

## Mechanical Activation of Nb75Al Powder Mixtures with different Process Control Agents

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**Abstract:** The behavior of different process control agents (PCAs) during mechanical activation of Nb75Al powder mixtures was investigated. Mechanical activation by high-energy ball milling was carried out on a shaker mill (SPEX<sup>®</sup>8000) for 1 hour. Each PCA (Stearic acid, ethanol and methanol) was added to the powder charge in two proportions (1 and 2 wt%). Shape and microstructure of activated powders (aggregates) were analyzed by scanning electron microscopy. Milled powder mixtures were uniaxially pressed in cylindrical compacts that were further vacuum reacted at a constant heating rate (30°C/min) in order to produce NbAl<sub>3</sub> intermetallic compound. The temperature of the samples was monitored by an S-type thermocouple. The results show that the shape and the microstructure of the milled powders were strongly affected by the type and quantity of PCAs, therefore changing the reaction behavior and the densification of the produced pellets. Although ethanol was more effective to control aggregate size, best densification results were attained with 2 wt% of stearic acid.

### Introduction

Intermetallic compounds, such as NbAl<sub>3</sub>, have been considered for structural applications owing to their interesting properties at elevated temperatures associated with a low density [1,2]. Among the techniques to synthesize these materials, combustion synthesis, conducted in thermal explosion or SHS mode (Self-sustaining High-temperature Synthesis), has attracted considerable interest as an alternative and promising method, due to the possibility to attain products of high purity with relatively short processing times and inexpensive equipments. In this technique, strongly exothermal reactions are initiated when constituent elements of the desired product are put together and brought to favorable conditions of pressure and temperature [3,4].

In order to obtain materials with improved properties, some process variables of this technique must be controlled. It is well known that size, shape and component dispersion of solid constituent elements represent an important role in the kinetics of the reaction, as well as in the densification and microstructure homogeneity of the final products [5,6]. It was verified by previous works that the mechanical activation of powder mixtures causes a significant influence in the reaction mechanism of NbAl<sub>3</sub> intermetallic compounds, particularly by lowering the ignition temperature, as well as in the final density of compacted pellets [7,8]. This can be done very efficiently by high-energy ball milling, a technique developed by John S. Benjamin and characterized by successive events of cold welding and fracturing of powder particles under high-energy collisions [9].

To successful attain products with fine dispersion and good homogeneity; it is essential to establish a balance between cold welding and fracturing. However, for ductile systems, as in the milling of aluminum particles, this balance does not occur naturally, resulting in non-uniform microstructures and properties. One of the effective methods to avoid excessive cold welding reported in the literature is the addition of surface-active substances, known as process control agents (PCAs) [10]. These surfactants are mostly organic compounds and are usually added to the

powder charge in proportions that vary from 1 to 5 wt% [11]. PCAs can help to prevent excessive cold welding due to organic molecules adsorbed on the metal surface [10]. However, this process of absorption is not yet well understood. Many researchers have investigated the effects of PCAs in high-energy ball milling, particularly in mechanical alloying process and reactive milling, emphasizing their main effects on powder particle size and contamination. It has been reported that the addition of these agents can introduce contaminants, mainly C, O and H, that can alter the formation rate of amorphous and metastable phases as well as the mechanical properties of the final products [12-18]. Moreover, a study conducted on nanostructured aluminum alloys, indicated that prevention of excessive cold welding of Al particles could impair reductions in the grain size and microstructural refinement, slowing down the mechanical alloying process [19]. Recently, previous work on the effects of stearic acid as a process control agent in high-energy ball milling of Nb-Al and Ni-Al powder mixtures indicated a significant decrease in ignition temperature for Ni-Al samples reacted by combustion synthesis when stearic acid content was changed from 1.0 to 0.33 wt% [20].

In the present study, the influence of different PCAs (stearic acid, ethanol and methanol), usually encountered in the literature and chosen according to their distinct physical properties, was investigated through combustion synthesis of mechanically activated powder mixtures of Nb75Al. This work aims for a preliminary and better understanding of the effects of these surfactants in the milled powders and in the reaction behavior, as well as in the final density of NbAl<sub>3</sub> reacted pellets.

