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# Development of Nano-$TiO_2$ by Mechanical Milling

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**Abstract:** ***This paper reports the results of an investigation aiming at finding what affects the grain size of nano-$TiO_2$ powder during synthesis. Nano-sized $TiO_2$ powders have been prepared by a Mechanical milling method. The crystalline structures and morphologies of the powder have been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The result shows that the different preparation conditions such as wet, dry and milling time have a lot of influences upon the properties of nano-$TiO_2$ powders. The smallest grain size of $TiO_2$ powder we have obtained is ~12nm by controlling the process conditions.***

**Keywords:** Milling time; Nano-$TiO_2$ powder, XRD, TEM

## 1. Introduction

Since Gleiter's report [1] on the nano-materials, more attention has been paid upon the research of nano-materials. Compared with the traditional materials, nano-phase materials processes unusual chemical, mechanical, optical, electrical and magnetic properties [2].

Titanium dioxide is mainly applied as pigments, adsorbents, and catalytic supports. In almost all of these cases, the size of the titanium dioxide particles is an important factor affecting the performance of the materials. It is not surprising; therefore, that much research has been focused upon the reduction of particle size. Mechanical milling route is regarded as a good method to synthesize ultra-fine metallic oxide [3]. Mechanical milling process is a high-energy ball milling operation that involves the repetitive welding, fracturing, and rewelding of powder particles. Now the process has been regarded as an effective tool to synthesize metastable phases, e.g. supersaturated solid solution amorphous alloys and nanocrystalline materials [4-6]. It was usually found that different routes often produce different results. Even for the same route, using different amount of the starting materials the powder size obtained is different [7]. So it is regarded as necessary for us to investigate in detail the factors which may have important effect upon the particle size. In this paper, titanium dioxide nano-powders were prepared by the Mechanical milling. Using various techniques, including transmission electron microscopy (TEM), X-ray diffraction (XRD), powders obtained were studied in order to find the possible elements of affecting the microstructures and grain size.

## 2. Experiments Detail

Nano-sized TiO2 powders have been prepared by a Mechanical milling method. The structures and morphologies of the powder have been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

### 2.1 Material Synthesis

Commercially available micron sized powders of TiO2 (99%Pure, LOBA Chemic Pvt Ltd, Mumbai) were used. The milling was performed in a planetary ball mill (FRITSCH, GERMANY). Initially the particle size of the TiO2 were measured with the help of a Particle size analyzer (FRITSCH Particle Sizer Annlysett-22) During milling the weight ratio of the ball to the powder was maintained at 10:1. The balls and vials are made of tungsten carbide. The rotating speed for milling of the vials was maintained at 300 rpm for all the experiment. Primarily acetone was used as the wet milling medium. After milling for a predetermined time e.g. 20h and 35h, a small amount of ball-milled powder were taken out for analysis. Another set of nano TiO2 powders was prepared by dry milling without using any liquid milling medium. Samples were drawn after predetermined time intervals 20h and 35h.

### 2.2 Characterization

The particle size of the $TiO_2$ before milling was measured with the help of a particlesize analyzer (Fritsch Particle Size Analyzer-22). As receive and milled powders were characterized by X-ray diffraction (XRD) technique. X-ray diffraction analysis was carried out using CuKα radiation on a Philips PW1840 diffractometer using a step size of $0.05^0$ (2θ). Prior to these analyses, XRD peaks were corrected for the effects of the $K\alpha_2$ radiation and instrumental broadening. The particle size of the ball milled $TiO_2$ powders (wet & dry) were computed by the XRD technique using single line profile analysis. [8] It is imperative to briefly mention about the principle of SLA technique. The X-ray diffraction pattern ofnanoc-rystalline materials exhibits considerable peak broadening with reduced intensity due to the combined instrumental effects and structural factors like reduced crystallite size and strain at the atomic scale, caused by the lattice distortion. Therefore, the measured line profile 'h' is considered to be the convolution of the standard profile 'g' with the structurally broadened profile 'f' and is represented by

$$H = g*f. \quad (1)$$

The contribution of g, arising due to the instrumental effects, is computed by recording the XRD pattern of a polycrystalline large grained, strain free standard sample. In the present study, Si is used as the standard, where the crystallite size and strain effects are insignificant. The broadening of the pattern is thus only due to the instrumental effects. The contribution of the size and strain profiles in the structurally broadened profile f can be found by fitting Cauchy and Gaussian distribution, respectively. Again considering h, f and g profiles to be Voigt functions we can write

$$H_c = g_c * f_c \text{ and } h_G = g_G * f_G. \quad (2)$$

The subscripts C and G represent the Cauchy and Gaussian component of the respective Voigt profiles. The integral breadth (β) of $f_c$ and $f_G$ are given by

$$B^f_c = \beta^h_c - \beta^g_c \text{ and } (\beta^f_G)^2 = (\beta^h_G)^2 - (\beta^g_G)^2 \quad (3)$$

The constituent Cauchy and Gaussian components were obtained from the ratio '2w/ β for h and g profiles, where'2w' is full width at half maximum intensity of the peak and β is the integral breadth. Considering the most intense XRD peak, the crystalline size D, computed using SLA analysis, is given by

$$D = \lambda / \beta^f_c \cos\theta \text{ and strain } e = \lambda / \beta^f_G \, 4\tan\theta, \quad (4)$$

Where β is measured in radians, λ is the K∞1 radiation used and θ is the Bragg angle.

