

Effect of high energy ball milling on titanium–hydroxyapatite powders

S. Tsipas, P. Goodwin, H. B. McShane and R. D. Rawlings

This paper reports on an investigation of the potential use of high energy ball milling (HEBM) for the production of homogeneous mixtures of titanium/hydroxyapatite powders. This system is of considerable interest for the production of functionally graded material (FGM) components for use in implants in the body. In order for these FGMs to have satisfactory properties homogeneous mixtures of the titanium and hydroxyapatite (HA) powders must be produced prior to consolidation. In this investigation Ti/20 wt-% and 40 wt-% HA powder mixtures were produced by high energy milling for times of 15 minutes and 1 hour. Mixtures were also prepared on a conventional turbula powder mixer for reference purposes. The mixtures were consolidated by either cold pressing, cold isostatic pressing or hot pressing under various conditions. Selected specimens were also subjected to sintering over a range of temperatures (400–1100°C). The resulting microstructures were characterised using scanning electron microscopy, X-ray diffraction, dilatometry, differential thermal analysis and thermogravimetry.

Following the HEBM process, the resulting powders consisted of Ti particles coated with continuous surface layers of HA. It had been hoped that the process would produce a homogeneous product consisting of HA particles evenly distributed within the Ti particles and so the results were disappointing. There was some indication that the longer milling time of 1 hour produced a limited amount of HA surface layer breakup but also lead to amorphisation of the HA. A possible way forward may be to use extrusion as the consolidation process as this would provide substantial amounts of shear deformation, which in the past has been shown to be effective in breaking up surface oxide layers. An additional advantage is that the relatively high speed of the extrusion process would minimise the time available for HA amorphisation. PM/1013

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INTRODUCTION

Bioactive materials are designed to produce a specific biological response in the surrounding tissue when implanted in the body, such as inducing chemical activity that leads to a strong bond being formed with bone. The most successful bioactive structural materials as far as bonding

to bone are concerned are brittle materials as exemplified by hydroxyapatite and 'Bioglass'. Bioactive coatings are employed on metal implants to facilitate bonding to bone while retaining the good combination of mechanical properties associated with the underlying metal substrate. However, failure of the coating can arise due to thermal stresses, service stresses and poor adhesion (see for example Ref. 1). One possible solution would be to eliminate the abrupt bioactive material/metal interface and employ a functionally graded material in which the bioactive material content increases gradually from zero in the interior of the implant to the level required for formation of an adequate bond with the bone at the surface. Such functionally graded materials may be produced by a powder metallurgical route^{2,3} and at Imperial College preliminary research on the PM production of titanium/hydroxyapatite components has been undertaken.^{4,5} Of great importance in the successful production of these materials is the achievement of a homogeneous (on a very fine scale) mixture of the elemental powders prior to consolidation. This paper reports on an investigation of the potential use of high energy ball milling (mechanical alloying)^{5,6} to produce homogeneous powder mixtures.