## Experimental Procedure

Nb75Al (at%) powder mixtures were individually prepared from weighting the required proportions (according to the stoichiometry of NbAl<sub>3</sub>) of elemental powders of gas-atomized aluminum (-325 mesh, 99.7% in purity) and hydrated-dehydrated niobium (-325 mesh, 99% in purity). Different types of PCAs, stearic acid (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COOH), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and methanol (CH<sub>3</sub>OH), were added to each sample of 10 g in different proportions (1 and 2 wt%), in order to prevent excessive cold welding of powder particles. Powder mixtures in the desired composition were mechanically activated in a shaker ball mill (SPEX<sup>®</sup>8000) at room temperature for 1 hour. The ball-to-powder weight ratio was fixed in 10:1. Milling was conducted on a stainless steel vial and balls with 7.14 mm in diameter, under argon atmosphere.

Milled samples of about 4 g were uniaxially compacted in a cylindrical floating die with an applied pressure of 300 MPa. Green densities of compacted pellets (14 mm in diameter) were evaluated from weight and geometrical measurements, assuming cylindrical geometry. 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 consisted of an initial heating at 5°C/min to 400°C, followed by an isothermal treatment for 4 hours and a final heating at 30°C/min up to the end of the reaction. Density of reacted pellets was determined by Archimedes method, according to ASTM C 373-88 with 1 hour of boiling water.

Shape and microstructural characterization of the milled powders and polished cross-section areas of reacted pellets were performed in a scanning electron microscopy (SEM), using the signals emitted by secondary and backscattered electrons.

## Results and Discussion

**Powders Shape and Microstructure.** SEM micrographs of as-milled powders with different types and contents of PCAs are shown in Fig. 1. With 1 wt% of PCA, ethanol produced the finest aggregates, whereas methanol was insufficient to prevent excessive cold welding, forming very large aggregates of niobium and aluminum. Aggregates size decreased when the amount of each

PCA increased from 1 to 2 wt%. This decrease was more effective with ethanol and methanol additions.

It is well known that one of the consequences of the use of PCAs is a delay on the welding stage of aggregates formation [21]. This can be observed through the presence of isolated elemental particles as reported before by Rocha et al. [20]. Here the powders milled with 1 wt% of PCA exhibited a less quantity of white isolated niobium particles (i.e. not associated with aluminum which get easier welded) when compared with 2 wt% of PCA. These differences were greater for stearic acid and much less pronounced in the case of methanol, indicating that the former is more effective to impair cold welding.

