

## An Investigation of the use of Stearic Acid as a Process Control Agent in High Energy Ball Milling of Nb-Al and Ni-Al Powder Mixtures

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**Abstract:** High energy ball milling of powders involves successive events of fracture and welding promoting mechanical alloying, fine and homogeneous dispersions could be attained. To minimize excessive cold welding during milling of ductile particles, the so called process control agents (PCAs) are added to the powder charges. These additives, mostly organic compounds, act as a coating of the particles inhibiting welding. It is known that PCAs are a source of contamination, so under this point of view its quantity must be the lowest possible. Moreover performing combustion synthesis of a powder mixture with PCA requires a pretreatment during the heating for extracting the PCA before reaction takes place, otherwise it can impair densification. In this work the use of stearic acid as PCA in milling Nb-Al and Ni-Al powder mixtures was investigated. The aim was to find a optimum quantity of that additive concerning milling action and decreased contamination.

### Introduction

High-energy ball milling is a powder process that has a great potential on control the component dispersion, and even on alloy synthesis in the solid state. Based on a sequence of deformation, welding and fracture of powder particles occurring during the collisions of media parts, the properties of the materials involved as well as the energy conditions of the system play an important role on milling process [1]. It is known that when ductile materials are milled the welding event is preponderant on fracture, leading to an increase on powder aggregate size and a considerable material sticking on media parts with loss of powder yield. For this reason, a process agent control (PCA) is added to the starting powders in order to minimize these effects [2,3]. A very common PCA used for this purpose is the stearic acid. Depending on the milling conditions, a fraction of this compound, like other organic ones, decomposes during milling, reacting with milled material to form carbides and oxides. Recently, Lee and Kwun [4] observed that the mechanism of formation of amorphous and metastable phases in the Ti-Al system changes with an increase of PCA content. Other works had already shown the presence of PCA during milling causes a delay effect on the alloying process [2,5]. These results accentuate that the effects of PCA are beyond those related only with particle size or powder yield.

Previous work on the combustion synthesis of milled powder from Nb-Al system indicates a significant effect of milling on the ignition temperature and final density of compacted pellets [6]. It is well known that size, shape and surface conditions of powder particles, as well as its distribution, are critical when the goal are the densification and microstructure homogeneity [7]. Despite some articles discuss the effect of milling on the intermetallics synthesis [8-11], it was noticed that not always the use of PCA is adopted and there is a lack of discussion about how the PCA addition can affect the combination of milling and combustion synthesis.

In the present study, the influence of PCA content on the particle (aggregate) size and microstructure, as well as its effects on combustion synthesis process has been investigated through high-energy ball milling of Nb-Al and Ni-Al elemental powder mixtures.

## Experimental

Nb-75 a/o Al and Ni-25 a/o Al samples were prepared from weighting the required proportions of elemental powders of commercial purity aluminum (Alcoa), niobium (FTI – CBMM) and nickel (Riedel-de Haën). Different quantities of stearic acid were added to each sample of 10 g, e.g., 0.1 g (1.0 wt. %), 0.05 g (0.5 wt. %) and 0.033 g (0.33 wt. %). Samples were milled in a vibratory ball mill (Spex 8000) Milling was conducted on a stainless steel vial sealed with argon. Two sets of stainless steel balls were used: 9/32-in. diameter balls for Nb-Al samples and 7/32-in. diameter balls for Ni-Al samples. The reason for that is to take into account differences in the plastic behavior between both mixtures that cause Ni-Al samples to be more sensible to the impact of the balls. The milling time was 1 hour for Nb-Al samples and 20 min for Ni-Al samples. Loading and unloading of the samples were always done in an argon-filled glove box. Some milled samples suffered a degassing treatment before compaction, in order to investigate the influence of this procedure on the powder characteristics and final product density. As-milled and degassed powders were characterized by X-ray diffraction and scanning electron microscopy (SEM). Moreover, differential thermal analysis (DTA) was performed on small as-degassed samples (~200 mg) under argon flux (40 ml/min) at a heating rate of 15°C/min. Combustion synthesis were carried out on cylindrical compacted samples under vacuum at a heating rate of 30°C/min. The bulk density of the reacted pellets was measured by geometrical means or by Arquimedes method in those cases where high distortions from cylindrical geometry were observed.

