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Hydrogen Addition Effect on 3D Porous Titanium Produced By Powder Metallurgy

N.A. Braga[1a], N.G. Ferreira[1b], F. Piorino Neto[2c], M.R. Baldan[1d], C.A.A. Cairo[2e]

[1]Laboratório Associado de Sensores e Materiais – Instituto Nacional de Pesquisas Espaciais, 12245-970, São José dos Campos - SP – Brasil
[2]Divisão de Materiais, Comando Geral de Tecnologia Aeroespacial (CTA), 12228-904, São José dos Campos - SP, Brazil
[a]neila@las.inpe.br, [b]neidenei@las.inpe.br, [c]fpiorino@iae.cta.br, [d]baldan@las.inpe.br, [e]ccairo@iae.cta.br

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Abstract:Titanium is an attractive material for structural and biomedical applications because of its excellent corrosion resistance, biocompatibility and high strength-to-weight ratio. Power metallurgy was used in this work to prepare 3D porous titanium. The powders became fragile from hydrogenation process and were able to be used to obtain compacts with different porosities by uniaxial pressing and sintering without applied pressure. Since hydrogen dissolves easily in titanium to form titanium hydrides which have a strong influence on the microstructure coarsening and mechanical properties, the study of the porous compacts hydrogenation was carried out by hydrogenation at different temperatures (870 K up to 1070 K) in a hot filament reactor. Titanium surface morphology changes were investigated by scanning electron microscopy. High resolution x-ray was used to characterize the present phases. Evaluation of the porous titanium hydrides mechanical behavior was realized by flexion assay performed at three points.

Introduction

Titanium (Ti) metal presents some important properties, such as high strength-to-weight ratio, low density, high melting point, inertness and biocompatibility which make it an important material for different applications [1-4]. Regrettably, its high chemical reactivity at high temperature is a disadvantage on its processing in liquid phase [5]. That is the reason why titanium production and machining are expensive. Powder Metallurgy [6-9] emerges as a potential technique where all these difficulties have been solved by the production of titanium at lower temperatures and under some conditions that allow consolidating the metal in the solid phase diminishing the problems related to its high reactivity.

In order to obtain titanium with 3D porosity the sintering of preforms is a powder metallurgy available method. It is a way of producing materials by compacting, binding and sintering metal powders. The volume fraction of porosity is associated with the degree of particle interconnectivity and particle size. It can be controlled by process variables such as compacted powder density, sintering temperature and time, and alloying additions. Oh *et. al.* [10] sintered spherical unalloyed titanium powders with and without applied pressure and achieved a porosity range of 5-37 %. This porosity degree can be increased up to 50 % by using irregular particle powders as that produced by HDH technique [11]. Ricceri *et al*., [12] by using isostatic pressing showed the variation of the porosity level with the compacting pressing. Therefore, the lower the compacting pressing, the higher the material porosity.

Titanium exhibits good properties of hydrogen absorption and storage. These characteristics are an advantage for the applications of hydrogen storage, but a disadvantage for many others engineering applications due to hydrogen embrittlement [13,14]. Since titanium and its alloys have a high affinity for hydrogen, being capable of absorbing up to 60 at. % hydrogen at 873 K and even higher contents can be alloyed with titanium at lower temperatures [15]. This hydrogen absorption decreases the allotropic transition temperature from α-Ti (hcp) to β-Ti (bcc). In addition, hydrogen has also a significant effect on the microstructure of the titanium samples changing the well defined polygonal grain structure into a coarsening structure during α-β transformation [16].

There are no studies reporting hydrogen influence on titanium compacts containing three-dimensional porosity. In this work we are reporting the influence of such process as a function of the temperature and the hydrogen concentration in three-dimensional porous titanium compact produced by the powder sintering process.

Experimental Procedure

Power metallurgy was used to prepare Ti compacts by controlling the porosity. Ti powders with different particle sizes were prepared from the HDH technique. Hydriding was carried out at 770 K in a vertical furnace for 3 h under a pressure of 10^{-5} Pa. After cooling to room temperature, the friable hydride was milled in a titanium container with protective atmosphere for 30 minutes. The powders were sieved to use similar sizes of powder in the range of 250-350 μm. In order to fabricate the three-dimensional porous compacts, Ti powders were uniaxialy pressing in an inflexible mold by applying a pressure of 100 MPa and sintering at 1470 K under a vacuum of 1 x 10^{-5} Pa. A heating/cooling rate was 0.17 K/s in the sintering treatment. Sintered porous Ti compact crystal structure was examined from grazing incident diffraction (GID) at 3° from X'PERT Phillips system and the morphology was analyzed by SEM using a Jeol equipment JSM-5310.