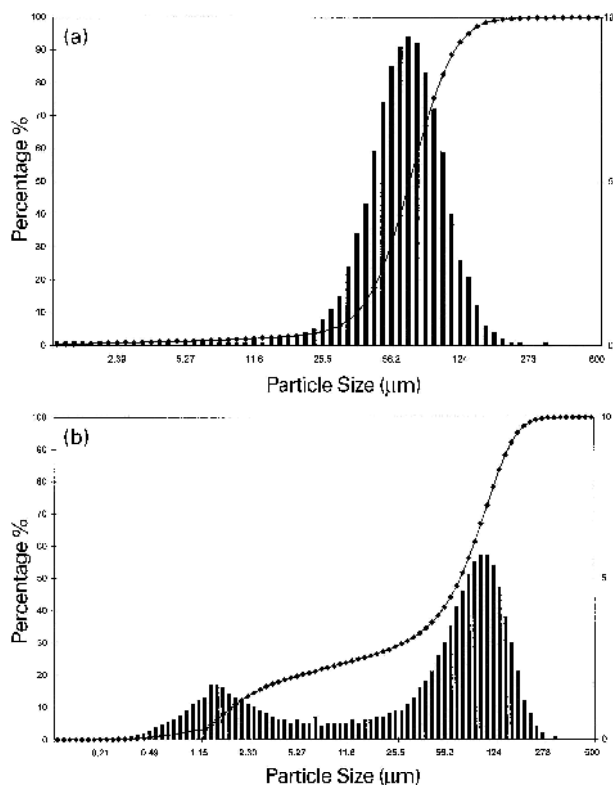
EXPERIMENTAL PROCEDURE

Processing

The nominal composition of the titanium powders used, supplied by Deeside Titanium Ltd, UK, is given in Table 1. The nominal composition of the hydroxyapatite, supplied by Biocomposites Ltd, UK, was $< 0.02\text{SiO}_2 - < 0.01\text{TiO}_2 - < 0.02\text{Al}_2\text{O}_3 - 0.01\text{Fe}_2\text{O}_3 - 54.5\text{CaO} - 1.07\text{MgO} - 0.74\text{Na}_2\text{O} - < 0.01\text{K}_2\text{O} - 41.1\text{P}_2\text{O}_5 - 0.01\text{ZnO} - 0.02\text{BaO}$.

Mixtures of 20 wt-% and 40 wt-% HA were processed in a high energy ball mill, under an inert atmosphere using a proprietary process, at DERA, Farnborough, UK. Both powders were milled for 15 minutes and an additional batch of the Ti–20% HA mixture was milled for 1 hour. At the end of ball milling the mixtures were easily removed from the mill, there was no smearing of material on the balls and the walls or significant agglomeration. A Ti–20 wt-% mixture was also produced using a Turbula 3D path rotating mixer (termed conventional mixing) for comparison purposes. Particle size distributions for the elemental powders and the mixtures were obtained using a laser particle size analyser (Malvern Mastersizer) and scanning electron microscopy was used to confirm the particle sizes and for observation of particle shape and topography.

A range of compaction methods (cold pressing, cold isostatic pressing and hot pressing) under a variety of conditions were employed. For cold pressing the powders were compacted in an 8 mm diameter, zinc stearate lubricated steel die, to a pressure of 300 MPa. The nominal height of the compacts was 12 mm. Some of the cold pressed compacts were subsequently isostatically pressed at 350 MPa for a period of 2 minutes. Finally a number of the isostatically pressed compacts were hot pressed at 500°C to a pressure of 800 MPa.



a Ti–20 wt-%HA, conventionally mixed; *b* Ti–20 wt-%HA, ball milled for 1 hour

1 Particle size distributions for powder mixtures

Sintering, under an argon atmosphere, was carried out on selected compacts at temperatures in the range 400 to 1100°C for times up to 48 hours.

