

Mechanical activation of Nb75Al Mixtures using Shaker and Planetary Ball Mills

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Abstract. Different types of high-energy ball mills can be applied to promote mechanical activation of powders mixtures for further combustion synthesis of intermetallic compounds. In this work, Nb75Al powder mixtures (for NbAl₃ synthesis) were mechanically activated in shaker and planetary mills by 1 and 3 hours. Remarkable differences in shape and microstructure of the activated powders resulted in distinct reaction behaviors (e.g. ignition and combustion temperatures). Temperature profile of the samples during the reaction showed that mechanical activation was higher in the shaker mill. Higher densities were obtained with samples activated in shaker mill by 1h.

Introduction

Combustion synthesis is a very powerful method to synthesize and consolidate compounds through a single heating step of a compacted blend of elemental powders. The compound enthalpy formation and the process-material parameters like particle size distribution, green density, heating atmosphere and heating rate are fundamental to the success of the consolidation process [1].

The effect of high-energy ball milling of elemental powders on combustion synthesis mechanisms has received a considerable attention on the last decade [2-7]. Previous work on mechanical activation of powder mixtures in shaker mill showed clearly a decrease on the ignition temperature by simultaneous combustion (thermal explosion) mode that was associated to a better dispersion and intimate contact between the reactant powder particles through the formation of agglomerates [6]. Gauthier *et al* pointed out the same effect on mixtures processed in a planetary ball mill and reacted through the SHS mode and emphasized that the level of energy stored in the reactants due to plastic deformation has an important contribution to the reaction [5]. The conditions of milling are greatly affected by parameters like ball-powder mass ratio and ball size. Thus, an effort has been made to show clearly the set up of milling process. However, when different mills are used it becomes very difficult to establish the same conditions.

The aim of this work is to compare the mechanical activation level of mixtures, processed in shaker and planetary mills, through observation of the agglomerate shape and microstructure, and verify its influence on simultaneous combustion synthesis of NbAl₃, by determination of ignition and combustion temperatures as well as final density.

Experimental Procedures

The starting mixtures were made of 75 at% of aluminum powder (-325 mesh, 99,7 % pure) and 25 at% of niobium powder (-325 mesh, 99 % pure). Stearic acid was used as process control agent (PCA) added on proportion of 1 wt% of total mass of metallic powders. The shaker mill was from SPEX (model 8000), which has no rotation speed control. The planetary mill was from Fritsch (Pulverisette 5) with the speed of supporting disc fixed at 400 rpm. In both shaker and planetary milling, the ball-powder mass ratio was kept at 10:1. Powder charges were 10 g for shaker mill and 38 g in planetary mill. The whole milling operation was carried out in argon atmosphere. Table 1 resumes the materials and quantities used in both mills.

The combustion synthesis was conducted in pellets of 4g compacted in a cylindrical floating die of 14 mm in diameter at 300 MPa. The heating cycles had two parts and were carried out in vacuum. In the first part the heating rate was 5°C per minute until 400°C, holding for 4 hours at this temperature for degassing. In the second part the heating rate was 30°C/min until the end of the reaction. Temperature was monitored by a S-type thermocouple located inside a small hole drilled at the pellets central axis. A thin alumina-based coating was applied to the thermocouple tip to avoid reaction with the combustion materials. Temperature-time profiles were provided by a data acquisition system operating at 10 Hz (scanning speed). Milled powders and pellets were characterized through scanning electron microscopy and EDS analysis. Green and reacted densities were determined by geometrical and weighting measures and by Archimedes method, respectively.

Table 1 – Balls and vial materials used for both mills in this work.

Mill	Material		Balls	
	Balls	vial	diameter	quantity
shaker	Inox steel	Inox steel	7,14 mm	68
planetary	Inox steel	inox steel	20 mm	15

Results

Microstructure of Milled powders

The shape and size of Nb75Al powder agglomerates activated in both mills for 1h and 3h can be compared on the micrographs (backscattered electrons) of Fig.1 (A). Micrographs in Fig. 1 (B) show the microstructure of these agglomerates. In this figures aluminum particles are gray and niobium particles are white. After 1 h, a strong formation of large flakes is verified from planetary-milling, particularly on more ductile aluminum particles. Flakes are predominantly constituted from aluminum or niobium, with little association between them (Fig. 1-B). Shake milling produced a completely different powder after 1 h. Agglomerates are rounded and composed by aluminum and some niobium, and a layered microstructure started to form. A lot of isolated particles of niobium are still observed.

