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Mechanochemical effects on the kinetics of zinc titanate formation

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In this work, mixtures Zn-TiO_2 (anatase) in molar ratio 1:1 were mechanochemically activated in air atmosphere, and submitted to thermal treatments in order to study its thermal transformations. The behavior of the system during the milling was followed by X-ray diffraction (XRD), differential thermal analyses (DTA) and thermogravimetric analyses (TGA).

Mechanochemical activation produces a progressive loss in crystallinity of the starting powders, with simultaneous oxidation of metallic Zn. However, the formation of neither $ZnTiO_3$ nor Zn_2TiO_4 could be detected. At temperatures above 600°C, the thermal treatments resulted in the formation of $ZnTiO_3$ and Zn_2TiO_4, at lower temperatures and shorter holding times for samples activated during longer times. The non-activated mixture exhibited a very different behavior, yielding $Zn_2Ti_3O_8$ and Zn_2TiO_4 without evidence of $ZnTiO_3$ formation. The obtained results are explained on the basis of reaction mechanisms taking place in the activated and non-activated samples.

1. Introduction

Since two decades, mechanochemical activation of crystalline solids performed in high-energy mills has become a very useful method to control the reactivity in the solid state [1, 2]. In numerous publications, the ability of this powder processing method to create defects in the crystalline structure of the activated reactants has been demonstrated. These treatments also accelerates the diffusion processes, which in many cases govern the kinetics of solid state reactions [3, 4]. The activation of a reactive mixture can induce chemical reactions during the same mechanical treatment at about room temperature [5] or make easier the same (or a different) chemical reaction, in a subsequent thermal treatment at much lower temperatures than those generally utilized in the conventional ceramic method [6]. In spite of the extensive work dedicated to mechanochemistry, an exhaustive model allowing to describe the mechanisms through which this method works does not exist yet.

Zinc titanates ($ZnTiO_3$ and Zn_2TiO_4) are electroceramic materials with interesting dielectrical properties and low sintering temperatures, which make them applicable in the microwave frequency range [7, 8]. The attempts to synthesize pure $ZnTiO_3$ by thermal treatment of ZnO:TiO_2 mixtures are generally unsuccessful because this titanate decomposes at temperatures close to that preparation (950°C) [9]. For this reason, the study of new routes of synthesis of these compounds needs to be explored.

In this work, the behavior of the Zn-TiO_2 system under mechanochemical and thermal treatments is studied in relation with zinc titanates synthesis. The effects of high-energy milling on the reaction kinetics is analyzed with the aim to elucidate the different mechanisms that operate in each case and to contribute to the understanding of mechanochemical processing.

2. Experimental method

2.1. Preparation and activation of reactive mixtures

A powder mixture of metallic Zn (commercial reagent, 98% wt.) and anatase (commercial reagent, 99% wt. TiO_2) was prepared. The reactants were mixed in a molar ratio 1:1. This powder mixture (60 g) was mechanically treated in a Herzog HSM100 oscillating

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mill under air atmosphere. This equipment consists of a 200 cm^3 milling chamber, which also contains a disk (10 cm diameter and 5 cm height) and a concentric ring (both made of Cr steel), reaching a milling media-to-powder mass ratio of about 60. The chamber was submitted to planetary movement with a frequency of 12.5 Hz during times up to 30 min. Small portions of powder (about 2 g) were withdrawn from the mill every 6 min in order to follow the evolution of the activation process. These samples were named ZTx, where x is the activation time, in minutes.

2.2. Thermal treatments and determination of the reaction kinetics

The non-activated sample, ZT0, and the activated samples ZT6, ZT18 and ZT30, were heated in an electrical furnace at temperatures between 600 and 800°C in air atmosphere during several holding times. The samples were heated as loose powders and quenched at room temperature after reaching the corresponding time.

The contents of $ZnTiO_3$ and Zn_2TiO_4 as crystalline phases were determined in each thermally treated sample, through quantitative analysis by XRD, according to the external standard method [10]. The diffraction peaks at interplanar spaces $d = 0.2729$ nm and $d = 0.2993$ nm were selected to perform the measurements of $ZnTiO_3$ and Zn_2TiO_4, respectively. The integrated area of these peaks were measured, excluding the continuous background, using a computer program.

