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Transformation and powder Characteristics of TiO_2 during high energy milling

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Ball-milling is a way of inducing phase transformations, chemical reactions and changes in the reactivity of solids. Anatase to rutile phase transformation was studied by milled samples. Ball milling was carried out by planetary milling with different milling medium, Ball-to-Powder Ratio (BPR), and different milling time. The results revealed that the anatase to rutile transformation completed after 20 hours by dry milling whereas there is no phase transformation by wet milling even after 60 h milling time. The amount of energy by using (BPR 5 : 1) during all dry milling periods was not enough to transfer the phase from anatase to rutile while anatase phase completely transferred to rutile by using BPR (10 : 1 and 20 : 1). The Crystallite size decreasing with increasing milling time. Crystallite size estimated from X-ray Diffraction (XRD) data. Scanning Electron Microscopy (SEM) micrographs clearly show more agglomeration by using BPR (20 : 1). less agglomeration and smaller size of the powder particles were obtained by wet milling compared to dry milling.

Key words: Ball milling, Anatase, Transformation, Titanium dioxide, Rutile.

Introduction

Titanium dioxide (TiO_2) is a crystalline material, commonly known as titania. The natural amorphous of titania are Rutile, Anatase and Brookite [1]. The stable form of titania is Rutile, other forms of titania transform at sufficiently pressure or temperature. Rutile has a tetragonal crystal structure in which the octahedra share four edges while Anatase has a tetragonal crystal structure in which the Ti-O octahedra share four corners [2]. Rutile has a more compact crystal structure and this explains why it has a higher specific gravity and harder for some applications [3, 2]. For outdoor durability as well as optimal hiding power in coating and plastics application TiO_2 pigment must be composed of rutile due to its higher refractive index (2.72) than that (2.52) of anatase [4, 5].

High energy ball milling is a way of inducing phase transformations in solids. Polymorphic transformations may take place during dry milling in various oxides. In the ball-milling process, powders are plastically deformed under high-energy between balls and the wall of the vial. In this process, three simultaneous phenomena are reported to occur: cold-welding, fracturing and annealing of powder grains. Ball milling is thus a complex process, depends on many factors, like the type of mill, dynamical condition of milling, temperature, atmosphere during milling, chemical composition of powder and properties of grinding media.

Many reports are available on the transformation of TiO_2 by mechanical milling from anatase [6, 7, 8].

Very few researchers pointed to effect of BPR and wet milling medium on transformation of anatase to rutile [9, 10, 11].

In an attempt to make this transformation possible at lower BPR (10 : 1) with lower milling speed (400 rpm), and study the effect of BPR and wet milling medium on transformation of anatase to rutile the present work was undertaken.

Experimental

In the present study, TiO_2 powder (purity 99.5%, 80-250 μm) was used as raw material. High-energy ball milling of anatase TiO_2 was milling by a planetary ball milling (Model P5, Fritsch) with the following parameters:

Stainless steel balls size	BPR	Rotational speed	Milling time	Milling medium
20 mm	5 : 1 to 20 : 1	400 rpm	10 h to 60 h	Dray and wet

The milled powder were tested using SEM-EDAX, and XRD.

Results and Discussion

Effect of wet milling on morphology of TiO_2

TiO_2 powder was used as raw material with maximum particle size 250 nm as shown in fig. 1, the titanium oxide powders are present at submicron scale with regular shapes.

Less agglomerated and smaller size of the powder

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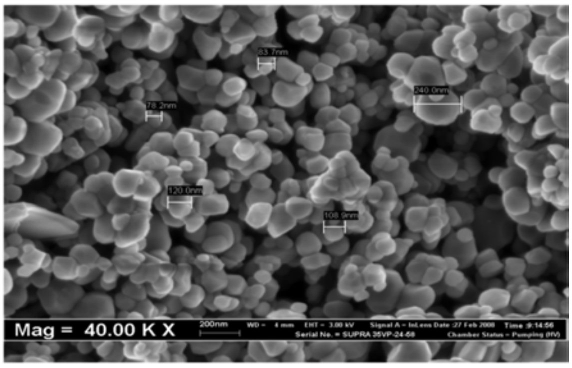

Fig. 1. SEM micrographs of as received powders of TiO_2 (40000x).