After 3 h of shaker or planetary milling, agglomerates become very different in shape and microstructure compared with 1 h of milling. Rounded agglomerates were produced on planetary mill, but are still larger than those obtained in shaker mill. Microstructure produced in both mills is very close to each other. Agglomerates exhibit compositional homogeneity and a very fine lamellar structure. Isolated particles of niobium are rarely seen.

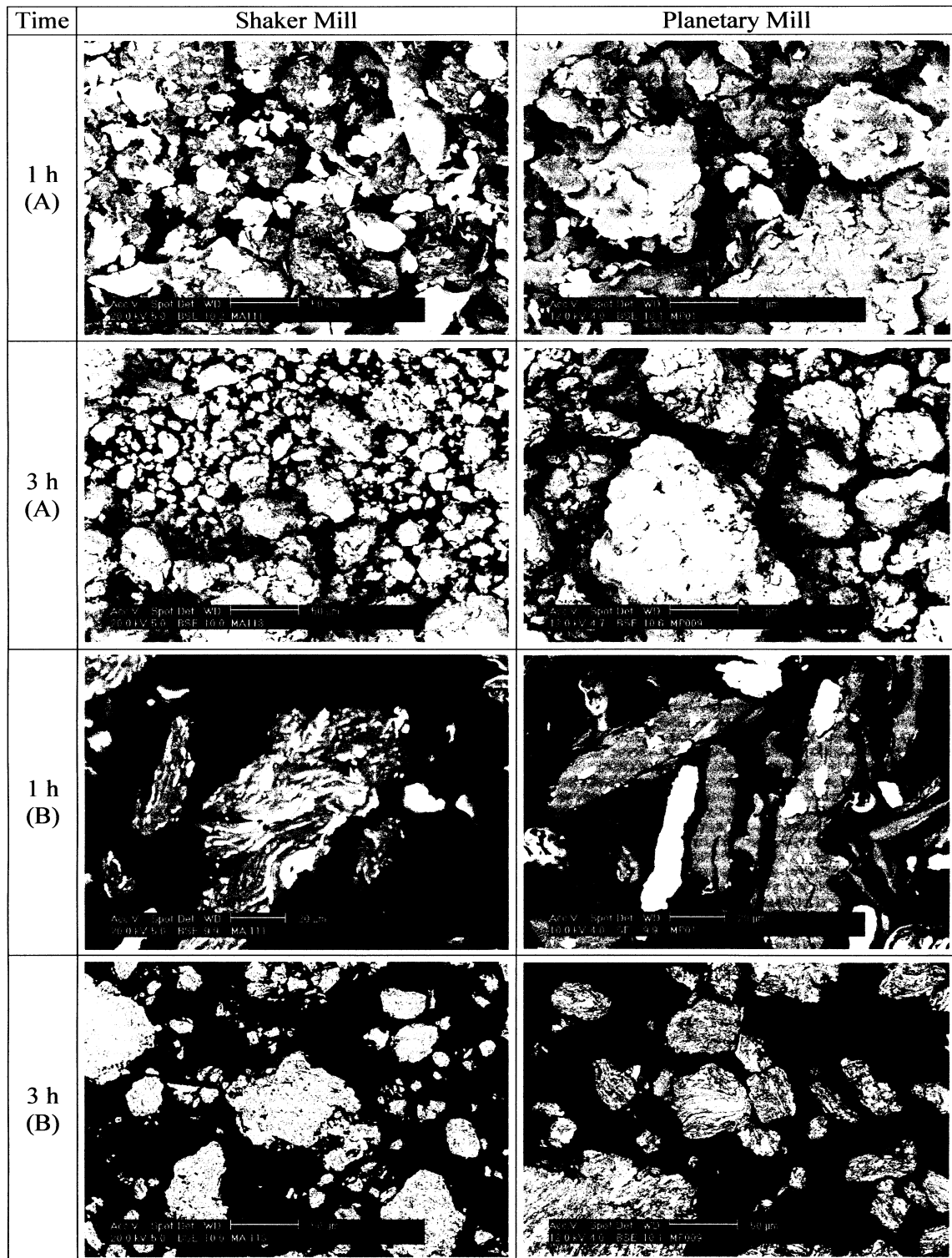


Figure 1 – Backscattered micrographs of Nb75Al powder mixtures after activation in shaker and planetary ball mills for 1 h and 3 h (A= surface aspects; B=agglomerate microstructures).

