

Combustion Synthesis of High-Energy Ball-Milled Nb + 3Al Powder Mixtures

Ricardo Mendes Leal Neto; Cláudio José da Rocha

Francisco Ambrozio Filho

Instituto de Pesquisas Energéticas e Nucleares
Centro de Ciência e Tecnologia de Materiais
PO Box 11049 - Zip Code 05422-970 - São Paulo - SP - Brazil
Fax: +55 (011) 816-9370 - e-mail: lealneto@net.ipen.br

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Abstract: A major concern on making products by combustion reactions is to obtain high densities. In this work the combustion synthesis of Nb + 3Al powder mixtures is investigated with emphasis on densification behaviour. Two sets of mixtures were compared: high-energy ball-milled and simple mixtures. Milling was conducted on a vibratory mill at different times, to promote a highly refined dispersion of aluminum and niobium powders, avoiding in situ reaction. Cylindrical pellets were obtained by uniaxial compaction and reacted by thermal explosion mode under vacuum. Besides milling time, green density, degassing procedures and heating rates were also varied. Reacted pellets of NbAl₃ were characterised in terms of final density, geometrical distortion and phases present in the microstructure. The results shown a great dependence of final density on milling time and that is possible to attain dense pellets with little dimensional distortion as compared to the ones from non-milled mixtures.

Introduction

For long time combustion synthesis, or SHS (Self-sustaining High-temperature Synthesis), has been utilized for processing a great variety of materials, including ceramics, composites and intermetallic compounds [1,2]. This method starts when the constituent elements of the desired product are put together and brought to favourable conditions (pressure and temperature) for strong exothermic reactions can take place. In condensed systems, particularly when starting elements are all solid, the kinetics of the reaction is very dependent on the initial dispersion of the reactant powder particles [1,3], once an intimate contact is provided between them. It is well know that it can be done very efficiently by high-energy ball milling, specially in ductile-brittle systems [4]. Beside the increase on the interfacial contact area between the reactants, the milling action generates large defect densities, both factors contributing to drive the reaction into a critical ignition temperature [5]. Thus, depending on milling conditions, the reaction can occur yet during the milling operation, when the process is called reactive milling or mechanosynthesis.

NbAl₃ in a powder form, like other compounds of Nb-Al system, has been obtained by milling elemental powders, producing amorphous or nanocrystalline material [6,7,8,9,10,11]. Recently, a variation of classical SHS process, named MASHS (from "Mechanically Activated SHS"), was applied to NbAl₃ by Gaffet et alli [12,13,14,15]. This process uses mechanical activation, imposed by co-milling the powder reactants, as a preparation step to the self-propagating high-temperature synthesis (SHS) reaction. On doing this, nanostructured NbAl₃ were produced and it was also verified a decrease on melting time of aluminium (the ignition temperature in that case was always higher than aluminium melting temperature), melting time and ignition temperature [12]. The influence of high-energy ball milling on reaction synthesis of NbAl₃ was also recently

investigated by Leal Neto e Rocha [16], who performed thermal explosion mode of combustion (simultaneous combustion) in place of SHS mode. It was demonstrated, by performing thermal analysis, that ignition temperature could be reduced to levels even lower than aluminium melting temperature depending on milling conditions (actually only milling time was changed, other parameters being fixed.)

A major concern doing combustion synthesis, whatever the combustion mode is, is to produce dense bulk materials. Previous work on NbAl_3 reported a MASHS end-product density of 60% of theoretical density [12]. The low density was attributed to the expansion of the adsorbed gases in the sample, not properly evacuated because the reaction was performed in argon atmosphere. It was shown before, on doing NbAl_3 combustion synthesis from simply powder mixtures, that higher densities can be obtained by reacting under vacuum [17,18,19].

Following a previous investigation about the influence of the high-energy ball milling on the combustion synthesis of NbAl_3 , the aim of this work is to verify this influence on reacting pellets, concerning mainly the attained densities.

