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The Effect of Mechanical Activation and Mixing Procedures of Elemental Powders on Combustion Synthesis of $NbAl_3$

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Abstract: The effect of mechanical activation procedures on the combustion synthesis of $NbAl_3$ was investigated. The activation was carried out by a two-step high energy ball milling procedure. In the first milling, niobium was milled separately (pre-activation). The mixtures of pre-activated niobium and small amounts of aluminum were then activated in the second milling. After $NbAl_3$ stoichiometry adjustment of mixtures with non-activated aluminum, reaction synthesis was conducted on compacted pellets, by simultaneous combustion mode. The thermal behavior of the compacted pellets upon heating was recorded and the main thermal combustion reaction characteristics were evaluated. The two-step procedure produced aggregates with a globular dispersion of niobium due to increased particle hardness and decreasing mean particle size during pre-activation milling. Analysis of pellet thermal behavior showed that the two-step milling procedure could enhance reaction performance by increasing maximum reaction heating rate and temperature gain during reaction.

Introduction

High energy ball milling has been applied as a process step for powder materials in order to obtain differentiated properties [1,2]. The sequence of deformation, fracture and cold welding during milling can produce high density crystalline defects and increase the surface area. This results in a mechanical activation. In the case of milling mixtures of ductile materials, the contact surface area between components can increase significantly, leading to the formation of a new material [3].

Mechanical activation of mixtures with high content of aluminum is a challenging task because of its high reactivity, ductility and capability to cold weld. The control of particle size distribution is often obtained by adding an amount of organic compounds called process control agents (PCA). However, the use of PCA's can increase the contamination by reacting with the aluminum [4-8].

The effects of mechanical activation over combustion synthesis technique have been reported in the literature as a key to carry out successful results [9-10]. In the case of mixtures of niobium and aluminum, the mechanical activation reduces de ignition temperature and enhances reaction rate between the components. However, the use of PCA's, to become feasible the mechanical activation, results in a formation of oxides and carbides dispersed on $NbAl_3$ matrix after combustion synthesis.

This study deals with different procedures of mechanical activation of niobium and aluminum mixtures, to synthesize the intermetallic $NbAl_3$. The combustion synthesis thermal behaviors were recorded and the main characteristics were evaluated.

Experimental Procedure

The initial materials, aluminum (-325 mesh, 99.7%) and niobium (-325 mesh, 99,8%), were purchased from the Atlantic Equipment Engineers (AEE – Micron Metals, INC). Stearic acid ($CH_3(CH_2)_{16}COOH$) was used as a PCA in amounts of 2 wt%, 1 wt% and 0.5 wt%.

Three different routes were adopted to carry out the mechanical activation. The first one was the conventional one-step mechanical activation. In this procedure, mixtures of aluminum and niobium were prepared according to the stoichiometry of $NbAl_3$, and two different amounts of PCA, 2wt% and 1wt% were added. The mixtures were milled for 120

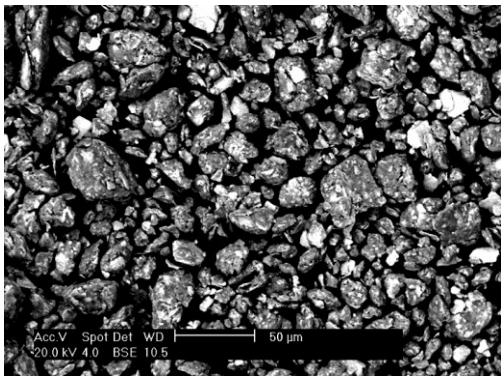
minutes in a shaker mill (©SPEX□8000), with ball-to-powder ratio of 5:1. The second and third procedures are based on two-step mechanical activation. In the first activation, niobium was milled separately (pre-activation). The mixtures of pre-activated niobium and aluminum were then activated in the second milling. The niobium pre-activation was carried out in a planetary mill (©Pulverisette 5) for 50 h, with ball-to-powder ratio of 5:1 and 0.5wt% of PCA. In the second procedure, the mixtures of pre-activated niobium and aluminum were milled for 120 minutes in a shaker mill, with ball-to-powder ratio of 5:1 and 2wt% PCA. In the third procedure, the pre-activated niobium was mixed with aluminum in the atomic proportion of 40% aluminum. These mixtures were then milled in the planetary mill for 180 minutes, with ball-to-powder ratio of 80:1 and 0.5 wt% of PCA. After the milling, the stoichiometry according to $NbAl_3$ were adjusted by adding aluminum. All millings were done under argon atmosphere.

