

Determining the Optimal Conditions for Calcium Titanate Nanostructures Synthesized by Mechanical Alloying Method

S. Manafi*^a, M. Jafarian^b^aDepartment of Engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran^bDepartment of Material Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran

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In this research, calcium titanate nano-particles were synthesized via mechanical alloying. To synthesize this compound, a mixture of calcium hydroxide and titanium dioxide, rotation speed of 250 rpm and diffenet ball to powder weight ratio (10:1, 20:1, 30:1 and 50:1) were used. Phase investigation, morphology and structure of calcium titanate powder obtained were evaluated by X-ray diffraction, scanning electron microscopy and Energy-dispersive X-ray Spectroscopy respectively. The results of the X-ray diffraction analysis confirmed the formation of single-phase calcium titanate nano-particles with cubic crystal structure. The agglomeration of powder has been shown in scanning electron microscope images. According to the results, the minimum of ball to powder weight ratio to synthesize this compound was 50:1 and milling time of 60 hs. The results of Zeta-sizer showed that the major part of the particle size distribution was in the range between 60 to 80 nm and this confirms the results of Williamson-Hall equation and scanning electron microscope images. Also, by using of Nelson-Riely and Cohen equations for calculating the lattice parameter, it was found that increasing milling time to 60 hs, leads to lattice parameter values to be closed to ideal values of calcium titanate phase.

1. INTRODUCTION

Calcium titanate (CTO) is recognized as the founding father of the materials with perovskite structure [1]. This compound with cubic structure is extensively used in electronic ceramic materials and also used as catalysts for partial oxidation of light hydrocarbons. It is also a key component of Synroc (synthetic rock) used for inhibition of high level radioactive wastes [2]. Because this combination is able to form wide solid solutions with rare earth materials to be used for disposing of nuclear waste [3]. CTO has three polymorphic phases including cubic, tetragonal and orthorhombic. Kennedy et.al [4] reported that CaTiO_3 includes successive transformation from cubic phase (Pm3m space group) to tetragonal phase (I4/mcm space group) at about 1580 K, orthorhombic phase (Cmcm space group) around 1500 K, and orthorhombic phase (Pbnm space group) at about 1380 K [4]. In Figure 1. three phases of polymorphic calcium titanate are shown. CTO is one of the materials synthesized via wet chemical and solid state routes such as sol-gel [5], co-

precipitation [6], polymeric precursor [7], organic-inorganic solution [8], combustion [9] and mechano-chemical method [10].

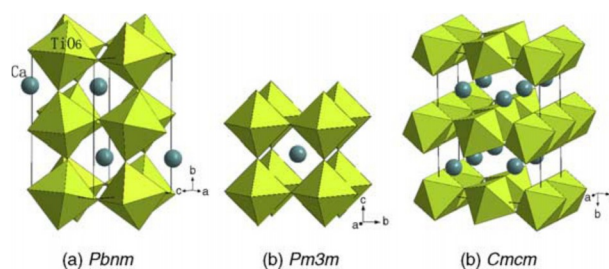


Figure 1. polymorphic phases of calcium titanate [4].

In addition, this compound is formed by heating a mixture of calcium oxide (CaO) or calcium carbonate (CaCO_3) with titanium dioxide (TiO_2) in temperature of 1650 K, but the problem of this process is heterogeneous product, contamination of impurities, performing process in high temperature, existence of coarse particles with different sizes and heterogenous distribution [11-13]. One of the synthesis methods of this matter is mechanical alloying method which includes a series of processes of breaking particles and cold fusion among them. By breaking each particle,

