

The Effect of Mechanical Activation of Elemental Powders on Combustion Synthesis of NbAl₃

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Keywords: High Energy Ball Milling, Combustion Synthesis, Nb-Al.

Abstract. The effect of mechanical activation procedures on the combustion synthesis of NbAl₃ was investigated. The activation was carried out by a two-step high energy ball milling procedure. In the first milling, aluminum and niobium were milled separately (pre-activation). The mixture of pre-activated powders was then activated in the second milling. Reaction synthesis, by simultaneous combustion mode, was conducted on compacted pellets made of powder mixtures with and without pre-activation. 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 the two-step milling procedure could enhance reaction performance by increasing maximum reaction heating rate and temperature gain during reaction.

Introduction

Ever since well dispersed oxides in metallic powders were first produced using high energy ball milling [1], this technique became widely used in research laboratories to obtain materials in conditions far from equilibrium. In the case of milling mixtures where components are all ductile, the intense particle deformation and fine lamellar structured aggregate formation may result in new materials due to diffusion and reactions at interfaces between components [2, 3]. These new materials can be formed during milling or annealing heat treatment of milled mixtures [4, 5].

A combination of high energy ball milling and combustion synthesis techniques has been used to produce materials, especially intermetallics, in a consolidate form [6-10]. The activated state due to well dispersed components with high density crystalline defects increases the reaction kinetics, lowers the ignition temperature and optimizes the thermal balance during the reaction [6-8]. In the simultaneous combustion mode, where the entire sample is heated until reaction, the lower ignition temperature contributes to minimize the dimensional distortion of the compacted pellets [7].

In the case of non-mechanical activated mixtures, the ignition temperature for the combustion synthesis of NbAl₃ is well above the aluminum melting point (850°C to 900°C). This characteristic is a consequence of poor wettability of niobium particles by liquid aluminum [11]. The mechanical activation of Nb-Al mixtures produce aggregates with lamellar structures that enhance wettability, thus lowering the ignition temperature to the same level of aluminum melting point or even lower. Thus, the thin lamellar dispersion of niobium into aggregates produced by intense plastic deformation of both elemental powders might change the reaction ignition mechanism to a solid state reaction. However, a solid state reaction ignition may induce low reacted pellet densities [10].

This article presents a two-step mechanical activation procedure which was applied to Nb-Al mixtures in order to produce an alternative dispersion of niobium with less activated Nb-Al interface. The effects of the aggregate microstructure on the reaction performance were observed when simultaneous combustion synthesis was applied.

Experimental Procedures

Mechanical activation was carried out using two different routes. The first route, considered here as standard procedure, was to prepare Nb75Al (at%) powder mixtures of gas-atomized aluminum (-325 mesh, 99.7% in purity) and hydrated-dehydrated niobium (-325 mesh, 99% in purity). Stearic acid was then added to each mixture of 19g in a fixed amount of 1.0 wt%, in order to prevent excessive cold welding of powder particles. Powder mixtures were mechanically activated in a shaker ball mill (SPEX®8000) at room temperature for 2 h. The ball-to-powder volume ratio was fixed at 5:1. Millings were conducted on a martensitic stainless steel vial, with AISI 52100 balls of 5.55 mm and 3.17 mm in diameter, under argon atmosphere.

The second route, here called as the two-step procedure, consisted of mechanically activating the elemental powders separately (pre-activation) in the first step. These pre-activations were carried out in a planetary mill (Fritsch Pulverisetti®5) for 50 h, with a ball-to-powder volume ratio fixed at 5:1 and stearic acid addition. Millings were conducted on a martensitic stainless steel vial, with AISI 52100 balls of 9.52 mm, 5.55 mm and 3.17 mm in diameter, under argon atmosphere. The second step follows the standard procedure however no stearic acid was used in the mixtures since the pre-activated elemental powders already contained this process control agent.

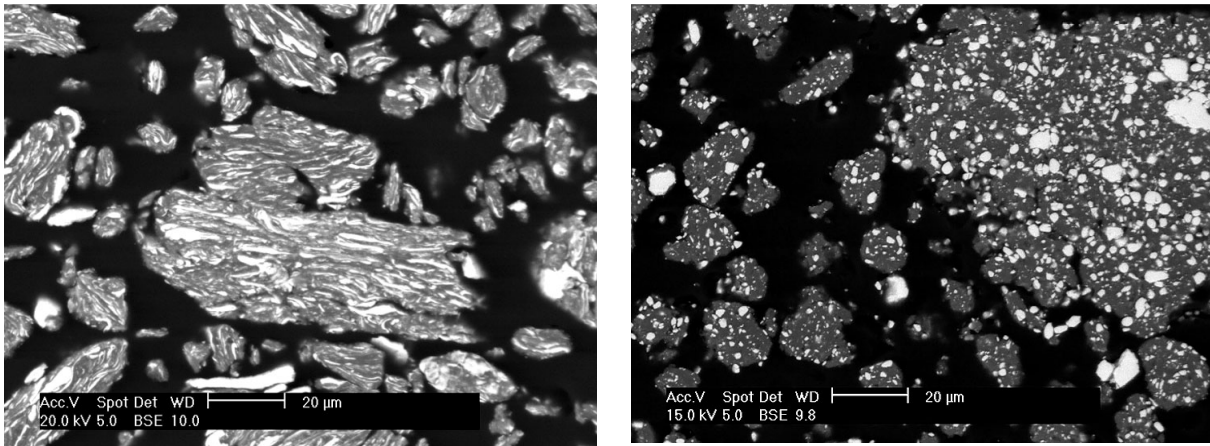
Milled samples of about 4 g were uniaxially compacted in a 14 mm cylindrical floating die with enough pressure for a 75% green pallet density. Simultaneous combustion syntheses were conducted in a tubular resistive furnace under vacuum. The heating cycles started from room temperature with heating rate of 5°C/min until 200°C and of 2°C/min until 450°C. After 10 minutes of temperature stabilization at 450°C, the pellets were then heated at 30°C/min until the end of the reaction.