Experimental

Samples were individually prepared by blending elemental powders of gas atomized aluminum (99.7 % pure, -325 mesh) and hydrated-dehydrated niobium (99 % pure, -325 mesh). The proportion of each powder was calculated according to the stoichiometry of NbAl_3 , i.e., Nb-75 at. % Al (Nb_75Al). Milling of each sample (10 g) was carried out at room temperature in a SPEX 8000 mixer/mill with forced air-cooling. A stainless steel vial was used with 9/32-in. diameter stainless steel balls. Loading was done in an argon-filled glove box. The ball-to-powder weight ratio (10:1) and the quantity of stearic acid (1 wt. %), for preventing excessive welding, were fixed during all the experiments. Samples were milled for 1, 2 and 3 hours. Possible phase formation was checked by X-ray diffraction and SEM analysis.

Milled samples of about 4g were uniaxially compacted in a cylindrical die in order to attain green densities between 65 and 75 % of theoretical. In another set of experiments the powders were first degassed under vacuum (400°C for 4 hours) and then compacted. Combustion reactions were conducted on a tubular resistive furnace under vacuum (thermal explosion mode). The heating cycle for samples not previously degassed consisted of a initial heating at 5°C/min to 400°C for 4 hours followed by heating to the ignition temperature, initially at 15 and later at 30°C/min. The combustion reaction of the pellets was detected by three almost simultaneous events: First, by a decrease of the vacuum level, slow at the very beginning of the self-heating and then abrupt, coinciding with the sudden increase of the pellet temperature. Second, by the intense light emission from the hot pellet that could be seen through the quartz tube. Last, by a small temperature increase detected by the thermocouple outside the quartz tube. Furnace were heated up just to the ignition temperature and then turned off. Pellets were allowed to cool inside the tube, which by its time were removed out of the furnace. Density of the reacted pellets was estimated by weight and geometric measurements. Microstructural characterization was carried out by x-ray diffraction and scanning electron microscopy on polished cross-section areas, performing elementary analysis using energy dispersive X-ray spectroscopy (EDS).

Results and discussion

At a heating rate of 15°C/min, the reaction of pellets, came from milled powders, was not complete, but NbAl_3 was the major phase, as detected by x-ray diffraction analysis. At a heating rate of 30°C/min, x-ray diffraction analysis detected only NbAl_3 phase. Microstructure of the pellets heated at 30°C/min is shown in Fig. 1. SEM analysis was able to detect an aluminum-rich phase

(probably unreacted aluminum) founded in grain boundaries, as shown at higher magnification in Fig. 1d (dark phase), along with niobium-rich white particles, finely dispersed inside the grains. Precise composition measurements by EDS of that phases were not possible to attain due to their very small size. In other regions (not shown in Fig. 1), mainly in the pellets that came from powders milled for 3h, it was found very fine particles containing oxygen and aluminum (probably Al_2O_3 formed from a reaction between aluminum and residual oxygen). X-ray diffraction analysis was unable to detect these particles. It was also observed that in the pellets from 1h-milled powders porosity (Fig. 1a) is finely distributed along NbAl_3 grain boundaries, associated with aluminum-rich particles (Fig. 1d). There are few pores resultant from gas entrapment. Porosity increases with milling time so that pellets from 3h-milled powders exhibits a highly interconnected porosity, as shown in Fig. 1c.