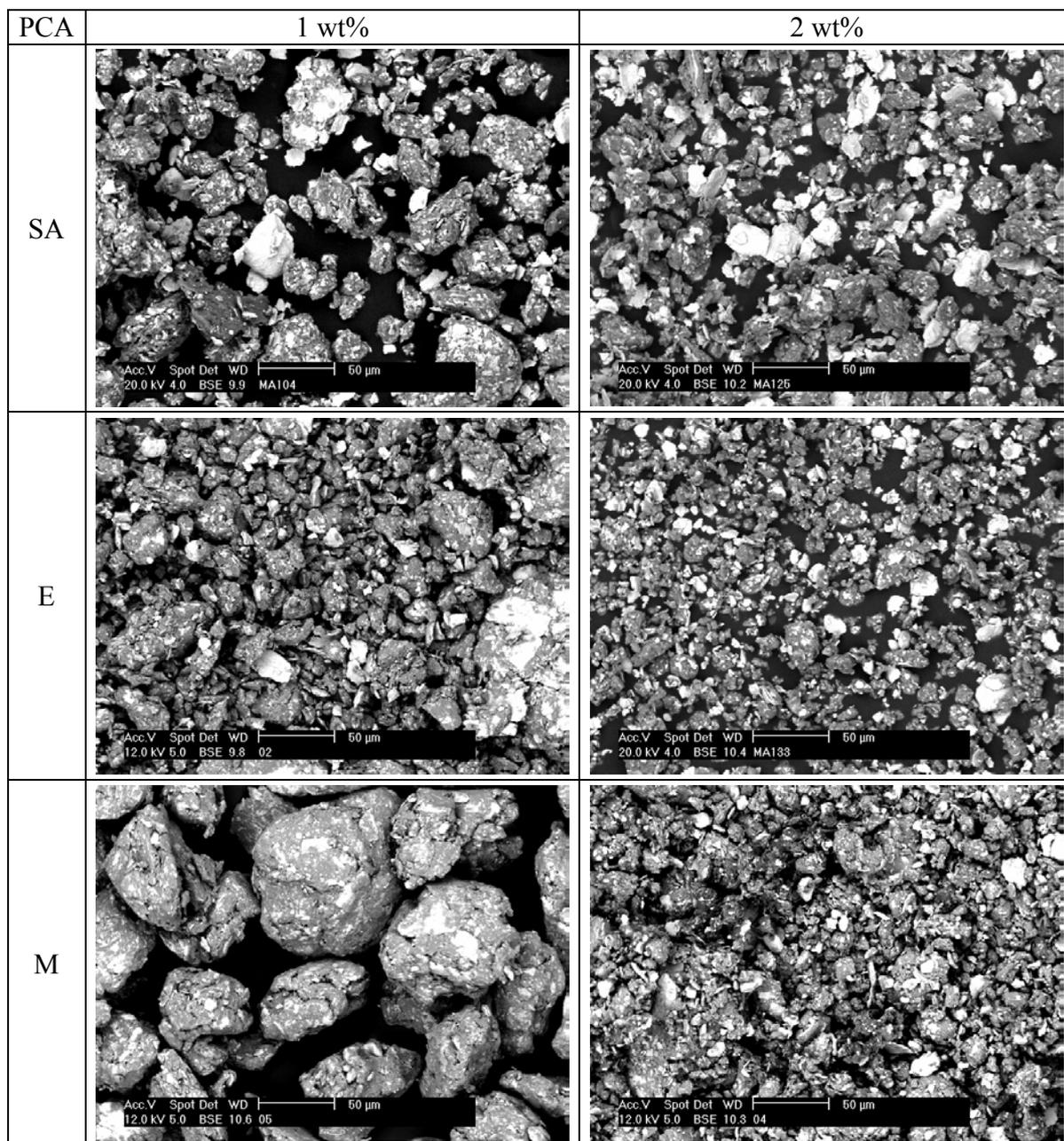


Figure 1 – SEM images (backscattered electrons) of as-milled powders with different types and amounts of PCAs (SA = Stearic Acid; E = Ethanol; M = Methanol).

By increasing the amount (e.g., 1 to 2 wt%) of each PCA no significant changes in microstructure of the aggregates were introduced, as shown in Fig. 2 for the case of stearic acid. It also can be noticed that the isolated niobium particles (white) present a flake shape, attained during the flattening stage of milling [21]. A very similar lamellar structure was produced with methanol. The addition of ethanol, however, produced aggregates with not to layered internal structures, as can be observed comparing high-magnification micrographs (Fig. 2) of powders with 2 wt% of methanol and ethanol.

