additional methods such as DMTA.

The analysis of SEM micrographs of the neat PET-D copolymer (FIG.2a) and of systems containing 0.4 and 0.6 wt% TiO2 (Fig.2 b,c) indicates differences in the topography of fracture surfaces: the neat copolymer sample shows features typical for elastomeric material (smooth fracture surface which indicates ductile deformation behaviour) while addition of TiO_2 leads to a surface topography typical for plastic deformation (b,c).

The analysis of static tensile properties indicates that the polymer-nanofiller system achieves the highest values of stress-strain characteristics at 0.4 wt% TiO_2 (FIG.3). The stress at break increased by 160% and the at break by 220%, comparing with the neat polymer, respectively. At higher concentrations of TiO_2 (0.6 wt%) tensile properties dramatically decreased, probably as the result of agglomerates formation (FIG.2c).

Conclusions

It has been demonstrated that the in situ polycondensation method in the presence of TiO_2 nanoparticles is a very interesting method for production of PET-D/TiO_2 nanocomposites. The in situ polycondensation method is a versatile and solvent-free technique to produce materials of interesting properties. Combination of a soft, elastomeric polymer matrix with crystalline ceramic nanoparticles gives an interesting material of enhanced mechanical properties as compared to the neat polymer. It is also expected that incorporation of TiO_2 nanoparticles will influence the degradation rate and bioactivity of these novel nanocomposites.

Acknowledgements

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PRODUCTION OF TITANIUM AND HYDROXYAPATITE COMPOSITE BIOMATERIAL FOR USE AS BIOMEDICAL IMPLANT BY MECHANICAL ALLOYING PROCESS

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Abstract

Mechanical alloying is a ball milling process where a powder mixture placed in the ball mill is subjected to high energy collision form the balls. As the power particles in the vial are continuously impacted by the balls, cold welding between the particles and fracturing of the particles take place repeatedly during the ball milling process. In this article you will be presented with the case of mechanically alloying a metal such as titanium with hydroxyapatite, a ceramic consisting of calcium, phosphate and hydroxyls. The composite material will be used as a biomaterial used for implants. The starting powders were weighted, mechanically alloyed in an inert atmosphere, pressed and then thermally treated up to 1150°C in a thermal cycle. The samples were then analyzed by TGA-TG, optical microscope, XRD, and SEM.

After the thermal treatment, the samples had an outer shell that was composed of hydroxyapatite, and an inner core that consisted of titanium. Mechanical alloying of titanium and hydroxyapatite did not give a uniform distribution of the powders, but titanium particles were covered by hydroxyapatite fragments only on the surface of the specimens.

Keywords: Titanium, hydroxyapatite, mechanical alloying, biocompatibility

Introduction

Mechanical alloying was invented in the 1970's as a method to develop dispersion-strengthened high temperature alloys with unique properties [1]. With the discovery of formation of amorphous alloys using this technique, it has received new research interest in developing different material systems.

Mechanical alloying is a ball milling process where a powder mixture placed in the ball mill is subjected to high energy collision form the balls. The process is usually carried out in an inert atmosphere [2]. The two most important events involved in mechanical alloying are the repeated welding and fracturing of the powder mixture. The alloying process is successful only when the rate of welding balances that of fracturing and the average particle size of the powders remains relatively coarse [3]. Alloys with different combination of elements have been synthesized, including at least one ductile metal to act as a host or binder to hold together the other ingredients [4]. The mechanical alloying process is a solid state process where the powder particles are subjected to high energetic impact by the balls in a vial.

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As the power particles in the vial are continuously impacted by the balls, cold welding between the particles and fracturing of the particles take place repeatedly during the ball milling process [5]. Change in structures of mechanically alloyed powder mixture can be divided into three stages according to measurement of the lattice spacing. They are grain refinement, solution diffusion, and formation of new phase. At the first stage, no solid solution takes place between the particles. Solid solution occurs as evidenced by the broadening of the x-ray diffraction peak patterns indicating the dissolution of different elemental atoms. New phases may be formed at the later stage, an occurrence manifested by the formation of new peaks in x-ray measurement [6].

