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PREPARATION OF NANO-STRUCTURAL Al_2O_3-TiB_2 IN-SITU COMPOSITE USING MECHANICALLY ACTIVATED COMBUSTION SYNTHESIS FOLLOWED BY INTENSIVE MILLING

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Abstract: *Nano-structural synthesized materials can be fabricated utilizing intensive milling after combustion synthesis. The Al_2O_3-TiB_2 ceramic composite has been synthesized by aluminothermic reactions between Al, Ti (TiO_2), and B (B_2O_3 or H_3BO_3). Boric acid (H_3BO_3) is less expensive than boron oxide, and after being dehydrated at 200°C, boron oxide will be obtained. In this study, Al, TiO_2, and boric acid were used as the starting materials to fabricate an Al_2O_3-TiB_2 ceramic composite. After mechanical activation and thermal explosion processes, intensive milling was performed for 5, 10, and 20h to assess the formation of a nano-structural composite. The X-ray phase analysis of the as-synthesized sample showed that considerable amounts of the remained reactants incorporated with the TiO phase were present in the XRD pattern. The results showed that the average crystallite size for alumina as a matrix were 150, 55 and 33 nm, after 5h, 10h, and 20h of intensive milling, respectively. The SEM microstructure of the as-milled samples indicated that increasing the milling duration after combustion synthesis causes a significant reduction in the particle size of the products, which leads to an increase in the homogeneity of particles size. A significant increase in the microhardness values of the composite powders was revealed after intensive milling process.*

Keywords: *Ceramic matrix composite, Combustion synthesis, X-ray analysis, Milling*

1. INTRODUCTION

TiB_2 ceramic material has good physical, chemical, and mechanical properties such as a high melting point, a high level of hardness, high Young's modulus, good corrosion resistance, and excellent electric conductivity. Such properties give a wide application area to TiB_2 material such as advanced engineering ceramics and ballistic protection materials [1, 2]. The addition of Al_2O_3 to TiB_2 can improve its fracture toughness, flexural strength, sinterability, and impact resistance [2].

There is a growing interest in the production of nano crystalline materials because of their excellent physical and mechanical properties compared with coarse-grained materials [3]. Fine-grained materials possess a higher reactivity, catalytic activity, and hardness compared to bulk materials, and frequently offer new optical, electronic, magnetic, and other properties. The growing commercial-scale production of nano materials stimulates a search for new approaches to their synthesis and the optimization of the known synthetic procedures [4]. Common methods for the preparation of nanocrystalline materials are, e.g., inert gas condensation (IGC), chemical vapor deposition (CVD), and ball milling [5]. The advantages of ball milling (mechanochemical synthesis) are easy handling, the possibility of producing large quantities, and the applicability to a wide range of different classes of materials. However, as a result of the long milling times (tens and even hundreds of hours), the final products become contaminated by substances erased from the walls of mill vials and balls. Moreover, for the systems considered, it is normally impossible to obtain nanocomposites with ceramic particles by mere mechanochemical treatment of the reagents, and additional high-temperature annealing is necessary. Thus, the drawbacks of this process lie in high-energy consumption and low product purity [3, 6].

From an economical point, there have been some attempts during the past few years to fabricate nano-structural composites using the combustion synthesis technique. It has been shown that the formation of nanostructured materials from mechanically activated reactants is possible after combustion synthesis [6, 7]. Combustion synthesis (CS), one of the rapidly emerging cost-effective technologies used to synthesize monolithic and composite in situ ceramics, has numerous advantages. These include very high-reaction rates, the formation of very pure products, and the elimination of the need for high-temperature furnaces used in conventional material fabrication methods due to the immense energy release. With the advantages of low energy consumption and short reaction periods, combustion synthesis appears to be an efficient technique for large-scale industrial production [7, 8]. However, it is not an easy task to produce nano materials by conventional CS, where the scale of heterogeneity for the initial solid reactants is approximately 10–100 μm. This feature, coupled with high reaction temperatures (usually >2000 K), makes it difficult to synthesize nano sized structures with a high surface area. Several methods were suggested for the synthesis of nano materials by using one of the following approaches: (i) CS, followed by intensive milling; (ii) CS + mechanical activation (MA); (iii) CS synthesis followed by chemical treatment, so-called chemical dispersion; (iv) CS with additives; (v) carbon combustion synthesis (CCS) [6-8].

