Effect of ball powder ratio on microstructure and compressive behaviour of porous Ti-4wt %Al alloy

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Abstract. Ti and Al powders were milled in the weight proportion 24:1 using horizontal planetary ball mill. The ratio of ball to powder amounts (BPR) was varied (10, 15, and 20) in the milling process. Powder mixture milled with different BPRs were characterized by the XRD and FESEM to probe the evolution of phase and particles shape and size. Further, these mixtures were used to make porous cylindrical samples through space holder method. The used space holder amount was 60 v%. Compression test of the samples were performed on Universal Testing Machine. It was analysed that crystallite size, shape and size of the powder particles considerably affected by the used ball to powder ratio. XRD confirms that phase formation is invariant with the BPR. The observed relative density is about 10% higher than the used space holder content. Porous sample synthesized by the powder milled with 15 BPR has higher plastic collapse stress and energy absorption capacity as compared to the samples made of the powder milled with 10 and 20 BPRs.

Keywords: Metal foam; Mechanical alloying; Ball Milling; Space holder

1. Introduction

The alloys of Ti are commonly used in the area of orthopaedic to make bone implant screw, bone scaffold, and stents for their distinctive properties of bio-inertness, lightweight and excellent noncorrosive nature[1]. However, life of the implant is limited due to the higher young modulus of the alloy than human bone which is the prime reason of stress shielding [2, 3]. Therefore, it is required to decreases the young modulus of the alloy in the range of human bone. Space holder technique is an easy and economical method to modify the young modulus of the material by the creation of porosity in its bulk [4]. Space holder (SH) like NaCl, NH4HCO3, starch, urea are prominently mixed with the metal powder to produce the pores in the final product [5-8]. However, strength of the material also reduces due to the reduction of density which is a prime concern. It was found that for the similar porosity, the compressive strength of the Ti alloy is comparatively lower than the natural bone [9]. Lower strength bounds to employ in load bearing bio implants where high strength is required.

Strength of the materials can be increased by reducing their grain size. Ball milling is extensively employed for the reduction of grain size of the material powder by the action of impact, cold welding and fracturing [10]. There are several ball mills such as high energy ball mill, attrition mill, spex mill.
are commonly used for the synthesis of nanomaterials. High energy ball mill is the equipments in which various types of materials can be transformed in the nano range due to the high grinding energy[11]. The extent of grain size reduction depends on the time and speed of the powder milling, BPR, types of used surfactant. In the literature, effects of milling time, surfactant, and milling speed are properly discussed[12]. But, variation of powder grain size and morphology of the particles in the influence of BPR are not discussed in details. Therefore, it is essential to explore the effect of BPR on grain reduction and behaviour of mechanical properties of the product made of milled powder.

This work deals with the effect of BPR on the evolution of Ti and 4%Al powder mixture characteristics due to milling in planetary ball mill for 16 h. The variation in crystallite size and lattice strain of the powder mixture milled by the use of different BPRs (10, 15, and 20) was discussed properly. The change in particles shape and size of the milled powder and their effects on the green density were analysed in detail. To reduce the young modulus of the final product, 60 v% of SH was blended with different BPRs milled powder mixtures and compacted, dried and sintered to obtain final product. The behaviour of compressive deformation of the sintered products were examined.

2. Experimental Procedure

2.1. Materials and Methods

The powders of Ti and Al (both 99.9 wt% pure and supplied by Alfa Aesar Company) were selected for the milling purpose. The average particle size of as received Ti and Al powders was 8 μm and 20 μm respectively. High energy planetary ball mill with four stainless steel cylindrical containers (volume 200 ml) was used for the milling. Ti and Al powders were filled in the three cylindrical containers in the proportion of 24:1. The stainless steel balls of 5 mm diameter were also added in containers with the metal powder in an appropriate proportion. The proportions of stainless steel balls and metal powder was chosen as 10:1, 15:1, and 20:1. 100 ml of propanol was also added in the powder + balls filled container to prevent excess heating during the milling operation. Containers were tight sealed and clamped in the planetary ball mill. The speed of the ball mill was fixed as 200 rpm for 16 h running time. After completion of milling (16 h), the powder mixtures milled with different BPRs were removed from the container and dried in an oven for 4h at110 °C for the elimination of propanol and moisture. After drying, milled powder samples were separated from the stainless steel balls by the strainer. The milled powder samples were used to prepare the cylindrical porous products. The powder mixtures milled with 10, 15 and 20 BPRs were assigned as the powder A, B, and C respectively, while unmilled Ti powder was assigned as U.

The method of preparation of porous product via powder metallurgy and space holder technique is discussed in the previous work [13]. To prepare the porous product, milled powder was mixed with 60 v% of ammonium bicarbonate particulates (average particulate size 245 μm) SH. Further, the milled powder and SH mixture was compacted in a hardened steel cylindrical shaped die (diameter = 12 mm) by applying 200 MPa compaction pressure. The compacted powder and SH mixture was removed from the die and green cylindrical compacts were found. To create porosity in the green compacts, they were dried in a vacuum oven at 200 °C for 4 h. During drying of green compacts at 200 °C, ammonium bicarbonate particulates got vaporized and the pores created at the place of particulates. The number of pores and their shape and size directly depends on the amount, shape and size of the ammonium bicarbonate particulates. Porous dried green compacts were sintered at 1100 °C for 90 minutes in a high temperature vacuum furnace. The foam samples produced by the use of A, B, and C powder mixtures, were given the name as A_f, B_f, and C_f.