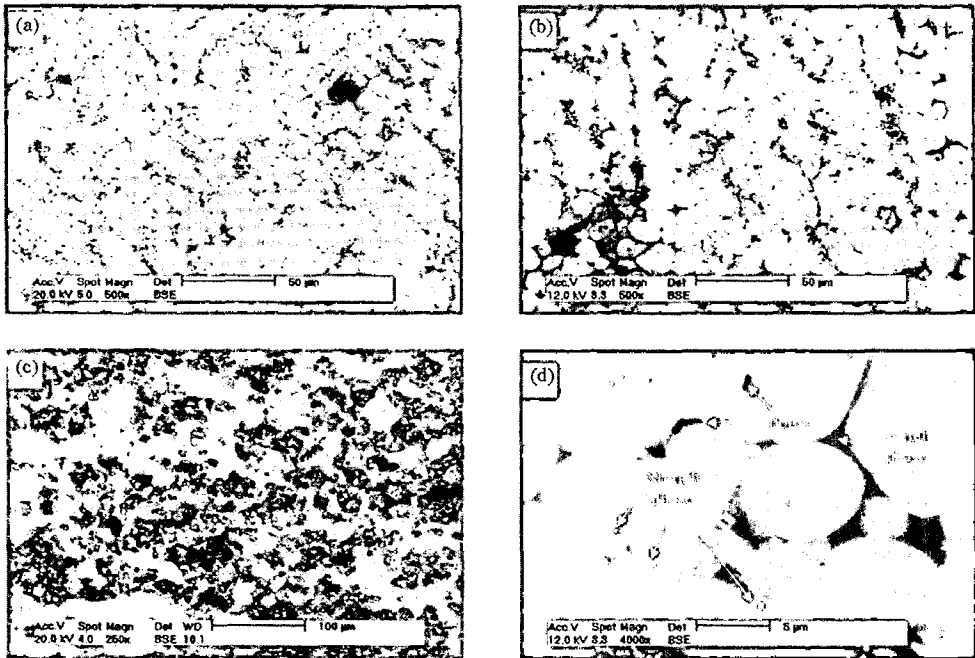


Fig. 1 – SEM micrographs of reacted pellets from powders milled for different times: (a) 1h; (b) 2h; (c) 3h; (d) higher magnification region from (a).

Macrographs of polished cross-sections of the reacted pellets are presented in Fig. 2. Densities before and after reaction, ignition temperatures and densification of the pellets processed at various conditions tested in this work are listed in Table 1. Densification D , shown in Table 1, is defined as the relative change in density (of the reacted pellet over the green compact) compared to the maximum possible density change [20].

Fig. 2a shows a pellet reacted from simple mixed powders (compacted at 50 MPa), added here for comparative analysis. It represents the best density result attained after a previous investigation (e.g., compaction at 50 MPa, degassing at 400°C for 4h and heated at a rate of 15°C/min) [21]. Heating rate and degassing procedures were the same of that used in the pellet shown in Fig. 2b, made of powders milled for 1 h. Pellet came from simple mixed powders has a high density (Table 1) and shows significant geometrical distortion. This non-uniform contraction

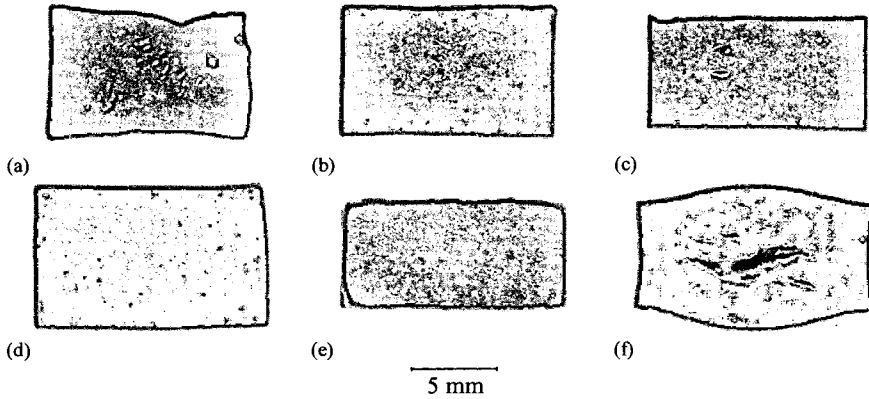


Fig. 2 – Optical macrographs of the polished cross-sections of the reacted pellets came from powders processed at different conditions: (a) simple mixture (pellet degassing; h.r.=15°C/min); (b) milled for 1h (pellet degassing; h.r.=15°C/min); (c) milled for 1h (pellet degassing; h.r.=30°C/min); (d) milled for 3h (pellet degassing; h.r.=30°C/min); (e) milled for 1h (powder degassing; h.r.=30°C/min); (f) milled for 1h (powder degassing; h.r.=30°C/min; higher compaction pressure).

Table 1 – Ignition temperature (T_{ig}) and density results obtained with combustion synthesis reaction of pellets processed in various conditions.