The microstructure, crystallite size were studied using the JEM 2100 HRTEM operated at an acceleration voltage of 200 kV in bright field modes. Selected area diffraction (SAD) patterns were obtained to identify the phases at specific locations using appropriate aperture and tilt.

## 3. Results and Discussion

The particle size distribution of the $TiO_2$ powder prior to mechanical milling is shown in Figure 1. The size distribution profile of the powder clearly shows that the distribution is fairly wide ranging from 0.195μm to 23.08μm

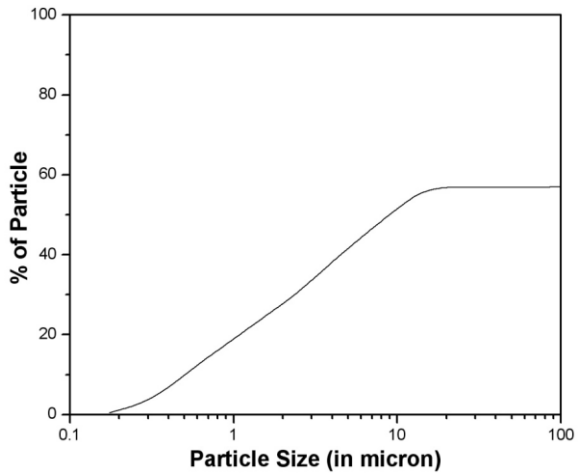


**Figure 1:** Particle size distribution of $TiO_2$ powder sample before ball milling

Figure 2 and 3 shows the results of XRD analysis of the mechanical milled $TiO_2$ powders in dry and wet condition. The pattern clearly shows that initially $TiO_2$ particles possess tetragonal crystal structure, which transform partially to orthorhombic and hexagonal crystal structure with the increase in dry milling and wet milling time. It has been further observed that the XRD pattern gets broadened with the increase in milling time, which suggest reduction in $TiO_2$ particle size and increase in lattice strains in the crystallites. This effect appears to be more prominent in the XRD pattern of the dry milled sample than the XRD pattern of the wet milled $TiO_2$ powder. This can be further corroborated by the results of the XRD pattern of the ball-milled sample by analyzed by the single line profile analysis technique.

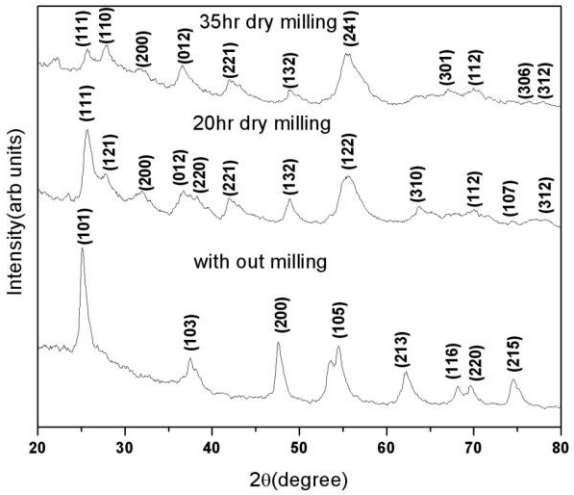


**Figure 2:** XRD spectra of $TiO_2$powder (a) After 20h dry milling (b) After 35h dry milling (c) without milling.

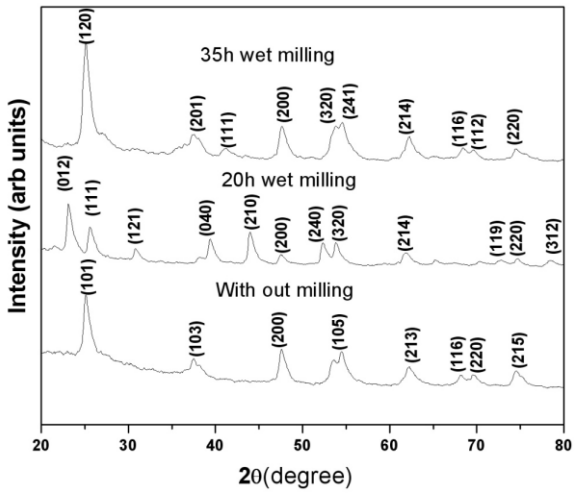


**Figure 3:** XRD spectra of $TiO_2$powder (a) After 20h wet milling (b) After 35h wet milling (c) without milling

**Table 1:** Influence of different milling condition and time on the variation of particle size and strain as measured by single line profile analysis of XRD spectra

| *Milling time (hrs)* | *Milling condition* | *Particle size (nm)* | *Strain* |
|---|---|---|---|
| 20 | Dry | 16.15 | 0.012 |
| 35 | Dry | 11.86 | 0.0109 |
| 20 | Wet | 893 | .0019 |
| 35 | Wet | 16.17 | .0091 |

