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Effect of Oxygen Content and Distribution on the Compression Properties of Titanium Foams

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ABSTRACT

The effect of interstitials (mainly oxygen, nitrogen, carbon) on the mechanical properties of dense titanium and titanium based alloys is well documented. Their effects on the yield stress and the deformation is important, the effect of nitrogen being the most significant followed by oxygen and carbon. While nitrogen and carbon are usually not found at high concentrations in dense titanium, oxygen is a common contaminant due to the high affinity of titanium for oxygen and the high solubility of oxygen in titanium.

While porous titanium has been used for many years as coating for orthopaedic implant applications and titanium foams are presently considered in many other applications, the effect of oxygen concentration on the mechanical properties of porous titanium is not well documented. The deformation behaviour of metallic foams is very different from that of dense metals. In addition, since metallic foams have large surface area, oxygen coming from surface oxide can be a significant contributor to the global oxygen concentration of the foams. The objective of the present work is to present the effect of oxygen concentration and distribution on the compression properties of pure titanium foams.

INTRODUCTION

It is well established that the mechanical properties of titanium and titanium alloys are sensitive to the presence of interstitial solutes such as oxygen, nitrogen, carbon and hydrogen. Conrad provided a good review of the effect of these interstitial on the strength and ductility of titanium [1]. These interstitials increase the elastic modulus, the yield strength and reduces the ductility of titanium.

The high solubility and relatively high diffusivity of interstitial elements in α -titanium are contributing to high potential of pick-up of such elements during thermal processing. The maximum solubility of oxygen, nitrogen, carbon and hydrogen in α -titanium is 30%at., 19%at., 2%at. and 8%at. respectively [2]. The activation energy for the diffusion of the interstitial increases from: hydrogen, carbon, oxygen to nitrogen, with values for oxygen and nitrogen approaching those for titanium self diffusion [1]. The activation energy for oxygen diffusion in α -titanium is approximately 50 kcal/mole [1].

Because of the strong influence of interstitial elements on the mechanical properties of titanium, chemical requirements have been established for the use of titanium in orthopedic and dental applications. Since porous titanium is also commonly used in orthopedic applications, chemical requirements have been established for such coating (Table 1). The ASTM standard for porous coating for orthopedic implants, the maximum content of oxygen must be lower than 0.4wt%.

TABLE I : ASTM chemical requirement [3] for titanium for coatings of surgical implants.

Element	Concentration max (%)
O	0.4
C	0.1
N	0.05
H	0.05

Titanium forms an inert and adherent oxide layer on its surface at exposure to aqueous solutions or air. This oxide layer has a thickness of approximately 2-7 nm thick. The oxide layer contains primarily TiO_2 and act as a barrier for the oxygen, which cannot attack more metal atoms beneath and the oxide formation is quickly stopped.. This provides the good corrosion resistance to the material.

For porous structure obtained by powder metallurgy processes, the thermal cycling is contributing significantly to the increase in oxygen. Indeed, at high temperature, the increased diffusivity of oxygen in titanium leads to the oxide film dissolution and solubilization of oxygen. The dissolution of the oxide layer creates highly reactive surfaces to react with very small concentration of contaminant in the atmosphere (namely O and N). This contribution is directly enhanced by the high surface area of the porous structure.

In addition, the oxygen coming from the surface oxide can be a significant contributor to total oxygen content of high surface area structures. Therefore, the distribution of the oxygen between the surface and the bulk in the porous structure has to be considered for the control of the mechanical properties.

This paper presents an evaluation of the effect of oxygen concentration and distribution on the compressive properties of titanium foams produced with a powder metallurgy process.

EXPERIMENTAL PROCEDURE

Titanium foams were produced using the process described in Figure 1. Plasma atomized CpTi spherical powder (-180 μ m, 0.12 wt.% oxygen) was admixed with a polyethylene binder and a chemical foaming agent (p,p'-oxybis[benzenesulfonyl hydrazide]). The resulting powder mixture was poured into a mold and foamed at 210°C in air. The resulting material was debinded at 450°C in Ar and sintered at 1400°C under vacuum.

