed oxide film. The nature, composition and thickness of the film should be similar to the one formed after sintering since its formation occurs under similar conditions (exposure to air at room temperature).

From Figure 6(a), the oxygen pick-up per cycle associated with the formation of the oxide film in air after the solutionizing heat treatment is 0.06 wt%O. For the as sintered specimens having a 0.05 m²/g surface area, this amount of oxygen corresponds to a 5 nm thick oxide film on the surface of the foam (see Fig. 2). This thickness corresponds to the typical thickness of an oxide film naturally formed at room temperature (i.e. 2–7 nm) and confirms that the oxide was mostly formed at low temperature when the vacuum furnace was opened to air at the end of the treatment.^[7]

Since the specific surface area of the foam is high, the contribution of this thin oxide film is significant and must be extracted from the global oxygen content of the foam to determine the contribution of the oxygen in solution. In the present study, the amount of oxygen in solution in titanium foams was determined by subtracting the surface contribution as calculated in Figure 6 (0.06 wt%O) to the total amount of oxygen determined using inert gas fusion techniques. For the as-sintered foams, the total oxygen content was 0.30 wt%O (LECO) and, therefore, the oxygen in solution is 0.24 wt%. Table 3 resumes the characteristics of the as-produced titanium foams characterized in this study before oxidation and solutionizing treatments.

Characterization of the Foams after Oxidation

Figure 7 shows the oxygen concentration measured with the LECO analyzer on the foams treated at different temperatures. After the oxidation treatments for 1 h in Ar-20%O₂, the foams had different colors, from yellow to light blue-green (Fig. 8). The same surface coloration was apparent in the inner pore surfaces of the foam sample confirming a relatively uniform oxidation throughout the specimens. The modification of the color is attributed to a modification of the oxide thickness. While before the oxidation treatment, the oxide film was very thin and was not clearly visible on the surfaces observed with SEM (Fig. 5), a thick oxide film was clearly visible after the oxidation treatment at 450 °C (Fig. 9). After

Table 3. Properties of the as-produced titanium foams.

Density	51%th. density
Porosity	Open
Surface Area	0.05 m ² /g
Total oxygen	0.30 wt%
Surface oxide contribution	0.06 wt%
Oxide thickness	5 nm
Oxygen in solution	0.24%

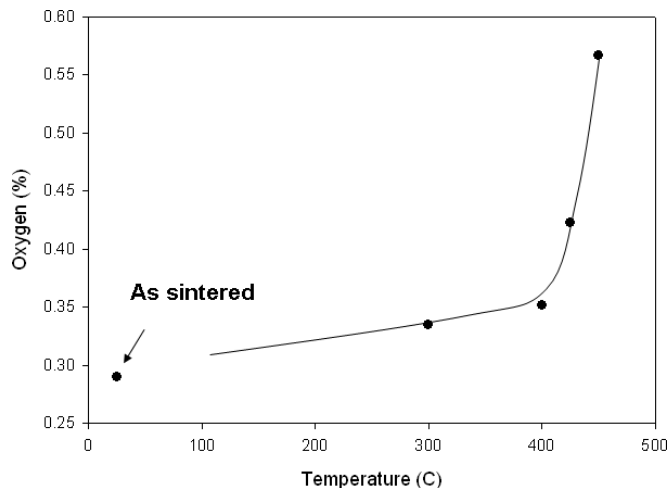


Fig. 7. Total oxygen concentration after the oxidation treatment at different temperatures for 1 h in Ar-20%O₂ atmosphere.



Fig. 8. Specimens after the different oxidation treatments for 1 h in Ar-20%O₂ atmosphere at temperatures ranging from 300 to 450 °C (color: silver, golden, dark purple, blue, light blue-green).