In this paper you will be presented with the case of mechanically alloying a metal such as titanium with hydroxyapatite, a ceramic consisting of calcium, phosphate and hydroxyls. The composite material will be used as a biomaterial used for implants, and was chosen for the good mechanical properties of the bio-inert titanium, and the excellent biocompatibility of the bio-active hydroxyapatite.

Generally, a wide range of metals and ceramics are used as biomaterials today. Metals such as titanium, chromium, aluminium, fluoride, vanadium, nickel, copper and its alloys are used as well as ceramics such as hydroxyapatite, alumina, bioglass, A-W glass ceramic, boron, and glass fibres. Pure titanium implants are widely used today too [7]. Due to the fact that they consist of metal, the implants are bio-inert and have very good strength but they weaken the natural bone. This is called stress protection and is due to the fact that titanium, as more electronegative, attracts ions from the bone on its surface with a resultant weakening of the bone above and below the position of the implant. Not only titanium but titanium alloys as well have been used increasingly over the last 10-15 years, in the area of bone replacement and orthopaedic surgery, and dental implantation [13]. Solid hydroxyapatite implants are being used today also [8]. It is thought that due to the porous nature of these implants they lack strength but they are bioactive that means that bone tissue grows into the pores of the implant once inserted. Over time they are partially resorbed and replaced by natural bone [9].

In order to overcome the stress protection problems of pure titanium implants and the brittleness of hydroxyapatite implants titanium matrix composites with bioactive reinforcement such as hydroxyapatite, bioglass and apoceram were manufactured [12].

Similar composites to the one featured in this paper were manufactured by Watari et al. by means of powder metallurgy [14]. T.Zhu, T.C Lowe, V.V Stolyarov, R.Z Valiev manufactured titanium and hydroxyapatite composite biomaterial by ECAP technique and cold extrusion [15]. W.Shi et al. manufactured a titanium- hydroxyapatite coating to pure titanium matrix [16]. Bishop et al. manufactured titanium- hydroxyapatite FGM biomaterials by powder metallurgy [17]. ?doba et al. manufactured titanium- hydroxyapatite FGM biomaterials by cold compression and sintering in controlled atmosphere [18]. Best et al. used an organic binder for better adhesion of the titanium and hydroxyapatite powders in the final composite biomaterial [19]. Mechanical alloying, with the aim of producing homogeneous mixtures of titanium /hydroxyapatite powders was studied by S. Tsipas et al. [20].

Experimental procedure

Mixtures of 160 grams pre-mixed titanium from Texas Ltd, USA and hydroxyapatite powders from Biocomposites Ltd, UK, with 50 μm particle diameter, were loaded on batches of 10 grams into a vial with 20 hardened steel balls 7.98 mm in diameter, giving a ball to powder ratio of about 4:1. Each batch was milled in a spex 8000 mill for 10 hours.
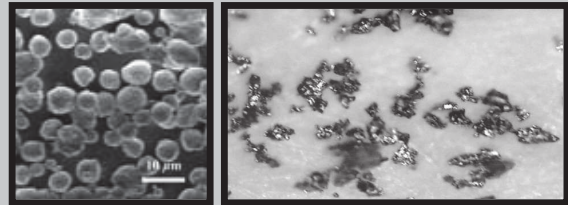

FIG. 1. Micrographs oh the hydroxyapatite and titanium powders x50 respectively.

The powders were sprayed with an organic binder PEG from Polysciences Inc, USA, layered into a steel die and pressed up to 0.67 GPa in a Rex Roth Hydronorm electric press. The intermediate products were 2 cm high and had a diameter of 1.5 cm.

The samples were heated in an argon atmosphere in a Thermavatt electric furnace to 350-400°C with a rate of 2°C /min for the removal of the binder, then to 800°C in 5.3hours and remaining in that temperature for 1 hour, and in the end to 1150°C in 2.5hours and remaining in that temperature for 1.5 hours. The billets were allowed to cool to approximately 200°C. The samples were then removed from the furnace and allowed to cool in air to room temperature.