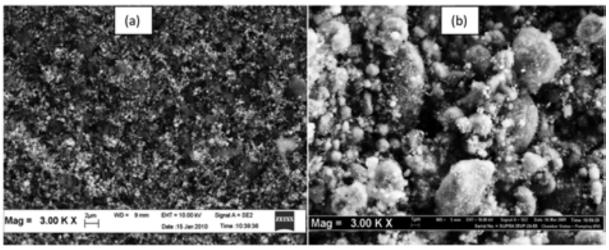

Fig. 2. SEM micrographs of TiO_2 after (a) 20 h wet milling (b) 20 h dry milling with BPR 10 : 1 (3000x).

particles were obtained with 20 h wet milling as shown in Fig. 2(a) compared to dry grinding as shown in Fig. 2(b).

Morphology changes in as-milled powder with dry milling at BPR 10 : 1 and BPR 20 : 1

The SEM technique was used to examine the changes in shape and size of the milled powders during the different stages of milling. At early stage, the powders were fine as shown in Fig. 3(a and b). Continuous deformation created new surface on par-ticles and particle size goes down to nanometer range and hence their specific surface energy increases significantly. On the other hand, the micro- strain produced in the particles increases as the milling time of the powder increases. Both these processes lead to enhance instability in the powder particles. A critical stage of instability is reached in the system with prolonged grinding when the particles start coalescing to form bigger particles by way of releasing the excess energy [12]. This stage indicated that cold welding was dominant than fracturing leading to the generation of large particles as shown in Fig. 3(c). SEM micrographs clearly show the different morphologies of powders milled for short milling time and for long milling time.

Suryanarayana (2001) has reported that increasing the ball-to-powder weight ratio (BPR) to 20 : 1 results in a faster rate of decrease in particle size; and a lower BPR of 10 : 1 decreases the rate of reduction. As a result of the rapid decrease in particle size, the surface energy of the powder increases and leads to rapid

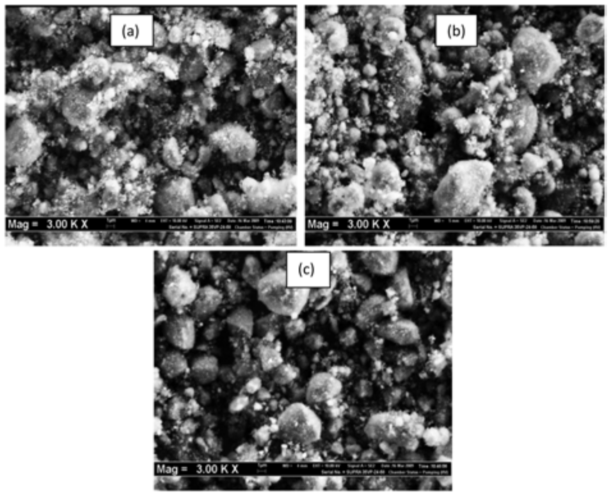

Fig. 3. SEM micrographs of TiO_2 after milling for (a) 10 h (b) 20 h (c) and 30 h, with BPR 10 : 1 (3000x).

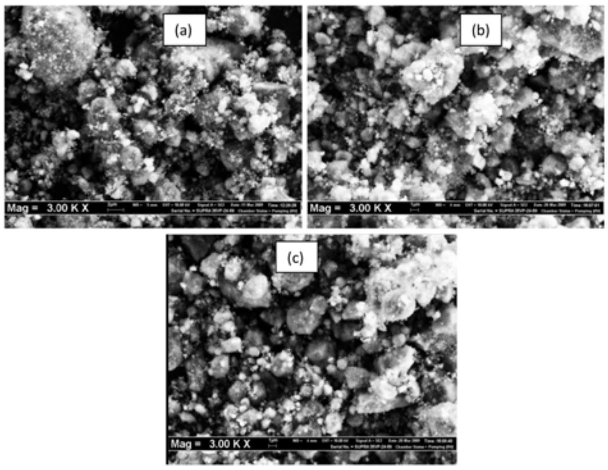

Fig. 4. SEM micrographs of TiO_2 after milling for (a) 10 h (b) 20 h (c) and 30 h, with BPR 20 : 1 (3000x).

recombination of nanoparticulate into agglomerates also by high BPR balance was achieved between the rate of welding, which tends to increase the average particle size, and the rate of fracturing, which tends to decrease the average particle size as shown in Fig. 4.