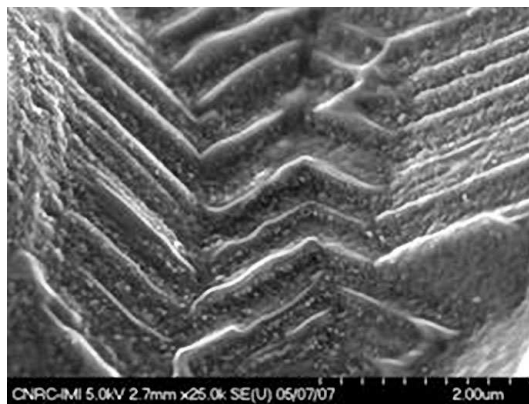


Fig. 9. High magnification SEM micrograph of the surface of a foam oxidized at 450 °C.

the treatment at 450 °C, the oxygen pick-up of 0.27 wt% corresponds to a 30 nm thickness increase of the film on the surface of the foam. This value represents the average thickness and important variations of the thickness have been observed. Indeed, oxide films of approximately 75 nm thick were observed at some locations (Fig. 10(c)). When this average increase in oxide thickness is added to the initial oxide

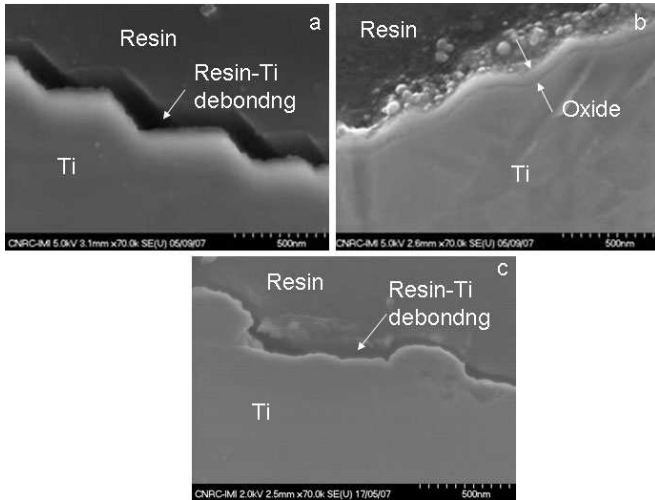


Fig. 10. High magnification SEM micrographs showing the surface of the foam on polished cross sections a) as produced specimens, b) after oxidation at 450 °C and c) after oxidation and solutionizing treatments.

thickness of the oxide (i.e. 5 nm), the average total thickness of the oxide film is 35 nm and the amount of oxygen coming from this oxide layer represents 0.33 wt%O after the treatment at 450 °C.

Microhardness measurements were done to determine the extent of the oxygen diffusion in titanium after the different oxidation treatments (Fig. 11). The microhardness does not increase with the oxygen content after oxidation. This result confirms that limited amount of oxygen diffused in titanium during the oxidation treatment and most of the oxygen pick-up was coming from the increase of the oxide thickness.

Characterization of the Foams After Oxidation and Solutionizing Treatment

After solutionizing treatment at 1000 °C, the specimen color returned to the same gray color as the as-produced foam

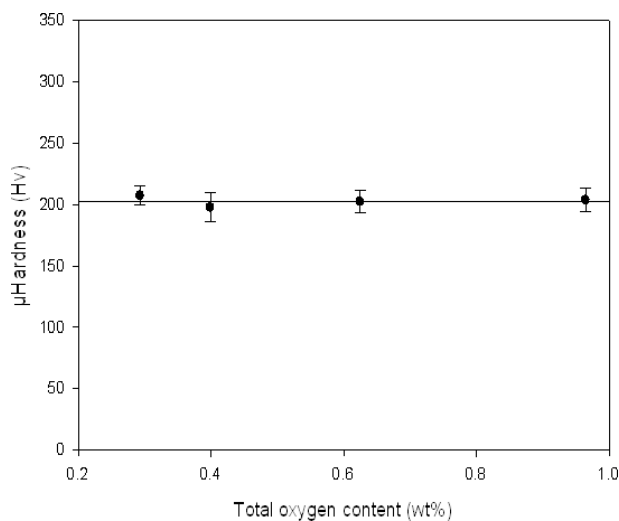


Fig. 11. Effect of the total oxygen content on the microhardness (after oxidation treatments).

and the oxide film was no longer visible on the specimen cross sections (Fig. 10(c)). The oxide film was dissolved during the solutionizing treatment at 1000 °C and the oxygen went into solution in the matrix. After air exposure at room temperature, the surface was re-oxidized with a very thin oxide film, not visible on the cross sections (Fig. 10(c)). As state before, the oxygen concentration slightly increased after the solutionizing treatments due to the formation of this new oxide film on the surface of the foam after air exposure.