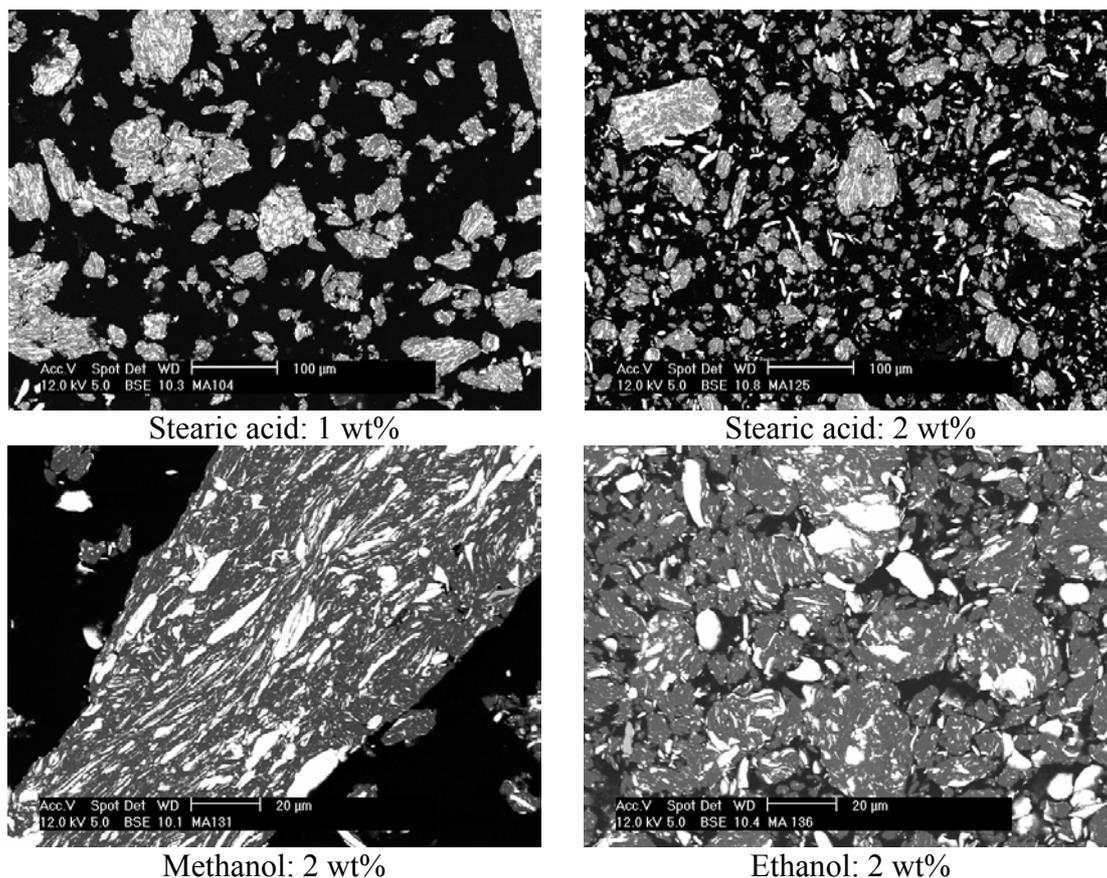


Figure 2 – Microstructure of aggregates produced after milling with different PCAs.

**Temperature profiles.** Temperature profiles of the pellets (Nb+3Al) heated at 30°C/min can be visualized in Fig. 3, grouped by content and type of PCA. All the pellets suffered ignition at melting plateau of aluminum, indicating a similar level of mechanical activation. Comparing thermal curves from samples with 1wt% of PCA (Fig. 3a) it can be noticed that sample with methanol ignites a little bit earlier. With 2 wt% of PCA (Fig. 3b) reaction starts first when stearic acid is added. This behavior can be explained by different ability of these agents in preventing cold welding, as seen before. Being less effective against cold welding, methanol is better for joining aluminum and niobium particles into aggregates (1wt%), providing intimate contact between the reactants and so anticipating the reaction in relation to the other PCAs. The influence of PCA amount is better seen when curves are grouped by type of PCA (Fig. 3c, 3d, 3e). As a general tendency, the increase from 1 to 2wt% retards the reaction, translating curves to the right. This effect is quite insignificant for stearic acid (Fig. 3c), meaning that 1 wt% of this PCA is already effective to prevent excessive welding. However for ethanol (Fig. 3d) and methanol (Fig. 3e) the delays are increasingly higher. Two possible reasons can be pointed out: first, the content of these PCAs need to be higher in order to be effective to impair welding; second, these agents aid the formation of stronger barriers at niobium-aluminum interfaces. Further analysis by TEM should help to understand these results.