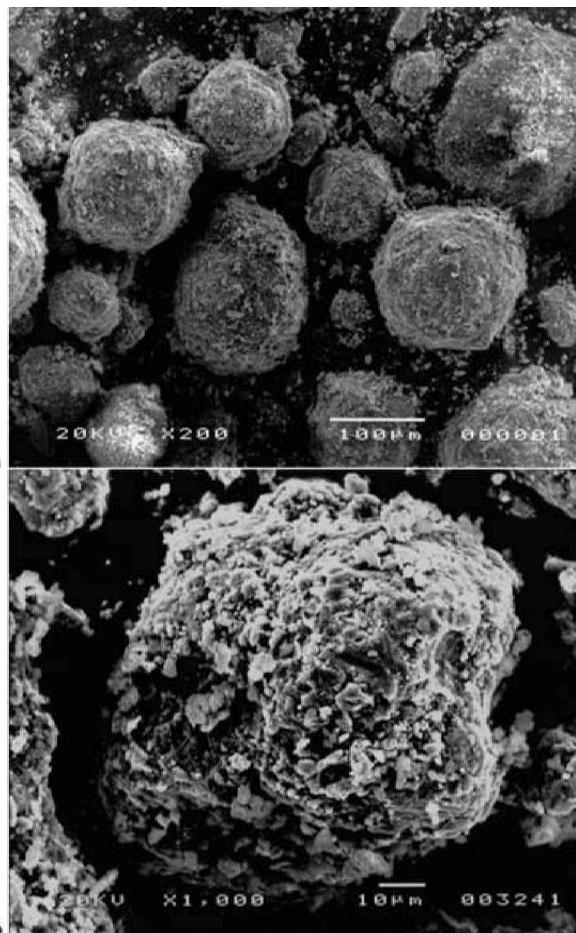
Characterisation

X-ray diffraction (XRD) was employed to study the effect of high energy ball milling and of any subsequent heat treatment on the phases present. Room temperature XRD was conducted in a Philips PW1710 diffractometer with monochromated Cu K_{α} radiation. High temperature (up to 920°C) XRD runs were performed in a Philips X'Pert machine with a high temperature, vacuum, attachment (Balzers). For an isochronal run upon reaching each successive temperature, 1 minute was allowed to pass before commencement of data acquisition. Isothermal runs were carried out at 785°C and 920°C for a holding time up to 3.5 hours.

The effect of the different processing methods on sinterability was assessed by density measurements (Archimedes method) and dilatometry. For the latter, specimens were heated up in an argon atmosphere to 1100°C at 10 K min⁻¹ in a Netzsch series 402E dilatometer.

The thermal stability of the compacts was assessed by means of differential thermal analysis (DTA) and thermogravimetry (TG) (Stanton Redcroft STA-780 series). The samples (powder mixtures and isostatically pressed) were heated in an argon gas flow from room temperature to 1000°C at a rate of 20 K min⁻¹ with Al₂O₃ as a reference.

Selected samples were sectioned, ground and polished to a 1 µm diamond finish and carbon coated. Microstructural



a Ti–20 wt-%HA, 15 minutes ball milling; *b* Ti–20 wt-%HA, 1 hour ball milling

2 Scanning electron microscope secondary electron images of powder mixtures

examination was carried out in a JEOL JSM scanning electron microscope in both secondary and backscattered electron imaging modes.