*Corresponding Author's Email: manafi@iauh-shahrood.ac.ir (S. Manafi)

new active surfaces are created that are ready for the chemical reactions and the required energy for starting a chemical bond between each pair of this surface is provided when the balls impact [14]. Some of the advantages of this method include reducing the temperature of sintered and annealed, reducing temperature of phase transformation, reducing the temperature of thermal decomposition and increasing the reactivity of powders [15]. The mechanical alloying method is performed in high intensity grinding mills such as Vibratory Mill, Attritor Mill, Tumbler Horizontal Mill, Tumbler Rod Mill, oscillating mill and planetary mill. Using the grinding mills, depending on the amount of shear and impact energy through the grinding media to the mixture of powder, can affect the process of reducing the grain size and the microstructure changes. Some of affective parameters on the microstructure of the final product in this method are the type of mill, speed and time of milling, the temperature of milling, ball to powder weight ratio, the milling atmosphere and control agent of process. Hence, some studies are performed in the field of calcium titanate nanoparticles [16,17] by mechanochemical method and using different raw materials and high energy planetary mill, but determining the optimal conditions for the synthesis this compound with simultaneous changing the ball to powder weight ratio and the milling time is not that polestar. In previous researchers, increasing energy applied to powder mixture was performed by increasing the milling speed, whereas in the present study by assuming milling speed constant and increasing the amount of BPR and milling time, the synthesis way of calcium titanate nanoparticles were studied. It was also tried by removing heat treatment and using the minimum energy and the synthesis of this compound get done by changing the process parameters. In the study that performed on synthesis of calcium titanate by mechanical alloying from the mixture of CaCO_3 and TiO_2 [18], because of more Gibbs free energy in the formation of calcium titanate from the powder mixture and adding barium carbonate decomposition stage, higher ball to powder weight ratio was required. Furthermore due to the high ball to powder weight ratio, use the heat treatment on final powder were essential. But In this paper evidences show the positive effects of increasing the parameters of mechanical alloying on calcium titanate synthesis and the nanopowders were synthesized without the need for heat treatment.

2. MATERIALS AND METHODS

To synthesize calcium titanate by mechanical alloying, planetary ball mill was used. The device contains 2 cups and 12 balls in each cup made of stainless still with average diameter of 16 mm. According to the ball to powder weight ratio, the mixture of raw materials

including Ca(OH)_2 (99 % < 1 μm , 99% purity) and TiO_2 -anatase (99 % < 1 μm , 99% purity) with molar ratio of 1:1 was placed in the planetary mill cup. Also, as a process control agent (PCA) 1 cc ethanol was added to the mixture. Milling process rotational speed (cup speed) of 250 rpm took place in different times. The amount of BPR was considered 10:1, 20:1, 30:1 and 50:1. To avoid excess heat production, after every 1 h of milling, the device was turned off for 30 minutes. After the milling process, to remove Fe/Cr contamination of powder mixture, 30 mL aqueous solution containing 2 mL of HCl (36.5 wt.%), 5 mL of H_2O_2 (30 wt.%), and 20 mL of distilled water at room temperature was stirred for 12 hs. The crystal phases were determined with X-ray diffraction analysis device (PW1800, 40 kV and 30 mA) with the $K_{\alpha 1}$ radiation of Cu ($\lambda = 1.5406 \text{ \AA}$) which was done in $2\theta = 10 - 70$ and step size = 0.01. Observing microstructure and particle size was performed by scanning electron microscopy (VEGA//TESCAN-LMU) equipped with EDS chemical analysis and secondary electrons. In mechanical alloying method for reducing the error in determination of the grain size, the share of fine grains and increase of strain in band width must be considered simultaneously. Therefore, The crystalline size (D) and lattice strain were estimated by Williamson-Hall [5]:

$$\beta \cos \theta = 2\varepsilon \sin \theta + 0.9 \frac{\lambda}{D} \quad (1)$$

Where λ is the wavelength of the X-ray, β is the full width at half-maximum (FWHM), θ is the Bragg angle, and ε is the micro strain. Also, the exact value of the lattice parameters was determined by using the Nelson-Riely equation and Cohen. Eventually, the particle size distribution of the produced powders was measured by zeta sizer instrument (Malvern Co, ZEN3600, England).

3. RESULT AND DISCUSSION

Figure 2. shows the XRD patterns of raw materials and the milled samples with BPR equal with 10:1. As it can be seen, the first diffraction pattern is related to mixture of raw materials in which the reaction and diffusion between materials has not occurred due to lack of the supplement of energy. Just by increasing of milling time to 25 hs, the intensity of the peaks of raw materials decreased due to reduce the size of the particles or creation of amorphous phase, and no new phase has been produced.