The conversions, α, were calculated considering the maximum percentage that can be formed of each phase (100% for $ZnTiO_3$ and 75.2% for Zn_2TiO_4) as $\alpha = 1$.

Standards of $ZnTiO_3$ and Zn_2TiO_4 were specially prepared to be used as reference. The first one, was synthesized by calcination during 3 h at 800°C of a Zn:TiO_2 mixture (molar ratio 1:1) activated by 42 min. The last one, was prepared starting from a Zn:TiO_2 mixture, in a molar ratio 2:1, activated by 30 min and thermally treated at 800°C during 1 h.

2.3. Characterization techniques

XRD analyses were made in a Philips PW1830/00 diffractometer, using Cu K_α radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA. Thermal analyses were performed in a Shimadzu DTA/TG-50H equipment in flowing air, using a heating rate of 10 K/min and platinum sample holders.

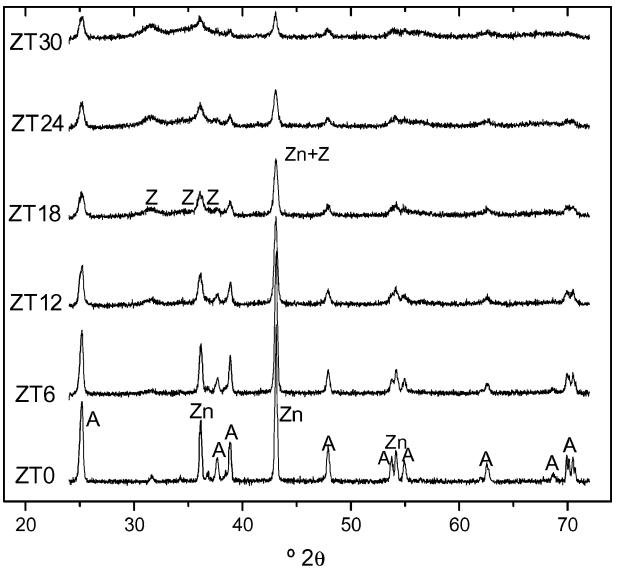

Figure 1 XRD diagrams of the series of samples ZTx. A: anatase (TiO_2); Z: zincite (ZnO).

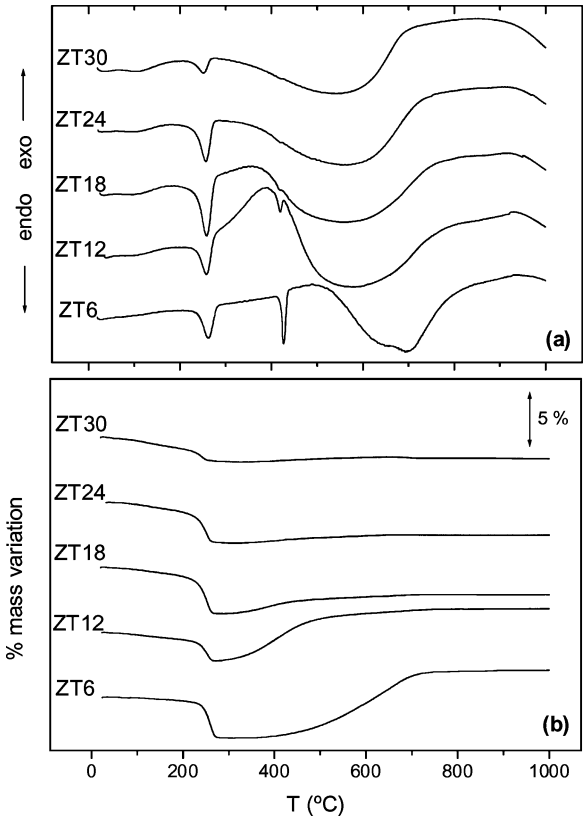

Figure 2 DTA (a) and TGA (b) analyses of the activated mixtures.

