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Porous titanium foil by tape casting technique

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There were presented method of manufacturing titanium porous objects in a shape of sponge or foil during the sintering process in vacuum. The unique combination of a reducing chemical agent and vacuum in one processing step were applied to improve sinterability of titanium. The main novelty of proposed technique is using reactive component for sintering that result in decreasing of temperature of the process. The developed technique allows manufacturing of strong titanium products, porous or fully dense.

1. INTRODUCTION

Titanium metal is the ninth most abundant element in the earth's crust. It is also present in meteorites and in the sun. Pure titanium (Ti) is a silvery-white, lustrous metal with low density (4.51 g/cm^3) and good strength. Titanium is as strong as steel with only 45 % of its weight, so when combined with other metals, it greatly improves the strength and the ability to withstand extremes of temperature. Ti has low thermal and electrical conductivity and is one of the most corrosion-resistant structural metals. In powder form, it is dark grey. Because of its high strength-to-weight ratio, titanium and its alloys are widely used in both aerospace and non-aerospace applications. Aerospace applications include the use in gas turbine engines for both military and commercial aircrafts, airframes, and in various applications in missiles and space vehicles. In most aircraft engines, Ti-based alloys parts account for 20 – 30 % of engine weight. Non-aerospace applications include the use of Ti in specialty chemical, pulp and paper, oil an gas, marine, medical, and consumer goods industries. A very thin layer of titanium dioxide formed on the surface of Ti products makes it so corrosion resistive. The thickness of this protective layer is in the range of few to tens angstroms. Titanium dioxide formed on the surface of the Ti products is characterized by very high melting point (1640 ^{o}C) and, in general, its sinterability is low. Therefore the application of the typical powder metallurgy processes for processing of the Ti powder into the dense or porous objects is very limited. The process for manufacture of Ti powders is slow and costly, and this has resulted in slow growth of P/M as a means of manufacturing titanium parts. One of the most important considerations in manufacture of a Ti powder metallurgy product is control of oxygen content. Powders must be handled very carefully, because they have a very high affinity for oxygen. The porous 3D Ti components are manufactured at this moment by reduction of sodium fluorotitanate (Na_2TiF_5) by an aluminum-zinc alloy to produce a molten Ti-Zn alloy. The zinc is then reduced from this by evaporation. Another process uses electrolysis to reduce either $TiCl_4$ or titanium dioxide (TiO_2) to titanium metal [1].

2. EXPERIMENTAL

The technology of manufacturing the titanium porous objects in the shape of porous sponge or porous foils was based on an unique combination of a reducing chemical agent and vacuum applied in one processing step. The use of a neutral atmosphere (Ar), reducing atmosphere ($Ar+H_2$) or vacuum separately during the sintering process was not successful for a good sintering of the compacted Ti powder to a dense component. It was necessary to clean off effectively the surface of the Ti particles from the passivated titanium dioxide layer before the process of sintering will takes place. This was achieved by using the well know reductant, titanium hydride TiH_2, which decompose at 288°C to very high reactive hydrogen form, H^+ ion [2]. The in-situ formed hydrogen ions react with the layer of passivating layer of TiO_2, decompose it to the Ti metal and water vapour. The water vapour is removed by vacuum and the active form of very fine Ti promotes effectively the sintering process of the Ti components.

The reaction goes in two steps:

$$2TiH_2 \rightarrow Ti + 4H^+ \quad (1)$$

$$TiO_2 + 4H^+ \rightarrow Ti + H_2O \uparrow \quad (2)$$

Combined reaction can be written in such way:

$$2TiH_2 + TiO_2 \rightarrow 3Ti + 2H_2O \uparrow \quad (3)$$

The types of the Ti powders, fine -325 mesh and coarse – 60 + 100 mesh from Alfa Aesar and commercial binder B-33305 from Ferro, were used in the performed experiments. The organic binder is a mixture of polymer polyvinyl butyral (PVB) with solvents (toluene/ethanol), surface active agent and plasticizer. The binder solids was 22.4 wt.%, resin/plasticizer ratio – 1.7/1 and viscosity of 450 cPs. The tape casting method was applied as a shaping technique. This technique commonly used in the ceramic and electronic industries. The composition of the paste for tape casting was: 55 vol. % Ti powder and 45 vol. % binder. Additionally 0.1 wt % TiH_2 was added to the mixture. All components of the paste was mixed by shaking in a Turbula mixer for 45 min and then the tape was casted on the glass plate coated with the Teflon foil. Doctor blade tape casting technique was used for shaping a tape with the thickness of 0.5 mm and width of 30 cm. The tape was dried in ambient atmosphere for 4 hours to remove the majority of the solvents and then was kept for 1 hour in an electric oven at the temperature of 60 ^oC. The elastic tape was cut for samples of sizes 12x12 cm^2. The samples were placed between the molybdenum plates coated with BN thin layer and then sintered in an electric oven under vacuum (10^{-5} hPa) at 1000 ^oC for 1 h. The rate of heating was 200 $^oC/h$, cooling was together with the oven. The sintered tape was very flexible, strong, with the open porosity of 39 %. Average pore size measured from the SEM photograph is approximately 22 μm (Fig. 1). Coefficient of thermal expansion measured in the temperature range 20 – 1000 ^oC is 8,3 x 10^{-6} 1/^oC. Particles of titanium are sintered together as it was shown in Fig. 2.