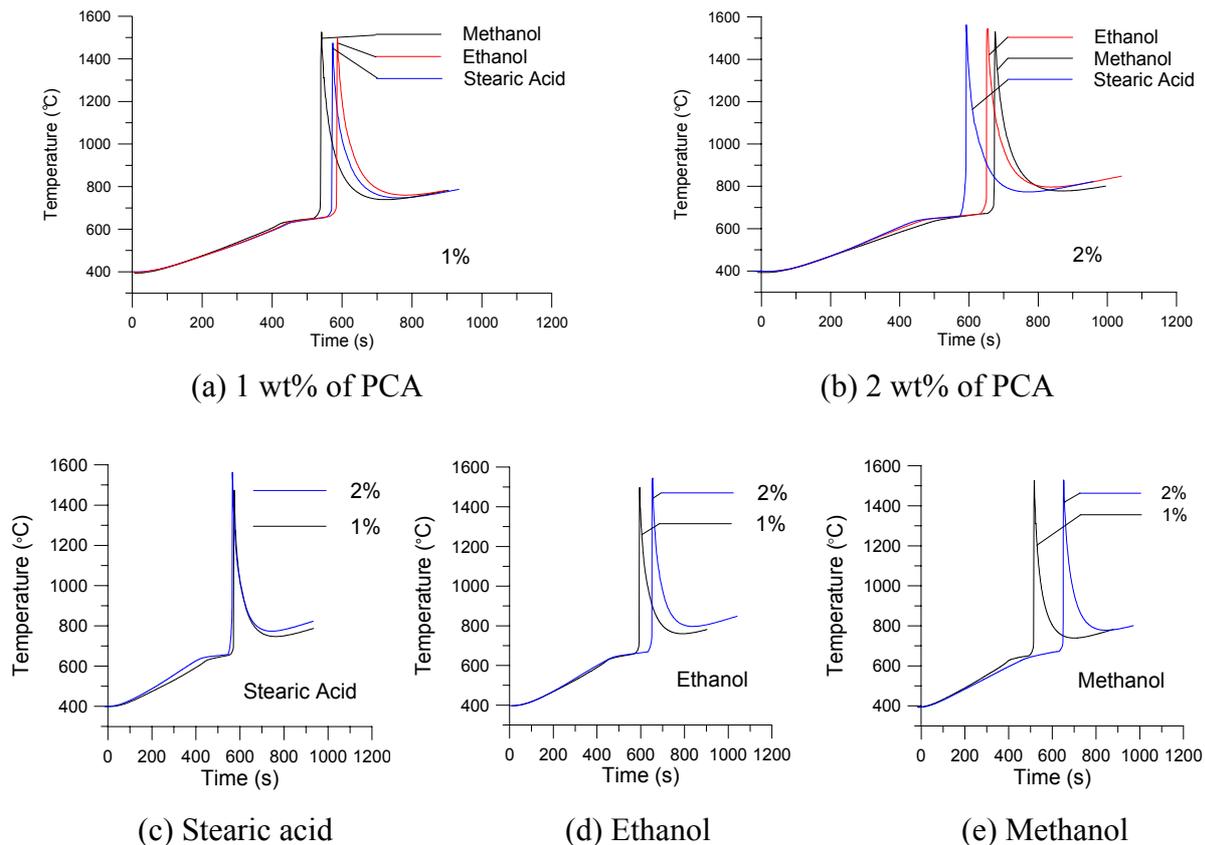


Figure 4 – Temperature profiles of pellets grouped by content (a, b) and type of PCA (c, d, e).