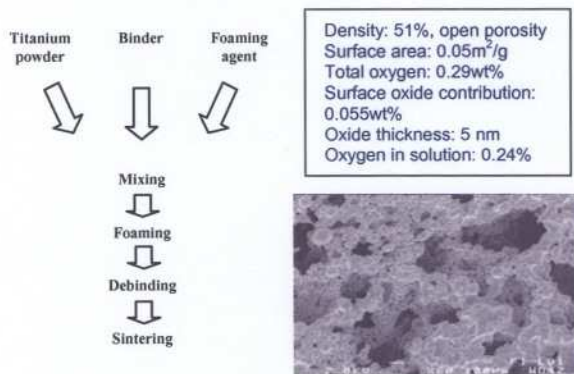


Figure 1: Schematic description of the process (further described in [4]) and characteristics of the foams evaluated in this study.

Foams containing different oxygen content were produced by heat treating the specimens in Ar-20%O₂ at different temperatures (300 to 500°C) for 1 hour to oxidize the foams. Some of the oxidized foams were solution treated at 1000°C under vacuum to dissolve the oxide layer and increase the oxygen content in solution in titanium.

The density of the specimens was evaluated using the weight and physical dimensions of the cylinders.

Specimens were observed using a JEOL 6100 Scanning Electron Microscope (SEM). 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 using a LECO analyzer.

Compression tests were done on a MTS 100 kN testing machine using a crosshead speed of 1.25 mm/min.

RESULTS

The titanium foam evaluated in this study is presented in Figure 1 before any oxidation and oxide dissolution treatments. The porosity is 49% and the pore size is typically between 50 and 400 μ m. The porosity is open and the material is permeable. The foam has high specific surface area (around 0.05 m²/g, evaluated by BET). The high surface area is associated with the powder metallurgy process used. The starting material is a powder having a specific surface area around 0.03 m²/g. The surface of the initial powder is smooth and reveals grains boundaries (Figure 2a). During sintering at high temperature under vacuum, solid diffusion occurs and sintering necks are formed. Thermal etching also occurs and reveals the crystallographic planes of the titanium crystals. This thermal etching effect generates the fine submicronic features observed on the surface of the titanium foam (Figure 2b) and also contributes to the high surface area of the material.

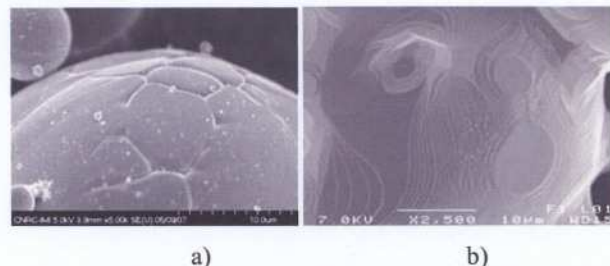


Figure 2: SEM micrographs of the surface of the initial powder and b) the foam.

The surface of the foam is covered by a thin oxide film. The oxygen contribution of the film was evaluated to be around 0.055 wt% [5]. Using the specific surface area of the foam (0.05 m²/g, evaluated with BET), this contribution correspond to an oxide film with an average thickness of 5 nm. This corresponds to the thickness of a naturally grown oxide film on the surface of titanium [6]. Indeed, this film is very thin can hardly be observed on the specimen cross sections (Figure 3a).

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 amount of oxygen in solution. When the surface contribution (0.055 wt%) is extracted from the total amount of oxygen determined using inert gas fusion techniques (LECO; 0.29 wt%), the amount of oxygen in solution can be determined (0.24 wt%).

After the oxidation treatments, the foams had different colors, from yellow to blue. The oxidation appears to be uniform throughout the specimens (i.e. all the internal surface appears the same color). The modification of the color of the specimens is attributed to a modification of the oxide thickness.

Microhardness measurements were done to determine the extent of the oxygen diffusion in titanium during the oxidation treatments. The results suggested that limited amount of oxygen diffused in titanium and most of the oxygen pick up during the oxidation treatment was associated to the increase of the oxide layer thickness [7]. For the specimens treated at 450°C, the oxygen pick up (i.e. 0.27 wt%) corresponds to an increase of the oxide layer of around 30 nm. SEM observations showed that the oxidation is not uniform and the film thickness can be thicker at some location. Figure 3b shows a cross section of the foams where the film is clearly visible.