3. Results

3.1. Mechanical activation

Fig. 1 shows the XRD diagrams of the activated samples. A notable decrease of the diffracted peak intensity of anatase between ZT0 and ZT30 can be observed, as a consequence of the loss of crystallinity produced by the distortion and accumulation of defects in the structure. For the sample ZT30, whereas the diffracted intensity of TiO_2 dropped to about 50%, in the case of Zn the intensity was lowered to 25% of the initial value.

In Fig. 2 the curves of the DTA/TG analyses for the activated samples are shown. At about 250°C an endothermic peak accompanied by a mass loss can be noticed with variable intensity for all the samples. Between 300 and 600°C the TG traces (Fig. 2b) show a mass gain for all the samples, whose intensity decreases for more activated mixtures (in fact, for ZT30 this event is hardly detectable). In this temperature range, the DTA curves (Fig. 2a) reveal the presence of an exothermic band, which is also more intense for the more activated samples.

Finally, an endothermic peak at 420°C corresponding to the melting of metallic Zn can be observed by DTA for the samples activated up to 18 min.

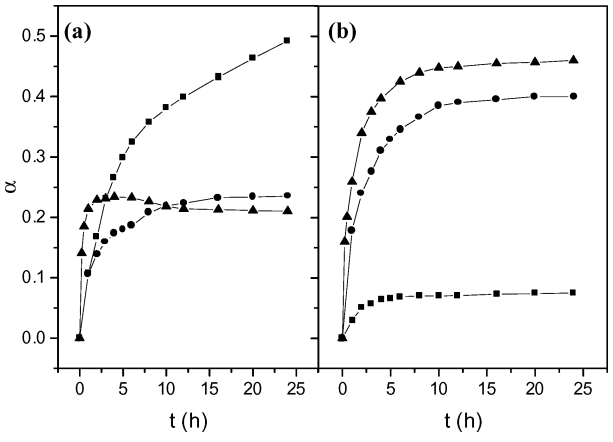

Figure 3 Conversion curves of Zn_2TiO_4 (a) and $ZnTiO_3$ (b) at 600°C for samples ZT6 (-■-), ZT18 (-●-) and ZT30 (-▲-).

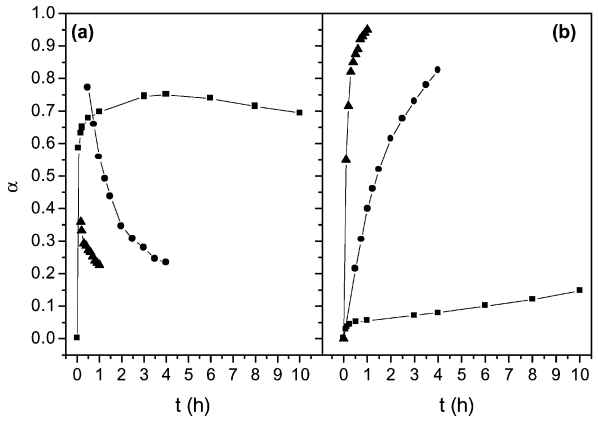

Figure 5 Conversion curves of Zn_2TiO_4 (a) and $ZnTiO_3$ (b) at 800°C for samples ZT6 (-■-), ZT18 (-●-) and ZT30 (-▲-).

3.2. Thermal treatments and reaction kinetics

Fig. 3 shows the conversion-time curves to Zn_2TiO_4 (a) and $ZnTiO_3$ (b) for the samples ZT6, ZT18 and ZT30 treated at 600°C. For sample ZT6, a continuous increase in the Zn_2TiO_4 formation can be observed, reaching a conversion close to 0.50 at 24 h of heating. For samples ZT18 and ZT30 the maximum conversion into Zn_2TiO_4 does not overcome 0.23. In ZT18 this value is reached at 18 h of heating, remaining constant until 24 h. In contrast, in ZT30 the formation of this phase increases up to its maximum value at 2 h of heating, and after that the conversion diminishes very slowly. The $ZnTiO_3$ formation reveals a completely different behavior, as it can be seen in Fig. 3b. For the three activated mixtures, a gradual increase in the conversion is observed. However, there are significant differences between them. Whereas ZT6 exhibits very low conversion values (not higher than 0.07), ZT18 and ZT30 present a much stronger tendency to form $ZnTiO_3$, giving maximum values of 0.37 and 0.44, respectively, between 10 and 12 h of thermal treatment.