After the solutionizing treatment, the microhardness increased with the increased total amount of oxygen in the specimens (Fig. 12). Other researchers demonstrated that the hardness increases with the amount of oxygen content in solution.^[2,10–12] The trend is similar to that reported by Wood and the results confirmed that the oxide was dissolved during the solutionizing treatment and the oxygen went into solution.^[2]

Figure 13 schematizes the distribution of oxygen in the titanium foam after the different treatments. The initial titanium foam has 0.30 wt%O total (0.24 wt%O in solution and 0.06 wt%O in the 5 nm thick oxide film). During oxidation,

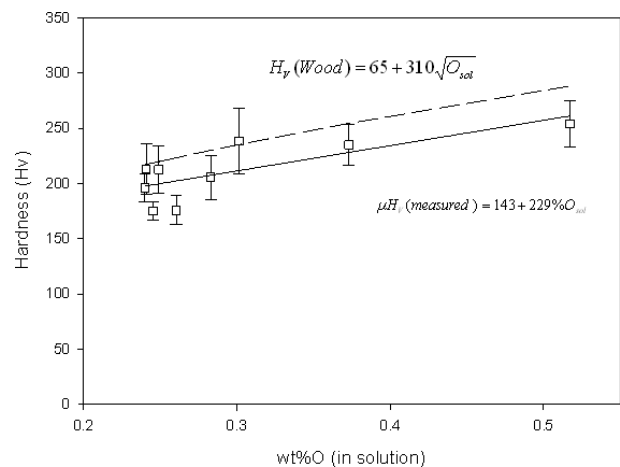


Fig. 12. Variation of the hardness as a function of oxygen in solution after the solutionizing treatment at 1000 °C under vacuum (μhardness measured on the foams and values obtained with Wood model for Vickers hardness).

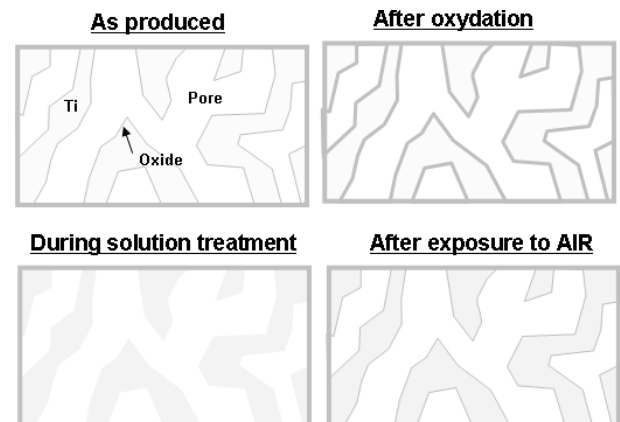


Fig. 13. Schematic representation of the oxygen distribution in the foams after the different treatments.

the oxide grows up and insignificant amount of oxygen goes into solution. For example, for the 450 °C oxidation treatment, the total amount of oxygen increases to 0.57 wt% and the oxide layer thickness grows up to approximately 35 nm. During the solutionizing treatment at 1000 °C, the oxide film is dissolved and the oxygen goes into solution. After the solutionizing treatment, a new oxide layer is formed when the foam is exposed to air. This oxide film contributes to 0.06 wt%O increase in the foam despite its small thickness (~ 5 nm).

Effect of Oxygen and Oxygen Distribution on the Mechanical Properties

Figure 14 presents the compression behavior of the foams before and after the oxidation and solutionizing treatments. A series of unloading was done at every 2.5% of deformation to follow up the elastic modulus as a function of the plastic deformation. For all specimens, a smooth curve was obtained suggesting a ductile behavior. However, observation of the specimens after compression showed that deformation behaviors were very different. While the specimens containing low level of oxygen in solution were plastically deformed, the specimens containing large amount of oxygen in solution showed brittle fractures and were disintegrated at the end of the tests (Fig. 14).