## Results and Discussion

Fig. 1 shows the DTA curves of milled powders with different contents of PCA after degassing treatment. For Nb-Al samples (Fig 1a), the combustion reaction was seen to occur in two steps as described previously by Leal Neto and Rocha [6]. First exothermic peak occurs just after the melting of aluminium (endothermic peak) followed by a weak second exothermic peak. A little decrease on ignition temperature was observed as PCA content is diminished to 0.5 and 0.33 wt.%. Ignition (first exothermic peak) occurs just before the melting of aluminium. For Ni-Al samples, a dramatic decrease on ignition temperature was observed when the PCA content is changed from 1.0 wt. % to 0.33 wt. %.

Fig. 2 shows SEM micrographs of as-milled powders with 0.33 and 1.0 wt. % of stearic acid. As general tendency, higher the stearic acid content, smaller the aggregate of both powder mixtures. As Nb-Al mixtures have much more aluminum than Ni-Al mixtures, the aggregate size is much higher in the former due to the strong tendency of aluminum to welding. The combustion synthesis of Nb-Al mixture with 0.33 wt. % of stearic acid was discarded, as aggregate size distribution is much heterogeneous, having aggregates as high as 0.5 mm.

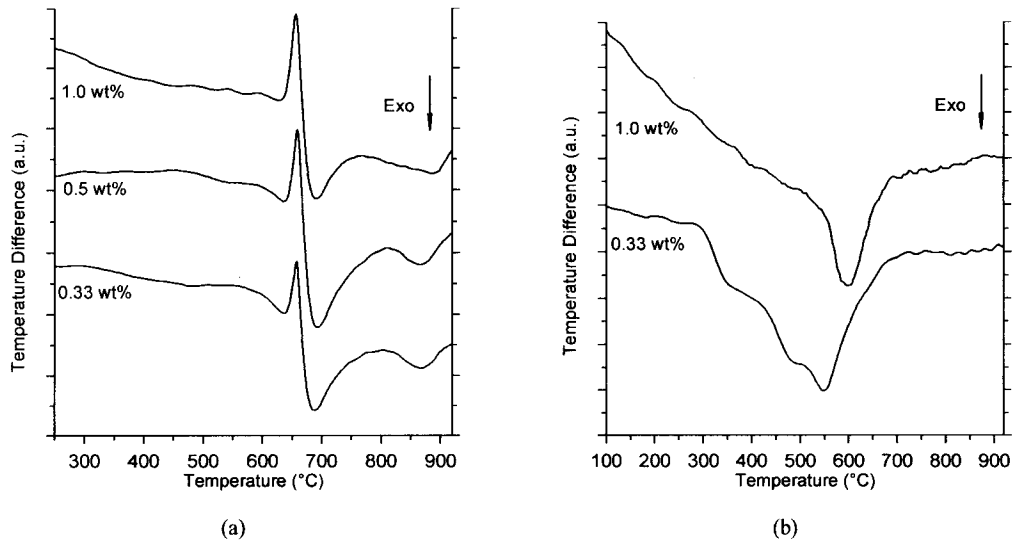


Fig. 1 - DTA curves of milled powders with 0.33, 0.5 and 1.0 wt. % PCA. (a) Nb75Al; (b) Ni25Al.

