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High-energy ball milling of Al_2O_3–TiO_2 powders

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Abstract

High-energy ball milling of Al_2O_3–13 wt% TiO_2 and Al_2O_3–44 wt% TiO_2 powders have been studied and more precisely the effect of the addition of a milling agent and the relative speed of the vials. The evolution of the microstructure of the milled powders has been studied by X-ray diffraction and the evolution of the specific surface areas has been determined. The pressure and the temperature inside the vials have been recorded. The milling of the powders induces the transformation of the anatase TiO_2 phase into the high-pressure TiO_2(II) phase and partly into the rutile TiO_2 phase. A decrease in the corundum crystallite size is also evidenced. The addition of PVA as a milling agent in order to avoid severe agglomeration appears to be efficient to enhance the milling effect. The formation of the TiO_2(II) phase can be controlled thanks to the vials speed and the milling time in order to obtain quite exclusively this high pressure TiO_2 phase that could be interesting to manufacture nanostructured deposits.

Keywords: Nanostructures; High-energy ball milling; X-ray diffraction

1. Introduction

The manufacturing of nanostructured materials presents an increasing interest. Indeed, they are very promising materials due to their enhanced properties. In the case of Al_2O_3–TiO_2 coatings, they present superior properties like higher hardness and enhanced fracture toughness as compared to their counterparts containing microscale grains [1]. Our work, dedicated to this system, is part of the NAMAMET European program that deals with the manufacturing of nanocrystalline materials through metastability. More precisely our aim is to study the effect of high-energy ball milling of powders in this system and afterwards its impact on the characteristics of powders and deposits obtained by the plasma spraying process.

In the present work, we focus on the effect of the milling parameters (like shock energy, friction energy to total energy ratio, addition of a dry milling agent to prevent severe agglomeration) on the structural parameters (nature of the phases, grain size) of the powders. Two compositions have been chosen: Al_2O_3–13 wt% TiO_2, that is often studied concerning the manufacturing of coatings by thermal spray from commercial powders [1–4] and Al_2O_3–44 wt% TiO_2 that corresponds to the composition of the definite compound Al_2TiO_5.

2. Experimental

The titania powder (Tiona® AT-1, purity ≥98.5%, anatase ≥98%, Millenium Inorganic Chemicals) and the alumina powder (P152SB, corundum, Aluminium Pechiney) were ball milled in air using a Fritsch planetary ball mill, Pulverisette 4 so-called Vario-Mill, with vials and ball made of steel. The absolute speed of the disc is of 250 rpm and the one of the vials was of −50, −127.5 or −300 rpm, the corresponding relative speeds being of, respectively, −1.2, −1.51 and −2.2. Thirty grams of powder were milled with 15 balls of 15 mm. The milling time varied from 30 min to 24 h.

X-ray diffraction (XRD) was used to determine the structural changes as phase transformation and crystallite size evolution. The data were collected using a D5000 Siemens diffractometer (Cu Kα radiation). The evolution of the specific surface area according to the milling conditions was determined by the N_2 BET method, using a Quantachrome Autosorb Automated Gas Sorption System, Quantachrome Corporation. The pressure and the temperature inside the vials were recorded during the ball milling by a GTM system, kindly provided by Fritsch.

3. Results and discussion

3.1. Effect of the milling conditions on the microstructure

The addition of a milling agent in order to prevent a severe agglomeration during milling and the relative speed of the vials

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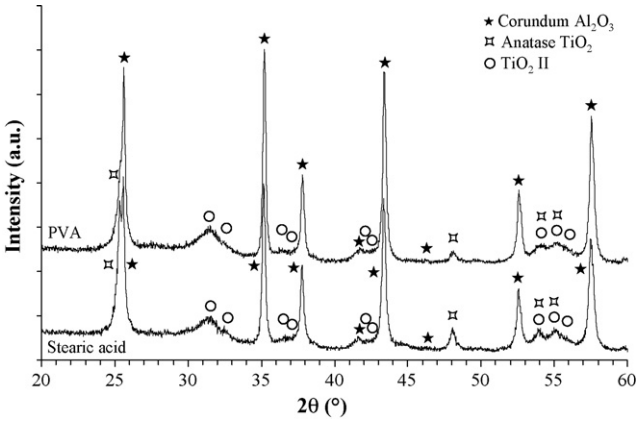

Fig. 1. XRD patterns of Al_2O_3–44 wt% TiO_2 powders ball milled at 250 and −127.5 rpm for 12 h with 1% of PVA or stearic acid. Curves are arbitrary vertically shifted for clarity.