According to the literature [9-11], MA may decrease or increase the crystallite size of the products, depending on the system. It is well known that MA will enhance the reactivity of the reactants, and therefore further heat will be released, resulting in an increase in the final temperature. On the other hand, the final combustion temperature also depends on the initial temperature (ignition temperature). In some systems, especially in the binary ones, MA causes a significant decrease in the initial temperature by even hundreds of degrees, meaning that the final temperature, and consequently the crystallite size, will be decreased. In some other systems, especially in the thermite systems that contain more than two reactants, MA may lead to an increase in the initial temperature due to a decrease in the interfacial area between the reducing agent and metal oxides. In the former systems, MA will lead to an increase in the crystallite size [9-11]. However, despite the high heat content of the composition, it is extremely difficult to initiate combustion in the initial samples that were not subjected to MA, even if a high-temperature primer is used [9]. Thus, for the systems in which MA causes an increase in the combustion temperature, an optimized MA duration should be found to obtain nano-structural products.

A potential route to the combustion synthesis of Al_2O_3-TiB_2 in situ composite uses the aluminothermic reduction of oxides of Ti and B, according to reaction (1) [1].

$$10Al + 3TiO_2 + 3B_2O_3 \rightarrow 5Al_2O_3 + 3TiB_2, \Delta H_{(298)} = -2725 (kJ/mol) \qquad (1)$$

An important benefit from combining thermite-based displacement reactions with conventional combustion synthesis is the cost savings, since the metallic oxides like TiO_2, B_2O_3, and ZrO_2 are considerably less expensive than elemental titanium, boron, and zirconium [1, 2]. The other benefit is that the replacement of elementary reagents by compounds normally leads to the formation of a structure with finer grains [9].

Recently, Deqing [1] fabricated Al_2O_3-TiB_2 in situ composite using boric acid instead of B_2O_3 as a boron source, in synthesizing Al_2O_3-TiB_2 in situ composite, reaction (2).

$$10Al + 3TiO_2 + 6H_3BO_3 \rightarrow 5Al_2O_3 + 3TiB_2 + 9H_2O, \Delta H_{(298)} = -2518.9 (kJ/mol) \qquad (2)$$

To the best of our knowledge, the fabrication of nano-structural Al_2O_3-TiB_2 in situ composite using a combination of methods (i) and (ii), and Al, TiO_2, and boric acid as starting materials has not yet been studied. We aimed to assess the formation of nano structural ceramic composite using boric acid instead of boron oxide after intensive milling after combustion synthesis. In addition, changes in purity, thermodynamic stability, and microhardness of the final powders were investigated in this work. This study indicates that intensive milling after combustion synthesis has some useful effects on the grain size, purity, and structure of the final products as well as their microhardness.

2. EXPERIMENTAL

The starting materials used in this study included Al (average particle size< 45 μm, 99.5% purity) as the reducing agent, TiO_2 (anatase, average particle size< 1 μm, 99% purity), and H_3BO_3 (average particle size< 100 μm, 99% purity) as the thermite reagents. The powder blend was made according to the reactions (2).

Based on our experiments, in the Al-TiO_2-H_3BO_3 thermite system, MA up to 5h will cause an initial temperature reduction by about 140 °C, which indicates that the final temperature will be reduced. However, after 5h of MA, due to the agglomeration and a depression in the interfacial area between the particles of the reactants, the initial temperature will be increased. Thus, whereas no combustion synthesis would occur for an inactivated sample, and the final temperature will be decreased up to 5h, the MA process has been done for 5h as an optimized MA time. The MA process was performed at a milling speed of 250 rpm using Fritsch planetary ball-mill with an alumina vial and a blend of alumina balls (10mm and 20mm diameters) in argon atmosphere. No process control agent (PCA) was used in this system, as the boric acid is able to reduce the effect of cold-welding and can inhibit agglomeration [12]. The ball to powder weight ratio was 10:1. To prevent a significant temperature rise in the mechanically alloyed powders, the 10min run (milling)-5min stop (natural cooling) milling cycle was used. After the milling process, the mixture was oven-dried at 80 °C for 2h. The dried powders were then sieved through a 100-mesh to reduce the number of agglomerates. The powder mixture was uniaxially pressed without a binder at 400MPa into a cylindrical compacted billet 2cm in diameter and 1cm height to approximately 60 % relative density using mass and geometry calculations. The thermal explosion was carried out in a preheated furnace in air at 800 °C. When a sample with an ambient temperature is put in a preheated furnace, the nonequilibrium defects and internal stresses generated due to the intense plastic deformation during the MA do not have enough time to be eliminated. It is worth mentioning that in the Al-TiO_2-B_2O_3 system, the synthesis was carried out in less time (about 30 seconds) because there is no water to evaporate.