After solution treatment at 1000°C, the specimen color returned to gray and the oxide film was no longer visible on the specimen cross sections (Figure 3c). At the end of the solution treatment, the oxygen concentration in the foams slightly increases due to the formation of a new oxide layer on the surface of the foam after air exposure. Experiments confirmed that there was no oxygen pick up during the solution treatments.

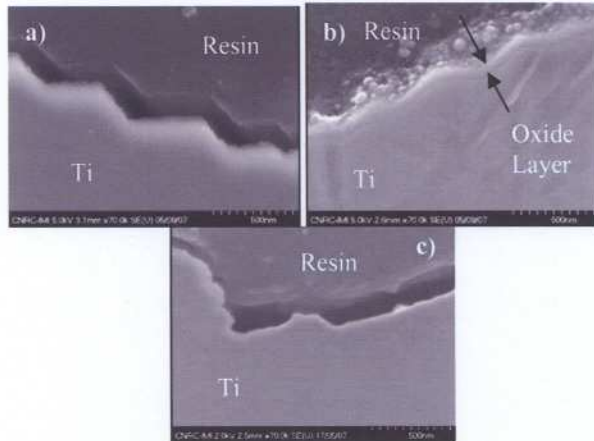


Figure 3: High magnification SEM micrographs showing the surface of the foam on polished cross sections a) as produced, b) after oxidation at 450°C and c) after solution treatment.

Figure 4 schematize the distribution of oxygen after the different treatments. The initial titanium foam has 0.29 wt%O total (0.235 wt%O in solution and 0.055 wt%O in the 5 nm thick oxide film). For the 450°C oxidation treatment, the oxide layer grows up by 35 nm and the total amount of oxygen increases to 0.57 wt%. The oxygen in solution remains approximately the same during the oxidation treatment. During the solution treatment, the oxide film is dissolved and the oxygen goes into solution. After the solution treatment, a new oxide

layer is formed (additional 0.055 wt%O) when the foam is exposed to air.

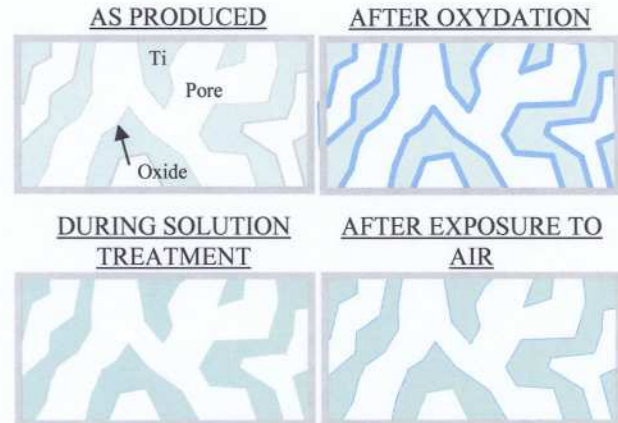


Figure 4: Schematic representation of the oxygen distribution in the foams after different treatments.

Figure 5 presents the compression behavior of foams before and after the oxidation and solution 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 (results to be presented in a separate study). For all specimens, a smooth curve is obtained suggesting a ductile behavior. However, observation of the specimens after compression shows that deformation behaviors are very different. When the foam contains large amount of oxygen in solution, brittle fractures are observed and the specimens are disintegrated during the tests.

The effect of the oxidation and solution treatments on the initial portion of the compression curve can be seen in Figure 5b for specimens as-sintered, oxidized at 450°C and solution treated 1000°C. The compressive yield strength remains the same after the oxidation treatment, while it increases significantly after the solution 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 solution treatment, the oxygen is approximately the same but is dissolved in titanium and its impact on the compressive behavior is significant.

Figure 6 presents the effect of oxygen on the compressive properties of titanium foams after the different oxidation treatments, before and after solution treatments. In the oxidized state, the difference of oxygen concentration mainly comes from differences in the oxide layer thickness and the oxide thickness has little impact on the yield strength. On the other hand, after the solution treatment, the difference of oxygen concentration comes from differences of concentrations in solution and 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%.