Effect of Wet Milling Medium on phase transformation

Transformation of energy which causes phase transformation is affected by milling parameters such as type of mill, milling speed, type of milling media, ball to powder ratio, dry or wet milling and duration of milling. During wet milling, the reduction reaction was noticed to start after long milling time compared to that with dry milling [13].

Anatase to rutile transformation has not been noticed even after 60 h during wet milling as in fig. 5(a), whereas the transformation completed after 20 h during dry milling due to higher transformation of energy during dry milling compared to wet milling as shown in Fig. 5(b).

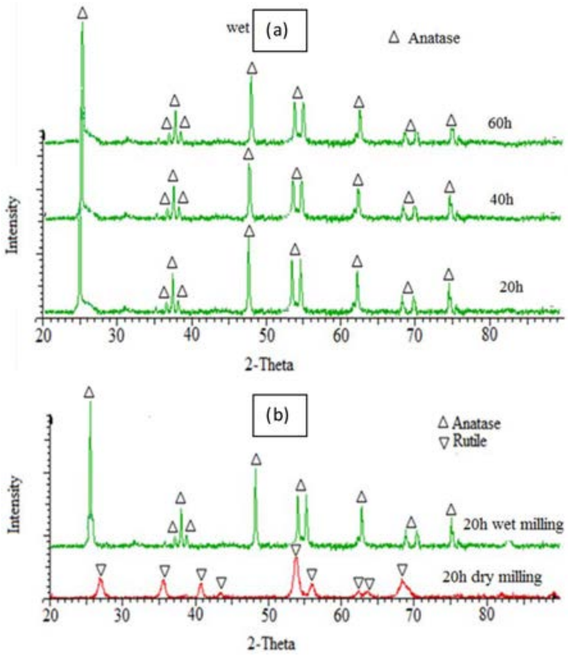

Fig. 5. XRD patterns of TiO_2 powders with (a) 20 h milling time in wet medium (b) 20 h milling time in dry and wet media.

Effect of ball-to-powder ratio (BPR) on phase transformation

BPR is an important variable in the milling process, which has been studied from as low as 5 : 1 to 20 : 1 BPR ratio. The use of BPR at 5 : 1 during all milling periods where the amount of energy transferred to powder was not enough to transfer the phase from anatase to rutile as indicated from Fig. 6(a). BPR has significant effects on the time required to achieve a particular phase in the powder being milled, and higher the BPR, the shorter is the time to achieve a particular phase (rutile) as shows in the Fig. 6(b and c). Increasing BPR causes increasing number of collisions per unit time and consequently more energy is transferred to the powder particles leading to decrease in grain size and consequent increase in grain boundary area. It therefore increases the mechanical activation of the system, thus leading to easier transformation and formation of new phases as a means of reducing the free energy of the system [9, 10].

It was reported that the BPR has a strong effect on the amorphous phase formation and on the subsequent recrystallization during continuous milling too, milling at higher BPR leads to much faster kinetics of amorph-ous phase formation and more contaminations compared to the sample milled at lower BRP [14, 15, 16, 17]. Amorphization also occurs during milling [18, 19]. Also high BPR still poses as the major limitation towards amount of rutile product using mech-anochemical route because the productivity of rutile decreases with higher BPR. Most of the MA/MM operations have been carried out by BPR 10 : 1. From Fig. 6(b and c) all peaks for TiO_2 after milling 30 h were rutile, whereas