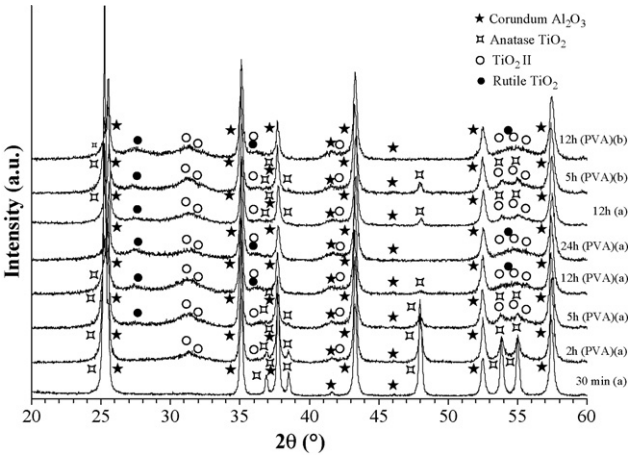

Fig. 2. XRD patterns of Al_2O_3–44 wt% TiO_2 powders according to the milling times and (a) $\omega = -127.5$, (b) $\omega = -300$. The addition of 1 wt% of PVA for a part of the samples is noted at the spectrum. Curves are arbitrary vertically shifted for clarity.

are the main investigated parameters in order to study their effect on the microstructure.

3.1.1. Effect of a dispersing agent on the milling

As an important agglomeration was observed after high-energy ball milling, mostly for the Al_2O_3–44 wt% TiO_2 mixtures, the addition of a dispersing agent was considered. The effect of the addition of 1 wt% of two agents has been determined, the studied compounds being a polyvinyl alcohol (PVA) and a stearic acid.

After a milling at 250 and −127.5 rpm for 12 h, the powders are less agglomerated with both agents. In order to determine the effect on the microstructure, the powders have been characterized by XRD. The XRD patterns (Fig. 1) allow to observe that the transformation of the anatase TiO_2 phase into the high pressure TiO_2(II) phase is less important with the addition of stearic acid. The stearic acid leading to a lower transformation of the anatase phase and PVA being afterward used for the granulation of the powders in order to obtain sprayable grains, we have chosen PVA as a dispersing agent for our milling study.

3.1.2. Effect of the milling parameters

In this part we will focus on the effect of the milling speed and time. For a speed of the disc (Ω) of 250 rpm and for absolute speeds of the vials (ω) of −50, −127.5 and −300 rpm, the shock energy is of 0.084, 0.085 and 0.099 J, the power per ball of 0.37, 0.41 and 0.32 W/g and the friction energy to the total energy ratio of 9, 32 and 26%, respectively. The milling times (Δt) were of 30 min, 2 h, 5 h, 12 h and 24 h. A milling condition is noted in the following ($\Omega/-\omega/\Delta t$).

The nature of the crystalline phases and an estimation of the evolution of the size of the corundum crystallites have been determined by XRD. The XRD patterns collected between 15° and 90° in 2θ are presented in Fig. 2 for the Al_2O_3–44 wt% TiO_2 powders and in Fig. 3 for the Al_2O_3–13 wt% TiO_2 powders, between 20° and 60° in 2θ for a better understanding. For the Al_2O_3–44 wt% TiO_2 powders, from a milling time of 2 h, the transformation of the anatase TiO_2 phase into the TiO_2(II) phase is noticeable. For longer times, the stable rutile TiO_2 phase is also identified, more particularly for milling times of 12 and 24 h. The general sequence of phase transformation: anatase → high-pressure TiO_2(II) → rutile has already been reported in the literature for the milling of the anatase TiO_2 phase [5–6]. The mechanisms responsible for the transformation of anatase into rutile are not well understood. As mentioned by Jentoft et al. [7] some authors have proposed a local heating whereas others have claimed that the pressure produced by the balls on the material during milling, is the driving force. They also indicate that the decrease of the average particle size may also affect the phase transition. In order to determine the effect of milling on the stable corundum Al_2O_3 phase, we have estimated the evolution of the crystallite size (Fig. 4) from XRD broadening using the Scherrer equation, after correction for instrumental broadening. As the contribution of the strains to the broadening is neglected in that calculation, the crystallite size may be under estimated. However, it gives a trend of the evolution of the crystallite size and in all cases it evidences the importance of the

