Preparation of Al_2O_3/ZrO_2 and $Al_2O_3/ZrO_2/ZrN$ nanocomposite by mechanical activated combustion synthesis: effect of milling time and synthesis atmosphere

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Combustion synthesis has been developed as a simple and economically viable technique for the preparation of composites, nanomaterials and intermetallics. In this paper, by combining two methods (milling and combustion synthesis) the effects of milling time and combustion furnace environment on the synthesis of the mixture consists of aluminium and industrial Zirconia powders was investigated. By milling, the average crystallite size of powders was reduced to 20nm. Particle morphology and powder composition were observed by SEM and were analysed by X-ray diffraction respectively.

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Keywords: Combustion Synthesis; Milling; Zr Compounds; Al_2O_3; Nanocomposite

1. Introduction

Powders as raw materials are very important to manufacture the mixture that consists of ceramic parts. Therefore, they greatly attract the attention of scientists for both types of synthesis methods for the preparation of micro and Nano- particles [1]. One of the compound materials which has been widely used as a useful source of industrial and household materials is Ceramic composites [2]. Chemical and thermal stability, relatively good strength, thermal and electrical insulation characteristics combined with availability in abundance have made alumina (Al_2O_3) attractive for engineering application ă3î. Zirconia is the third most widely used ceramic material after alumina and silica. It is a good source for structural material because of its physical and mechanical characteristics [2].

Al_2O_3-ZrN Nanocomposite is used as a coating in medical devices and in the food industry that it prevents the formation of bacteria and germs on the surfaces. In addition, this coating has oxidation resistance property and is used in anti-scratch and hard coating in the automotive and aerospace components and other parts exposed to high wear and corrosive environments. Metal nitrides have high corrosion resistance and have applications in mechanical, thermal and chemical coatings [4]. By consideration unique properties of composite Al_2O_3-ZrO_2 such as high toughness, high wear resistance and relative low thermal expansion, it can be used in toughened ceramics, wear resistant ceramics, thermal barrier coating in gas turbine, oxygen sensor and the femoral head of hip replacement [5].

During the recent decades, a lot of attention has been focused on the producing of Nano-materials and Nano-powders because they show new electronic, optical, magnetic, photochemical, electrochemical and mechanical properties [5]. The researches display that an effective and efficient process to produce powders is Self-propagated High-temperature Synthesis, SHS, which has been taken as an important goal for the future of technology in the composites [6].

The use of SHS in ceramic technology, due to production of sinterable and Nano- sized or high purity micro powders, have been significantly developed [1]. SHS is an exothermic process in which the reaction occurs between two or more solid or gaseous reactants and this reaction occurs with a self-propagating regime during the formation of its solid product [7]. Therefor in order to reach the desired product, the parameters affecting the SHS should be studied. Various parameters which affect the SHS synthesis include: grain size, compact powder, raw material, and the reactant stoichiometry and atmosphere gas type and pressure [8]. But today, taking maximum advantage of the material properties is not possible without utilizing the benefits of nanotechnology [9-10]. On the other hand, the product of SHS procedures is fine enough, despite being ultra-nanostructures and provisions must be made to optimize the synthesis of nanostructures. One of the common methods used to achieve nanostructures is "Mechanical Alloying (MA)" however this method has proven its own ability to achieve stable compounds with nanostructure; the researchers have also faced some problems. For example: the synthesis of a broad pattern of main phases with intermediate phase, the entrance of impurity through balls and cups, use of too much energy and excessive length of the process [11]. During high-energy milling, the impact of the ball to the powder particles leads the powder particles to be repeatedly flattened, cold welded, fractured and rewelded. Because of repeated flattening and cold welding, the fine structure will be observed and as a result, the distance between layers is reduced, besides, increasing the local

temperature during particle collision lead to increase the diffusion rate in the structure of each other [12].