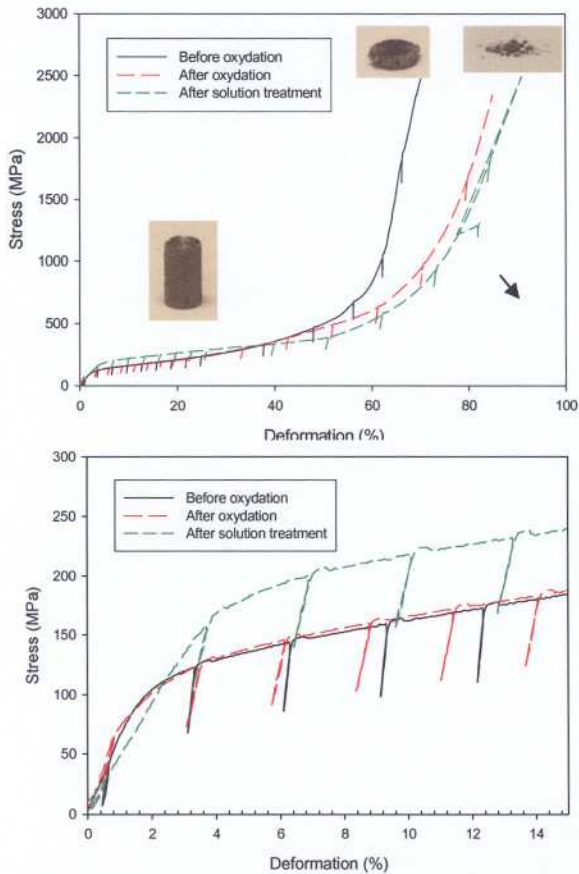


Figure 5: Compressive behavior of foams as-sintered (before) and after an oxidation treatment at 450°C in Ar-20%O and solution treatment at 1000°C under vacuum a) full curve and b) zoom on the initial portion of the curve.

Figure 7 shows SEM micrographs of the fracture surface of the foam after compression. Since the specimens containing 0.24%O in solution did not break during compression, a fracture surface was obtained by breaking the remaining specimens after the compression test. The effect of the oxygen content on the rupture mechanism 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. 0.51wt%O) present brittle cleavage-type rupture surface.

CONCLUSIONS

Titanium foams with different oxygen concentrations were produced by oxidation. The as-produced foams have 0.24 wt%O in solution. Due to the high specific surface area of the material, the contribution of the thin oxide film (5 nm) on the surface of the foam contributes significantly to the total oxygen content (0.055 wt%) and increase the total oxygen content to 0.29%. The contribution of the surface oxide on the compression

yield strength is minimal. However, the amount of oxygen in solution has important impact on the compression properties. The yield strength and ductility of the foams are significantly affected when the oxygen in solution increases from 0.24 to 0.51 wt%. While smooth compression curves are obtained for both specimens, the foams containing high oxygen concentration has limited ductility and brittle fractures are observed.

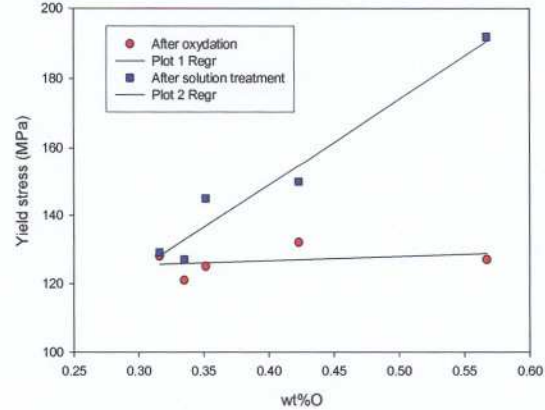


Figure 6: Effect of oxygen on the compressive yield strength before and after the solution treatments.

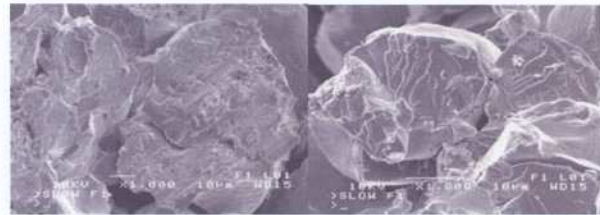


Figure 7: SEM micrographs of the fracture surface of foams with a) 0.24 wt%O and b) 0.51 wt%O.

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