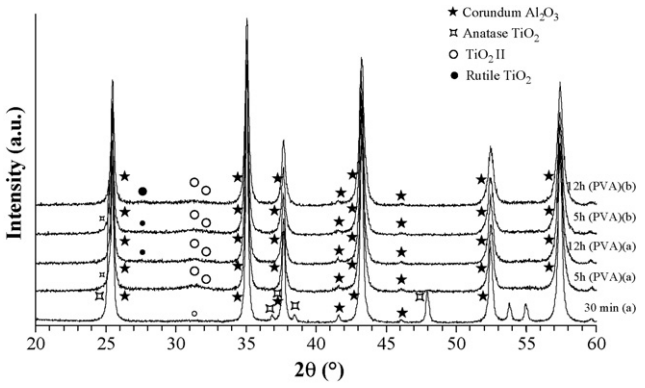

Fig. 3. XRD patterns of Al_2O_3–13 wt% TiO_2 + 1% PVA powders according to the milling times and (a) $\omega = -127.5$, (b) $\omega = -300$. Curves are arbitrary vertically shifted for clarity.

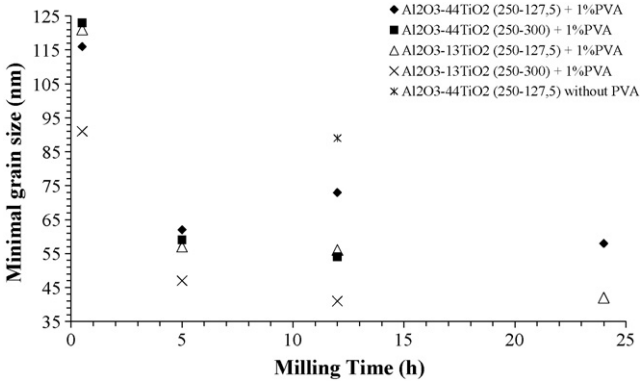

Fig. 4. Minimal corundum crystallite size as estimated from XRD line broadening by using the Scherrer equation.

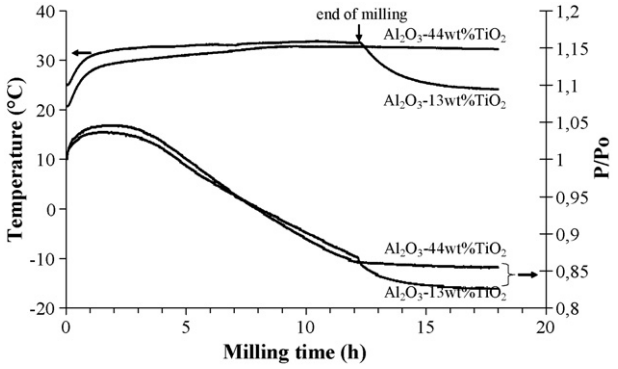

Fig. 5. In situ measurements of the pressure and the temperature during milling by a GTM system for Al_2O_3–13 wt% TiO_2 and Al_2O_3–44 wt% TiO_2 powders ball milled with 1 wt% of PVA at 250 and −127.5 rpm. For the Al_2O_3–13 wt% TiO_2 powders the milling has been stopped after 12 h.