After the thermal explosion, the porous sample was immediately removed from the furnace and crushed in a mortar. Intensive milling was carried out for 5, 10, and 20h in air (argon atmosphere was not used intentionally). For the intensive milling process, the ball to powder weight ratio of 20:1 was applied, the milling speed was 500 rpm, and alumina made balls and vial were used to prevent the entrance of unexpected impurities like iron. The microstructures of the as-synthesized and the as-milled powders were obtained using a scanning electron microscope (Camscan mv2300). The mean powder particle size was estimated from SEM images of the powder particles by image tool software. The average size of about 20 particles was calculated and reported as the mean powder particle size. The mechanically activated and as-synthesized powders just before and after thermal explosion, respectively, were characterized by an X-ray diffractometer (Bruker's D8 advance system, Germany) with Cu Kα(λ=0.15405 nm) radiation. In addition, the samples that were taken at selected time intervals (5h, 10h, and 20h) after thermal explosion were characterized by X-ray phase analysis. In order to analyze the results of the XRD experiments, X'Pert HighScore software (Netherlands) was used. The crystallite size analysis was made through X-ray diffraction (XRD) patterns using the Williamson-Hall method [13] and sigma plot software.

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

Where θ is the Bragg diffraction angle, D is the average crystallite size, ε is the average internal strain, λ is the wavelength of the radiation used, and β is the diffraction peak width at half-maximum intensity.

The hardness of cross-section of as-synthesized and as-milled powder particles was determined by microhardness test using a Vickers indenter at the load of 100 g and dwell time of 5 seconds. The average of ten measurements for each sample was calculated and reported as hardness value.

3. RESULTS AND DISCUSSION

The MA process before combustion synthesis has some important effects on the process. At the first stages of activation, harder particles (TiO_2 and boric acid) penetrate into the aluminum, which is accompanied by the failure of the oxide film always present on Al particles, and due to repeated welding, fracturing, and rewelding of the powder particles, higher interfacial regions will be obtained. In addition, MA brings about an increase in the energy level of the reactants mechanically. Therefore, the formation of new phases during this process is possible. Fig. 1 shows that no reaction took place during the MA process, as only the reactant peaks were revealed. In fact, it indicates that the mechanically activated powders had not been given enough energy to react with each other during this process. Nevertheless, it was found that no combustion synthesis occurred for any sample having had no mechanical pre-treatment. This means that the energy, which had been given to the reactants within 5h, was necessary for the combustion synthesis to occur.

Fig. 2 shows the X-ray phase analyses of the as synthesized and the as-milled samples after thermal explosion. The considerable presence of Al, TiO, and TiO_2 peaks in the patterns of the as-synthesized sample together with those of Al_2O_3 and TiB_2 confirms that the efficiency of the combustion synthesis reactions was not significant. Care should be taken that the boiling point of B_2O_3 is much lower than 2000 °C, although the final temperature exceeded this temperature. However, as no weight loss was measured in the sample, it is concluded that all the B_2O_3 powders were consumed during the combustion synthesis. Solid-state synthesis has one major drawback, the incomplete conversion of the product leading to the depression of products purity. Insufficient mixing of the reactants before combustion synthesis, formation of the oxide layer on the aluminum powders, and even a little amount of impurity in the reactants may lead to incomplete reactions. Although MA usually increases the intensity and the efficiency of combustion reactions, it seems that 5h duration for MA is not sufficient for this powdery sample to achieve a high chemical conversion of the reactants to the expected products. By increasing the MA duration, higher mixing will be obtained between the reactants. However, as mentioned, in this thermite system, increasing the MA time above 5h will lead to an increase in the ignition temperature of the combustion reactions and a higher final temperature will be obtained, causing an increase in the crystallite size of the products.