Recently, combining milling and SHS process has led to a faster and better combustion processes [13]. And it is important to mention that due to the SHS itself imposes very high temperatures (although in short time) usually does not have the ability to develop compounds with nanostructures; and should be combined with mechanical activation methods (MASHS)[1] as an auxiliary procedure. In this study, the effect of synthesis atmosphere type and activation time on the phase properties and microstructure of synthesized samples by MASHS were investigated.

2. Experimental

The starting powders were aluminum (Al) and ZrO_2. The powders were mixed in a composition of 30 wt. % Al and 70 wt. % ZrO_2. Powder mixing and milling was carried out by the planetary ball mill (Retsch, PM100, Germany) at 300 RPM for 1 and 6 hours in an Argon atmosphere. The jars and balls were made of stainless steel. The balls were weighed to achieve a ball to powder ratio (BPR) of 15:1. Samples of 10 mm diameter and 5 mm height were manufactured by uniaxial die pressing at 300 MPa. The samples were placed on a graphite substrate at 800°C in a tube furnace with flowing of different gases. Microstructures were studied by a VEGA\\TESCAN scanning electron microscope (SEM). Phase identification and measuring the crystallite size were carried out on a Philips X-ray diffractometer with Cu-Kα radiation operated at 30 KV and 25 MA.

Fig. 1 shows a schematic of this procedure. There are several methods for the calculation of the average grain size by using obtained spectra peaks from XRD analysis, such as Scherrer, Williamson-Hall, Warren Averbach and Rietveld Refinement Method [14].

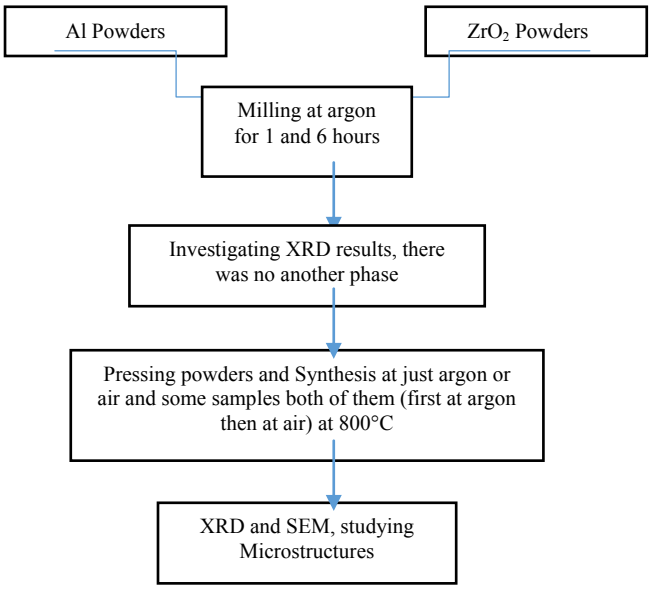


Fig.1. Schematic of experimental works

[1] Mechanical Activated SHS

3. Results and discussion

3.1. Mechanical Activation

The XRD analysis was taken after milling. Fig. 2 shows the XRD pattern. The results show no secondary phase has been formed during the milling process and just peaks of Al and ZrO_2 were seen in the pattern.

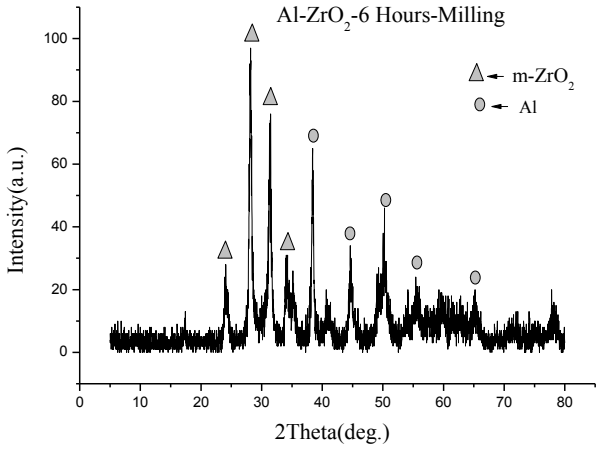


Fig.2.The X-ray diffraction pattern of mixed powders of Al and ZrO_2 which mechanically activated during 6 hours.