effect of the milling conditions on the alumina, a decrease of the grain size and an increase of the strains leading to mechanical activation [8]. The milling condition of (250/300), that corresponds to the higher shock energy, is more efficient than the one of (250/127.5) for the transformation of the anatase TiO_2 phase into the TiO_2(II) phase and for the decrease of the corundum crystallite size. An even lower efficiency was observed for (250/50), but no important investigations have been performed. Although phase transformations induced by ball milling have been widely reported, the effect of the milling conditions (ball-to-powder ratio, shock energy, friction energy-to-total energy ratio, etc.) has not been investigated in detail. However, Sort et al. [9] have already shown that the fcc–hcp transformation in ball milled Co powder can be tailored by varying the milling parameters. As expected, the addition of 1 wt% PVA has been found to improve the milling as the corundum crystalline size after a milling with (250/127.5/12 h) is smaller (about 75 nm instead of 90 nm without PVA) and the transformation of the anatase phase is increased. However, the formation of the definite compound Al_2TiO_5 is not evidenced. For the Al_2O_3–13 wt% TiO_2 mixtures, similar effect of the milling conditions is observed. However, the transformation of the anatase TiO_2 phase into the TiO_2(II) phase is quite completed after only 5 h of milling and the rutile TiO_2 phase seems to be noticed with milling condition (250/300/12 h). For these powders, the grain size of the corundum phase is smaller than in the previous system. This could be explained by the fact that in this system the percentage of titania is far smaller and the transformation of the anatase TiO_2 phase may need more energy than the decrease in size of the corundum. The higher decrease of the alumina grain size can also be due to the lower agglomeration of the Al_2O_3–13 wt% TiO_2 powders compared to the Al_2O_3–44 wt% TiO_2 powders, the efficiency of the milling thus being increased. Such behaviour could also explain the faster transformation of the anatase phase with higher alumina contents, no further correlation between the transformation kinetic of the anatase and the addition of alumina being yet possible.

Concerning the contamination of the powders due to the wear of the vials and balls, no iron has been observed by XRD as well as by EDX, even after a 24 h milling.

3.2. *In situ measurement of the pressure and temperature and evolution of the specific surface area*

In order to observe possible thermal phenomenon and the formation of new surfaces, in situ pressure and temperature have been measured during milling as well as the specific surface area by the BET method. The curves obtained with (250/127.5) are presented Fig. 5 for the Al_2O_3–13 wt% TiO_2 and Al_2O_3–44 wt% TiO_2 powders with the addition of 1 wt% of PVA. No specific thermal phenomenon is observed during milling. After about 2 h of milling, we can observe a decrease of the pressure after its stabilization, while the temperature remains constant. The decrease of the pressure may be due to the adsorption of oxygen on the new surfaces formed during the milling. The evolution of the specific surface area, shown in Fig. 6 is in good agreement with this conclusion for the Al_2O_3–44 wt% TiO_2 mixtures as the specific surface area increases during the milling. However, for the Al_2O_3–13 wt% TiO_2 powders, we do not observe a significant increase of the specific surface area. This could be due to the fact that while new surfaces are formed, particles stick together, resulting in no change of the surface area.

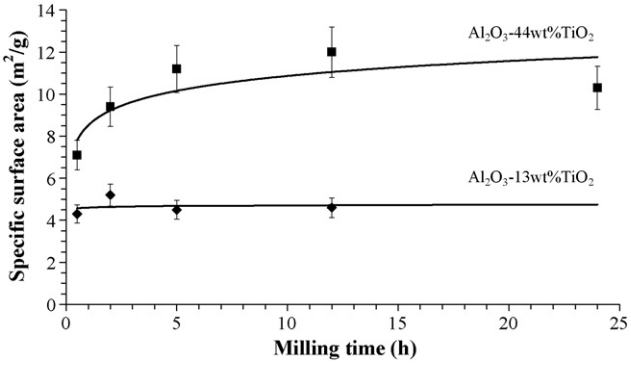

Fig. 6. Evolution of the specific surface area of Al_2O_3–13 wt% TiO_2 and Al_2O_3–44 wt% TiO_2 powders ball milled with 1 wt% of PVA for 30 min, 5 h, 12 h and 24 h at 250 and −127.5 rpm.

4. Conclusion

The effect of the addition of a milling agent and of the relative speed of the vials on the high-energy ball milling of Al_2O_3–13 wt% TiO_2 and Al_2O_3–44 wt% TiO_2 powders have been studied. The addition of the PVA as a dispersing agent in order to avoid a severe agglomeration favors the milling. The optimization of the speed of the vials also allows to enhance the transformation of the anatase TiO_2 phase into the high-pressure TiO_2(II) phase and the decrease in size of the corundum. These mechanically activated powders are very interesting for the manufacturing of nanostructured deposits through the plasma spraying process as they are constituted of another metastable phase, the TiO_2(II) phase that can be obtained quite exclusively according to the milling process.

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