Milled samples of about 4 g were uniaxially compacted in a cylindrical floating die with enough applied pressure to produce a green density around 75% of theoretical mixture density. Combustion synthesis in thermal explosion mode (simultaneous combustion) was conducted on a tubular resistive furnace under vacuum. Ignition and combustion (adiabatic) temperatures were monitored by an S-type thermocouple located inside the pellets. The heating cycle was composed of an initial heating at 5°C/min to 200°C, followed by heating at 2ºC/min until 450ºC and a final heating at 30°C/min up to the end of the reaction.

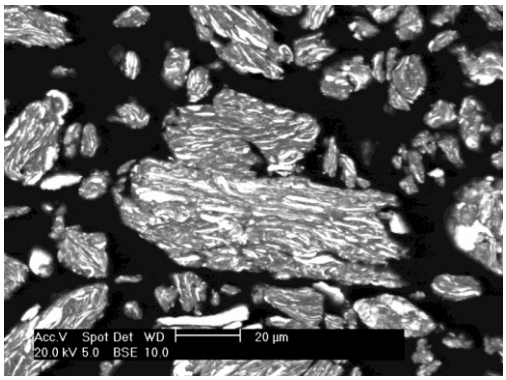
Milled powders were evaluated by scanning electron microscope in order visualize the dispersion of niobium and the particle microstructure.

Results and Discussion

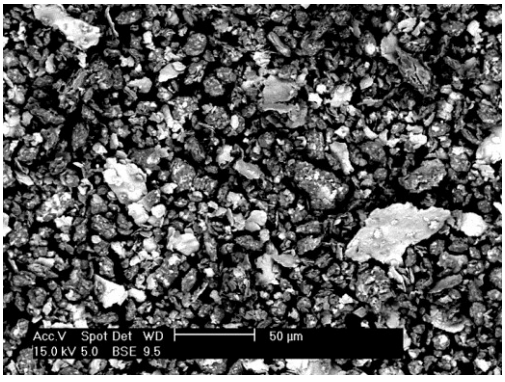
***Powder shape and microstructure*.** Scanning electron microscope (SEM) micrographs of as-milled mixtures for the first procedure are shown in Figure 1. The milling of the mixture with less PCA produced aggregates with homogeneous lamellar dispersion of niobium. The mixture with higher PCA content showed more isolated flake shaped niobium particles.



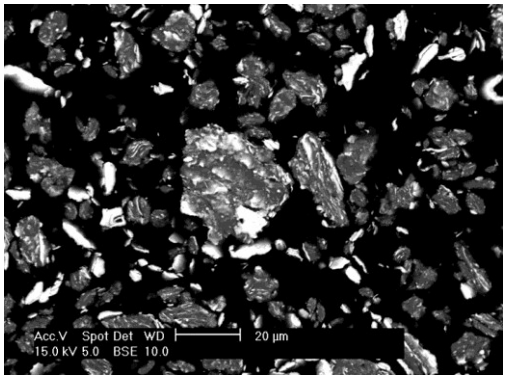
25Nb75Al + 1wt% PCA + 120 min



25Nb75Al + 1wt% PCA + 120 min



25Nb75Al + 2wt% PCA + 120 min



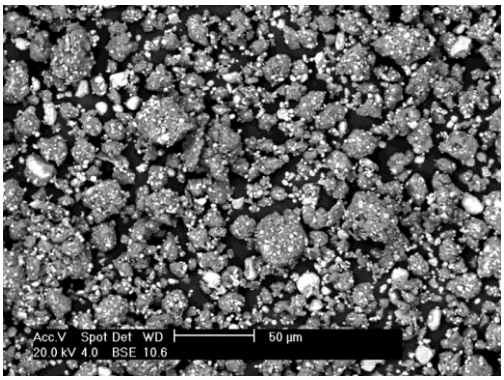
25Nb75Al + 2wt% PCA + 120 min

Figure 1 – Shape and microstructure of milled mixtures without pre-activation of niobium. Addition of 1 wt% and 2 wt% of PCA.