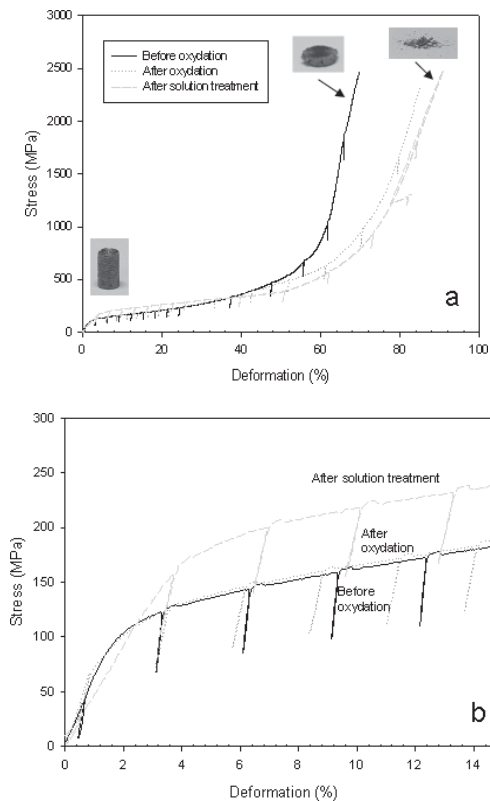


Fig. 14. Compressive behavior of foams as-sintered (before), after an oxidation treatment at 450 °C in Ar-20%O and after an oxidation treatment at 450 °C in Ar-20%O and solutionizing treatment at 1000 °C under vacuum a) full curve and b) zoom on the initial portion of the curve.

Figure 15 presents the evolution of the compression modulus as a function of the deformation for foams having different amounts of oxygen in solution. The general trend observed is that the modulus increases with deformation due to the densification of the material and its consolidation. However, the amount of oxygen does not seem to have a significant impact on the evolution of the modulus. The variations observed are within the variability of the results (precision on those measurements were not very good due to the small elastic recovery measured during the unloading). Oxygen can have an impact on the elastic modulus but, as reported by Conrad, such effect should only be seen with larger range of oxygen content variations.^[1]

The effect of the oxidation and solutionizing treatments on the initial portion of the compression curve can be seen in Figure 14(b) for sintered specimens, specimens oxidized at 450 °C and specimens oxidized at 450 °C and solutionized at 1000 °C. The compressive yield strength remains the same after the oxidation treatment while it increases significantly after the solutionizing treatment. After the oxidation treatment, the oxide layer contributes significantly to the oxygen concentration of the foams but has little impact on the yield strength. After the solutionizing treatment, the oxygen is approximately the same than after oxidation but is mostly in solution and influences the yield strength significantly.

Figure 16 resumes the effect of oxygen on the yield strength of titanium foams containing different amount of oxygen, before and after the solutionizing treatment. In the oxidized state, the difference of oxygen concentration mainly comes from the differences in the oxide layer thickness and the oxide thickness has little impact on the yield strength. On the other hand, after the solutionizing treatment, the difference of oxygen concentration mostly comes from differences of oxygen concentration in solid solution and it has an important impact on the yield strength of the foams. Indeed, the yield strength is increased by more than 50% when the oxygen content in solution increases from 0.24 wt% to 0.51 wt%.

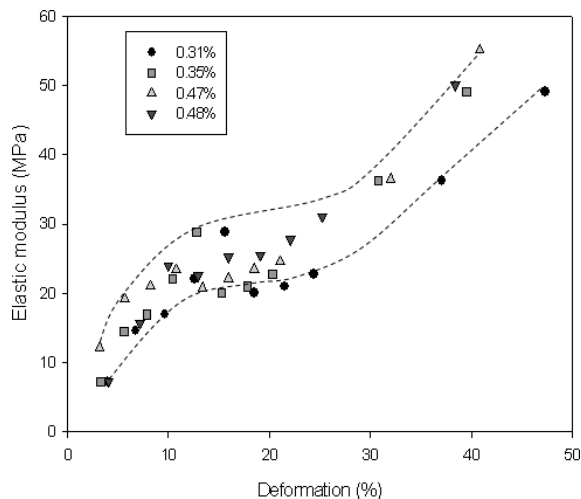


Fig. 15. Variation of the elastic modulus as a function of the deformation for foams having different oxygen content in solution.