In Table 1. The crystallite size before milling and crystallite size of phases after 6 hours of milling is given. As it can be seen in Table 1, crystallite size is reduced to nanometer scale by milling

Table 1. Calculation of the crystallite size before and after 6hours milling with BPR 15:1 by reitveld method

Element or compound	Before milling	After 6 hours milling
Al	<100nm	23 nm
ZrO_2	51nm	16 nm

3.2. Argon environment

Two samples with different milling time 1 and 6 hours were prepared under 300 MPa pressure by uniaxial pressing. Then the samples were synthesized under argon atmosphere at 800º C in tabular furnace, also they were cooled at argon atmosphere. XRD patterns of these samples are shown in Fig. 3. The results showed the presence of intermetallic phase Al_2Zr and monoclinic Zirconia. Considering that the samples were synthesized in argon atmosphere, the formation of intermetallic phase can be expected; because in fact, only aluminum and Zirconia can react to each other. The crystallite size of the phase

was calculated by Scherrer method [15], which is shown in Fig. 4. As it is expected, the crystallite size of the samples with 6 hours of milling was less than the sample with 1 hour milling; because in the initial hours of milling, the particles became finer and finer. SEM images of the synthesized samples are shown in Fig. 5. As SEM images show, the particle shape of sample with 1 hour of milling is seen as blade shape and contains relatively coarse particles. The sample with 6 hours of milling somehow changed its blade shape and became smaller and spherical. According to the mechanical milling mechanism, this process will result in fine particles and increased area, so during in this process the surface free energy (γ) increases and the trend of surface free energy increasing is more than the strain free energy (ΔG_E). With reduced the milling time, the rate of increasing of γ is less than G_E and therefore, the free strain energy overcomes the surface free energy of the system. So the system for reduction of the strain free energy, in accordance with the Nabbaro`s relationship (equation 1), tends to be more disc like (Fig. 5b) [16].

$$G_E = \frac{2}{3}\mu \Delta V^2 f\left(\frac{c}{a}\right) \quad (1)$$

In which ΔV is the percentage of change in volume, is the shear modulus of the matrix and f (c/a) is shaping factor.

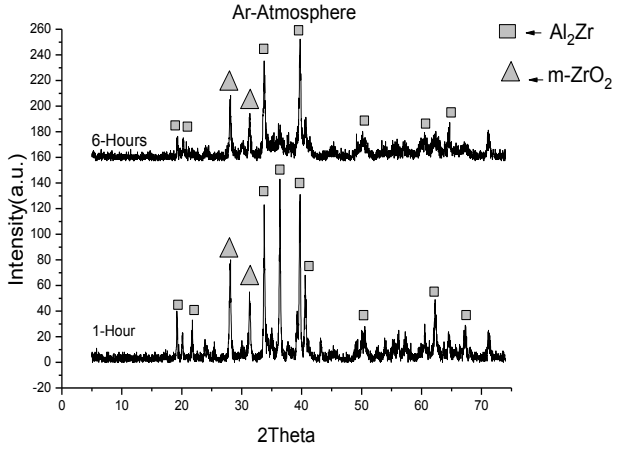


Fig.3.The XRD patterns of samples 1 and 6 hours milling with BPR of 15 to 1 and synthesized in an argon environment at 800 ˚C