Table 1 summarizes results of the single line profile analysis, which shows the variation of particle size and lattice strain with respect to milling condition and time. From the table it is quite clearly evident that with the increase in milling time the particle size of $TiO_2$ powder decreases and corresponding lattice strain increases. It has been also seen that dry milling is more effective technique in reducing the particle size to the nanometric length scale as compared to wet milling.

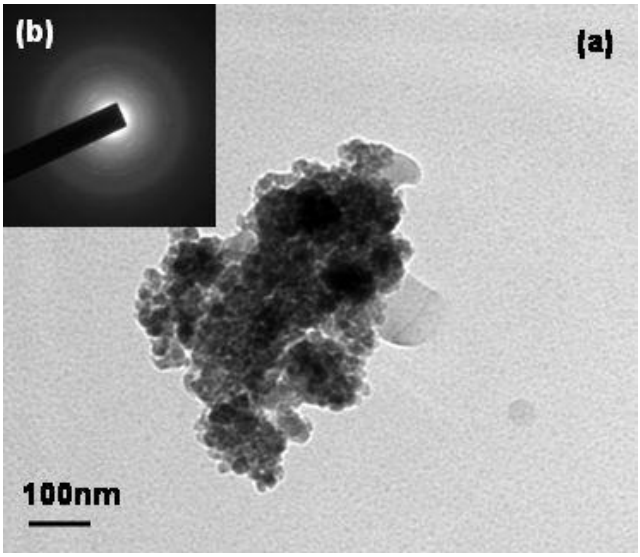


**Figure 4(a):** Bright field TEM image and inset (b) the corresponding SAD pattern of the powder dry milled after 35 hr.

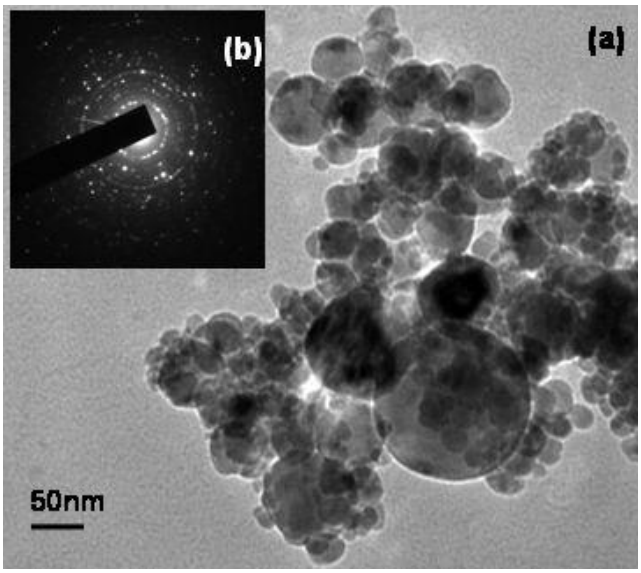


**Figure 5(a):** Bright field TEM image and inset (b) the corresponding SAD pattern of the powder wet milled after 35 hr.

A bright field TEM image and the corresponding SAD pattern from the powder dry milled after 35 hr are shown in Fig. 4. Examination of the TEM image (Fig. 4a) and indexing of the Debye rings in the corresponding SAD pattern (Fig. 4b) indicate that nano-sized (~10 nm). Fig. 5 shows the bright field TEM image and the corresponding SAD pattern of the dry milled after 35 hr. Comparison of the TEM images in Fig. 4a and 5a suggests that dry milling is the better process for obtaining minimum crystal size $TiO_2$. In fact, the SAD pattern from the powder wet milled after 35 hr (Fig. 5b) shows many spot with Debye rings which confirm larger crystallite Size.

## 4. Conclusion

The conclusions that are drawn from this investigation are:

a) Nano-$TiO_2$ powders have been prepared by mechanical milling method successfully. By controlling the conditions properly, nano-$TiO_2$ powders with the grain size less than 12 nm could be obtained.
b) Micron sized $TiO_2$ particles which initially possesses a tetragonal crystal structure, transform partially to orthorhombic and hexagonal crystal structure with the increase in milling time.
c) Dry milling technique has been found to be more effective method of particle size reduction of $TiO_2$ then the wet milling technique

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