**Density of reacted pellets.** Table 1 presents density results obtained from compacted and reacted pellets, along with temperature (ignition and combustion) values. Densification, according to Rabin and Wright [22], is defined as the relative change in density compared to the maximum change that is possible to be achieved. In this study, the effects of PCAs on combustion temperatures, although listed in Table 1, will not be discussed, once their results were not very conclusive. In general, higher PCAs contents resulted in higher densities and densifications. An exception was observed for 2 wt% of ethanol, whose pellet swelled due to a pronounced gas entrapment. With 2 wt% of methanol some gas entrapment although not very significant was also observed. The highest densifications were attained with 2 wt% of stearic acid followed by 1 wt% of ethanol. These results, combined with powder shape and microstructural analyses, are indicative that fine powders and a certain amount of isolated particles are beneficial to sintering.

Table 1 – Ignition ( $T_{ig}$ ) and combustion ( $T_c$ ) temperatures, and density results of reacted pellets processed with different PCA additions.

PCA	Quantity (wt%)	$T_{ig}$ (°C)	$T_c$ (°C)	Green Density $\rho_g$ (g/cm <sup>3</sup> ) / % $\rho_m$	Reacted Density $\rho_r$ (g/cm <sup>3</sup> ) / % $\rho_t$	Densification $(\rho_r - \rho_g)/(\rho_t - \rho_g)$
Stearic acid	1	654	1491	3.23 (75.6)	3.99 / 87.9	58.0 %
	2	657	1563	3.11 (72.8)	4.40 / 96.9	90.2 %
Ethanol	1	658	1502	3.18 (74.5)	4.31 / 94.9	83.1 %
	2	668	1545	3.06 (71.7)	3.91 / 86.1	57.4 %
Methanol	1	650	1534	3.22 (75.4)	3.77 / 83.0	41.7 %
	2	671	1533	3.08 (72.1)	4.14 / 91.2	72.6 %

$\rho_m = Nb + 3Al$  mixture theoretical density (4.27 g/cm<sup>3</sup>);  $\rho_t = NbAl_3$  theoretical density (4.54 g/cm<sup>3</sup>)

**Microstructure of reacted pellets.** SEM micrographs of polished cross-sections of reacted pellets are shown in Fig. 4. As commented previously, severe gas entrapment, resulted from the addition of 2 wt% of ethanol, led to the formation of large voids. The degassing treatment (400°C for 4 hours) was not suitable in this case to extract volatile materials before the reaction. This observation was supported by the fact that less amount of ethanol (1 wt%) resulted in good densification and smaller rounded pores. For the other PCAs however the general tendency goes to the opposite direction: the higher the PCA content, the higher the density of the reacted pellet. The pores remained in the microstructure of the pellets produced from the mixtures containing stearic acid and methanol show that the increase of the PCA content promotes a decrease of their size. This decrease can be associated to the decrease of the aggregates size, enhancing the escape of volatiles matters. NbAl<sub>3</sub> was the major phase formed in all cases. Energy-dispersive spectroscopy (EDS) analysis was able to detect the presence of very fine particles of aluminum oxide and niobium carbide.