Hydrinding process was carried out in a hot filament reactor [17] by varying the temperature from 770 K up to 1070 K in controlled hydrogen flux. The pressure in the reactor was kept at 6.6 kPa for a time of 1 h. A K-type thermocouple located inside the substrate was used to measure the substrate surface temperature. Top view images of the hydrogenated compacts were performed by SEM analyses from the same Jeol equipment above described. The TiHx crystalline phases were analyzed from grazing incident diffraction (GID) at 3°.

The 3-point bending tests were carried out on a INSTRON 4301 universal testing machine with 500 Kgf charging cell at a rate of 0.5 mm/min.

Results and discussion

Fig. 1a shows a general view of the Ti compact morphology produced from Ti powders obtained by HDH technique. That image is focusing the sample region represented by a skeletal structure among porous, with their struts in random directions. It might be observed that sintered Ti compact presents neck formation between the powder particles by the densification process due to the mass transfer mechanisms. Because the sintering temperature slightly affects the densification [10] in this process, the initial powder size and shape have verified to be a dominant factor governing the porosity level. Second plane pores evidenced on such image indicate that porosity is not concentrated only in the compact surface, but propagates itself to its inner in an interconnected three-dimensional net. An image with higher magnification of the compact surface is showed in the Fig. 1b. It can be seen the angular pore shape which is a feature of the sintering of performs. The Ti roughness surface morphology is better evidenced in the Fig. 1a inset were a stairs-like structure is evidenced. This texture may be attributed to the volume shrinkage during the sintering process and the cross slip of the planes in the Ti crystal structure.

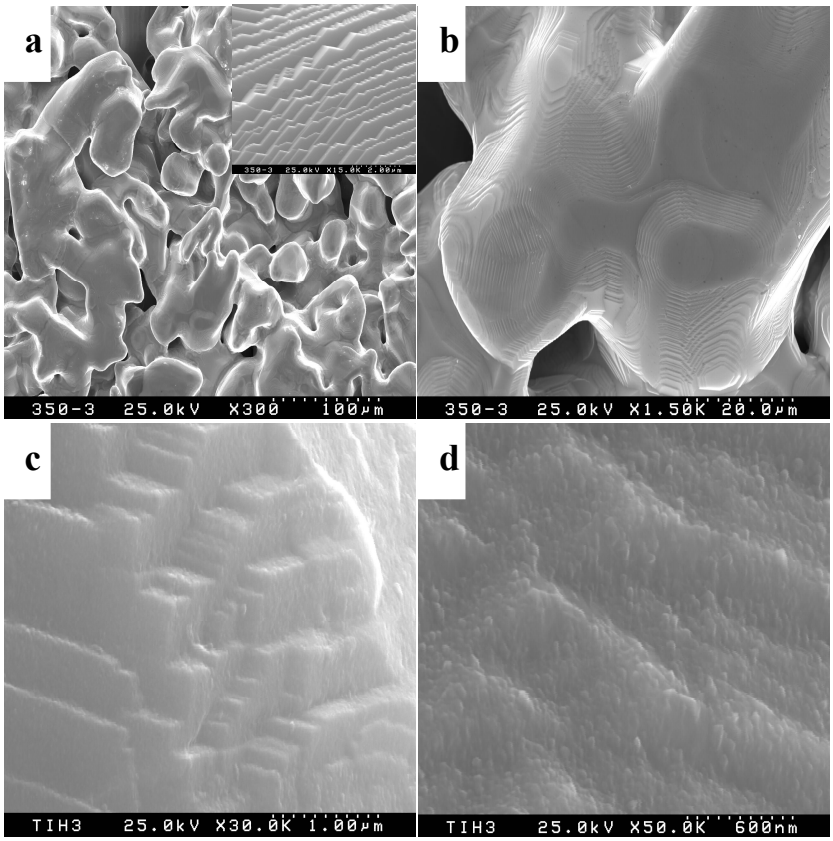

Fig. 1 – SEM images: (a) sintered Ti compact showing its detailed texture in the inset; (b) Ti surface morphology in a higher magnification; (c) Hydrogenated Ti compact surface morphology at 870 K; (d) Hydrogenated Ti in a higher magnification evidencing the roughness.