The samples were then analyzed by TGA-TG, optical microscope, XRD, and SEM.

Results and discussion

Optical and SEM

Samples that were mechanically alloyed, microscopically showed the titanium particles covered with hydroxyapatite, but hydroxyapatite particles were not homogeneously distributed throughout the titanium and were only located on the surface. Mechanical alloying has caused in some way the re-distribution of the titanium and hydroxyapatite particles. Mixing times did not play an important role in the structure of the final composite biomaterial, but lead to amorphisation of the hydroxyapatite.

After the thermal treatment, the samples had an outer shell that was composed of hydroxyapatite, and an inner core that consisted of titanium. The outer shell was very brittle and deflating, and generally all the specimens were fairly sensitive to handling and had less fracture toughness than the starting materials. Titanium particles had an angular morphology and were considerably larger than the granules of hydroxyapatite, which appear melted. Study of the photographs from SEM showed that the HA particles were in agglomerates of small particles, these agglomerates were then broken during milling, and then the fragments were attached to the surface of the more ductile titanium.

In one specimen, visible crystal structures appear in the outer shell during a SEM analysis. These crystals were found to be titanium oxides. The schematic appearance of the final samples shown in FIG. 2:

The monolithic material as well as the final material had increased porosity. In the final samples, increased porosity was observed in the hydroxyapatite outer shell and less in the titanium core. This indicates that sintering was achieved
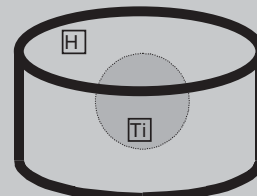

FIG. 2. Schematic presentation of the final sample where the different areas are shown consisting of Ti and HA.
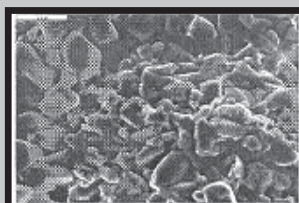
FIG. 3. SEM micrograph of the titanium core after the thermal treatment (x700).
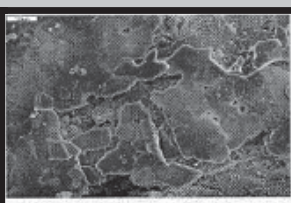
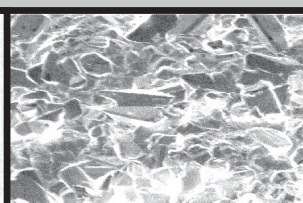**FIG. 4. SEM micrograph of the hydroxyapatite shell after the thermal treatment (x1500).**

FIG. 5. SEM micrograph of the crystal structure, possibly titanium oxide, after the thermal treatment (x400).
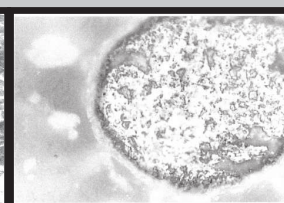
FIG. 6. Typical micrograph from optical microscope of the final sample x100. In the centre, the titanium core can be seen, covered with hydroxyapatite shell.

in the titanium core in high degree of volume fraction, but not on the hydroxyapatite shell. There are no indications of formation of secondary phases from the SEM photographs. That might indicate that there were no intermediate reactions between titanium and hydroxyapatite, even though titanium has high reactivity in elevated temperatures.

In the micrographs below (FIGs. 3-6), a clear bilayer between titanium and hydroxyapatite can be seen, that shows that the composition constant changes steeply. This makes the connection between the different layers weak and explains the defilamation of the hydroxyapatite layer from the titanium matrix in almost all the samples.

XRD analysis

The typical XRD pattern of the mechanically alloyed Ti and hydroxyapatite before and after thermal treatment are shown in FIGs. 7 and 8. The three main peaks for hydroxyapatite are 2.8330, 2.7369, 2.7976 for the angular hydroxyapatite and 2.8133, 2.7189, 2.7782 fro the spherical hydroxyapatite. The main peaks for the titanium are 2.2468, 2.3456, 2.5594.