The conversion vs. soaking time curves for the activated mixtures heated at 700°C are displayed in Fig. 4. There are well-marked differences among the three samples in relation to Zn_2TiO_4 formation (Fig. 4a). Sample ZT6 shows a fast conversion into this phase, reaching a value as high as 0.65 after only 8 h of calcination; from then on, a slight decrease is observed. Samples ZT18 and ZT30 also undergo a fast reaction, but in contrast to ZT6, the conversion reaches a much lower level and begins to decrease at shorter times. In fact, for ZT30 the maximum conversion is below 0.30 and takes place at a holding time as short as 30 min. Regarding the conversion into $ZnTiO_3$, a similar tendency to that observed in the treatments at 600°C can be seen. The main distinction between both thermal series is the higher conversions obtained for mixtures ZT18 and ZT30 heated at 700°C. The behavior of sample ZT6 at this temperature is almost identical to that described at 600°C.

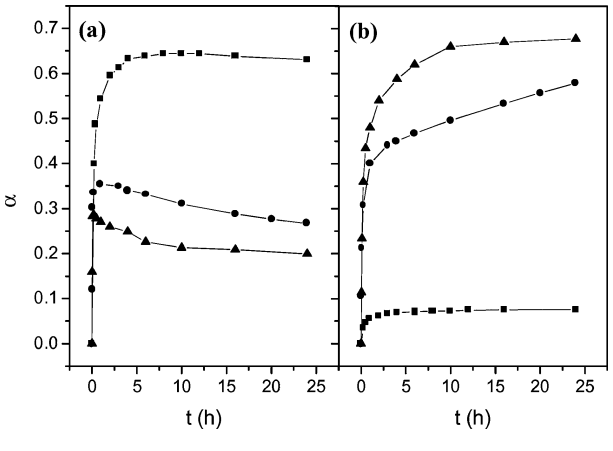

Figure 4 Conversion curves of Zn_2TiO_4 (a) and $ZnTiO_3$ (b) at 700°C for samples ZT6 (-■-), ZT18 (-●-) and ZT30 (-▲-).

At 800°C, the conversion into both zinc titanates follows the same general behavior observed in Figs 3 and 4. The Zn_2TiO_4 formation (Fig. 5a) is notably influenced by the previous activation treatment of the reactive powders. Samples ZT18 and ZT30 react very fast producing this phase, after which its gradual decomposition takes place, reaching conversion values close to 0.20 in both cases. For ZT6, the Zn_2TiO_4 formation occurs until 3 h of heating, giving a maximum conversion of 0.75; after that, a slow diminution of the quantity of this phase in the system can be observed. In the case of $ZnTiO_3$, there are important changes in the reactivity of the analyzed samples (Fig. 5b). Sample ZT6 continues showing a very slow reaction to produce $ZnTiO_3$ (note that after 10 h at 800°C the conversion hardly overcomes 0.14). However, for samples ZT18 and ZT30 the production rate of this titanate increases considerably. For ZT18 the results evidence a maximum conversion of 0.80, attainable at a holding time of 4 h. For sample ZT30 the reaction is much faster; after only 1 h of calcination, the formation of $ZnTiO_3$ is almost complete.

Fig. 6 displays a XRD diagram of the sample ZT0 calcined at 800°C for 4 h. Besides Zn_2TiO_4, the presence of remaining anatase and ZnO can be observed, together with the titanate $Zn_2Ti_3O_8$. However, the phase $ZnTiO_3$ could not be detected in ZT0. The insert in the figure shows the conversion into Zn_2TiO_4 of the non-activated sample, ZT0, heated at 650, 725 and 800°C. At 650°C the conversion is very low ($\alpha = 0.25$ for 8 h), but at 725 and 800°C the reaction rate increases