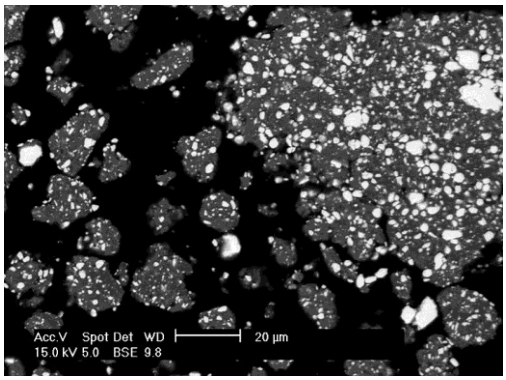
SEM micrographs of as-milled mixtures for the second and third procedure are shown in Figure 2. The mechanical activation using pre-activated niobium produced a globular dispersion of niobium. In fact, the shape of the niobium particles, after mechanical activation, was essentially the same shape obtained after pre-activation. This result suggests that the pre-activation procedure reduced the ductility of the niobium particles. This behavior might be related to an increase of the crystalline defect density and possibly to the formation of solid solution of carbon, oxygen and hydrogen from PCA addition. In this context, the Nb-Al aggregates might be formed mainly by aluminum plastic deformation.

***Temperature profiles*.** The temperature behavior of the pellets recorded during heating is shown in Figure 3. The pellet temperature was plotted against furnace temperature to show the temperature difference with only one profile for each pellet. A profile of pellet without mechanical activation was plotted as a reference. The visual analysis shows that the maximum temperature reached, also called combustion temperature, was decreased with mechanical activation as well as the extension of aluminum melting plateau. The pellets prepared in only one step showed a degree of self heating before aluminum melting. This behavior is a clear evidence of exothermic reaction started without liquid phase.

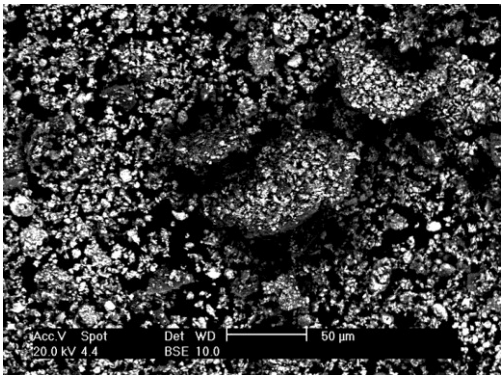
More quantitative data could be extracted from these profiles and were presented in Table 1. The ignition temperature was considered as the temperature of aluminum melting plateau. Exceptions were made to pellet without mechanical activation and the pellet prepared with 1 wt% of PCA and in one step. For these, the ignition occurred much after and before aluminum melting, respectively.



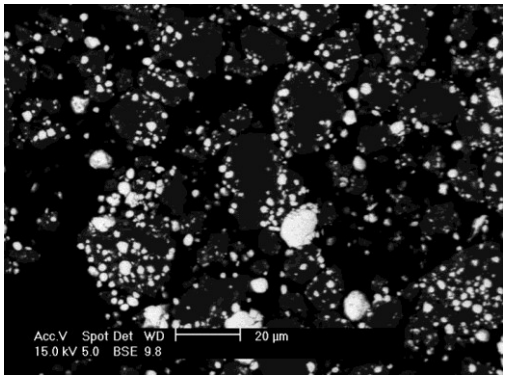
25Nb75Al + 2wt% PCA + 120 min
With pre-activated Nb



25Nb75Al + 2wt% PCA + 120 min
With pre-activated Nb



60Nb40Al + 0.5wt% PCA + 180 min
With pre-activated Nb



60Nb40Al + 0.5wt% PCA + 120 min
With pre-activated Nb

Figure 2 – Shape and microstructure of milled mixtures with pre-activation of niobium and different amounts of aluminum and PCA.

