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Mechanically induced polymorphic phase transformation in nanocrystalline TiO_2 powder

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ABSTRACT

Microstructural evolution of nanocrystalline TiO_2 powders during mechanical milling was evaluated via Rietveld refinement method. Fully anatase phase nanocrystalline TiO_2 powders were mechanically milled using a high-energy planetary ball mill. Milling the powders, employing two types of balls with different sizes, and annealing at three different temperatures, led to the formation of equiaxed nanocrystalline TiO_2 powders with the mean crystallite size in the range of 10–80 nm, based on the Rietveld refinement results. According to the X-ray diffraction and scanning electron microscopy results, it was found that phase structure, composition, and crystallite size of the resulting particles were dependent on annealing temperature. The transformation kinetics is properly described by the standard first-order model of Avrami–Erofeev equation with activation energy of $E = 28$ kJ/mol which implies at the random nucleation of rutile phase on the surface of anatase crystallites followed by an instantaneous growth of the nuclei.

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1. Introduction

Owing to their wide range of applications in photocatalysis, pigments, cosmetics [1–3] and sensor industries [4], TiO_2 nanocrystalline particles have been of much interest in recent years. TiO_2 exists in three common crystalline polymorphs: anatase, rutile and brookite [1,3,5,6]. Under ambient conditions, coarse-grained rutile is thermodynamically more stable compared to coarse-grained anatase or brookite [7]. However, thermodynamic stability is particle-size dependent, and at particle diameters below ca. 14 nm, anatase is more stable than rutile [8]. This may explain why anatase can be synthesized at ultrafine sizes. If nanocrystalline titania is heated, crystal growth leads to the alteration of phase stability and, ultimately, conversion of both anatase and brookite to rutile. However, it is unclear whether brookite firstly transforms to anatase, or vice versa [9]. The properties of TiO_2 are closely related to its crystal structure, which makes phase transformation one of the most important issues in the practical application of the material.

In the study of nanocrystalline materials, the crystallite size is usually the sole factor of interest. Effective introduction of nanocrystalline particles in different applications requires careful investigation on the crystallite size of these particles to make the most out of their exceptional properties. The reason behind the importance of the crystallite size lies in the fact that the performance of TiO_2 in these applications is strongly influenced by its crystalline structure, morphology and especially crystallite size [1,3,4,10]. On the other hand, calorimetric data for the transformation enthalpies of anatase-to-rutile and brookite-to-rutile suggest that the thermodynamic phase stability for the three polymorphs is: rutile > brookite > anatase. Thus, anatase may either transform directly to rutile, or to brookite and then to rutile [11].

The ease of data collection in the powder diffraction instruments and their availability and versatility make them indispensable tools to obtain compositional, structural, microstructural and many other types of information. The extensive peak broadening and possible overlapping inherent in the studies of the patterns acquired from nanocrystalline particles make the phase determination process a very demanding and time-consuming process. Misidentification of the multiple phase systems, co-existing in closely related phases, as being single phase ones, can lead to fallacious results [12]. Therefore, full-pattern profile fitting techniques are extensively employed to assist in the phase identification process for quantification purposes. Among various established methods for the analysis of X-ray diffraction patterns, Rietveld refinement [13] method (a full-pattern profile fitting method) is highly considered as an elaborate and rigorous method for the size–strain analysis in order to evaluate the microstructural parameters like domain size $\langle D \rangle$, microstrain $\langle \varepsilon^2 \rangle^{1/2}$, etc. Rietveld method exhibits advantages over all the other methods. It takes into account the whole fitting methodology for size–strain analysis, simultaneous refinement of crystal structure, and microstructural parameters. It is also capable of eliminating the preferred orientation effect (if there is any) [14,15]. Considering the benefits of the whole profile fitting

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Table 1
Initial microstructural parameters used in Rietveld refinement of experimental XRD patterns.