In the XRD pattern from the intermediate green products before the thermal treatment, it is observed that the main titanium and most of the hydroxyapatite peaks remain. Overall XRD graph with patterns of the mechanically alloyed samples in comparison to the patterns for pure titanium and hydroxyapatite is given in FIG. 9.
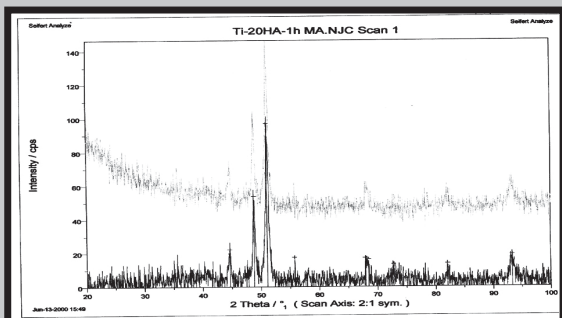

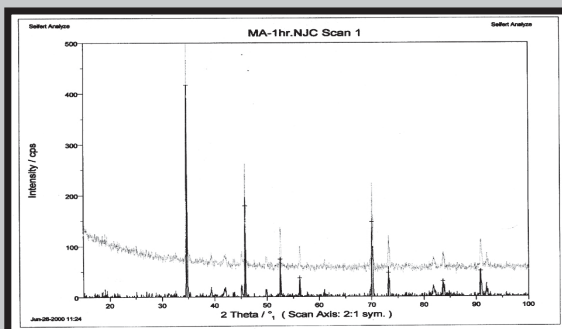**FIG. 7. Typical XRD pattern of mechanically alloyed specimen before the thermal treatment.**

FIG. 8. Typical XRD pattern of mechanically alloyed specimen after the thermal treatment.

In the XRD pattern from the final products after the thermal treatment, there is very little overlap with the initial titanium peaks and relatively better with the initial hydroxyapatite peaks. However, MA reduced the intensity of the HA diffraction peaks. In these diagrams, there is a shift of the titanium peaks towards larger angles. In addition, new peaks appeared that didn't belong to hydroxyapatite or titanium. There are little differences between the XRD patterns of the mechanically alloyed samples.

After comparison with an electronic data library the possible compounds that can be in the final composite material where found. These are, according to 3 greatest peaks (d spacing): TiO_2 (Rutile), TiO, TiH, CaP_2O_6, Ti_3O_5, TiH_2, $TiO_1.O_4$, TiO_2 (Rutile, syn), CaO, P, Ti(HPO4)2-, $CaTi_{21}O_{38}$, H_2O.

The new peaks that appeared match with $CaTiO_3$ and to $Ca_4Ti_3O_1$, but the peaks are board so the distinction between them is difficult.

DTA-TG analysis

The DTA curves of titanium and hydroxyapatite before and after thermal treatment are shown in Fig. 10. The DTA curves of the starting powders present peaks for the angular hydroxyapatite at 412.48°C, at 576.33°C, at 669.64°C and at 1130°C, after 1330°C hydroxyapatite decomposes. For the spherical hydroxyapatite at 343.88°C, at 422.13°C, at 630.73°C and at 1200°C. Above 800°C decarbonisation and dehydroxylation is observed for the primary powders. Above 1200°C hydroxyapatite is decomposed to ß-TCP, then to α-TCP, and finally melts. Due to the presence of titanium in the starting mixture hydroxyapatite decomposes in an even lesser temperature near 800°C.
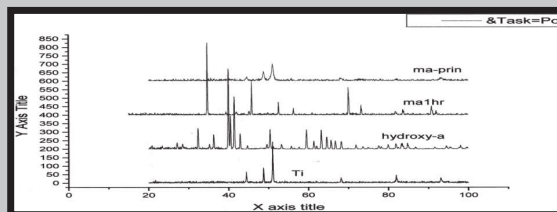

FIG. 9. Overall XRD patterns of the mechanically alloyed samples in comparison to the patterns for pure titanium and hydroxyapatite.