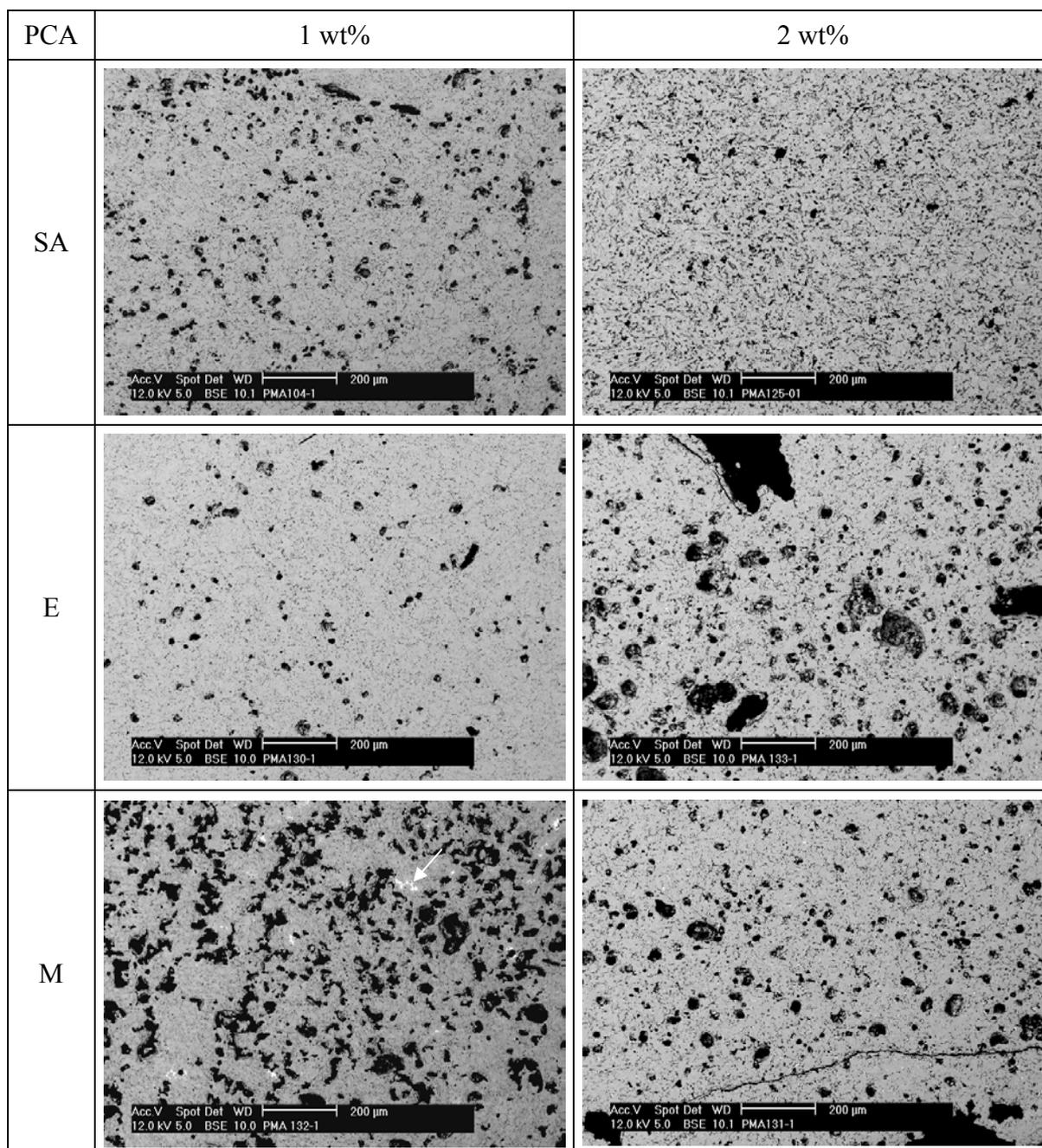


Figure 4 – Microstructure of reacted pellets for different PCAs additions.

The eutectic component Nb<sub>2</sub>Al-NbAl<sub>3</sub> (white regions indicated by the arrow in Fig. 4) was formed in the reacted pellets relative to the addition of 1 wt% of methanol. The presence of this structure can be attributed to deviations in the local stoichiometry inside the strong cold welded aggregates of the milled powders.

### Concluding Remarks

The results presented here allow the conclusion that the type and quantity of the PCA used strongly affect the shape and the microstructure of the aggregates formed during the activation process (milling). As a consequence, the densification of the NbAl<sub>3</sub> pellets produced by combustion synthesis is also affected, which justify a careful study concerning the type and quantity of the material chosen as a process control agent. The following observations can be summarized:

- (a) The addition of 2 wt% of PCA (compared to 1 wt%) produces in general smaller aggregates and more niobium particles not welded to aluminum. The reduction of the aggregate size was seen to be better for densification. Ethanol showed to be more effective in reducing particle size, even with 1 wt% of addition, but not so good to be extracted by the degassing treatment adopted;
- (b) The increase of the amount of PCA caused some delay on the ignition of the reaction, which was more significant for methanol, probably a stronger barrier former at Al/Nb interfaces;
- (c) For each PCA should be exist an optimum quantity concerning densification.

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