In order to apply more energy in the mixture of raw materials, the BPR was increased to 20:1 and 30:1. Figures 3. and 4. respectively show the XRD patterns of milling samples with values of 20:1 and 30:1 BPR.

Based on results the energy required for the formation of a new phase to powder mixture after 30 hs milling with ball to powder weight ratio of 30:1 has not been

entered but the intensity of peaks has been reduced aggressively.

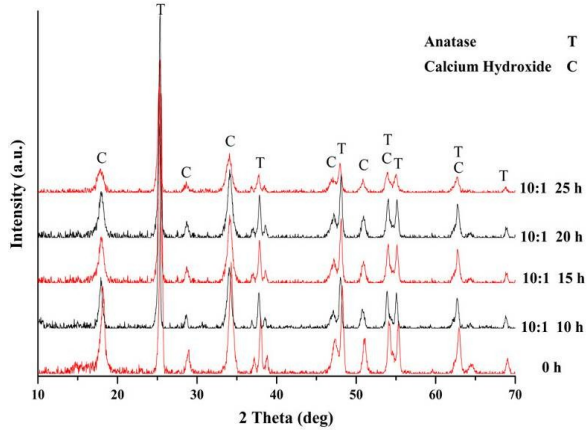


Figure 2. The X-ray diffraction spectra of mechanically alloyed $\text{Ca(OH)}_2/\text{TiO}_2$ powders with BPR equal to 10:1.

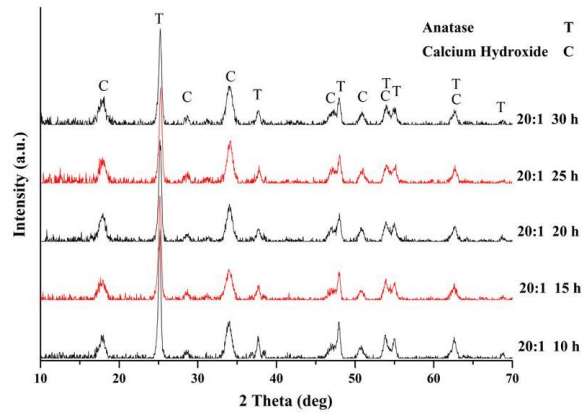


Figure 3. The X-ray diffraction spectra of mechanically alloyed $\text{Ca(OH)}_2/\text{TiO}_2$ powders with BPR equal to 20:1.

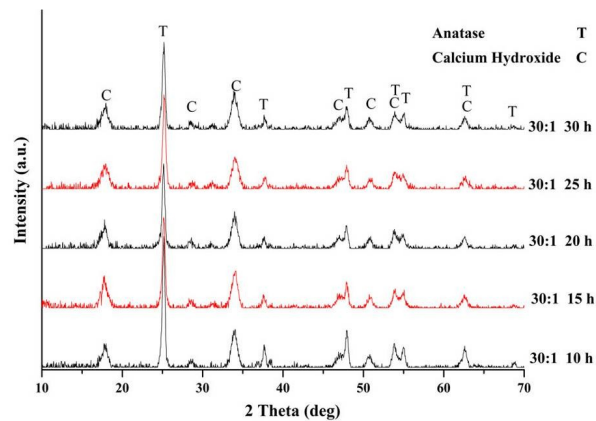


Figure 4. The X-ray diffraction spectra of mechanically alloyed $\text{Ca(OH)}_2/\text{TiO}_2$ powders with BPR equal to 30:1.

In the mechanical alloying method, the amount of applied energy depends on some factors like the ball to power weight ratio, mill speed, mill time and mill diameter. By increasing of BRP and milling time, the

rate of formation of structural defects has increased in raw materials and it leads to the partial formation of amorphous materials and in the following the formation of calcium titanate compound through a chemical reaction between the components. Increasing of formation ratio of structural defects leads to reduction in peak intensity and peak base broadening. to produce CaTiO_3 , the variables of time and BPR proportion increased. Figure 5. shows the XRD patterns of milling samples in times of 30, 40, 50 and 60 hs.