The TG curves for the initial powders, present a weight loss for the angular hydroxyapatite at 600° dm:-1.730% and 1130°C dm:-1.730%, and for spherical hydroxyapatite at 630°C dm:-0.234%, and at 1000°C dm:-0.228%.

The main features of all the DTA-TG plots for the mixed powders were the same: there was a large exothermic peak, starting at low temperatures ,accompanied by a weight gain. The DTA curves of the intermediate green products before the thermal treatment presented peaks in 600°C and 830°C to 1100°C.

The TG curves of the intermediate green products before the thermal treatment showed a 5% increase in weight from 650°C to 1250°C.

The DTA curves of the final products after the thermal treatment generally present a broad exothermic behavior for all the specimens from 400°C to 700°C. As an example, the mechanically alloyed sample for 1 hour, presented a negative peak at 375°C, a peak at 850°C, at 950°C, a negative peak at 1125°C and finally a peak at 1188°C.

The TG curves of the final products after the thermal treatment present a 3.2% approximately from 375°C to 1450°C for all the samples.
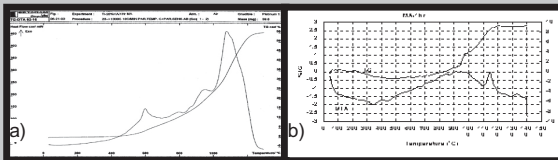

FIG. 10. Typical DTA-TG curves for the 1 hour mechanically alloyed sample: a) before thermal treatment, b) after thermal treatment.

Discussion

The morphology of the starting powders lead to a composite material with medium to poor mechanical properties.

Mechanical alloying of titanium and hydroxyapatite lead to a decrease in the size of the particles, especially of titanium particles, in relation to the starting powders and to a more fine and uniform distribution of the powders before sintering [10].

Mechanical alloying of titanium and hydroxyapatite did not give a relatively uniform distribution of the powders as was stated in bibliography[11] after the sintering. Macroscopically, titanium particles were covered by hydroxyapatite fragments only on the surface of the material and not throughout the whole volume of the material.

Thermal treatment of the mechanically alloyed material above 1000°C lead to the formation of new compound. The new peaks that were observed in XRD diagrams couldn't be related to new phases clearly. If those peaks were associated with the crystallization or decomposition products of the amorphised HA, then there is some matching of the peaks with those associated with $CaTiO_3$ and to $Ca_4Ti_3O_1$.

The microstructure after sintering shows that titanium was fully sintered, but hydroxyapatite remained intact as it was before the thermal treatment, containing a significant amount of pores.

In the composite material of titanium and hydroxyapatite the interface between the layer of titanium and of hydroxyapatite is weak, with micro-cracks horizontally, which maybe due to the presence of titanium oxides produced by the increased reactivity of the titanium as a result of the destruction of the HA coating. Mechanical alloying did not enhance the sinterability of the composite material. Reduction of HA particles was observed, but mixing proved to be ineffective due to the HA coating of the titanium particles that reduced the titanium -titanium contact.

A steady and not very uniform change in the composition of the composite biomaterial form the centre to the outer of the sample has been noticed.

It is believed that mechanical alloying for 10 hours reduced the spheroidicity of the particles in the composite biomaterial in relation to the starting powders.

Mechanical alloying of the HA for 10 hours led to its amorphisation.

XRD analysis showed that the crystal phase that was found in one specimen during the thermal treatment consisted of the titanium oxide routile.

Conclusions

To sum up with, these advantages of the mechanical alloying process can be observed in this paper:

i. Distribution of the secondary phase particles before sintering.

ii. Expansion of the solid solution limits.

iii. Decrease of the size of the particles in the order of nanometers.

iv. Formation of new almost crystalline phases.

v. Formation of amorphous phase.

vi. Re-distribution of graded intermetallic compounds.

vii. Possibility of diminishing the difficulty when mixing pure elements.

viii. Prompting of the translocation chemical reactions to start at lower temperatures.

Acknowledgments

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