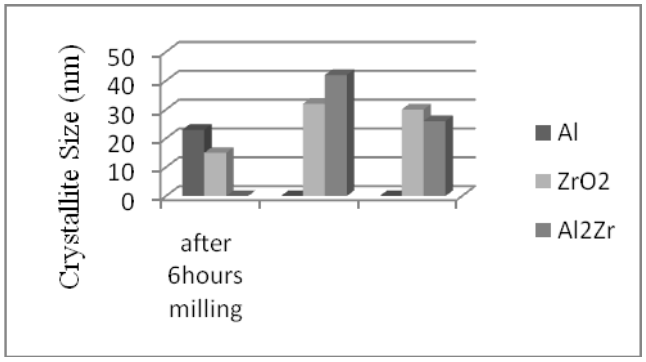
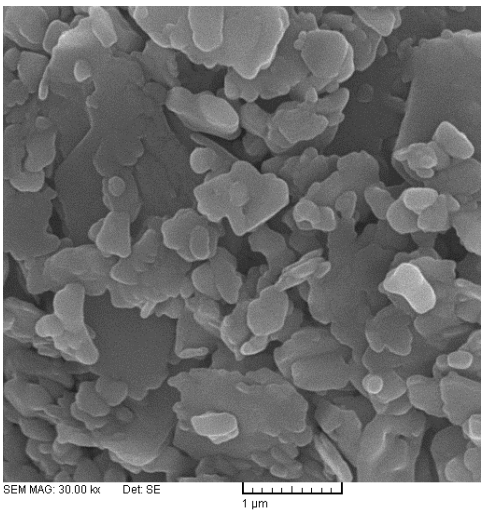
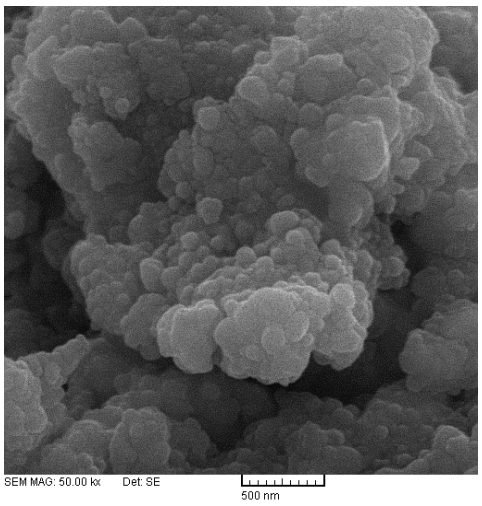


Fig.4. Comparison of crystallite size of the synthesized samples in argon environment at 800 ˚C



a)



b)

Fig.5. (a) SEM image of 1 hour milling sample (b) SEM image of 6 hours milling sample synthesized in an argon environment at 800 °C

3.3. Argon environment and then air environment

At this stage, the samples first were synthesized in Argon environment at 800º C in tabular furnace, and then as soon as samples were taken out from the argon to cool in air, again, they were synthesized in the air environment (the two-stage synthesis).

Fig. 6 shows the XRD sample analysis. As it can be seen in Fig. 6, in the synthesized sample pattern, after 1 hour of milling, there are alumina, cubic Zirconia and some unrequited monoclinic Zirconia phases. However, in the synthesized sample pattern after 6 hours of milling, there are alumina, zirconium nitride and some unrequited monoclinic Zirconia phases. The different results can be expressed that by 6 hours of milling, the powders have been become highly activated and the surface energy of the sample is highly increased in comparison of sample with 1 hour of milling. Aluminum existed in Al_2Zr compound formed in the argon environment (according to the thermodynamic data in 17 *Table 2. Thermodynamic data*) reacts with oxygen as soon as it is exposed to air (N_2 and O_2). It is necessary to note that Al has a greater tendency to combine with oxygen than Zr [17], especially in high temperature.

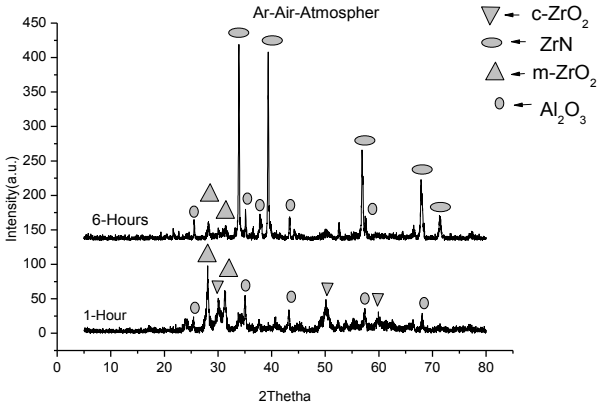


Fig.6.The XRD patterns of samples 1 and 6 hours milling with BPR of 15 to 1 and then synthesized in argon environment and ambient air environment at 800 ° C