Combustion Synthesis

Typical temperature-time curves obtained after the degassing treatment (400°C for 4h) and registering the NbAl₃ synthesis can be seen in Figure 2. Simple mixture data were again added for comparison. Fig. 2a and 2b illustrates what goes on samples milled for 1 h and 3 h, respectively.

Thermograms for simple mixture condition and for 1 h milling activation show some similarities and some differences. Melting of aluminum, indicated by a plateau observed on each curve, always occurred before the reaction corresponding to the NbAl₃ formation. The ignition time concept, reported in previous works [5,8] as the length of time between the end of aluminum melting and the ignition temperature, makes sense only for the simple-mixture curve and for the planetary curve shown here. In these curves, the plateau is lightly inclined and just after it there is a change of the heating rate registered by the thermocouple inserted in the pellet central hole. This behavior can be attributed to a thermal imbalance provided by the continuous heating of the furnace: after the end of aluminum melting, and endothermic event, the difference between the internal and external pellet temperature is higher compared to the beginning of melting (thermal delay), so increasing for some seconds (25 s) the pellet heating rate, which became lower again after the initial thermal balance is attained. Looking to the so-called ignition time, there is actually a noticeable decrease of it when comparing planetary and simple mixture curves. In fact this came from the anticipation of the ignition temperature, which is an effect of the mechanical activation. Analyzing now the curve corresponding to the shaker milling (1 h – Fig. 2a), there is no time of ignition, as defined before, because ignition occurs before the ending or, at least, just at the ending of the melting plateau.

It can be seen that the plateaus corresponding to the melting of aluminum occurred before the combustion reaction (Fig. 2a) are different. The plateaus from shaker mill and simple mixture curves are more clearly seen than that from the planetary mill curve. Also it can be noticed a heating rate change in the shaker mill curve from about 500°C. These different behaviors suggest differences in thermal conductivity of the samples aroused from different agglomerates microstructures, dispersion degree (both affecting aluminum particle contact, which is more conductible than niobium) and pore size distributions. However, these aspects were not yet investigated in this work.

Table 2 summarizes the results from densities of pellets (before and after the reaction), ignition and combustion temperatures.

Higher final densities were attained in pellets made with powder mixtures milled for 1 h in the Shaker mill. These densities were closed to the simple mixture condition, whose results were shown in Table 2 for comparison. The combustion temperatures were not so different considering the inaccuracy of this type of measure. However, the difference between combustion and ignition temperature of the milled sample is higher, indicating a strong activation process. Poor densification was attained in samples milled for 1 h in the planetary mill, which is attributed to the flake heterogeneous agglomerates preventing good aluminum wetting. The ignition temperatures of the samples milled in both mills for 3 h were very close, while combustion temperatures were clearly different, higher for the samples activated in planetary ball mill. Poor densification was observed in both cases. Combustion temperatures were low and the reaction started below the aluminum melting, impairing sintering.

Low magnification images from the microstructure of the reacted pellets (Fig. 3) show differences in pore structure from each case. Rounded and isolated powders are obtained after the reaction of shaker-milled sample for 1 h. Planetary-milled sample presents more irregular in pores shape and apparently more connected. By increasing milling time (3 h) a sponge-like structure is produced and the original agglomerates can still be seen in the microstructure.