XRD patterns surfaces are shown in Figs. 2 for pure titanium (Ti), Ti hydrogenated at 870 K (TiHx-870) and for Ti hydrogenated at 1070 K (TiHx-1070). The Ti XRD spectra clearly present the peaks at 35.17º, 40.17°, 52.99° and 63.02° corresponding to the (100), (101), (102) and (110) titanium diffractions planes respectively (JCPDS 89-5009). The diffractions patterns related to TiHx-870 and TiHx-1070, presented the same characteristics peaks related to titanium hydrides at 37.21º, 51.97° and 62.58 planes. These peaks can be attributed to the (111), (211) and (220) hydrides planes respectively. The main TiHx peak at 37,21 ° was more intense for the Ti hydrogenated at 1070 K which indicate that the higher the hydrogenation temperature the higher the hydride precipitation in the Ti matriz in the experimental conditions of this work..

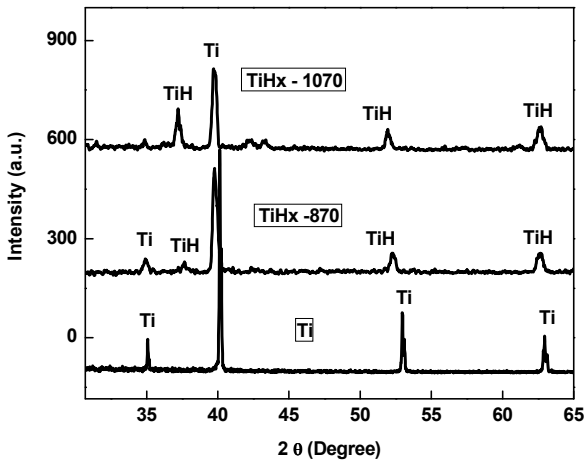

Fig. 2 – X-ray difractogramms obtained for Ti (pure titanium), TiHx -870 (Ti hydrogenated at 870 K) and TiHx-1070 (Ti hydrogenated at 1070 K).

Another important feature is that hydrogen absorption changes the composition and the phase equilibrium of the Ti substrate. Pure Ti possesses a polygonal α-grains structure Fig. 1b. The hydrogen absorption decreases the temperature for the α-β transformation [18]. The main consequence is the temperature decrease by which the coarsening β-phase occurs. These contributions might explain the coarsening process and morphology changes observed for titanium compacts obtained in temperatures higher than 870 K (Fig. 1c). It can be observed that the stairs-like angular edges were maintained in the Ti surface although an increase in the surface roughness is evidenced in the Fig 1d.

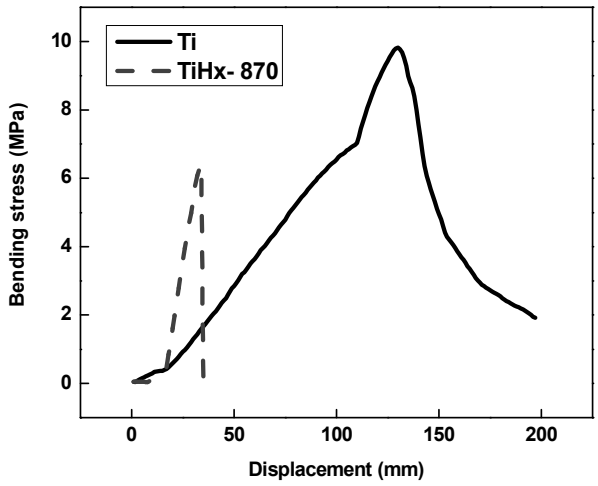

Fig. 3 – Bending tests results for a non-hydrogenated (Ti) and hydrogenated (TiHx -870) samples

Typical force-displacement curves from 3-point-bending tests are shown in Fig. 3 for non-hydrogenated and hydrogenated titanium samples with around 35 % porosity. It can be seen that the total displacement for the pure titanium curve is significantly higher than that for the hydrogenated sample. This feature became evident a more ductile behavior for the metallic pure porous titanium than for the hydrogenated sample. Therefore, the catastrophic rupture is found for the hydrogenated titanium specie. Besides, the deflection at rupture for the hydrogenated titanium is around 60 % of that for pure titanium. All these factors became evident that the hydrogen has a significant influence in the mechanical properties of the 3D porous titanium samples contributing for its fragilization.

Conclusion

Powder metallurgy is a potential technique to obtain Ti substrates with three-dimensional porosity by controlling the porosity level and surface area. Titanium hydrogenation promotes significant changes in the microstructure and mechanical properties of the titanium compacts. Titanium surface morphology suffers a coarsening process while titanium matrix was fragilized by the hydride formation.

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