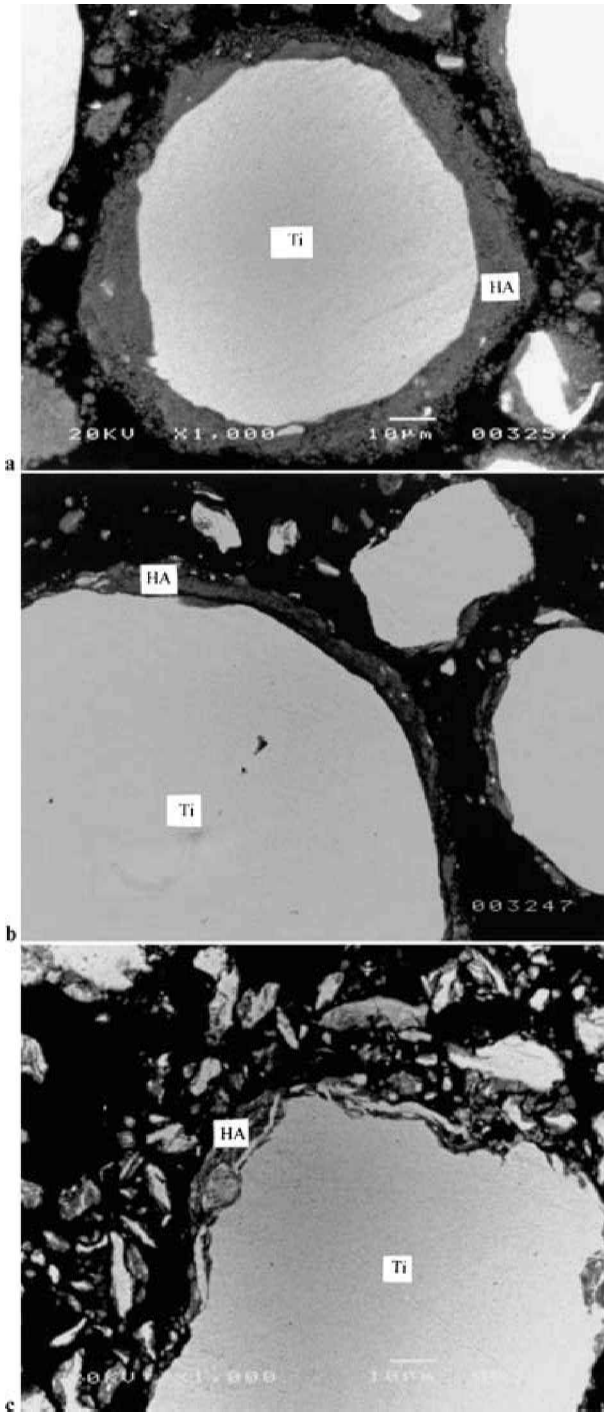
RESULTS

Of the titanium particles, 85 wt-% were in the size range 20–120 µm, with a weighted average of 56.6 µm. All of the HA particles were less than 120 µm and the weighted average was almost the same at 57.5 µm. Microscopy revealed that the HA particles were in fact agglomerates of small particles (about 1 µm). The size distribution of the conventionally mixed Ti–20 wt-%HA powder was as expected from the distributions of the constituent powders (Fig. 1*a*). In contrast the proportion of particles of less than 15 µm in size increased on high energy ball milling and after 1 hour a well developed bimodal distribution was observed (Fig. 1*b*).

Scanning electron microscopy (SEM) revealed that the large number of small particles was due to the brittle ceramic agglomerates having been broken during milling. Figure 2 shows that many of these small particles were attached to the surface of the more ductile titanium. The

Table 1 Nominal compositions (wt-%) of titanium powder

	C	Cl	Cr	Co	H	Ni	N	O	Si	Na	Sn
Typical	0.01	0.10	0.0005	0.001	0.008	0.0005	0.005	0.12	0.005	0.09	0.01
Maximum	0.02	0.15	0.0020	0.002	0.015	0.0010	0.010	0.15	0.010	0.15	0.02

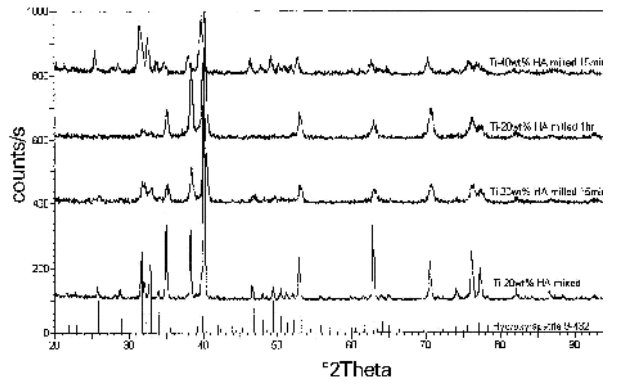


a Ti-40 wt-%HA, 15 minutes ball milling; b Ti-20 wt-%HA, 15 minutes ball milling; c Ti-20 wt-%HA, 1 hour ball milling

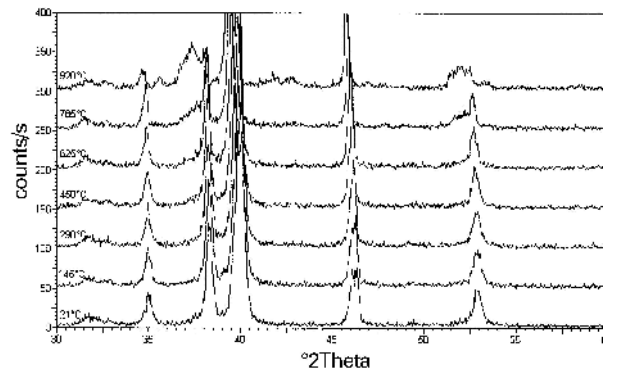
3 Scanning electron microscope back scattered electron images of cross-sections of powder mixtures

titanium particles after 15 minutes ball milling were more spherical than in the as received powder but further milling reduced the spheroidicity. SEM of cross-sections of titanium particles demonstrated that the small HA particles were not homogeneously distributed throughout the titanium but were only located on the surface (Fig. 3). In the case of the mixtures milled for 15 minutes the surface coating was fairly uniform and continuous (Fig. 3a and b) but after 1 hour (Fig. 3c) the coatings on the now more irregularly shaped particles were disrupted.