In Fig. 2, the most significant points that can be

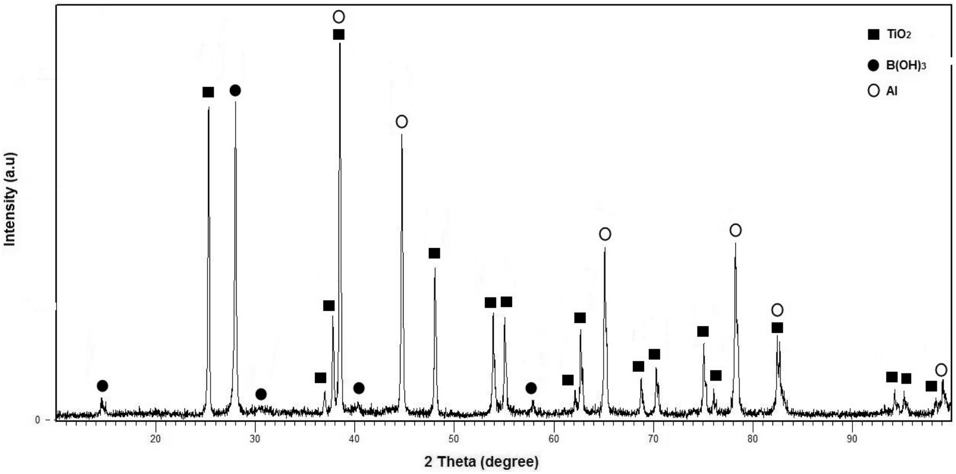

Fig. 1. The X-ray phase analysis of the mechanically activated powders.

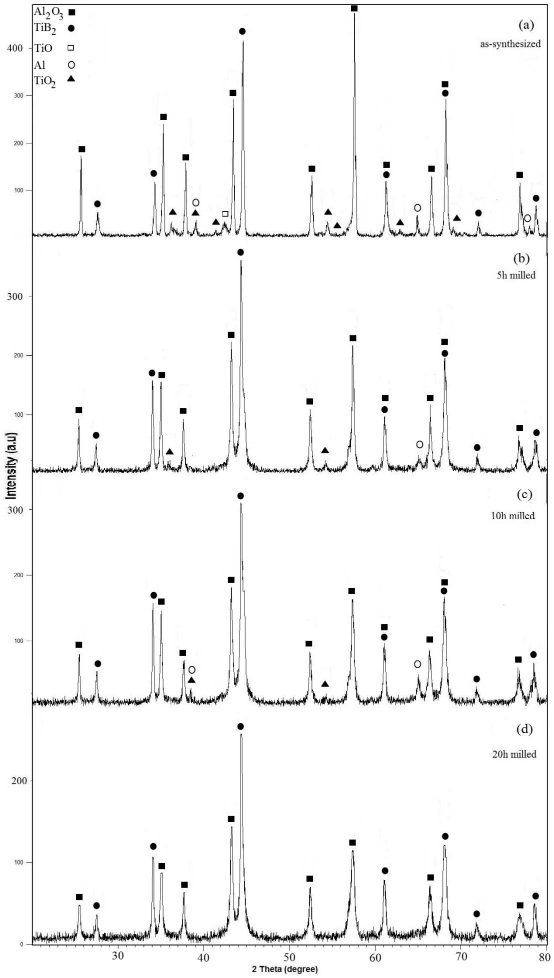

Fig. 2. X-ray phase analyses of: (a) as-synthesized sample, (b) after 5h of intensive milling, (c) after 10h of intensive milling, and (d) after 20h of intensive milling.

understood by increasing the milling time are the gradual elimination of Al, TiO_2, and TiO peaks in the patterns of the final products, the considerable peak shift toward lower angles for the alumina and titanium diboride, and the crystalline peaks broadening of the Al_2O_3 and TiB_2 phases.