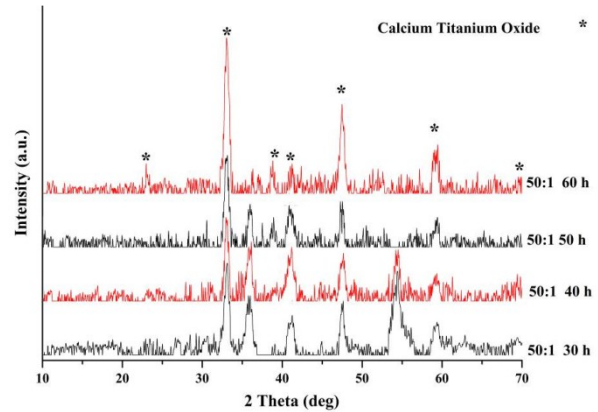


Figure 5. The X-ray diffraction spectra of mechanically alloyed $\text{Ca(OH)}_2/\text{TiO}_2$ powders with BPR equal to 50:1.

As it can be seen, the peaks of calcium titanate and rutile appeared after 30 hs milling with weight ratio of ball to powder of 50:1. By increasing of milling time from 30 to 60 hs, the peaks of calcium titanate got wider and the intensity of peaks of rutile phase decreased and the reason is desordering process of raw materials during milling in more periods of time. By increasing the milling time, the reaction rate increased indicating that the performance of this process is occurred by nucleation and growth mechanism. Since the activation of energy depends on the deformation, it can be concluded that energy barrier decreases by increasing of defection due mechanical activation. Finally, after 60 hs of milling with ball to powder weight ratio of 50:1, the combination of single phase calcium titanate was obtained. So far, In previous studies related to Calcium titanate synthesis, increasing energy applied to powder mixture is performed by increasing the milling speed while in the present study by assuming milling speed constant and increasing the amount of BPR and milling time, the synthesis way of calcium titanate nano particles were studied. Also it was tried by removing heat treatment and using the minimum energy, the synthesis of this compound get done by changing the process parameters. Diffraction patterns of calcium titanate compound were well correlated with standards card No. 001-1055 and dominant peaks at $2\theta=33.11, 47.49, 59.35$ and 69.48 were respectively related to (220), (400), (422) and (440). The sample milled for 60

hs by using Williamson-Hall equation the mean size of the grains and the strain percentages were respectively obtained 82 nm and 0.68. In order to determine the lattice parameter after 60 hs milling, the combination of Nelson-Reily and Cohen were used. By combining Nelson-Riely and Cohen equations, the following equations are obtained in a cubic system [5]:

$$\sin^2 \theta - \frac{\lambda^2}{4a^2} [(h^2 + k^2 + l^2)] = -\frac{k}{2} \left(\frac{\sin^2 2\theta}{\sin \theta} + \frac{\sin^2 2\theta}{\theta} \right) \quad (2)$$

In this equation, a is value of laticc parameter, θ is Bragg angle, hkl is miller indices and K is a constant quantity. With defining the following new quantities we have:

$$C = \frac{\lambda^2}{4a^2} \quad (3)$$

$$\alpha = h^2 + k^2 + l^2 \quad (4)$$

$$A = -K/2 \quad (5)$$

$$\delta = \left(\frac{\sin^2 2\theta}{\sin \theta} + \frac{\sin^2 2\theta}{\theta} \right) \quad (6)$$

Equation 2 can be rewritten as follows:

$$\sin^2 \theta = C\alpha + A\delta \quad (7)$$

In equation 8, the experimental values of $\sin \theta$, α and δ are obtained for each peak in the X-ray diffraction patterns. To calculate unknown constants A and C , the square method is used and by using this method, the following normal equations are obtained:

$$\sum \alpha \sin^2 \theta = C \sum \alpha^2 + A \sum \alpha \delta^2 \quad (8)$$