Temperature-time profiles of furnace and pellets were recorded by a data acquisition system. The values of profile inflection points were determined by analyzing the changes of heating rate and when necessary, by the interception of two lines calculated using linear regression before and after of each inflection point. The main thermal characteristics were ignition temperature, flash temperature (pellet heating rate reaching 100 °C/s), maximum combustion temperature, maximum reaction heating rate, reaction time (time difference between ignition and maximum combustion temperatures) and aluminum melting time.

The microstructures of the milled mixtures were evaluated by scanning electron microscopy and X-ray diffraction. Crystallite size and microstrain were calculated by application of the Rietveld method [12] to the diffraction data. This task was done using the Maud program developed by Lutteroti [13-16].

Results

Microstructures of milled powders. Pre-activation in the planetary mill decreased mean particle size from 41 to 26 μm for aluminum and from 24 μm to 4 μm for niobium. The microstructures of the milled mixtures with and without pre-activation are shown in Fig. 1. The black color corresponds to epoxy resin used to obtain a flat and polished surface with dispersed particles and aggregates. The gray and white colors are aluminum and niobium, respectively. The two-step procedure produced a globular dispersion of niobium.



Without pre-activation

With pre-activation

Fig.1 - Milled mixture microstructures with and without elemental powders pre-activation. Backscattering electrons images.

The X-ray diffraction patterns are shown in Fig.2. In regards to the level of crystalline defects, the results of the Rietveld analysis, presented in Table 1, revealed that the pre-activation step was more effective for niobium than aluminum. Despite of the fifty hour pre-activation milling, the levels of crystalline defects of aluminum with and without pre-activation were quite similar. It is important to note that these values must be considered as relative values. Pre-activated niobium also presented a significant change of the lattice parameter which indicates that some solid solution occurred. It was also possible to observe small peaks, identified as niobium oxide, but only in mixture without pre-activation

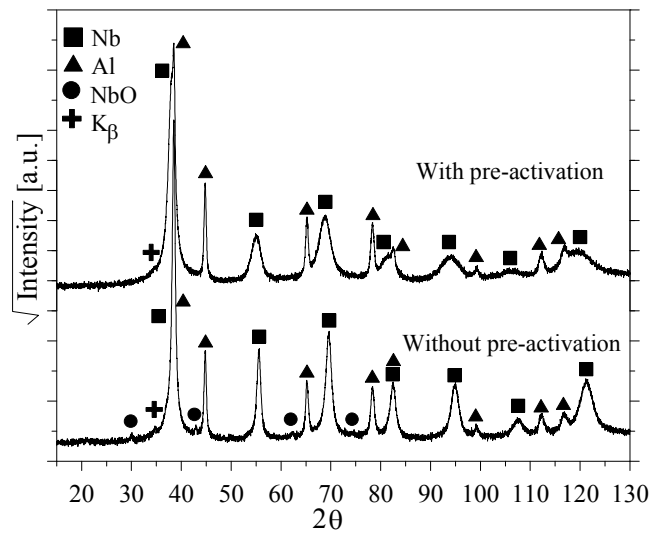


Fig. 2 – X-ray diffraction patterns of milled mixtures with and without elemental powder pre-activation.

Table 1 – Crystallite size, microstrain and lattice parameter of milled mixtures with and without elemental powder pre-activation.

Without Pre-Activation	Aluminum	Niobium
Crystallite size [nm]	43	20
Microstrain [%]	0,151	0,353
Lattice parameter [Å]	4,0478	3,3098
With Pre-Activation	Aluminum	Niobium
Crystallite size [nm]	34	6,3
Microstrain [%]	0,151	0,750
Lattice parameter [Å]	4,0483	3,3407

Combustion synthesis profiles. The thermal profiles recorded during the combustion synthesis procedure are presented in Fig. 3. Three pellets of each type of mixture were reacted but only one profile of each was presented in order to preserve a clear view of inflection points. Profiles were recorded as a function of time; however, the profiles presented here are as a function of furnace temperature. The dashed line in Fig. 3, represents a visual reference of furnace temperature and was drawn so that the relationship of furnace and pellet temperatures were easier observe. Profile analysis results are presented in Table 2.