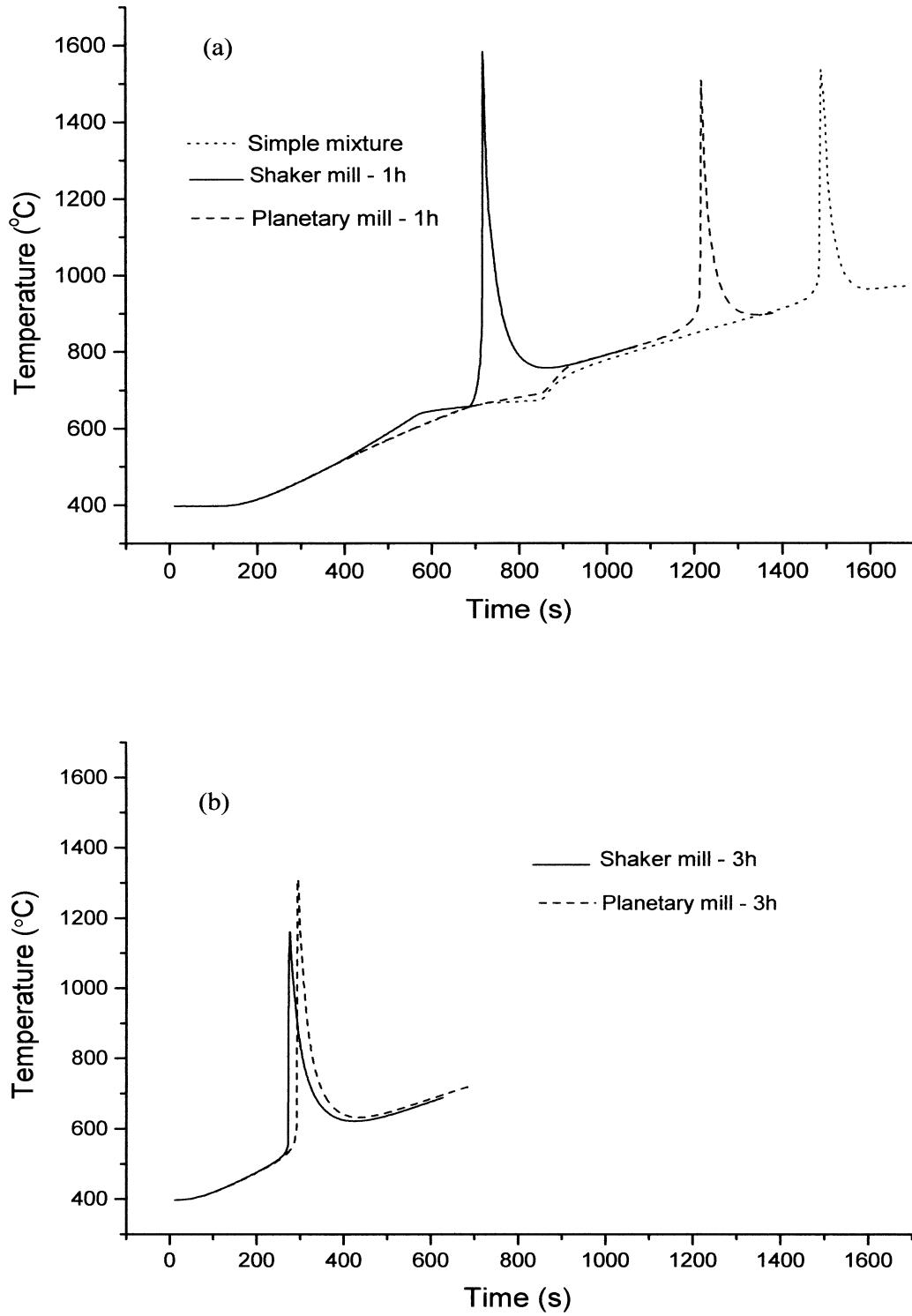


Figure 2 – Temperature profiles of the thermal explosion of pellets from Nb75Al mixtures differently processed: (a) simple mixture and 1 h milling; (b) 3 h milling.

Table 2 – Green and after reaction densities, ignition and combustion temperatures of pellets made from Nb75Al mixtures previously activated in shaker and planetary mills for 1 and 3 h. Simple mixture data has been added for comparison.