$$\sum \delta \sin^2 \theta = C \sum \alpha \delta + A \sum \delta^2 \quad (9)$$

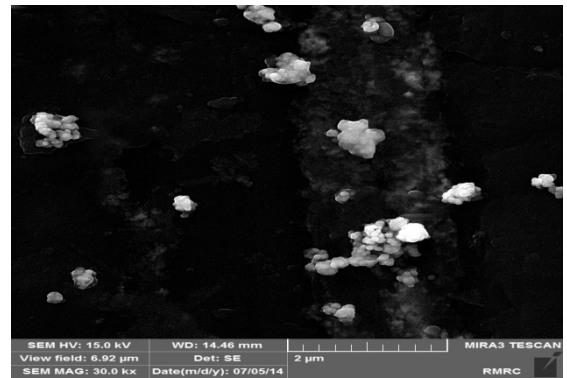
Finally, accurate lattice parameter (a) is directly obtained from the equation $C = \frac{\lambda^2}{4a^2}$. In Table 1 the

values of 2θ , $\sin^2 \theta$, α and δ are given for diffraction peaks of 60 hs milling sample. According to the results, the exact value of the lattice parameter is 3.51 Å.

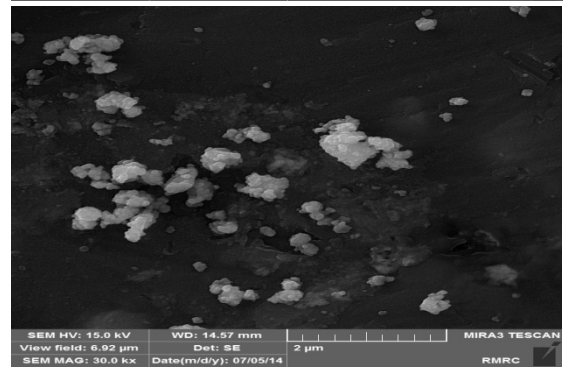
TABLE 1. the values of 2θ , α , δ and $\sin^2 \theta$ for the diffraction lines of the 60 h milling sample.

hkl	2θ	α	δ	$\sin^2 \theta$
220	33.02	8	1.0629	0.081
400	47.45	16	1.3717	0.162
422	59.11	24	1.5179	0.243
440	69.43	32	1.5644	0.324

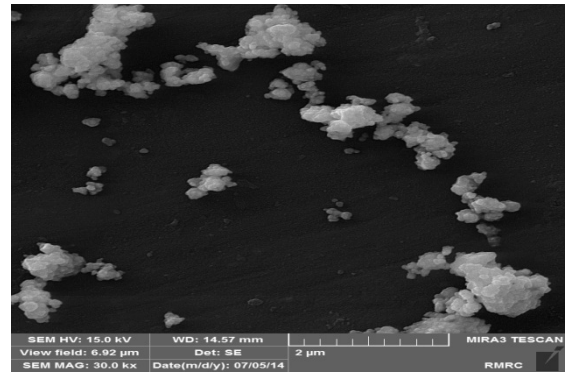
In mechanical alloying method, three main steps exist in interaction between particles including adherence, aggregation and agglomeration. In adherence step, the powder particles adheres to the body of mill and balls placed on them as a cover. In aggreration step, particles with weak Van der Walls force gather together that this condition is revisable. Finally, in the agglomeration step, chemical bonding between particles happens, this reaction is irreversible. Basically, aggreration of particles was common in dry grinding and was usually explained by the agglomeration of structurally modified particles following the initial reduction of particle size. By increasing the ball to powder weight ratio and milling time, the surface area increases tremendously. In this case, particles due to reduction of their excess free surface energy start to agglomeration and gather together. Figure 6. shows SEM images of milled sample in, 30, 40, 50 and 60 hs. As can be seen in Figures 6d and 6e, particles are agglomerated and placed next to each other.



(a)



(b)



(c)