As the reactions were not performed thoroughly after thermal explosion, the system is not thermodynamically stable, and during the initial stages of intensive milling, the remained reactants will react with each other to form alumina and TiB_2. Thus, the corresponding peaks of the reactants will disappear, and a substantial amount of heat will be released, causing decrease in the number of structural defects, and an increase in the crystallite size. On the other hand, the remained reactants may enter in the lattice structures of the alumina and TiB_2 after thermal explosion. We believe that both events have taken place. According to Fig. 3, a considerable number of peaks shifting toward lower angles can be observed for the alumina and TiB_2 during intensive milling, which indicates that their lattice parameters have been increased. Generally, these shifts that are observed in the patterns of XRD will be attributed to the formation of the solid solution and/or uniform strain [14]. However, it seems that the latter is more closely related to metals and alloys and consequently a solid solution should have been formed in this system. As can be seen in Fig. 3,

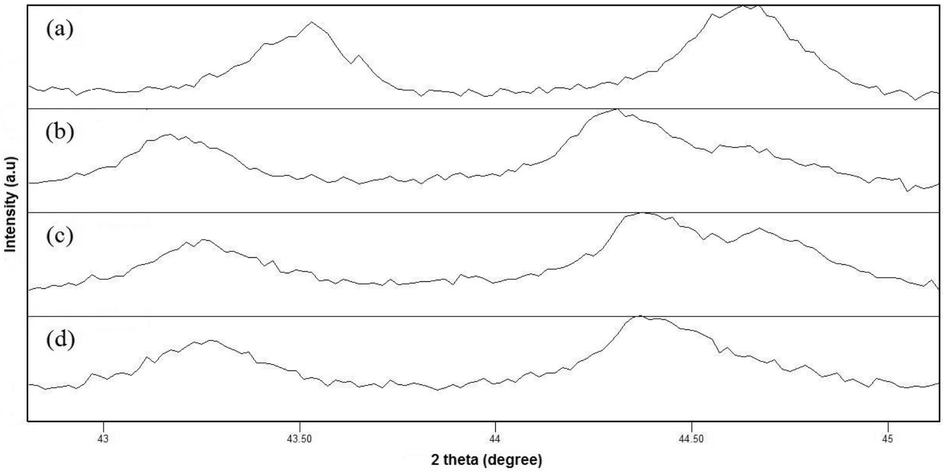

Fig. 3. The alumina and TiB2 peaks displacement during intensive milling, (a) as-synthesized powder, (b) after 5h of intensive milling, (c) after 10h of intensive milling, and (d) after 20h of intensive milling.

the main shift of these peaks is observed up to 5h of intensive milling, which demonstrates the entrance of the reactants in the lattice structures of alumina and TiB_2 that will also lead to the elimination of the reactants peaks in the XRD patterns. By further increasing the milling time to 10h, a peak shift to higher angles can be seen. On the other hand, more intensive aluminum peaks (around $2\theta = 65$ °C and 38.5 °C) are present in the pattern of 10h milled powders. In fact, from the thermodynamic point of view, the system tends to reduce its internal energy. The unreacted aluminum that entered into the lattice structures of Al_2O_3 and TiB_2 diffuse out to react with TiO_2 and B_2O_3 to form more thermodynamically stable phases and to decrease the lattice parameters of Al_2O_3 and TiB_2. In accordance with Fig. 3(c and d), no peaks shift is observed after 10h intensive milling, which indicates that the lattice parameters of Al_2O_3 and TiB2 did not change after this time. Fig. 2(d) shows only the presence of Al_2O_3 and TiB2 peaks and no corresponding peaks of aluminum and TiO_2 are observed. It should be stressed that the argon atmosphere was not used intentionally so that there would be no remained aluminum after 20h milling.

The other point as mentioned above is a gradual intensity fading pertaining to Al_2O_3 and TiB_2 diffraction peaks accompanied by an increase in the peaks width with increasing the milling time after thermal explosion. The background is also substantially increased. This gradual broadening is usually associated with combined instrumental effects and structural factors like reduced crystallite size, and strain at the atomic scale caused by the lattice distortion [14]. Upon milling, the mechanical energy is stored in the materials via the production of defects and dislocations, leading to an increase in the internal strain. At the same time, a part of the cumulated energy is partially relaxed when the dislocations come close to each other to form a new grain boundary, then the crystallite size decreases [14].