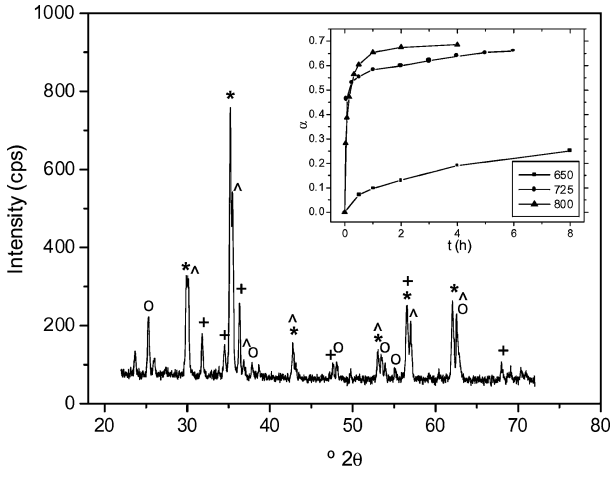

Figure 6 XRD diagram of the non-activated mixture heated at 800°C for 4 h. (O) TiO_2; (*) Zn_2TiO_4; (^) $Zn_2Ti_3O_8$; (+) ZnO. The insert shows the conversion curves to Zn_2TiO_4 at 650, 725 and 800°C.

notably and after 6 and 4 h, the conversion reaches 0.65 and 0.70, respectively.

4. Discussion

4.1. Effects of the mechanical activation

The results described in Section 3 for the XRD analyses indicate that the mechanochemical treatment produces several structural and chemical effects on both reactants of the powder mixture. The partial amorphization of the crystalline structures of TiO_2 and metallic Zn is evidenced by the significant drop in the diffracted intensity. In the last case, besides the structural amorphization, the oxidation of the metal with atmospheric O_2 takes place, which explains the larger diminution of the diffraction peaks of the metallic Zn. In fact, from ZT12 on, some very weak and wide peaks corresponding to ZnO were detected, confirming the oxidation of metallic Zn and the low crystallinity of the formed oxide. The broadening of the peaks of TiO_2 and Zn also come from different phenomena: for the oxide, it is mainly owing to the large decrease of the crystallite size; and for the metal, the plastic deformation becomes important too. In spite of these changes, the mechanochemical activation does not produce the formation of the zinc titanates in the investigated time range.

The results from the thermal analyses also allowed to explain other processes produced during the milling. The endothermic mass loss observed at about 250°C is attributed to the decomposition of zinc carbonate, which was formed during the mechanochemical treatment by absorption of CO_2 and H_2O from the atmosphere. In order to corroborate this assignation, a sample of commercial hydrozincite ($Zn_5(CO_3)_2(OH)_6$) was analyzed by DTA/TG, undergoing a mass loss of about 30% at the same temperature than the series ZTx. Moreover, previous investigations found the formation of zinc carbonate during the milling of Zn-Fe_3O_4 powder mixtures in similar conditions [11]. As it is deduced from the intensity of the DTA and TG bands, the formation of zinc carbonate increases with the activation time up to 18 min. For longer times, the formed carbonate begins to decompose during the selfsame mechanical treatment, giving weaker decomposition bands in the thermal analyses.

The exothermic mass gain evidenced by DTA/TG corresponds to the oxidation of metallic Zn, remaining from the milling. In both diagrams, this oxidation is displaced towards lower temperatures as the mechanoactivation time increases, proving that this chemical process is strongly favored by the milling. For the samples ZT24 and ZT30, this effect is no more noticeable, suggesting that most of the metal was oxidized during the mechanical treatment. This fact agrees with the analysis of the TG curves, where the mass gain assigned to the Zn oxidation clearly diminishes as the activation time increases.