Mill Apparatus	Milling Time (h)	Green density (g/cm ³ and % ρ_t)	Reacted density (g/cm ³ and % ρ_t)	Ignition temperature (°C)	Combustion temperature (°C)
No milling	0	3,30 (77,3)	4,21 (92,7)	940	1540
Shaker	1	3,28 (76,8)	4,17 (91,8)	657	1585
Shaker	3	2,91 (68,4)	3,07 (67,7)	520	1160
Planetary	1	3,65 (85,1)	3,95 (83,5)	870	1510
Planetary	3	3,00 (70,2)	2,95 (64,9)	535	1310

* ρ_t – theoretical density (Nb + 3Al mixture = 4,27 g/cm³ ; NbAl₃ = 4,54 g/cm³)

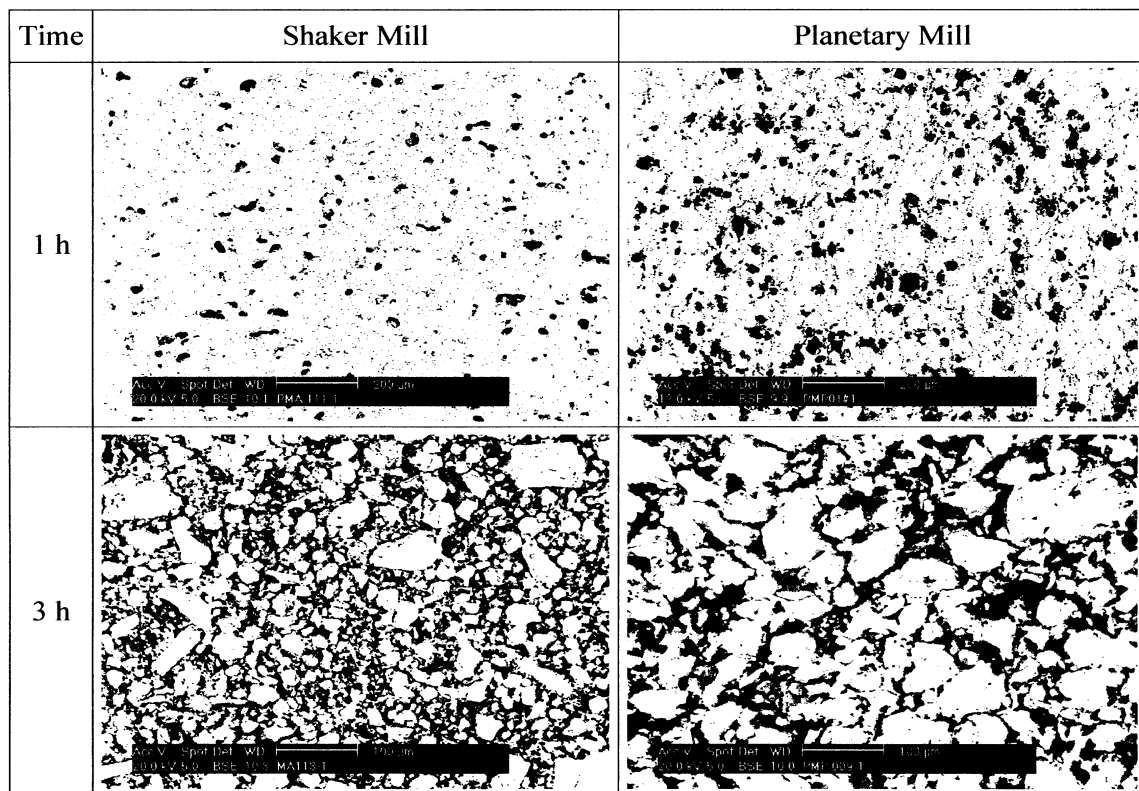


Figure 3 – Microstructure (low magnification) of reacted pellets (SEM - backscattered electrons) from powder mixtures activated in shaker and planetary mills.

In the higher magnification images from Fig. 4, NbAl_3 is the gray major phase. Very small intergranular pores can be seen in the microstructure of the shaker-milled sample for 1 h, along with fine white particles of niobium carbide. The microstructure of the planetary-milled sample (1 h) exhibits many white regions (Fig. 4) corresponding to the $\text{Nb}_2\text{Al-NbAl}_3$ eutectic component. This is also formed on simple-mixture samples as reported before [9]. It was suggested that the eutectic like structure could form from niobium rich liquid pools, which would be trapped at interstices between impinging NbAl_3 particles during its formation and growing. This argument is supported now as the combustion temperature is lower than the eutectic reaction temperature (1590°C) [10], meaning that the eutectic component was not formed by conventional reaction. The liquid pools enriched in niobium are probably caused by aluminum vaporization after the melting which increases with longer ignition times. Thus the absence of the eutectic component in the shaker-milled sample (1 h) resulted from lower exposure time of liquid aluminum to vacuum.