The values found for ignition temperatures came from different methodologies. In the case of pre-activated mixtures, the transition of aluminum melting plateau to reaction was quite clear and values could be read directly. However, the ignition temperature before melting point as observed in non pre-activated mixtures showed no clear transition and values taken were based on interception between pellet temperature profile and the furnace reference dashed line. In order to verify if ignition temperatures found were related with a self-sustainable reaction process, several interruption tests were carried out at this temperature by pulling out the pellets from the furnace. This procedure would not be able to stop reaction for all tests what indicates that ignition temperature was quite close to the values found.

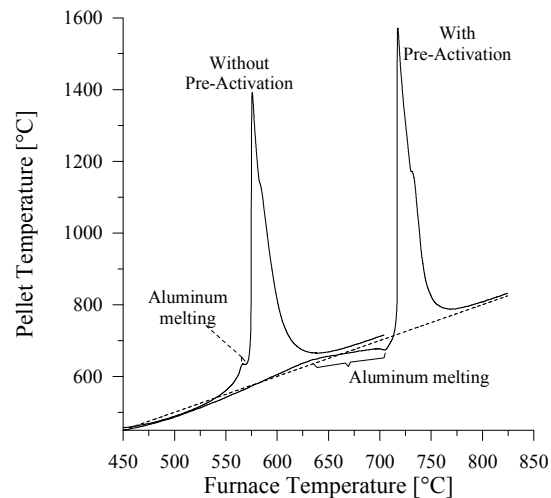


Fig. 3 – Temperature profiles of pellets prepared with milled mixtures of elemental powders with and without pre-activation.

Table 2 – Thermal characteristics of time- temperature profiles of pellets prepared with milled mixtures of elemental powders with and without pre-activation.

Thermal Characteristic	Without Pre-Activation	With Pre-Activation
Ignition Temperature [°C]	541 ± 3	669 ± 6
Flash Temperature [°C]	740 ± 23	805 ± 10
Combustion Temperature [°C]	1393 ± 1	1570 ± 2
Maximum reaction heating rate [°C/s]	626 ± 38	1667 ± 211
Reaction time[s]	75 ± 6	35 ± 2
Aluminum melting time [s]	11 ± 1	196 ± 9

Discussion

The mechanical activation of Nb-Al powder mixture without pre-activation produced thin lamellar structured aggregates with high interface area. The high level of plastic deformation of aluminum and niobium particles generated free oxide surfaces promoting strong bonded interfaces. This situation enhanced the diffusion at interfaces and was the main reason of lowering ignition temperature below the aluminum melting point. The solid state reaction was responsible for increasing the pellet heating rate from 525 °C. The short aluminum melting time observed was probably due to less aluminum available and intense energy release. The presence of more generalized liquid aluminum could then increase the reaction heating rate to its maximum. However, the presence of reacted NbAl₃ before aluminum melting acted as an inert mass and left less aluminum and niobium to react. This combination and the fact that reaction heating was not adiabatic limited the maximum combustion temperature, as well as, the maximum reaction heating rate. As the reaction was initially at solid-solid interface and this reaction type is much slower than at liquid-solid interface, the reaction time was increased.

In the case of pre-activated elemental powder pellets, the aggregated microstructure presented in Fig. 1 showed that niobium particles remained globular even after two hours of mixture milling. This indicates that the high level of crystalline defects observed in X-ray diffraction resulted in increased niobium particle hardness. Therefore, aggregates were mainly produced by aluminum plastic deformation and Nb-Al interfaces were created with limited niobium plastic deformation. This aggregate formation mechanism might be responsible for the delay of reaction ignition by producing interfaces with limited diffusion (due to the limited niobium plastic deformation) which hindered NbAl₃ solid state formation before reaction ignition.

The maximum heating reaction rate of pre-activated pellets was favored by small niobium particle size and reaction ignition occurring after almost all aluminum having been already melted. This combination can also be achieved in Nb-Al mixtures without any mechanical activation mainly by control particle size distribution and compaction pressure. However, the main difference between mixtures with and without mechanical activation is the interface quality which was the main reason of lowering ignition temperature [8,10].

The comparison of flash temperatures and their differences between ignition and combustion temperatures could help better understand the reaction stages of reaction kinetics. In the case of non pre-activated pellets, the difference between flash and combustion temperature was 653 °C and 765 °C for the pre-activated pellets. In terms of time, the corresponding differences were about two

seconds for all pellets. This result indicates that the reaction ignition delay was important to improve reaction performance.

Conclusions

The pre-activation of elemental powders increased particle hardness changing the niobium dispersion during mechanical mixture activation. The limitation on niobium particle plastic deformation resulted in limited diffusion at Nb-Al interfaces. As a consequence, the delay of the ignition temperature was close to the end of the aluminum melting plateau. The well dispersed small niobium particles produced by two-step mechanical activation procedure enhanced the reaction kinetics through decreasing reaction time and increasing the maximum reaction heating rate. These reaction characteristics led to a maximum combustion temperature 90 °C lower than NbAl₃ melting point.

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Advanced Powder Technology VII

doi:10.4028/www.scientific.net/MSF.660-661

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doi:10.4028/www.scientific.net/MSF.660-661.335