The essential features of the DTA and TG plots from the powders were the same. There was a large exothermic



4 XRD patterns showing the reduction in the intensity of HA peaks after 1 hour ball milling of Ti-20 wt-%HA



5 XRD patterns as function of temperature for Ti-20 wt-%HA, ball milled for 1 hour, showing the presence of additional peaks at 920°C

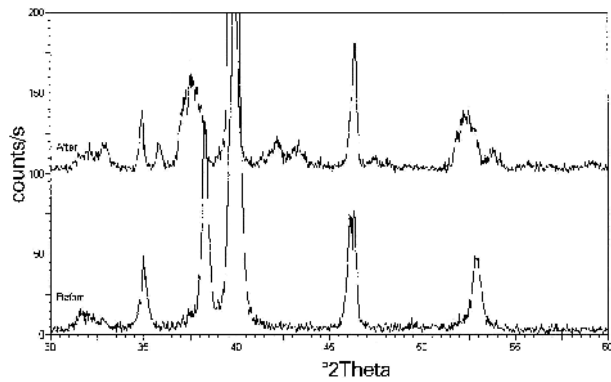
peak, commencing at a low temperature which was accompanied by a weight gain. The onset temperature, as determined from TG, and the total weight change to 950°C are given in Table 2. Note that the weight gain for titanium was normalised to a titanium content of 80 wt-% for comparison with the Ti-20 wt-%HA material.

Only diffraction peaks corresponding to titanium and HA were present in the room temperature XRD patterns from both the conventionally mixed and high energy ball milled powder mixtures (Fig. 4). The most noticeable feature of the patterns of Fig. 4 is the reduction in the intensity of the peaks for HA in the Ti-20 wt-%HA, 1 hour ball milled sample.

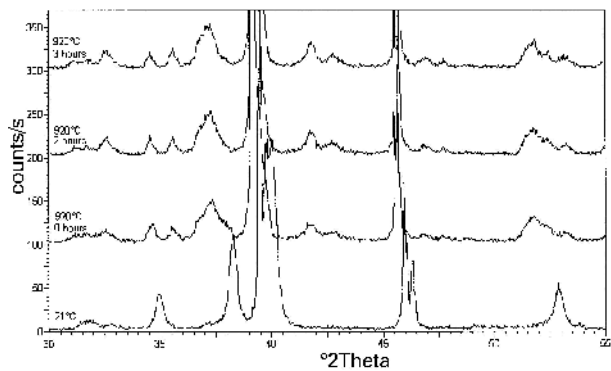
The XRD data at elevated temperatures for the Ti-20 wt-%HA and Ti-40 wt-%HA, both ball milled for 15 minutes, showed no significant changes up to the maximum temperature of the test of 920°C. The elevated temperature data for the Ti-20 wt-%HA, 1 hour ball milled sample, are presented in Fig. 5. In these patterns the peaks at about 40° and 47° are partly attributable to the platinum of the heating system. New peaks appeared at 920°C at around 35.5, 37.5, 42.0, 43.0 and 52.0°; there was also evidence of the existence of the 52.0° peak at 785°C. The

Table 2 Effect of mixing procedure (conventional or high energy ball milling) on weight gain for powders

Powder	Onset temperature, °C	Weight gain, %
Titanium	300	6.0
Ti-20%HA (Conventional)	525	3.6
Ti-20%HA (15 minutes)	525	3.2
Ti-20%HA (1 hour)	300	4.7



6 Comparison of room temperature XRD patterns for Ti-20 wt-%HA, ball milled for 1 hour, before and after the high temperature run to 920°C