4.2. Effects of the activation on the reaction kinetics

The formation of Zn_2TiO_4 in all the samples reveals that in the studied reactive system, the following reaction takes place:

$$2ZnO + TiO_2 \rightarrow Zn_2TiO_4 \qquad (1)$$

Although reaction (1) does not correspond to the stoichiometry of the starting mixture, Zn_2TiO_4 is formed very quickly in all the heated samples, reaching high conversions in some cases. This observation suggests that Zn^{2+} diffusion is very fast through the interphase ZnO/TiO_2 creating a concentration gradient, which has its maximum value in this interphase. In this way, the Zn/Ti molar ratio in this zone is higher than 1 and the Zn-richer titanate can be formed. As it can be observed in the Zn_2TiO_4 conversion curves, the formation rate of this phase is notably influenced by the mechanochemical activation of the starting mixtures. The observed trend is that the samples activated for longer times (ZT18 and ZT30) react more quickly, but they reach lower conversions than samples ZT6 and ZT0, since part of the produced Zn_2TiO_4, decomposes. In the particular case of the non-activated mixture (ZT0), the phase $Zn_2Ti_3O_8$ was also detected. According to previous studies [12], this titanate is a low-temperature form of $ZnTiO_3$. However, in sample ZT0, even after 4 h at 800°C (Fig. 6) this phase is present in a significant concentration, whereas $ZnTiO_3$ is not formed at all. This fact suggests that in the non-activated sample the compositional gradient is really very important, leading the reaction between ZnO and TiO_2 to unexpected products, one of them with a Zn/Ti molar ratio higher than 1 (Zn_2TiO_4) and the another one with a Zn/Ti molar ratio lower than 1 ($Zn_2Ti_3O_8$). This mechanism resembles that reported for the $BaTiO_3$ formation [13, 14], where phases rich in Ba and Ti were detected in some reaction stages.

From the conversion curves of the activated samples it can be stated that the gradual disappearance of Zn_2TiO_4 results in the appearance of $ZnTiO_3$. This means that $ZnTiO_3$ formation occur by two paths: the direct formation, in which ZnO and TiO_2 react according to Equation 2 and an indirect formation through the reaction of the Zn_2TiO_4 (produced by reaction 1) and

TiO_2, according to Equation 3:

$$ZnO + TiO_2 \rightarrow ZnTiO_3 \quad (2)$$

$$Zn_2TiO_4 + TiO_2 \rightarrow 2ZnTiO_3 \quad (3)$$

Taking into account the conversion curves obtained for both titanates, it can be concluded that the mechanochemical treatment has important effects on the reactivity and the reaction mechanisms of the investigated system. On one hand, it accelerates the direct formation reaction of $ZnTiO_3$ (Equation 2) through the increase in the ionic diffusion caused by the accumulation of defects in the activated reactants and the formation of highly reactive ZnO and $ZnCO_3$. On the other hand, these same structural and chemical changes also lead to an increase of the reaction rate of Zn_2TiO_4 formation. In those more activated mixtures, this effect is partially overlapped by the acceleration of Zn_2TiO_4 decomposition, which is possibly based on the higher reactivity of the ball-milled anatase, or the Zn_2TiO_4 formed very quickly during the first stages of the calcination. Therefore, the net observed effect of the mechanical treatment is to increase significantly the $ZnTiO_3$ formation, by acceleration of the two reaction paths.

5. Conclusions

The mechanochemical activation of Zn:TiO_2 (1:1) mixtures under air atmosphere produced, as main effects, the deterioration of crystalline structures, the absorption of CO_2 and H_2O from the atmosphere (yielding zinc carbonate) and the formation of poorly crystallized ZnO, by oxidation of the most part of metallic Zn.

Moreover, the mechanical milling notably affected the reactivity of the solid mixture when it was submitted to thermal treatments. Longer activations (30 min) favored the formation of $ZnTiO_3$, reaching almost complete conversion after heating at 800°C for only 1 h. In contrast, the non-activated mixture led to the formation of Zn_2TiO_4 and $Zn_2Ti_3O_8$ after 4 h of heating at the same temperature. This remarkable difference was explained on the basis of a reaction model, in which the differences in ionic diffusion rates generate compositional gradients in the solid. The mechanochemical treatment provides much more efficient diffusion paths, minimizing the compositional gradients and the formation of non-expected phases.

The kinetic study allowed to identify two routes for the $ZnTiO_3$ formation: the first one by direct reaction between ZnO and TiO_2 and the second one by decomposition of Zn_2TiO_4 formed at very short heating times. Both routes are accelerated by the mechanical action.

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