Both samples milled for 3 h show a quite similar refined microstructure inside NbAl_3 islands. As the whole reaction took place before aluminum melting (solid state reaction) no eutectic was formed.

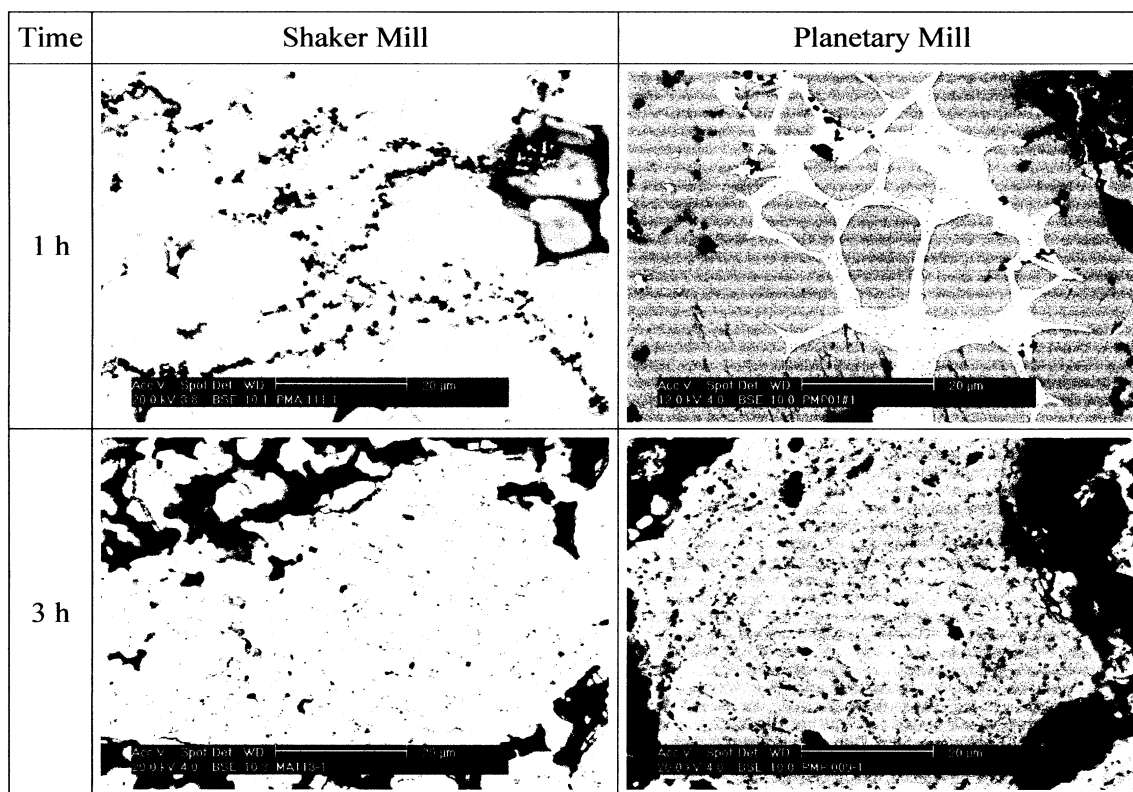


Figure 4 - Microstructure (higher magnification) of reacted pellets (SEM - backscattered electrons) from powder mixtures activated in shaker and planetary mills.

Conclusions

Formation of agglomerates from reactant powders strongly influences the activation by ball milling. The differences between milling apparatus arises from different agglomerate formation. A right combination of size and internal structure of agglomerates is necessary for good densification, which was better attained with shaker milling for 1 h. It is believed that this right combination could probably be attained also with planetary milling for a length of time higher than 1 h but lower than 3 h. Compositional homogeneity and lamellar structure of agglomerates enhance activation, which is denoted mainly by the decrease of the ignition temperature.

Some aluminum melting enhances densification as expected.

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