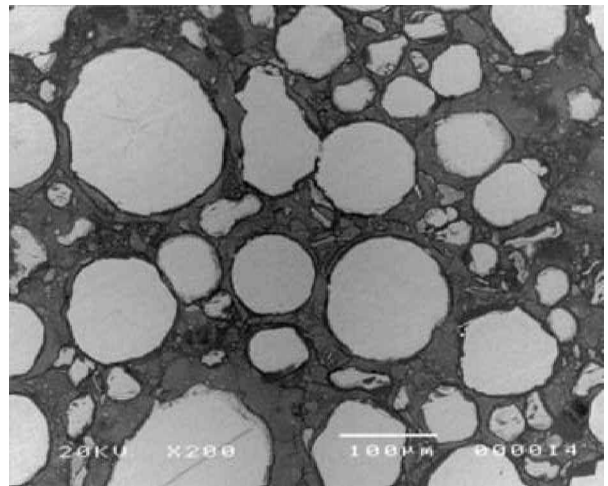


7 Effect of hold time at 920°C on XRD patterns of Ti-20 wt-%HA, ball milled for 1 hour

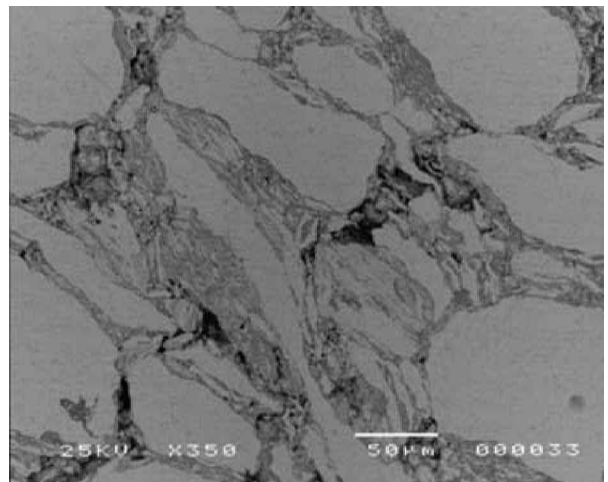
pattern from this sample after cooling to room temperature is compared with the original room temperature pattern in Fig. 6; the new high temperature peaks are still present at room temperature, although of course at slightly different 2θ values and intensities. An isothermal run for 3–5 hours at 785°C resulted in no further development of the 52.0° peak and the formation of no new peaks. In contrast at 920°C the new peaks became more marked with time (Fig. 7).

The density of the green compacts improved in the order: cold pressed, cold isostatically pressed, hot pressed. With appropriate sintering treatment densities of greater than 90% theoretical density were achievable irrespective of compaction method (Table 3). There is no evidence that high energy ball milling enhanced compaction or sintering.

Dilatometry data indicated that the onset temperature (defined as the temperature at which the length of the sample began to decrease) for sintering was about 800°C for isostatically pressed samples of Ti-20%HA, whether the powder had been ball milled or conventionally mixed



8 Scanning electron microscope back scattered electron image of Ti-40 wt-%HA, 15 minutes ball milling, isostatically pressed and sintered for 1 hour at 900°C



9 Scanning electron microscope back scattered electron image Ti-20 wt-%HA, 15 minutes ball milling and hot pressed

(Table 4). However the shrinkage from 800°C to the maximum temperature of 1100°C was found to decrease to only 0.4% for the Ti-40%HA ball milled material.

The microstructure of most of the materials consisted of fairly spherical titanium particles separated by a network of the ceramic phase as exemplified by Fig. 8. The only samples with a different microstructure were those of Ti-20%HA, ball milled for 1 hour, where the large titanium particles were significantly deformed and the ceramic network was broken down into an intimate lamellar structure of titanium and HA (Fig. 9).

Table 3 Effect of thermomechanical history on density (CP, cold pressed; IP, cold isostatically pressed; HP, hot pressed; Sint., sintered; x/y, time hours/temperature °C)

Powder	Density as % of theoretical density											
	CP	IP	HP	Sint. CP 48/600	Sint. CP 48/850	Sint. CP 2/1100	Sint. IP 1/800	Sint. IP 1/900	Sint. IP 1/1000	Sint. HP 48/600	Sint. HP 48/850	Sint. HP 2/1100
Ti-20%HA (Conventional)	73	77	92	95	92
Ti-20%HA (15 minutes)	72	78	88	78	77	93	92	93	93	91	91	93
Ti-20%HA (1 hour)	73	76	85	76	81	92	91	94	93	92	92	93
Ti-40%HA (15 minutes)	72	76	87	81	78	91	90	91	90	91	91	90

DISCUSSION

The high energy ball milling (HEBM) succeeded in breaking up the HA agglomerates as required. However instead of obtaining an even distribution of fine HA particles within the titanium, the HA coated the titanium particles. This contrasted with the seminal work of Benjamin⁸ that produced fine distributions of submicrometre size particles of thoria and yttria in a nickel superalloy matrix. Similarly more recent publications, e.g. that of Lai and co-workers and others,^{9–11} have reported that HEBM has been successful in producing aluminium alloys reinforced with SiC.