Table 2. Thermodynamic data 17

The standard free energy of formation (J/mole) ($\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}$)	Temperature (k) Range	Composition
-1682900 323.2 T	933-2315	Al_2O_3
-1100800- 50.4 T	298-1478	ZrO_2
-363000 92 T	298-2125	ZrN
-327100 115.5T	933-2273	AlN

Also Zr can react with nitrogen. Indeed, we can consider that, since oxygen consist of only 21% of the air, by an oxidation process of aluminum, around of the samples were depleted of oxygen and only nitrogen remains to react with Zr. On the other hand, about sample milled at 1 hour, Zr did not react with nitrogen. Likely, the required energy for this reaction has not been supplied. Fig. 7 shows the particle morphology of the synthesized samples in argon and air environments. According to Fig. 7, the sample micrograph can be clearly observed molten state that it is caused by extreme oxidation of aluminum, which result in the temperature increase and ultimately causes its melting. Fig. 7 shows when the sample is milled for 6 hours, in fact the surface free energy is increased and therefore the system tends to reduce it. As a result, the particle shape becomes spherical but when the sample is affected by combustion synthesis in the second step, it can be considered that combustion synthesis like the heat treatment, causes the reduction of the strain energy and their values almost equalize to each other [18].

So in this case, the particle shape will be between spherical shape and disc shape (Fig. 7b). The crystallite size of the samples was calculated by using Reitveld method that the results are given in Fig. 8. With notice that in the sample with 6 hours of milling, the crystallite size is smaller and it can be concluded that the particles are more active. The more activation of particles accelerates and intensifies the reaction and thus can increase the combustion temperature. On the other hand, in the sample with 6 hours of milling, two exothermic reactions take place which one of them is related to the oxidation of aluminum and the other is in accordance with nitridation of zirconium. However, in the sample with 1 hour of milling, only one exothermic reaction (oxidation of aluminum) can be seen. This situation leads to further increase in the combustion temperature and ultimately causes further increase crystallite growth in the sample with 6 hours of milling.

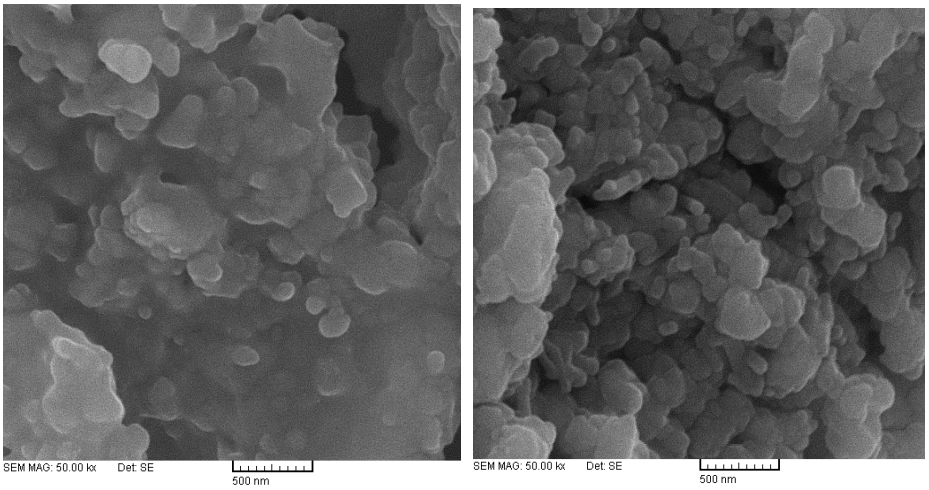


Fig.7. (a) SEM image of 1 hour milling sample (b) SEM image of 6 hours milling sample which synthesized two times in argon and air environment at 800 ºC