Phases	Symmetry	Space group	Lattice parameters (Å)		
			a	*b*	*c*
Anatase	Tetragonal	*I*41/*amd*:1	3.785	3.785	9.514
Rutile	Tetragonal	*P*42/*mnm*	4.594	4.594	2.958
Brookite	Orthorhombic	*Pcab*	9.174	5.449	5.138

methodology, the Rietveld's structure refinement procedure using MAUD software was adopted in the present study to evaluate the microstructural evolution of TiO_2 nanocrystalline particles during the mechanical milling process.

The present work addresses the solid-state polymorphic phase transformation in the nanocrystalline TiO_2 powder through a high-energy ball milling method, based on the X-ray diffraction (XRD) and scanning electron microscopy (SEM) results.

2. Experimental procedure

Nanocrystalline TiO_2 powder (Sigma–Aldrich) with mean grain size of lower than 25 nm was used as the starting material. In order to investigate the mechanical activation of the polymorphic transformation in TiO_2, powders were charged in a high-energy planetary ball mill. Powders were milled for 6 h. A 70:30 ratio (weight percent) mixture of 2 and 1 cm (diameter) hard chromated steel balls were used during milling. The milled powders were annealed at three different temperatures of 450, 750 and 1050 °C for 1 h to aid the anatase-to-rutile phase transformation.

Phase characterization of the obtained powder was conducted using a Philips Xpert pro X-ray diffractometer (XRD) with Co Kα radiation. The average crystallite size and relative weight percent of the anatase, brookite and rutile phases in the samples were calculated via Rietveld Refinement Method using Materials Analysis Using Diffraction (MAUD) program. The particle morphology was investigated using Philips XL30 scanning electron microscope (SEM).

3. Results and discussion

In order to determine the exact phase evolution in the TiO_2 powders, it is essential to fit the experimental powder diffraction pattern with a profile fitting function based on the crystal structure and microstructure information. This methodology takes care of all reflections of each phase present in such a multiphase material and provides a very accurate result.

The experimental patterns (I_0) (*i.e.* observed X-ray powder diffraction pattern of samples) are fitted with respective simulated patterns (I_c). Below each fitted pattern, the difference of calculated value to observed value ($I_0 - I_c$) at each point of observation is plotted. The lower $I_0 - I_c$ value plotted at the bottom points toward that the experimental pattern fitted well with the simulated one [16]. The use of the Rietveld refinement method requires proper knowledge of the approximate crystal structure of each phase present in the sample to be able to have a roughly initial approximation of the probable XRD pattern. Such crystal structure information as well as starting parameters of site occupancies and lattice parameters were taken from database of the Rietveld refinement program (MAUD). The initial parameters used in Rietveld refinement of XRD patterns are listed in Table 1. Site occupancies and atomic positions were kept fixed during the refinement because of the low quality of the diffraction patterns to refine the crystal structure. By the process of successive profile refinements, the values of different structural and microstructural parameters including crystal structure, phase analysis, mean crystallite size, root mean square (RMS) microstrain, and lattice parameters in the simulated pattern are modified to fit the experimental diffraction patterns. Profile refinement continues until convergence is reached in each case. The broadening of all phases' reflections was assumed due to a combination of isotropic and anisotropic size-microstrain broadening considering Popa rules [17].

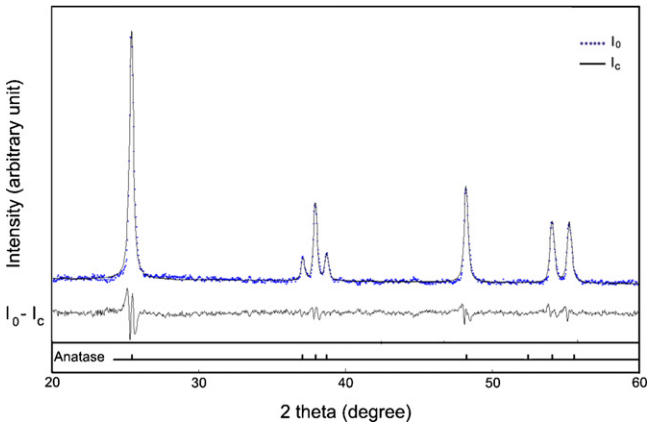

Fig. 1. XRD pattern of the initial TiO_2 powder fitted the corresponding simulated pattern based on the Rietveld refinement method.