The crystallite size for alumina as the matrix is calculated to be 150nm using Williamson-Hall method [13] and sigma plot software, and is not decreased below 100nm after 5h of milling time. According to the literature [1], the adiabatic temperature for the $Al\text{-}TiO_2\text{-}H_3BO_3$ system is above 2300 °C. During in-situ formation of the $Al_2O_3\text{-}TiB_2$ ceramic composite, alumina forms initially due to the occurrence of thermite reactions, and then TiB_2 will form, and the temperature rises to above 2300 °C. Therefore, the alumina will be melted immediately and solidified with large grains, and the defects that were generated at the stage of preliminary activation will be eliminated in the course of the CS process. Thus, 5h intensive milling time may be insufficient to decrease the crystallite size of alumina below 100nm, while further milling creates a high concentration of nonequilibrium defects owing to highly intense plastic strains, and its average crystallite sizes will be decreased to 55 and 33nm after 10 and 20h of intensive milling, respectively. It should be stressed that the heat released after the initial stages of intensive milling will prevent the significant decrease of the crystallite size, especially before 5h.

The microstructures of the as synthesized and the as-milled powders after 5h, and 20h of intensive milling are shown in Fig. 4. A porous structure (see Fig. 4a) with homogeneous distribution of the components is obtained for the final products after combustion synthesis. As can be seen in Fig. 4(b and c), the milling has caused a reduction in the particle size of the as-milled powders. In fact, both the Al_2O_3 and the TiB_2 are very hard and brittle ceramics, and during intensive milling, their particle sizes reduced due to continuous fracturing. The particles size seems more homogeneous and finer after 20h milling. The average size of about 20 particles was calculated to be about 4.7μm and 0.8μm after 5h and 20h of intensive milling, respectively.

Sharifi et al. [15] used the $Al\text{-}TiO_2\text{-}B_2O_3$ thermite system in order to fabricate a nano-structural $Al_2O_3\text{-}TiB_2$ ceramic composite via mechanochemical route. They showed that after 60h of ball milling, nano structural composite would be prepared with a crystallite size of less than 50nm. First, it was not possible to use boric acid at a lower cost than the boron oxide, as the boric acid will not be dissociated in the ball mill, in which the temperature increases locally. Therefore, using the combustion synthesis route will be more beneficial since a less expensive material (boric acid) could be used instead of boron oxide, and this material would decompose in the furnace. Second, one of the major advantages of the combustion synthesis is the formation of very pure products. In the Sharifi et al. [15] study, steel vial and balls, which would bring about impurities to the system, were used. Third, the products will form after thermal explosion within one minute, which is much less than that required for the mechanochemical synthesis (about 50h).