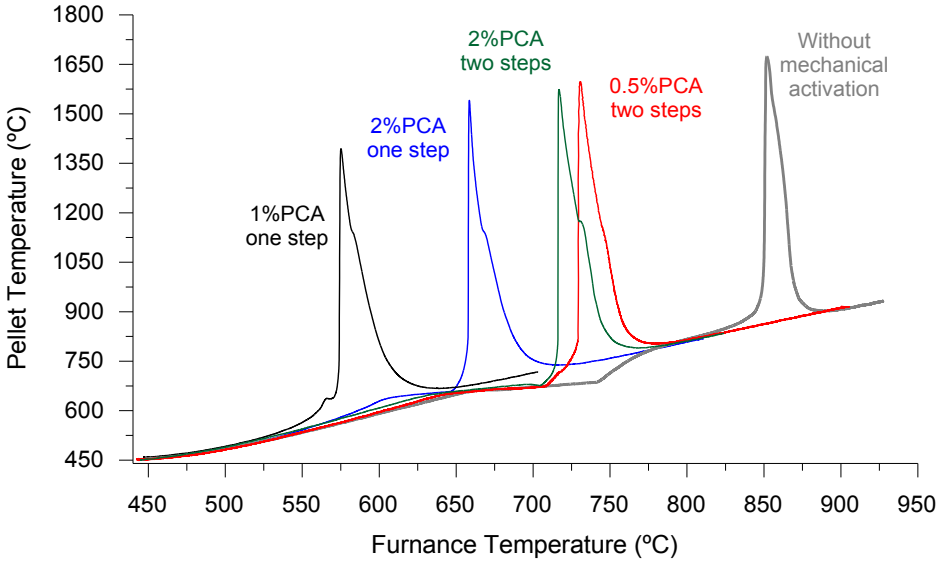


Figure 3 – Temperature profiles recorded during combustion synthesis of Nb-Al mixtures with and without mechanical activation.

	Without Mechanical activation	One step 1 wt% PCA	One step 2 wt% PCA	Two step 2 wt% PCA	Two step 0.5 wt% PCA
Ignition temperature (ºC)	878 ± 4	541 ± 3	659 ± 1	669 ± 6	670 ± 8
Thermal explosion temperature (ºC)	1071 ± 24	740 ± 23	813 ± 31	805 ± 10	815 ± 13
Combustion temperature (ºC)	1648 ± 22	1393 ± 1	1507 ± 32	1570 ± 2	1590 ± 8
Difference between combustion and ignition temperatures(ºC)	770 ± 25	852 ± 2	847 ± 32	901 ± 6	920 ± 8
Maximum heating rate (ºC/s)	330 ± 38	626 ± 38	1283 ± 262	1667 ± 211	980 ± 50
Reaction time (s)	35 ± 5	75 ± 6	24 ± 2	35 ± 2	54 ± 6
Average reaction heating rate (ºC/s)	23 ± 3	11 ± 1	36 ± 2	26 ± 1	17 ± 3
Aluminum melting plateau time (s)	236 ± 11	11 ± 1	101 ± 1	196 ± 9	170 ± 7

Table 1 – Main thermal characteristics of temperature profiles recorded during combustion synthesis of Nb-Al mixtures with and without mechanical activation.

The combustion synthesis of $NbAl_3$ can be divided in two stages. The first one begins with the ignition of the reaction and is characterized by a lower heating rate than in the second stage. When the pellet reaches the thermal explosion temperature, the heating rate increases abruptly, reaching a maximum and decreasing abruptly at the combustion temperature. The reaction time was defined here as the difference between ignition temperature and combustion temperature in terms of time. Considering that the second stage of combustion synthesis can take less than a second to a few seconds, the major part of reaction time is related to the first stage of reaction and its heating rate is closer to average heating rate.

The maximum heating rate in the second stage of reaction is possibly related to the niobium dispersion pattern. However, the analysis of the data presented in Table 1 must take in account that the pellets with lamellar distribution pattern of niobium had some degree of

reaction before aluminum melting. This amount of reacted product can decrease the heating rate by consuming a fraction of the released heat to increase its temperature and by decreasing the volume of reactant elements. Besides, in the case of pellet prepared with 1 wt% of PCA and only one step of mechanical activation a fraction aluminum melted during reaction, consuming more heat.

The evaluation of the level of mechanical activation can be done by checking the ignition and combustion temperature and the difference between them. In the case of pellets with one step of mechanical activation, the difference was slightly lower than pellets with two steps, but higher than pellet without mechanical activation. Again, with these parameters, the solid state reaction before melting of aluminum may hinder the temperature increase. Considering only the difference between ignition and melting temperatures the mechanical activation levels are quite similar. However, considering all parameter together the pellet with 0.5 wt% of PCA and two steps of mechanical activation can be highlighted due to its low PCA content.

Conclusions

The thermal behavior during combustion synthesis of the intermetallic $NbAl_3$ changed the elemental powders processed by different routes. The mechanical activation of niobium prior milling the mixture Al-Nb resulted in a globular dispersion of niobium. This type of dispersion increased the heating rate and combustion temperature, at the same time decreased the ignition temperature to the aluminum melting temperature. The two-step procedure, with less aluminum in the second step and adjustment of stoichiometry milling, made the mechanical activation possible using less PCA.

References

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