The experimental XRD pattern (dots) of the initial TiO_2 sample fitted with its calculated one (solid curve) is shown in Fig. 1. The pattern reveals that the sample is completely composed of anatase phase. A good fitting between the experimental and calculated patterns can be observed according to the I0−Ic plotted at the bottom of the pattern.

Fig. 2 presents the experimental XRD patterns of the as-milled and annealed samples fitted with the corresponding simulated patterns. The XRD pattern of the as-milled sample (Fig. 2(a)) demonstrates that the sample consists of both brookite and rutile phases. In fact, the initial anatase phase completely transformed to other polymorphic phases of TiO_2 through solid-state phase

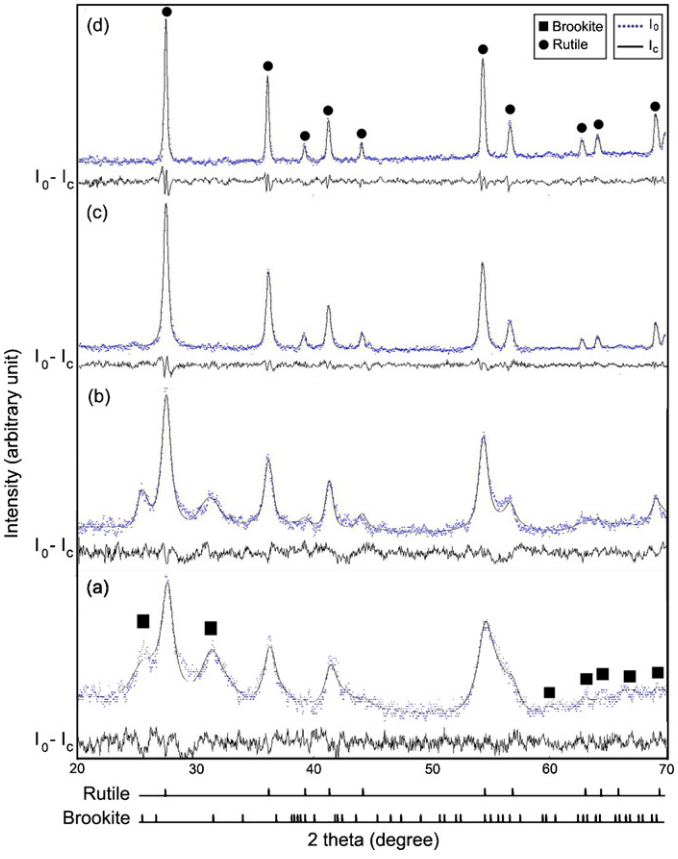

Fig. 2. XRD pattern of the (a) as-milled sample, milled and annealed at (b) 450 °C, (c) 750 °C and (d) 1050 °C fitted the corresponding simulated patterns based on the Rietveld refinement method.

transformation just as a result of the mechanical activation. From Fig. 2(a), it can be noticed that the experimental XRD pattern of the sample has a significant amount of background which affects the appeared peaks. This can be proved by the relatively big difference between the experimental (dots) and calculated (solid line) patterns in some angles like 2θ of ~24°.