Increasing the time of ball milling from 15 minutes to 1 hour disrupted the coating and led to more distortion of the titanium (Fig. 2). The structural evolution during HEBM of mixed powders is generally accepted to be:^{11,12}

- (i) flattening of the more ductile phase,
- (ii) occlusion of brittle particles in the ductile phase to give a lamellar microstructure,
- (iii) welding and fracture leading to breakdown of the lamellar structure and a more homogeneous distribution of the brittle constituent.

In the present work, stages (ii) and (iii) were not reached. This would suggest that the employment of longer milling times may have produced a more homogeneous distribution of the HA in the titanium matrix.

However, there are problems associated with this solution. High energy ball milling for 1 hour reduced the intensity of the HA diffraction peaks. This is attributable to amorphisation of the HA and it is assumed that longer milling times would enhance the degree of amorphisation.

After HEBM the powder has to be consolidated and this involves elevated temperatures, hence the stability of the powder is important. Attempts to monitor the stability of the amorphous phase and/or to determine whether any interaction took place between the titanium and HA by DTA were unsuccessful as the curve was dominated by the exothermic oxidation of titanium, even though the tests were carried out in a flow of commercial argon. The stability of the heavily ball milled powder was determined by means of high temperature XRD. Isochronal runs showed that new peaks were present at 920°C and perhaps at 785°C. Isothermal runs at these temperatures showed no further development of new peaks at 785°C in contrast to 920°C where the new peaks became more marked. However, it has not been possible to unambiguously identify the phase(s) responsible for the new peaks. If it is assumed the peaks are associated with crystallisation and/or decomposition of the amorphised HA, then the peaks could be assigned, to varying extents, to α -TCP (α -Ca₃(PO₄)₂), β -TCP (β -Ca₃(PO₄)₂), TCPM (Ca₄P₂O₉) and HA. It has been suggested that the decomposition of HA is catalysed by titanium and can occur at temperatures as low as 800°C.¹³ If the possibility of an interaction with titanium having taken place is considered, and there is evidence of such a reaction in the literature (or more strictly a reaction between TiO₂ and HA (Refs. 13 and 14)) then there is some matching of the peaks with those associated with CaTiO₃ and Ca₄Ti₃O₁₀.

It had been hoped that ball milling would have enhanced the sinterability of the Ti–HA mixtures, by reducing HA

particle size and improving mixing. It is evident from the dilatometry and density measurements that there is no benefit in ball milling as far as sinterability is concerned. This is due to the ceramic coating reducing titanium/titanium contact as is confirmed by the microstructures of compacted and sintered materials (Fig. 8). An alternative to the longer milling times discussed above, is to employ a high strain processing method, such as extrusion, that may break up the coating and better distribute the ceramic; the potential benefit of imposing a high strain has been demonstrated by the microstructure resulting from hot pressing (Fig. 9).

Finally, it is interesting to note that the oxidation resistance of the powder milled for 1 hour was inferior to that of the powder milled for the shorter time. This is a result of the disruption of the ceramic coating and increased activity of the titanium.

CONCLUSIONS

The results of the high energy ball milling trials with the Ti/HA powders were disappointing. Instead of producing a homogeneous distribution of HA particles within the titanium particles, continuous surface layers of HA were formed on the titanium particles leading to very poor sintering behaviour. Extended ball milling times provided evidence of limited surface layer disruption but at the cost of amorphisation of the HA. The specimens subjected to hot pressing prior to sintering showed some signs of breakup of the HA surface layers due to the plastic deformation of the titanium particles leading to the formation of regions with a lamellar structure. This suggests that one possible way forward might be to consolidate the material by hot extrusion using a suitable extrusion ratio. This process would have the advantage of subjecting the titanium particles to large amounts of shear plastic deformation thus causing the HA surface layers to disintegrate. At the same time the speed of the extrusion would be such as to minimise the opportunities for HA amorphisation to occur.

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Table 4 Sintering characteristics of isostatically pressed samples as determined by dilatometry

Powder	Onset temperature, °C	Shrinkage, %
Ti–20%HA (Conventional)	800	1.1
Ti–20%HA (15 minutes)	740	1.7
Ti–20%HA (1 hour)	800	1.0
Ti–40%HA (15 minutes)	800	0.4