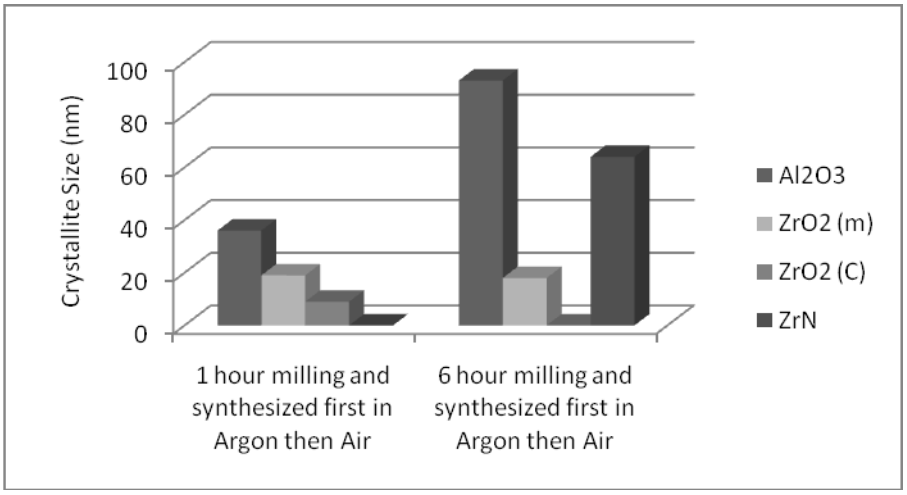


Fig.8. Comparison of the crystallite size of the synthesized samples in argon and in air environment at 800 ˚C

3.4. Ambient air environment

So in this case, two plates were prepared from 1 and 6 hours milled powders by 300 MPa press pressure. Then, the samples were synthesized under ambient air atmosphere at 800 ˚C. The XRD pattern of the samples is shown in Fig. 9.

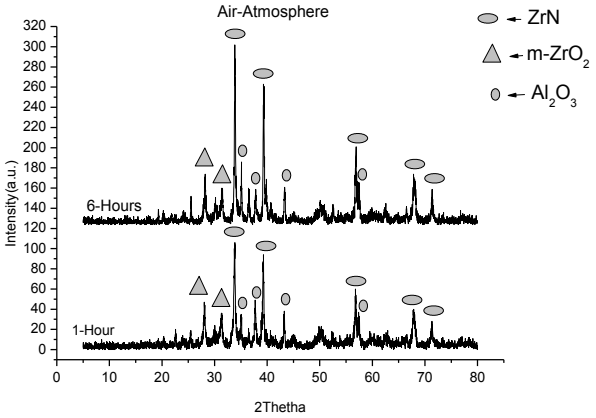


Fig.9.The XRD patterns of samples 1 and 6 hours milling with BPR of 15 to 1 and synthesized in an air environment at 800 º C

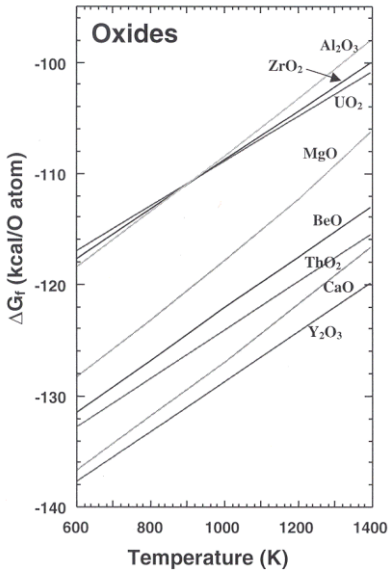


Fig.10.The standard free energy of formation of oxides as a function of temperature