Milling Time (h)	Heating Rate (°C/min)	T_{ig} range (°C)	Green Density, ρ_g (g/cm ³)	Reacted Density, ρ_r (g/cm ³ and %)	Densification Range *
0 (simple mixture)	15	890 - 910	2.80 - 2.93	4.31 - 4.49 (94.9 - 98.8)	86.7 - 96.6
1	15	660 - 680	3.0 - 3.3	3.8 - 4.0 (83.7 - 88.1)	51.9 - 56.4
1 (pellet degassed)	30	660 - 680	3.0 - 3.3	4.2 - 4.3 (92.5 - 93.8)	78.0 - 80.6
1 (powder degassed)	30	660 - 680	3.1 - 3.6	3.3 - 4.2 (72.2 - 92.5)	-28.4 - 76.4
2	15	540 - 550	3.0 - 3.1	3.2 - 3.3 (70.5 - 72.7)	12.9 - 13.8
2	30	535 - 545	3.0 - 3.1	3.25 - 3.35 (71.5 - 73.7)	16.2 - 17.3
3	15	515 - 525	2.88 - 2.91	3.11 - 3.14 (68.5 - 69.1)	13.8 - 14.1
3	30	510 - 520	2.87 - 2.92	3.13 - 3.16 (68.9 - 69.6)	14.8 - 15.5

ρ_t = NbAl₃ theoretical density (4,54 g/cm³);

$$\text{Densification: } D = \frac{\rho_r - \rho_g}{\rho_t - \rho_g} \times 100$$

can be attributed not only to density gradients in the compact but also to excessive liquid formation before the reaction beginning (aluminum melts at 660°C and the reaction started at about 900°C), thus leading to a higher contraction of those regions which had a lower green density. Densification of the pellet came from 1h-milled powder was not so high and almost no geometrical distortion occurred. The lower density can be attributed to the decreasing on ignition temperature (Table 1). Lowering the ignition temperature to values nearly or even below the melting point of aluminum may result in a reduction of the amount of melted aluminum, as seen before performing thermal analysis [16]. Densification (sintering) is enhanced when a liquid phase exists, so if the amount of liquid is diminished final product density will be lowered. Pellet from Fig. 2c was made with the same procedure of the previous one (Fig. 2b) except for the heating rate that was 30°C/min. The increase in heating rate accelerates the kinetics, and it was responsible for the higher density reached. At a heating rate of 15°C/min the lower density obtained can be explained by the intermetallic compound formation by diffusion, during the heating cycle and before the ignition, which work as a heat sink, impairing the temperature rise needed for sintering. Diffusion is enhanced in this case (which is not true for the simple powder mixture) due to the milling action, which increases the defect density, diminishing diffusion distance. This assertive need to be proved by doing specific experiments to interrupt heating before the ignition and thus performing microstructural analysis in the unreacted pellet to identify possible phase formation. However, higher density values obtained at 30°C/min are a strong indication of that. By increasing heating rate the time for diffusion is decreased and at ignition temperature there are less product formation by diffusion.

As a general tendency, higher the milling time lower the ignition temperature and density attained. The higher heating rate was only effective to increase density with 1h-milling time, probably due to the strong reduction in ignition temperature to values well below the melting point of aluminum.

An attempt to increase the final density was done by starting with a denser compact. Once this could impair the evacuation of gases (mainly coming from stearic acid added in milling), milled powders were first degassed (400°C for 4h) and then compacted at a higher pressure than before (450 MPa). Previous degassed powders were also compacted at a lower pressure as before and then compared. Two representative pellets of both procedures are presented in Fig. 2e (lower pressure) and 2f (higher pressure). They were reacted at 30°C/min with no degassing cycle. Higher green density pellets (Fig. 2f) have swelled spectacularly (negative densification in Table 1), having a central void that indicates severe gas entrapment. Lower green density pellets have contracted in very similar way as the pellets that were degassed (Fig. 2c).

Final comments

NbAl_3 combustion synthesis is severely altered by milling its elemental powder reactants. Although densification was not attained at the same level than reacting pellets came from simple powder mixtures, the results shown here indicate that it is possible to make dense products with little dimensional distortion, which makes the procedure studied here technologically attractive and promising.

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