In order to trace the evolution of TiO_2 particles during the polymorphic phase transformation, the as-milled powder was annealed at three different temperatures of 450, 750 and 1050 °C. The XRD pattern of the first annealed sample (at 450 °C) is shown in Fig. 2(b). A relatively good fitting can be seen between the experimental (dots) and simulated (solid line) patterns for this sample according to the low $I_0 - I_c$ value plotted at the bottom of the pattern. In comparison with the as-milled powder, it can be seen that the intensity ratio of rutile-to-brookite peaks increased with annealing. Increasing the rutile phase content by annealing the powder seems sensible according to the thermodynamics of the transformation. Above ~600 °C, anatase and brookite are found to transform irreversibly to rutile [18]. Transformation of the anatase to brookite and rutile during the mechanical milling and also of the brookite-to-rutile during annealing at a temperature lower than this limit can be attributed to the mechanical activation of the milled powder. Mechanical activation can be accumulated in the powders and plays the role of thermal activation in the thermally activated phase transformations. In turn, the mechanical activation can be considered as the driving force for polymorphic phase transformation of the TiO_2 powder.

Fig. 2(c) shows the XRD pattern of the milled powder annealed at 750 °C. As it can be seen, this sample almost consists of rutile phase and a hint a brookite phase. A good fitting can be seen between experimental (dots) pattern and the calculated (solid line) one obtained from Rietveld refinement method. Annealing the powder at a temperature higher than 600 °C results in the completion of the phase transformation. Since rutile is the most stable phase among different polymorphic phases of TiO_2 [7,8,18], it seems rational to obtain a almost fully rutile phase powder after annealing at 750 °C.

In order to check the thermodynamic stability of the rutile phase, the milled powder was annealed at higher temperature (1050 °C). Fig. 2(d) demonstrates the graphical Rietveld analysis of this sample. As it can be observed, it looks like to be the same as the XRD pattern of the sample annealed at 750 °C. It confirms the stability of the rutile phase at temperatures higher than the temperature limit (600 °C). There is a difference between these two XRD patterns. It seems that the peak width decreases by increasing annealing temperature which can be ascribed to the coarsening of the crystallite size of rutile phase. A good agreement between the experimental (dots) and simulated (solid line) data can also be observed in this case.

The variation of the rutile crystallite size and root mean square (RMS) microstrain in rutile phase with increasing the annealing temperature is shown in Fig. 3. As it can be seen, the crystallite size of the rutile phase increases with increasing the annealing temperature, while the RMS microstrain has a reverse trend. The microstrain content increases proportionally with the reciprocal of crystallite size, as occurs in other materials [19]. Thus, it is clear that the post-annealing treatment of milled powder produces the increase in crystallite size, but these large crystallites have a low content of microstrain. The particles of milled samples are formed by small crystallites welded together in a mosaic structure [19]. The grain boundaries constitute the main contribution to the microstrain. Therefore, the higher the number of grain boundaries in a particle, the smaller the size of the crystallites. Through mechanical processing, the number of grain boundaries substantially increases within a more defective structure. Annealing the milled particles, the microstructural defects tend to be reduced and grains tend to

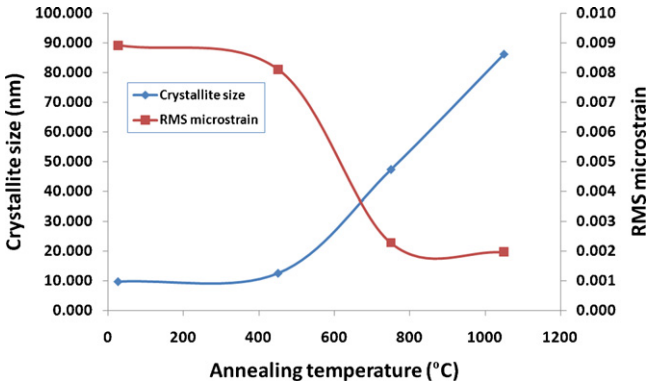

Fig. 3. Variation of rutile crystallite size and RMS microstrain with annealing temperature.

grow in order to reduce their surface energy. This coarsening of the crystallites can change the thermodynamic stability of the phases. Zhang and Banfield [9] studied the polymorphic phase transformation via enthalpy calculations and pointed out that the stability of the TiO_2 polymorphs is crystallite size dependent; anatase is the most stable phase at <11 nm, brookite is preferred between 11 and 35 nm, while rutile is favored at sizes greater than 35 nm. The same results have been obtained from calorimetry experiments [20]. As it can be seen in Fig. 3, the mean crystallite size of the powders is above the stability limit of the anatase phase. This may explain the absence of anatase phase peaks in the XRD patterns of the samples.