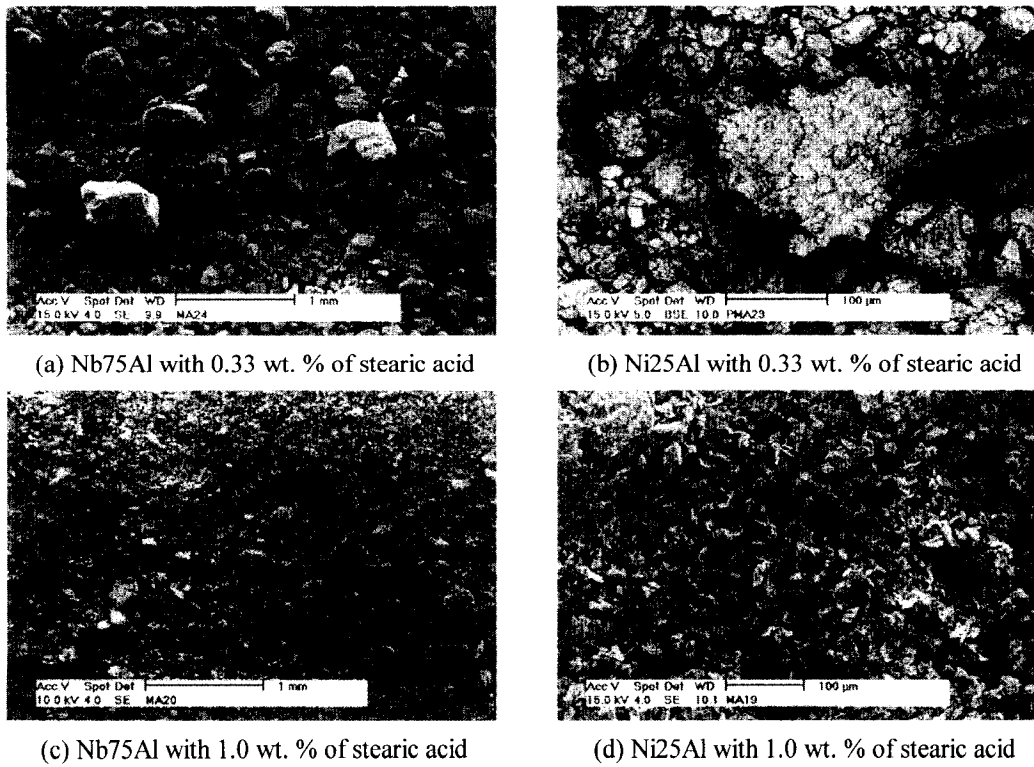


Fig. 2 – SEM micrographs of Nb75Al and Ni25Al powder mixtures after milling for 20 and 60 min, respectively. Stearic acid contents are indicated in each case.