2.2. Materials Characterization

Xray diffraction patterns of milled and unmilled powders were recorded by the XRD (Rigaku Miniflex ii, Japan) to investigate the phase and crystallographic evolution. Crystallite size, lattice strain were
calculated with help of Williamson Hall equation [14]. The evolution of shape and size of the powder particles due to milling was examined by FESEM (Nova Nano SEM 430 Model) micrographs. Compressive deformation behaviour of prepared foam samples were tested at UTM (model: Instron 8801) at 0.01/s strain rate. Engineering stress-strain curve was prepared by the data obtained from the test which was recorded by the software. Different mechanical properties like young modulus, yield strength, capacity of energy absorption and densification strain were analysed by engineering stress-strain diagram.

3. Results and Discussion

3.1. Analysis of XRD and crystallographic evolution

XRD patterns for the unmilled powder of Ti and milled powder mixture are shown in Fig. 1. In the XRD, only peaks of Ti was found for the unmilled Ti powder, which represents its high purity. The peaks of Ti, TiO₂, and Al₂O₃ were observed in the milled powder mixtures A, B, and C. However, intensity of TiO₂ and Al₂O₃ are very small. It shows that small amount of TiO₂ and Al₂O₃ were also present in the milled powder mixture. It may be due to the entrapment of oxygen during the milling. It can be observed that peaks related to the Ti are become broadened after the milling as compared to the unmilled Ti peaks. It is because of the crystallite size refinement and increased strain in the lattice. The crystallite size and lattice strain for the milled and unmilled powders are given in the Table 1. The size of the crystallite significantly reduces due to the milling. After milling, crystallite size of milled powders is 4 to 5 times lower than the crystallite size of unmilled one. However, in the group of milled powders, B has 6 % to 4% lower crystallite size than A and C.

Table 1: The value of the size of crystallites, lattice strain, and lattice parameters for the powders milled by different BPRs

| S/N | Powder Sample | Crystallites Size (nm) | Lattice Strain (%) | Lattice Parameter (Å) |
|-----|---------------|------------------------|--------------------|-----------------------|
| 1   | Unmilled Ti   | 99                     | 0.15               | 2.96226 4.71874      |
|   | A   | B   | C   |
|---|-----|-----|-----|
| 2 | 24.6711 | 20.3955 | 21.6703 |
| 3 | 0.24 | 0.31 | 0.27 |
| 4 | 2.95945 | 2.95978 | 2.95759 |

Also, the lattice strain is higher for the B powder as compared to U, A, and C. A reduction in lattice parameters were observed due to milling. It is caused due to the impact provided by the moving stainless steel balls in the container to the powder particles.

3.2. Microstructure and particle size analysis

Average particle size (APS) of the milled and unmilled powders were calculated by measuring the average of major and minor dimensions of 500 particles present in the related microstructures. The microstructure of the milled and unmilled powders are given in the Fig. 2. The APS are 10\(\mu\)m, 2 \(\mu\)m, 1 \(\mu\)m, and 1.5 \(\mu\)m for U, A, B, and C respectively. Aspect ratio represents the extent of circularity of a particle. For a circular particle, it is taken as 1. If the value of aspect ratio increases then particle shape goes beyond circularity. The aspect ratio of U was measured as 1.32 while after milling, aspect ratio for the powders A, B and C were measured as 1.48, 1.58 and 1.53 respectively. It indicates that the circularity of the particle is also reduced due to milling. Particles flattening (arrow marked)occurs because of the milling. The particles of A is more flattened as compared to the B and C (Fig. 2 (b), (c), and (d)). The B powder is the mixture of fine particles as well as some amount of circular shaped flattened particles with widen size range. It indicates that proper particle fracturing occurs in the B powder. The powder particles are subjected to the impact and rolling action in the influence of moving balls. Due to milling, various types of defects like vacancies, stacking faults, dislocations are generated in the particles. Fracturing of the particles occurs when these defects exceed beyond a limit. A fraction of fragmented particles also re-welded or reformed to make relatively bigger size particle. The extent of impact and shearing action is relatively less in case of A and C because of relatively high ball loading with respect to the powder used. A greater fraction of energy spent on re-welding of fragmented particles, causing increase in particle size and reduction in aspect ratio as compared to that of “B” particles.
3.3. Green density, dried density and sintered density of the cylindrical sample