On the other hand, it seems that the superimposition of brookite peaks with shoulders of rutile phase (see Fig. 2(a) and (b)) prevents the precise calculation of the mean crystallite size of this phase. In fact, this peak superimposition leads to wider peaks, and consequently, results in obtaining much lower values for this parameter, *e.g.* 4.6 nm for the mean crystallite size of as-milled sample. Therefore, the calculated values for brookite mean crystallite size cannot be reliable to be used as evidence for determining the mechanism of phase transformation.

The change in the lattice parameters of rutile phase of the milled samples versus annealing temperature is shown in Fig. 4. The corresponding lattice parameters of bulk rutile sample reported in database of MAUD software are also shown in the figure (Table 1). According to this figure, it can be concluded that the lattice parameters were lower at room temperature and reached the bulk values at temperature around 370 °C. These parameters remained almost constant and closely matched with the bulk values at higher annealing temperatures. This trend can be attributed to the decreasing the microstructural defects, caused by mechanical deformation during

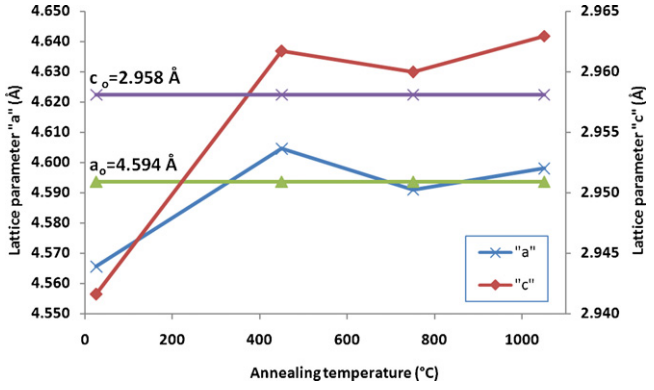

Fig. 4. Effect of annealing temperature on the lattice parameters of rutile phase of milled samples.

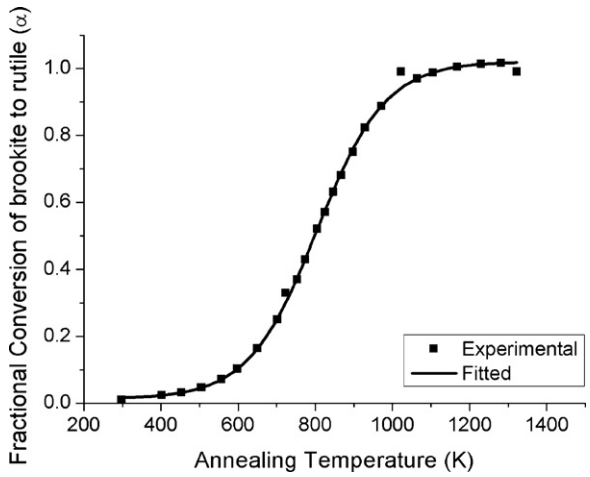

Fig. 5. Fractional conversion of brookite-to-rutile phase transformation versus annealing temperature curve.

milling, with increasing the annealing temperature. This conclusion seems logical with regards to the decrement of microstrain with increasing annealing temperature (Fig. 3).