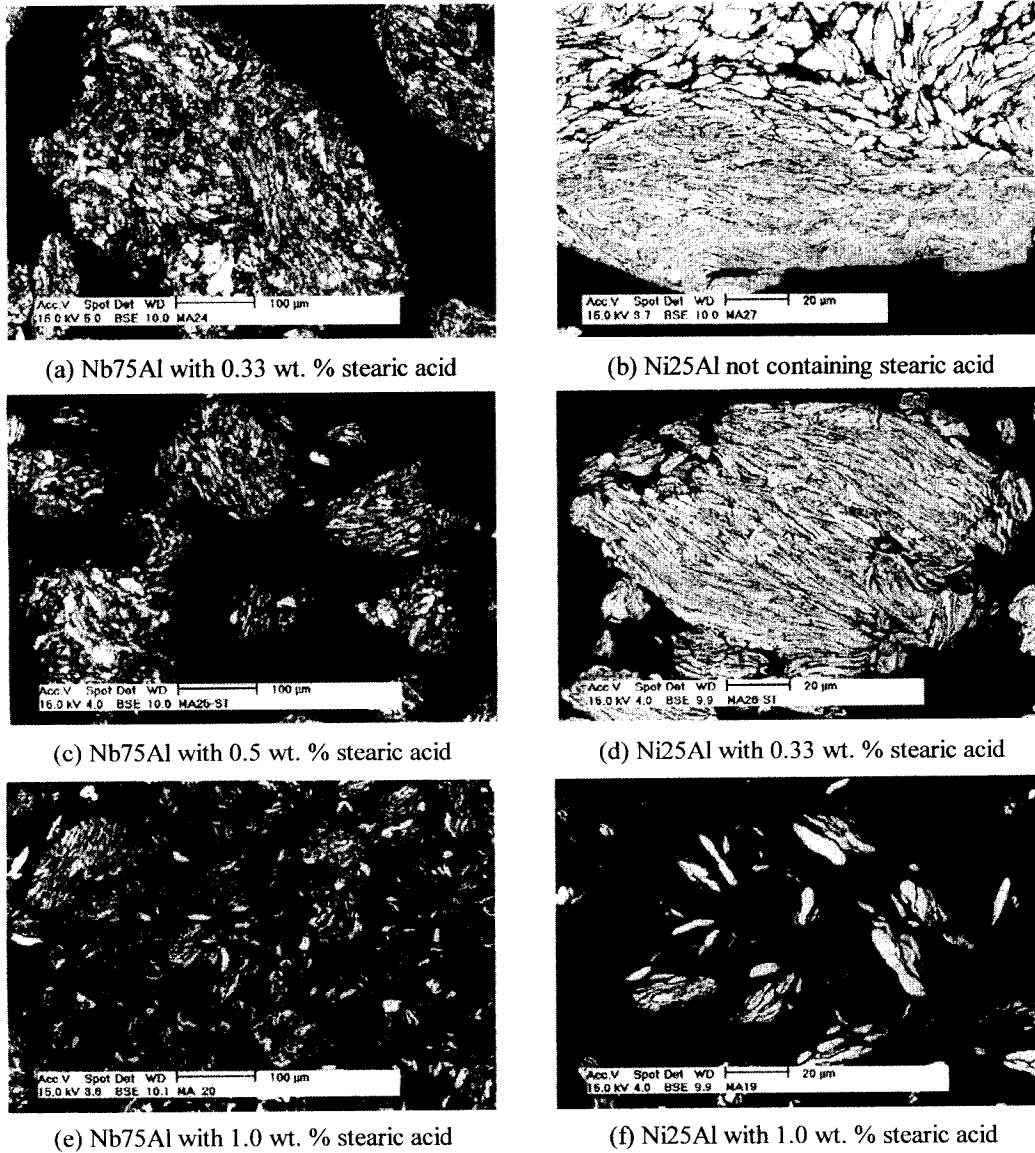


Fig. 3 – SEM micrographs (backscattered electrons) of polished sections from Ni25Al e Nb75Al powder mixtures after milling for 20 and 60 min. Stearic acid contents are indicated in each case.

The microstructure of milled powders is shown in Fig. 3. Micrographs from Figs. 3a, 3c e 3e refer to Nb-Al samples. As the content of stearic acid is increased from 0.33 to 1.0 wt. % no significant variation on the thickness of the alternated layers can be observed. Actually the outstanding change is the size of the aggregates, which decreases as the content of acid is increased. Moreover, this is followed by a substantial increase in the number of isolated (i.e., not associated with aluminium) white niobium particles. The last two aspects are consequence of a diminished welding action, notably from aluminium, that occurs when more stearic acid is added to the

powders. Higher the acid content, lower the size of the aggregates and higher the quantity of non-welded niobium particles. Reducing the number of isolated niobium particles increases interfacial areas between dissimilar particles, and contributes to the lowering of the ignition temperatures. Ni-Al samples exhibit similar behaviour concerning aggregates size and isolated nickel particles (Figs. 3b, 3d and 3f). However, microstructure is severely changed with the increase in the stearic acid content. Milling without acid produces heterogeneous aggregates that can contain portions of extremely thin layers of nickel and aluminium coexisting with thicker ones (Fig. 3b). With the addition of 0.33 wt. % acid (Fig. 3d) more homogenous aggregates are obtained and the layers are a little bit thicker than fine layers of Fig. 3b. The changes are more evident when 1.0 wt. % acid is added (Fig. 3f). The welding between aluminium and nickel particles was severely impaired and a lot of isolated particles are observed. This aspect can elucidate the very anticipation of the ignition temperature as observed by thermal analysis experiments.