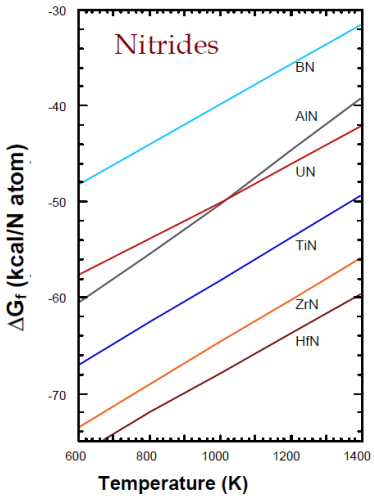


Fig.11.The standard free energy of formation of nitrides as a function of temperature

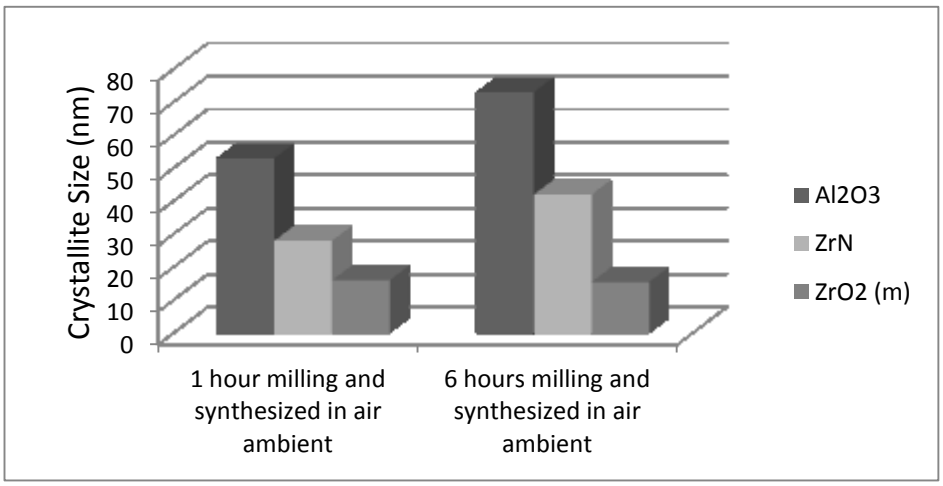
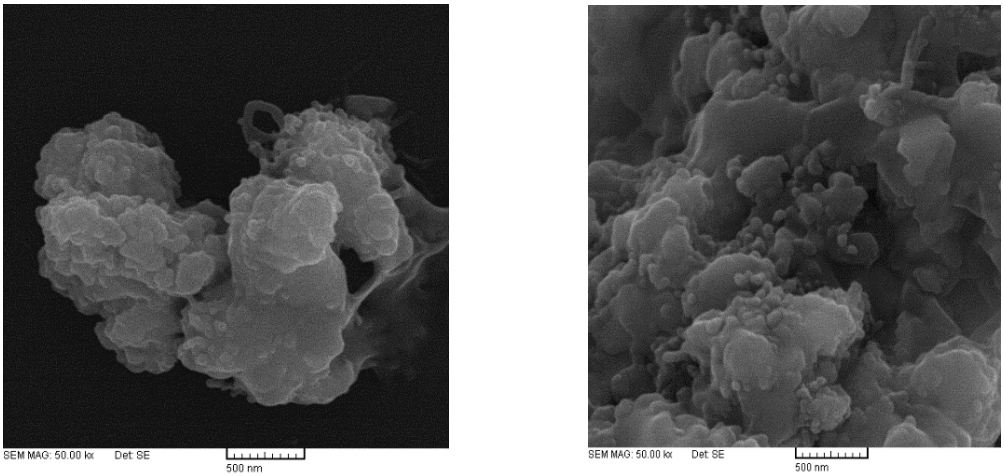


Fig.12. Comparison of the crystallite size of the synthesized samples in air environment at 800° C



a) b)

Fig.13. (a) SEM image of 1 hour milling sample (b) SEM image of the synthesized sample at 6 hours of milling in an air environment at 800° C