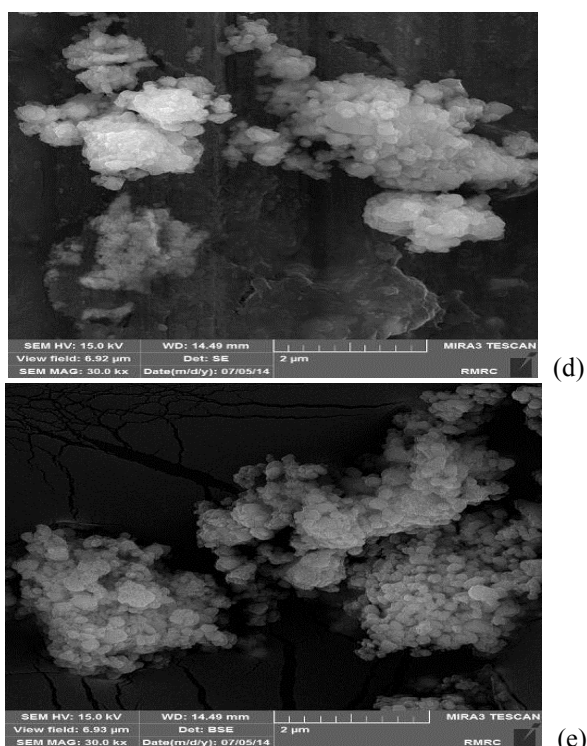


Figure 6. SEM images of milled sample in, a) 30hs, b) 40hs, c) 50hs and d,e) 60 hs.

According to the SEM images of 60 hs milling sample, in average particles are in the size range of 80 ± 20 nm. As a matter of fact, this method (MA) guarantees its production in the synthesis of CTO for different applications. EDS analysis were prepared from the powder that its result is shown in Figure 7.

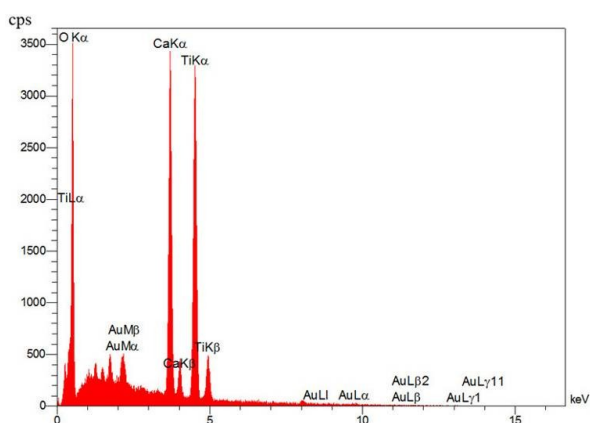


Figure 7. EDS analysis result of milled sample in 60 hs.

As can be seen, the results of EDS analysis of powder sample contains Ca (at.%12.24), Ti (at.%14.95) and O (at.%71.40) that with respect to the atomic constituent elements, forming calcium titanate phase is approved. The nanoparticle size of CTO milled for 60 hs was analyzed using a zeta sizer method. As seen in Figure 8. the existence of a spectrum in this picture represents a

uniform distribution of particles in the range between 20 to 110 nm. The result of this analysis confirms the results of scanning electron microscope images and the average of particle size has been calculated.

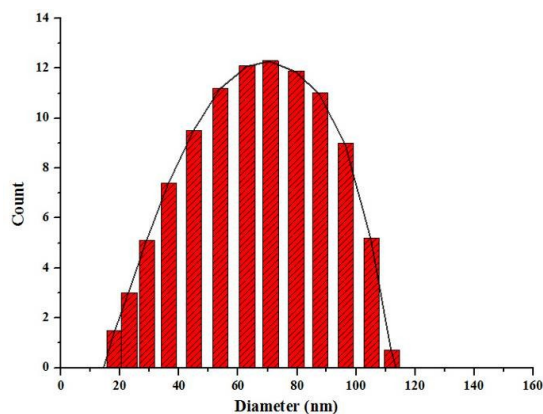


Figure 8. Zeta-sizer images of the CTO powders obtained after 60 hs milling.

4. CONCLUSION

The calcium titanate nanostructure was successfully synthesized via mechanical alloying from mixture of $\text{Ca}(\text{OH})_2$ and TiO_2 . Changing parameters of mechanical alloying method like BPR and milling time have a significant impact on the synthesis of the compound without the use of heat treatment. As a result, the minimum ball to powder weight ratio and milling time to synthesis of calcium titanate nanoparticles were respectively 50:1 and 60 hs. According to SEM images, nano-particles were produced in the form of soft agglomerates. This simple approach should promise us a future large-scale synthesis of this nano-structured material for many important applications in nanotechnology in a controlled manner. On the other side, due to the cubic crystal structure of the synthesized powder, it can be used as an option for using in Synroc.

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