Density of the green, dried and sintered products were calculated by the ratio of their weight and volume and shown in the Fig. 3. Green density of the compacted product made of the 10, 15, and 20 BPRs milled powders and 60 v% ammonium bicarbonate space holder is assigned as A<sub>g</sub>, B<sub>g</sub> and C<sub>g</sub>. It was observed that the value of B<sub>g</sub> is 1.68 g/cm<sup>3</sup>, which is 3% and 6% higher than the A<sub>g</sub> and C<sub>g</sub>. The particles of the B powder is finer as well as circular in nature. Also, the range of particle distribution is larger. The circular shaped with the particles of widen size distribution packed properly during the compaction[15]. Therefore, green density of B<sub>g</sub> is higher than A<sub>g</sub> and C<sub>g</sub>. From Fig. 3, it can be seen that the density of the each product being reduced after the drying process. It is because of the removal of ammonium bicarbonate particulates during drying at 200 °C. At this temperature, ammonium bicarbonate decomposed in ammonia and water vapour and carbon dioxide. Therefore, vacant sites generated at the place of ammonium bicarbonate particulates in the green product after drying. These vacant sites are uniformly distributed in the product and known as the pores. Due to generation of pores, weight of the product reduces without considerable volume change. Therefore, samples density also reduced after drying. The density of the product after sintering at high temperature is known as sintered density. Density for each sample was found to increase after sintering. During sintering, diffusion of the atoms takes place and the contraction of the dimension occurs. Hence, sintered density increases. The sintered densities of the porous product A<sub>f</sub>, B<sub>f</sub>, and C<sub>f</sub> are calculated as 1.42, 1.51, and 1.46 g/cm<sup>3</sup> respectively.

Figure 2. Microstructures of the unmilled Ti powder (a), milled powder mixture with 10 BPR (b), milled powder mixture with 15 BPR (c), and milled powder mixture with 20 BPR (d).
Figure 3. Variation of different densities during after compaction (green density), drying (dried density), and sintering (sintered density) for the product made of the powders milled by the use of 10, 15 and 20 BPRs.

Porosity present in the porous sample is found by the equation (1):

\[ \text{Porosity (Po)} = 1 - \text{Relative density} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \
its strength depends significantly. In the present case, the thickness of the cell wall was found in the range of 40-60 μm. Fig. 4 (b) shows the microstructure of cell wall after polishing and etching the surface of the porous sample. It can be easily seen that eutectic phase is formed in the material. The phase formation and pores present in the material is similar for the A, B, and C porous samples.

![Microstructure of porous sample](image)

**Figure 4.** Microstructure of the porous sample. (a) presence of pores and cell wall, (b) microstructure of cell wall containing eutectic phase.

3.5. Analysis of engineering stress-strain curve

Engineering stress-strain curve for the A, B, and C porous samples is shown in Fig. 5. The diagram contains three distinct parts known as elastic region; plastic region; and densification region. The region in which stress and strain vary linearly is known as the elastic region. The maximum stress attained by the porous product in this region is called as the plastic collapse stress. After the elastic region, stress oscillates along a mean value and this stress is recognised as plateau stress up to a definite strain. This region is identified as Plateau Region of the foam. Plateau region occurs due to the specific deformation behaviour. During the compression of foam, the surface that is direct contact with the compressive media experiences higher compressive force due to cellular structure. The depth of the material, up to where equal compressive force is experienced is known as a layer. Each layer has slightly different collapse stress due to the variation in number of pores and their orientation because of the inhomogeneity. When applied compressive force becomes higher than the collapse stress of the layer then it bursts. After collapsing the first layer at a certain stress, each layer goes to collapse at slightly different stress that is a cause of stress oscillation. After the plateau region, stress increase rapidly without considerable change in strain, known as Densification Region. This region starts when all the layers of the foam have been collapsed and densifies behaving as a dense material.
A comparison of plastic collapse stress, elastic modulus, specific energy absorption capacity and densification strain for the A_f, B_f, and C_f porous samples are shown in Fig. 6 (a), (b), (c), and (d) respectively. Plastic collapse stress is higher for the B_f than A_f and C_f in the range of reported RD. The value of plastic collapse stress attained by A_f, B_f, and C_f are 31 Mpa, 42 MPa, and 36 MPa. For the proper functioning of the porous material as a bone implant, elastic modulus should be in the range of natural bone. The value of elastic modulus for the prepared porous samples are in the range of 13-14 GPa, which match with the elastically modulus of cortical bone. The specific energy absorption capacity (SEAC) shows the shock absorption behaviour of the sample. For a good bio-implant, the SEAC should be high. The value of SEAC for B_f is 25% and 15% higher than the A_f and C_f with the of 21 MJ/m^3. Densification strain is approximately same for the each sample and varies from 0.59 to 0.61.
Figure 6. Comparison of different mechanical properties of A, B, and C porous samples. (a) Plastic collapse stress; (b) Elastic modulus; (c) Specific energy absorption capacity, and (d) Densification strain.

4. Conclusions

The microstructural and morphological evolutions have been studied on milled Ti4Al for different milling time by the use of varying BPRs in high energy planetary ball mill. After study, following points were concluded:

- Due to powder milling grain refinement occurs. The extent of grain refinement depends on the used ball to powder ratio.
- The powder particles change their shape from spherical to flaky. Sintered product made of flaky fine powders has about 10% higher porosity than the used space holder content.
- Plastic collapse stress is found maximum for the porous sample made of milled powder using 15 ball to powder ratio. Also, it has the elastic modulus in the range of natural cortical bone.

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