Fig. 5 shows the fractional conversion (α) of brookite-to-rutile versus annealing temperature. As it can be seen, a sigmoidal curve can be suitably fitted with the experimental data. In order to assess which model properly governs the kinetics of this solid-state transformation, the following general equation is applied [21]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (1)$$

where $d\alpha/dT$ is the ratio of fractional conversion to temperature, β is the heating rate (1/K), A is a constant, R is the universal constant of the gases, E is the activation energy and $f(\alpha)$ is the function of fractional conversion. In fact, $f(\alpha)$ elucidates the mechanism of the process and, therefore, different functions have been developed for $f(\alpha)$ in the case of solid-state transformations. These mechanisms have been suggested regarding some assumptions and simplifications such as the particles shape (spherical, cylindrical and planar) and driving forces (interface growth, diffusion, nucleation and growth of nuclei). Since brookite-to-rutile phase transformation, which occurs during both milling and annealing steps, is a solid-state transformation, Eq. (1) is applicable to investigate the kinetics of phase transformation in the present study. Fig. 6 depicts the values of $[\ln(d\alpha/dT) - \ln f(\alpha)]$ versus $1/T$ curve employing different models. This curve is obtained from the linear part of the sigmoidal curve shown in Fig. 5. The model which linearly fit $[\ln(d\alpha/dT) - \ln f(\alpha)]$ versus $1/T$ curve is then selected as the appropriate model (Avrami–Erofeev equation, $n = 1$). Based on Eq. (1), the slope of this line is equal to $-E/R$. Accordingly, the value of activation energy is calculated to be 28 kJ/mol.

Polymorphic phase transformation in TiO_2 needs a rearrangement of Ti and O atoms [22,23]. As Shannon and Pask [22] suggested, most of the atomic rearrangement seemingly occurs within a specific crystallographic planes. Ti–O bonds also must be broken during the atomic rearrangement. Thus, the mechanism of this polymorphic reaction has been described by Shannon and Pask [22] as "a cooperative movement of the Ti and O atoms", in contrast to a strict diffusion mechanism. The random nucleation followed by an instantaneous growth of the rutile nuclei (Avrami–Erofeev mechanism, $n = 1$) [23], as revealed in the present study, supports this argument.

Fig. 7 presents the SEM micrographs of the samples. As it can be seen, the samples consist of almost equiaxed particles with a narrow particle-size distribution. As the particles in the SEM micrographs seem larger than the mean crystallite sizes calculated by the use of Rietveld refinement method, one can conclude that the particles consist of individual grains. In fact, the powder particles are polycrystalline.

By comparison the SEM micrographs shown in Fig. 7 with each other, it can be observed that all the samples, except the one that was annealed at 1050 °C, consist of the particles with the same size. It might be due to the agglomeration of the powders. In the case of the fourth sample, it can be concluded that the particles have grown because of the very high annealing temperature. The size of the particles in this sample is in fairly good agreement with the results obtained from the XRD patterns.