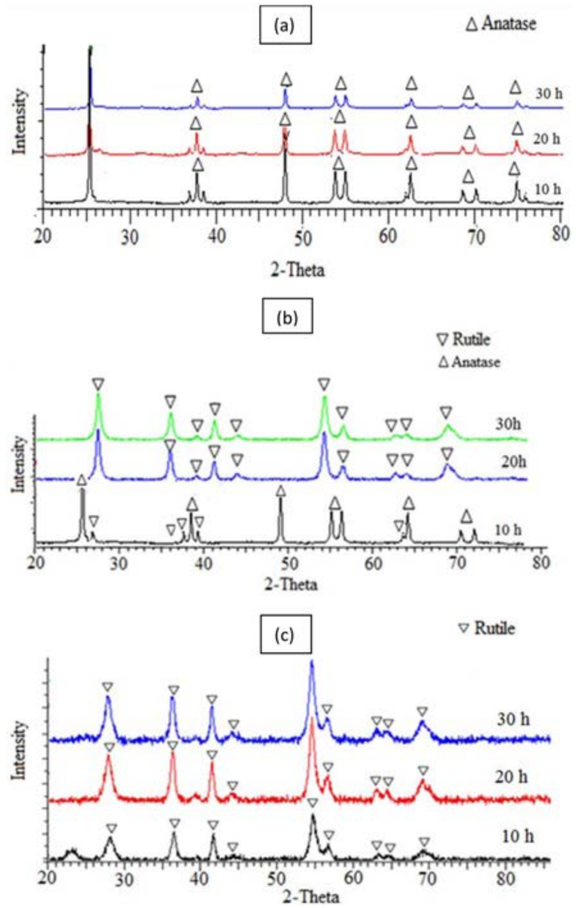

Fig. 6. XRD patterns of TiO_2 milled for different milling time by using BPR (a) 5 : 1 (b) 10 : 1 (c) 20 : 1.

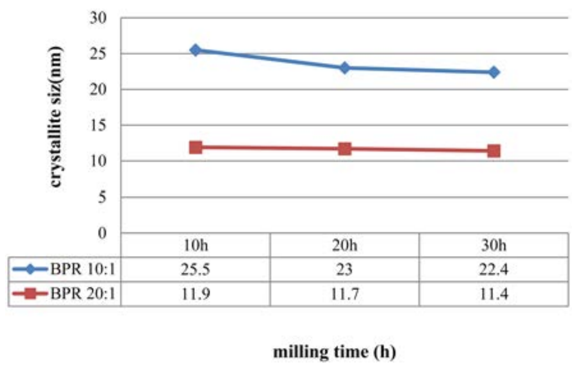

Fig. 7. Effect of milling time and BPR on crystallite size of TiO_2 powders.

no change in anatase peaks even after 30 h milling were noticed as in Fig.6(a) at BPR 5 : 1. From Fig. 6(c), it has been observed that the peaks with BPR 20 : 1 have less intensity and border peaks than peaks with BPR 10 : 1 The broadening of the peaks are due to decrease in crystallite size which occur by increasing milling time and higher BPR as shown in Fig. 6. The crystallite size of TiO_2 is a function of milling times and BPR. Crystallite size was estimated from the XRD data by using Scherrer equation as the following: $D = k/B \cos\theta$, Where D is the average crystallite size, k is the Cu K wave length, B is the diffraction peak width at half-maximum intensity and θ is the Bragg diffraction angle [20, 21]. From Fig. 7 it can be observed that BPR 20 : 1 at all milling durations achieved lower crystallite size due to the increase in the average frequency of collisions that causes an increase in the defect concentration.

due to the generally accepted theory of phase transformation in which two Ti-O bonds break in the anatase structure, allowing rearrangement of the Ti-O octahedra, which leads to a smaller volume and rutile phase [2].

Conclusions

Rutile has been transformed directly from anatase powder by lower BPR (10 : 1) and lower milling speed (400 rpm) through mechanical activation. In the proposed technique, the transformation of rutile was completed at dry milling with shorter milling time due to the mechanical activation process which enhanced the reactivity of the reactants as well as enhanced reaction kinetics. The milling conditions employed were also less severe. By using wet milling there is no phase transformation even after 60 h milling time while by using dry milling with increasing milling time, and PBR ratio lead to more rutile transformation due to increasing number of collisions per unit time and consequently more energy is transferred to the powder. The average crystallite size of the TiO_2 formed under all the conditions was in the nano range. The crystallite size of TiO_2 decreases with increasing milling time and PBR ratio.

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