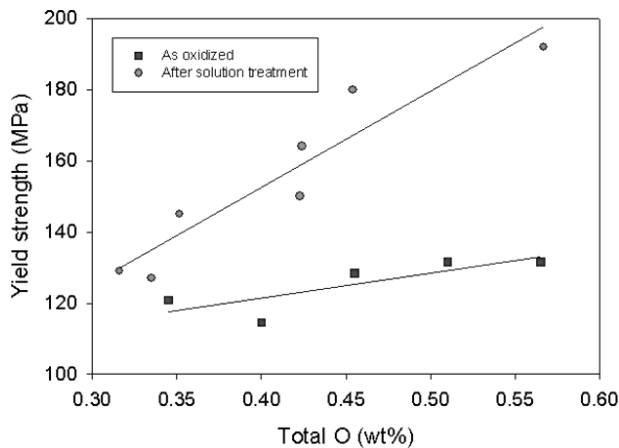


Fig. 16. Effect of oxygen on the compressive yield strength before and after the solutionizing treatments for foams oxidized at different temperatures.

Figure 17 shows SEM micrographs of the fracture surface of the foams after compression. Since the specimens containing 0.24 wt% O in solution did not break during compression, a fracture surface was obtained by manually breaking the remaining specimens by flexion with pliers. The effect of the oxygen content on the rupture mechanisms is clearly visible. The specimen containing 0.24 wt% O in solution shows ductile rupture surface while the foam containing high oxygen content (i.e. 0.51 wt% O in solution) presents brittle cleavage-type rupture surface.

Conclusion

Titanium foams were produced with a powder metallurgy process. Foams with 0.30 wt% total O were produced. The

evaluation of the distribution of the oxygen using cyclic solutionizing treatments showed that after sintering, the amount of oxygen coming from the oxide film was 0.06 wt% O with a thickness of approximately 5 nm. The resulting amount of oxygen in solid solution was 0.24 wt% O. During the oxidation treatments in Ar-20% O atmosphere, the thickness of the oxide layer increased significantly (up to 35 nm) but the amount of oxygen in solid solution remained unchanged. When these oxidized specimens were treated at 1000 °C under vacuum, the oxide layer was dissolved and the oxygen went into solid solution. After the solutionizing treatment, a new oxide layer, similar to the one formed after sintering, was formed and increased the total amount of oxygen in the specimens.

The thermo-processing of titanium powder and/or foams leads to an increase of the oxygen content in the material. Accordingly, the amount of oxygen in foams produced with powders can be significantly larger than that of the original powder used. Since the oxygen pick-up mostly comes from the surface of the material, the specific surface area does have an impact on the oxygen pick-up during the thermo-processing of titanium. The contribution of the oxide film on the total amount of oxygen can be important in materials with large surface area.

The oxygen content and distribution does have an impact on the compressive properties of titanium foams. Indeed, the yield strength and ductility are significantly affected when the oxygen in solution increases from 0.24 to 0.51 wt%. Besides, the contribution of the surface oxide on the compression properties is minimal. Since the amount of oxygen and its distribution have an impact on the mechanical properties of titanium foam, they are important characteristics to monitor. It is important to discriminate the amount of oxygen coming from the solid solution from that of the oxide layer.

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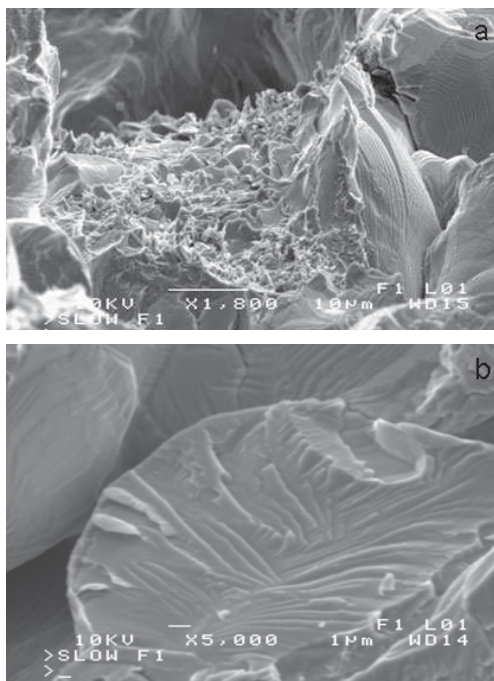


Fig. 17. SEM micrographs of the fracture surface of foams with a) 0.24 wt% O and b) 0.51 wt% O in solution.

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