The different behaviour between the two systems, concerning the microstructure of agglomerates, seems to be related to the differences of ductility and relative proportions of reactant elements. The lamellar aspect is more difficult to reach in the agglomerates with low volume content of harder element (in our case the niobium). This difficulty is probably related to the plastic deformation developed during milling, which is more concentrated in the softer element.

Table 1 shows the results obtained from reacting pellets in the furnace. The data refers to pellets compacted from previously degassed milled powders. Data from as-milled powders were shown in some cases just for comparing purposes.

Table 1 - Ignition temperature ( $T_{ig}$ ) and pellet density range attained with various milled powder mixtures (stearic acid contents and degassing treatments are indicated).

Powder Mixture	Conditions	$T_{ig}$ range (°C)	Density Range (g/cm <sup>3</sup> )
Nb75Al	0.5 wt. % PCA (powder degassing)	650-665	4.1 to 4.2
Nb75Al	1.0 wt. % PCA (powder degassing)	660-670	4.1 to 4.3
Nb75Al	1.0 wt. % PCA (pellet degassing)	660-670	4.2 to 4.3
Ni25Al	0.33 % PCA (not degassed)	300-350	4.7 to 4.9
Ni25Al	1.0 wt. % PCA (powder degassing)	465-475	4.7 to 4.8
Ni25Al	1.0 wt. % PCA (pellet degassing)	465-490	4.4 to 4.5

Observed ignition temperatures during combustion synthesis of the pellets at the furnace agree with the previous thermal analysis. In spite of lack of so high precision, as compared to thermal analysis, the tendency observed on measured temperatures was just similar. Thus, it was seen a slight reduction on ignition temperature as stearic acid content is decreased from 1.0 to 0.5 wt. % on Nb-Al mixtures. In Ni-Al mixtures however this reduction was about 170°C when stearic acid content was reduced from 1.0 to 0.33 wt. %. Previous powder degassing was not seen to change ignition temperatures.

Concerning the densities, table 1 show no significant change from one condition to another of Nb-Al pellets. On the other hand, changes were observed in the Ni-Al mixtures, where pellet degassing condition showed a slightly decrease of density. Previous powder degassing is believed to

be better than pellets degassing concerning the escape of gases coming from stearic acid volatilisation or decomposition. Thus it was hoped an increase on pellets density when degassing treatment was carried out on powder mixtures before compaction. This was true for Ni-Al mixtures but not for Nb-Al mixtures. This difference arises from different maximum degassing temperatures utilized in both powder mixtures. This maximum is the critical temperature to prevent ignition during the chosen dwell time (which was 4 hours in this work). According to this criteria Ni-Al mixtures containing 1.0 wt. % of stearic acid were degassed at 300°C. With 0.33 wt. % of stearic acid this temperature had to be so low (under 200°C) due to the reduction on ignition temperature, that previous powder degassing was not done. For Nb-Al mixtures the degassing temperature was 400°C and the treatment seemed to be similar in the powder and in the compacted pellets, resulting very close densities in both cases.

### Final Comments

The use of process control agents (PCA) on high-energy ball milling process is indispensable when the milled materials are ductile. The agglomerate size and powder yield are milling results that can be controlled by PCA additions. However, it was observed in this work that the distribution of elements, as well as its morphology, after milling can be strongly affected by PCA content. It can be envisaged that the ductility and the relative proportions of reactant elements play an important role on the extension of this effect. In the case of subsequent combustion synthesis, it was observed the differences of agglomerate morphology and elements distribution on Ni-Al mixtures have a marked influence on ignition temperatures with no significant effect on density. The variation of densities for high PCA content shows the relation of this parameter and the degassing treatment on powder or pellets is especially important for the Ni-Al system where the degassing temperature is lower than the Nb-Al system.

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## **An Investigation of the use of Stearic Acid as a Process Control Agent in High Energy Ball Milling of Nb-Al and Ni-Al Powder Mixtures**

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