Table 3. The results Summarized

Sample Ref.	Milling Time	Milling Atmos.	Heating Regime	Heating Atmos.	Cooling Regime	Cooling Atmos.	XRD Ref Fig.	Fig Ref.	SEM Ref.	Crystallite Size(nm)
Al-ZrO_2	6 Hours	Ar	----	----	----	----	2	----	----	Al: 23 m-ZrO_2:16
Al_2Zr- ZrO_2	1 Hour	Ar	800°C	Ar	50°C	Ar	3	4	5: a)	Al_2Zr:42 m-ZrO_2:32
Al_2Zr- ZrO_2	6 Hours	Ar	800°C	Ar	50°C	Ar	3	4	5: b)	Al_2Zr:26 m-ZrO_2:30
Al_2O_3-ZrO_2	1Hour	Ar	800°C	Ar	50°C	Air	6	8	7: a)	Al_2O_3:22 m-ZrO_2:19 c-ZrO_2:8
Al_2O_3 - ZrN - ZrO_2	6Hours	Ar	800°C	Ar	50°C	Air	6	8	7:b)	Al_2O_3:92 m-ZrO_2:18 c-ZrN:64
Al_2O_3 - ZrN - ZrO_2	1Hour	Ar	800°C	Air	50°C	Air	9	12	13:a)	Al_2O_3:53 m-ZrO_2:16 c-ZrN:28
Al_2O_3 - ZrN - ZrO_2	6Hours	Ar	800°C	Air	50°C	Air	9	12	13:b)	Al_2O_3:73 m-ZrO_2 :16 c-ZrN:41

As it can be seen in both cases, phases of alumina, Zirconia and zirconium nitride are formed. In accordance Ellingham diagram, ZrO_2 curve is placed under Al_2O_3 curve at above 900 K (Error! Reference source not found.) and it means ZrO_2 tends to be reduced [19]. So, ZrO_2 reacts to N_2 in air and Zirconium Nitride (ZrN) is formed. The tendency of Zr to form ZrN, according to Error! Reference source not found. is more than that of Al to form AlN, so ZrN formed is stable [15]. The average crystallite size of the grains is shown in Error! Reference source not found.. Error! Reference source not found. shows an SEM micrograph of the synthesized samples in air, which by considering Fig. 12, shows the particles of sample with 1 hour of milling are finer. Perhaps this is due to the fact that the samples with 6 hours of milling have higher activation and surface energy and also more defects and therefore they have a higher tendency to dissolve and also the grain boundary penetration, therefor they have higher growth of crystallite. According to the images, morphology of particles composed of spherical and blade shape. By considering that of microstructure there are three phases ZrO_2, ZrN and Al_2O_3 see in 6 hours samples milled and synthesized by combustion in air, so on the basis of Nabarro relationship, the volume percentage changes resulting from the three-phase (ΔV) increased and the amount of strain free energy becomes high. On the one hand, by 6 hours milling, the amount of surface free energy is high, but still in comparison of the strain free energy is lesser and it is not negligible. Therefore, in this case the particle shapes are between spherical and disk shape. The volume percentage of disk particles are more, due to higher strain free energy (Fig.13b). In order to access results quickly, see Table 3.

4. Conclusions

According to the results and discussions, the following conclusions are:

1) Nanopowders such as Al_2O_3-ZrO_2 and Al_2O_3-ZrN-ZrO_2 were successfully synthesized by mechanically activated self-propagating high-temperature synthesis (MASHS) under first argon then cooled at air atmospheres and air then cooled at air atmosphere respectively.

2) Nanoparticles have different shapes, in samples with 1 hour milling, shape of particles is disc like and by increasing milling time to 6 hours, the shape of particles becomes spherical. The atmosphere has an important effect on particle composition. Samples which exposured to air had different composition rather than samples were synthesized at argon atmosphere.

3) With regards to increase of milling time, particles tend to be spherical for reduction of surface free energy. Also in a second step, the number of phases in each sample has an important effect on the morphology type and its amount.

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