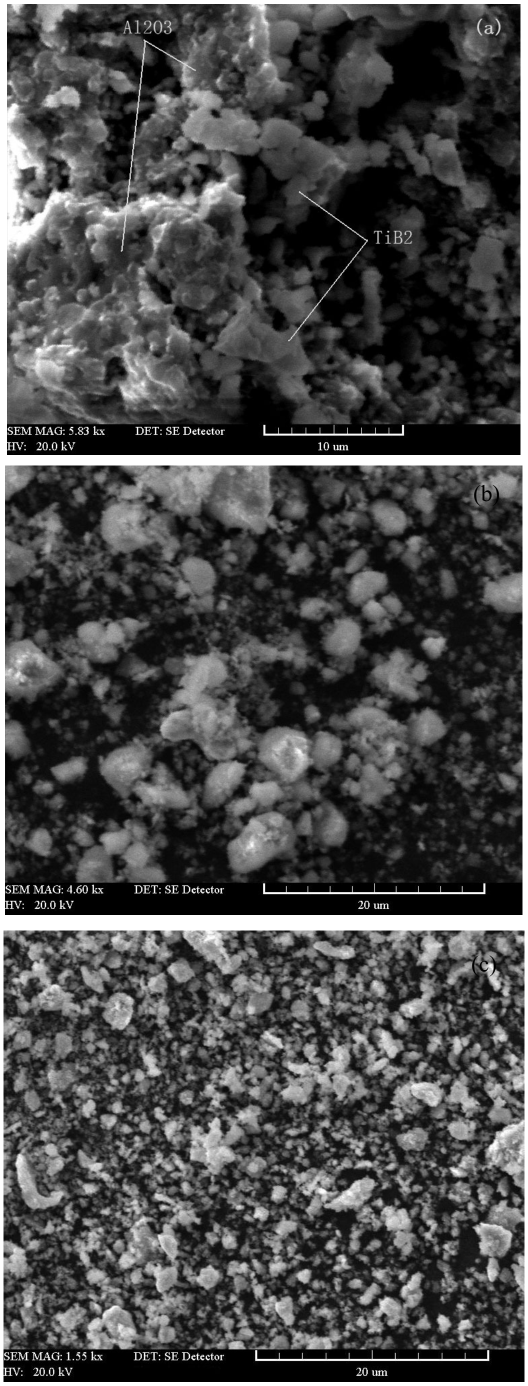

Fig. 4. The SEM microstructures of (a): as-synthesized composite, (b) after 5h of intensive milling, and (c) after 20h of intensive milling.

A low value of microhardness (1290 Hv) was obtained for the as-synthesized Al_2O_3-TiB_2 powders, which is not comparable with the literature [16]. In fact, a considerable presence of the remained reactants (especially Al) reduced the values of microhardness. However, as mentioned, by applying the intensive milling after combustion synthesis not only the crystallite size of the alumina as the matrix reduced, but also the purity of the ceramic composite increased. The measured values of microhardness confirmed these results. After 5h, 10h, and 20h of intensive milling, higher microhardness values of 1530, 1750, and 2020 Hv, were obtained. In fact, increasing the purity of the products and work hardening induced during intensive milling are the reasons of microhardness enhancement.

The features above allow us to hope that this technology may be implemented for much greater volumes of reactive mixtures and in devices with a much higher performance than that of the laboratory-scale mill used. Earlier, only laboratory planetary mills were in use, and at present, industrial planetary mills are commercially available. Industrial planetary mills of periodic action characterized by productivity up to 20-40 kg/h are promising for applications in powder metallurgy [17]. By using Non-equilibrium methods of compacting and sintering, it is possible to minimize the processes of the growth of the grains and particles. The results obtained by sintering in the plasma formed by a pulsed electric-spark discharge (SPS sintering), and by explosive compacting, seem to be the most promising to fabricate low cost nano-structural wear tools or ballistic protection components by using combustion synthesis followed by intensive milling [6].

4. CONCLUSIONS

In this study Al, TiO_2 and boric acid were used as raw materials. Al_2O_3-TiB_2 ceramic composite was successfully fabricated after mechanical activation and thermal explosion. After 10h and 20h of intensive milling after combustion synthesis, a nano-structural composite with an average crystallite size of 55nm and 33nm for alumina as the matrix was produced, but its crystallite size was not reduced below 100nm after 5h of intensive milling. The microstructural characterization of the powdery composite after different times of intensive milling indicated that the particle size decreased and a much more homogeneous microstructure was observed by increasing the milling time.

Summarizing the experimental data, the following conclusions can be drawn:

1. Irrespective of the results of the XRD analysis, it is almost impossible to have complete chemical conversion of the reactants in solid-state synthesis. It is shown in our study that, by applying intensive milling after combustion synthesis almost all the remained reactants will react with each other to increase the purity and the thermodynamic stability of the products. If a non-stable ceramic composite used as reinforcement in a metal-based composite, chemical reactions will take place at the matrix/reinforcing particle border of the metal matrix composite, and will lead to structure degradation during work at elevated temperatures.
2. Intensive milling after combustion synthesis will decrease the crystallite and particle size of the products to form a nano crystalline composite with fine particles.
3. The homogeneity in the particle size of the components in the final products will be increased after intensive milling.
4. As very pure products will be obtained after combustion synthesis within less than one minute, and intensive milling has very useful effects on the products, the method of combustion synthesis followed by intensive milling seems to be completely usable for industrial scale. Intensive milling after combustion synthesis is recommended highly to improve the final properties of the produced materials, especially for the Al_2O_3-TiB_2 ceramic composite.
5. As a result of purity enhancement and work hardening induced during intensive milling, a higher amount of microhardness was obtained after combustion synthesis.

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