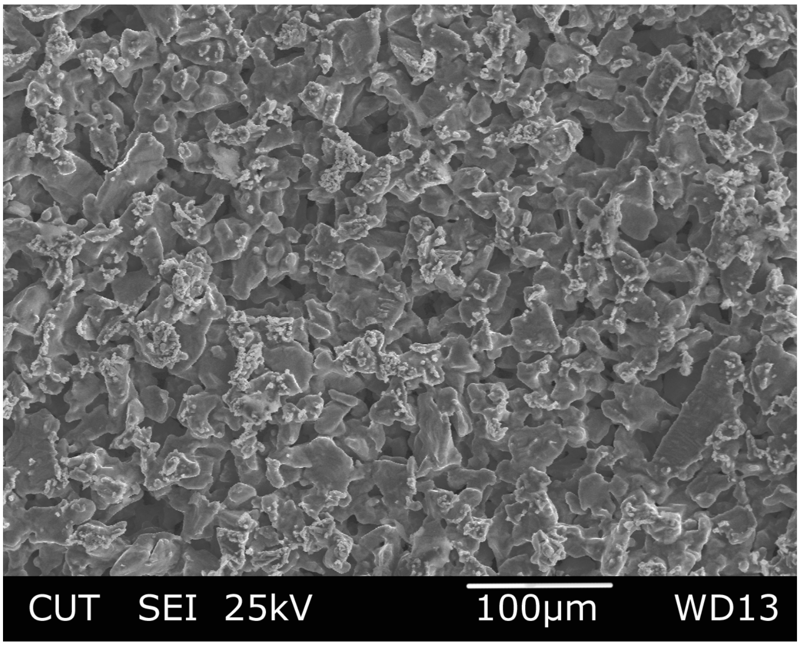

Figure. 1. The SEM image of the top view of Ti porous foil

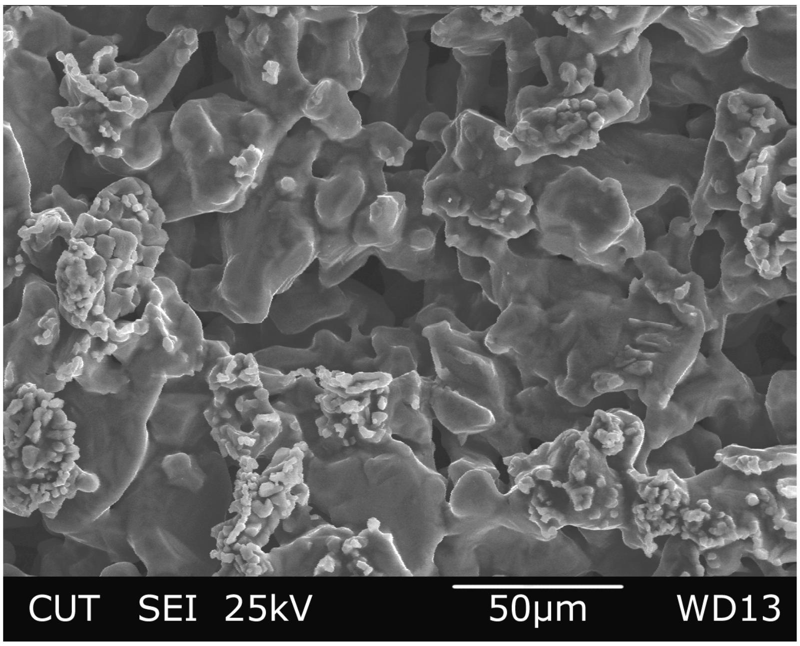

Figure. 2. The SEM image of necks among Ti particles

3. DISCUSSION AND CONCLUSIONS

The technology developed facilitates the manufacture of fully dense, or porous, strong titanium products. The tape casting technology, commonly used in the ceramic industry, was successfully applied for shaping the green Ti foil [3]. The organic binder system was used to protect the Ti particles from long contact with the surrounding air or water vapour. This reduced the risk of further growth of the titanium oxide on the surface of Ti particles. Two types of Ti powder were used in the experiments, fine and coarse with the average particle size respectively 25 and 100 µm. The highest flexibility and strength was achieved for the tape manufactured from the fine powder. The maximum sintering temperature was as low as 1000 ^{o}C. The crucial innovation was the use of the reducing agent, titanium hydride, and a vacuum, in one sintering step. The organic components of the tape (toluene, ethylene) were first evaporated at a temperature below 150 ^{o}C and the organic binder, plasticizer and surfactant were pyrolised to an amorphous carbon phase below 250 ^{o}C. The residual carbon and products of decomposition of TiH_2 and TiO_2 reacted together forming gaseous products, which were easily released from the Ti surface and were removed from the system with a vacuum pump. Therefore the surface of the sintered Ti was completely free from all contaminants (EDX analysis of tested samples) and allowed for a rapid sintering process between neighboring Ti particles forming a strong neck between separate particles (Fig 2). The developed sintering technique allows also for good sintering of Ti particles compacted by other shaping techniques such as uniaxial pressing, CIP, injection molding, impregnation of a polyurethane foam/squeezing, etc. Ti components were prepared by other shaping techniques and were also successfully sintered according to the described procedure [4]. The porous Ti foils are of interest for applications in PEM FC, solar reactors, chemical reactors, batteries, Ti electrodes and other devices.

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