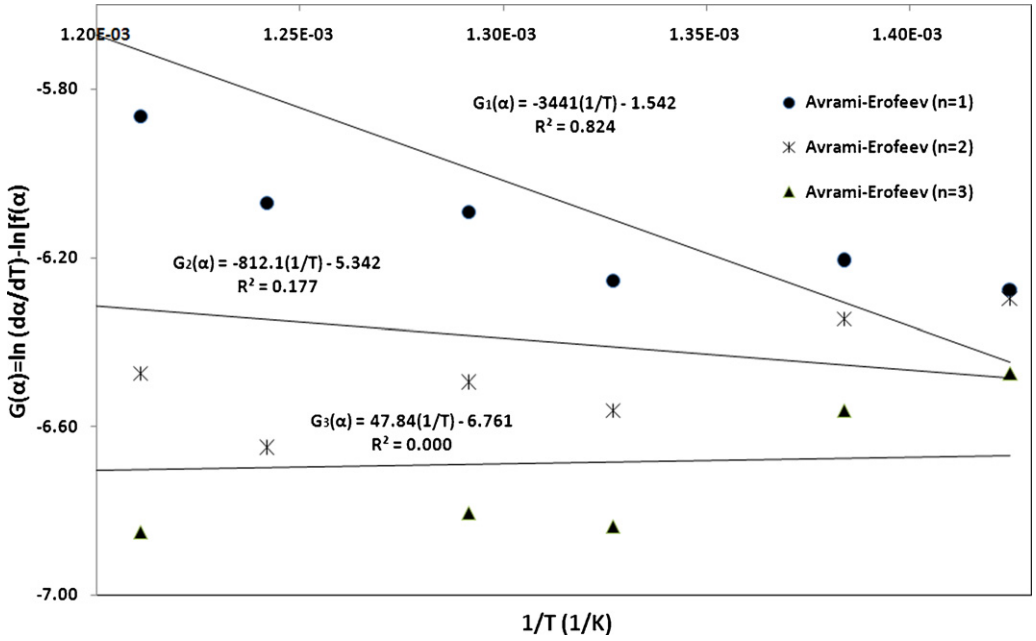

Fig. 6. $[\ln(d\alpha/dT) - \ln f(\alpha)]$ versus (1/annealing temperature) curve.

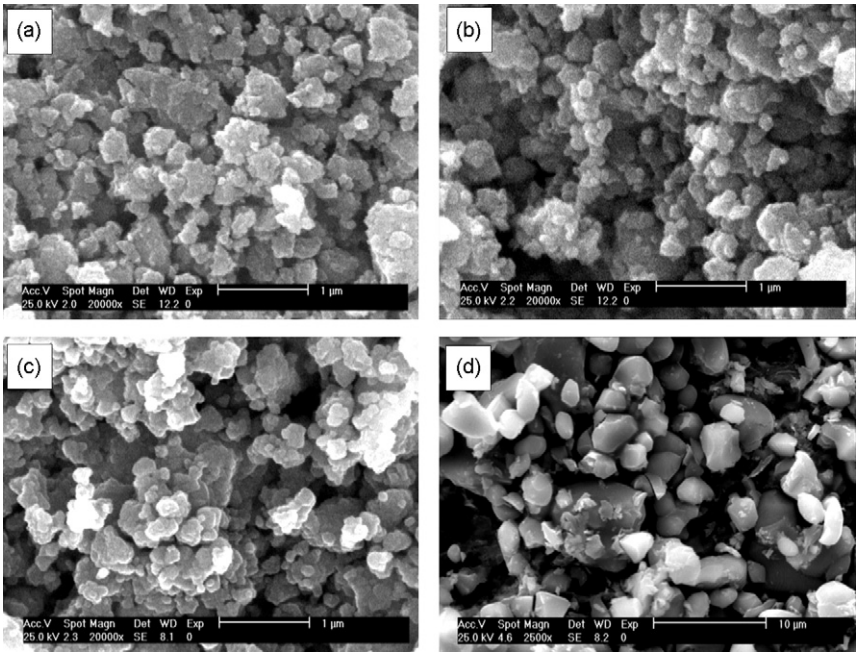

Fig. 7. SEM micrographs of (a) as-milled and annealed samples at (b) 450 °C, (c) 750 °C and (d) 1050 °C.

4. Conclusion

The mechanical activation of the polymorphic phase transformation of nanocrystalline anatase phase was investigated in the present work. It was found that the transformation of anatase phase to brookite and rutile can completely occur during mechanical milling and there is no need for further annealing. By annealing the powders, the brookite phase was completely transformed to the rutile phase at 750 °C, and there is no evidence of brookite phase at this temperature, based on the XRD results. The SEM micrographs show equiaxed particles with a relatively narrow size distribution. The brookite-to-rutile phase transformation rate is best expressed by Avrami–Erofeev kinetics model with an Avrami exponent value of $n = 1$ that indicates the random nucleation of rutile phase followed by an instantaneous growth of nuclei.

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