

Combustion Synthesis of Mechanically-Activated Nb-Al Mixtures

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Abstract: In this work shake milling were used to mechanically activate Nb – Al powder mixtures at different relative proportions (Nb80Al, Nb65Al, Nb54Al e Nb42Al). All milling process parameters were unchanged, e.g., powders mass, ball/powder mass ratio, balls diameter, quantity and kind of process control agent. Uniaxially compacted cylindrical pellets of milled powders were vacuum reacted. After a two-step degassing treatment (290°C for 0.5 h and 400°C for 4 h), samples were heated at 30°C/min. Ignition and combustion temperatures were measured by a thermocouple inserted in a hole drilled into the pellets. The microstructure of milled powders and reacted pellets were characterized by X-ray diffraction and SEM analysis. Bulk density of the pellets was measured by water immersion (Archimedes). The results showed a decrease of both ignition and combustion temperature with mechanical activation as seen by comparison with reacted pellets of the same composition not mechanically activated (simple mixtures). By increasing the heating rate the completeness of the reactions were improved. The lower the aluminum contents the lower the ignition and combustion temperatures and also the densification. The decrease on ignition temperature was caused by a more effective dispersion (and so more activation) attained by samples with lower aluminum content.

Introduction

Among Nb-Al intermetallic compounds, NbAl₃ has been gained increased attention as a candidate material for aerospace applications [1-3]. This came from its low density and good oxidation resistance due to its high aluminum content.

Monolithic NbAl₃ has been obtained by combustion synthesis from its elemental constituents [4,5], showing advantages over conventional processing like foundry or powder metal sintering.

Making a dense material by this process demands a very accurate control of the process variables. In previous papers it has been shown that it is possible to attain densities higher than 95% of theoretical value, but with significant dimensional distortion [5,6].

NbAl₃ combustion synthesis was verified to be severely altered by milling its elemental powder reactants, particularly by decreasing ignition temperature and dimensional distortion due to a lower (smaller) liquid phase formation during the reaction [7,8].

A good manner to have clues about the combustion of Nb75Al mixtures is to react other Nb-Al compositions and see what happens. In a previous work [9], non-milled Nb-Al mixtures (e.g. 42, 54, 65, 70, 75 and 80 a/o Al) were reacted. NbAl₃ was always the first phase to form. The reason for that is based on the ignition temperatures of the pellets, measured by a thermocouple placed outside the samples. They were very close together (from 850 to 860°C), at the same range of Nb75Al samples, indicating a similar event. Once aluminum is liquid at the ignition temperature, nucleation

of NbAl_3 begins at the niobium particles by diffusion of aluminum into them. Nucleus growth occurs by niobium dissolution and further reprecipitation of NbAl_3 . Nb_2Al formation mechanism is not very clear. It could be formed by niobium-enriched aluminum (liquid) or by liquid diffusion into the solid niobium. Densification was seen to decrease when mixtures different from Nb75Al were reacted. The question that arises at this moment is what will be the effect of mechanical activation on combustion of these mixtures.

Experimental

Gas atomized aluminum powder (ALCOA - 99,7 % pure) and hydrated/dehydrated niobium powder (FTI - 99 % pure) were screened and the size fraction utilized was that passing through 325-mesh sieve. Powder samples were individually weighted and blended according to the proportion of each composition desired, e.g. Nb-80 at.% Al (Nb80Al), Nb-65 at.% Al (Nb65Al), Nb-54 at.% Al (Nb54Al; eutectic composition) and Nb-42 at.% Al (Nb42Al). Each sample (10 g) was milled for 1 hour at room temperature in a SPEX 8000 shaker mill with forced air-cooling. A stainless steel vial was used with 9/32-in. diameter stainless steel balls. A ball-to-powder weight ratio of 10:1 were used in all the experiments as well as 1.0 wt.% (0,1g) of stearic acid. Loading/unloading procedures were done in an argon-filled glove box. Possible phase formation was checked by X-ray diffraction and SEM analysis.

Pellets of milled samples of about 4g were uniaxially compacted in a cylindrical die ($\varnothing = 14\text{mm}$) using a pressure of 300 MPa. Densities of the green pellets were measured by weight and dimensions measurements. Combustion reactions were conducted on a tubular resistive furnace under vacuum (thermal explosion mode), which was done in a quartz tube. For measuring ignition and combustion (maximum) temperatures, a type S thermocouple was inserted in a small hole drilled into the pellets along the cylindrical axis. The heating cycle consisted of an initial heating at $5^\circ\text{C}/\text{min}$ to 400°C for 4 hours (degassing step) [5,6] followed by heating at $30^\circ\text{C}/\text{min}$ to the ignition temperature. Pellets were allowed to cool inside the tube, which by its time were removed out of the furnace. Bulk density was measured by water immersion technique (Archimedes). The microstructure of the reacted pellets was characterized by X-ray diffraction and SEM analysis performed on polished cross-section areas.

Results and discussion

Figure 1 shows the microstructure of the as-milled powder mixtures. White areas denote niobium particles while dark gray areas denote aluminum particles. Eventually some inclusion from the milling media can be present, as seen in the Fig. Two main aspects can be noticed. The first one is that there is an increased refinement of the Nb/Al layers of the aggregates (composite particle) as aluminum content is lowered. Aluminum is more ductile than niobium, absorbing more impact energy from the balls to deform plastically. So as the volumetric fraction of the aluminum is lowered more energy from the balls can be transferred to the niobium layers (or particles), diminishing its thickness and increasing the interface area. The second aspect is related to the homogeneity degree of the aggregates. Nb80Al mixtures show a lot of niobium particles not associated with aluminum (better viewed at low magnification in Fig.1), having aggregates constituted mostly of aluminum. As aluminum content is lowered, the isolated niobium particles are rarely seen and more homogeneous become the aggregates. Both aspects indicate different stages of milling, according to the analysis of Benjamin and Volin [10], in spite of the same milling time. More advanced stages are attained by the lower aluminum content mixtures.

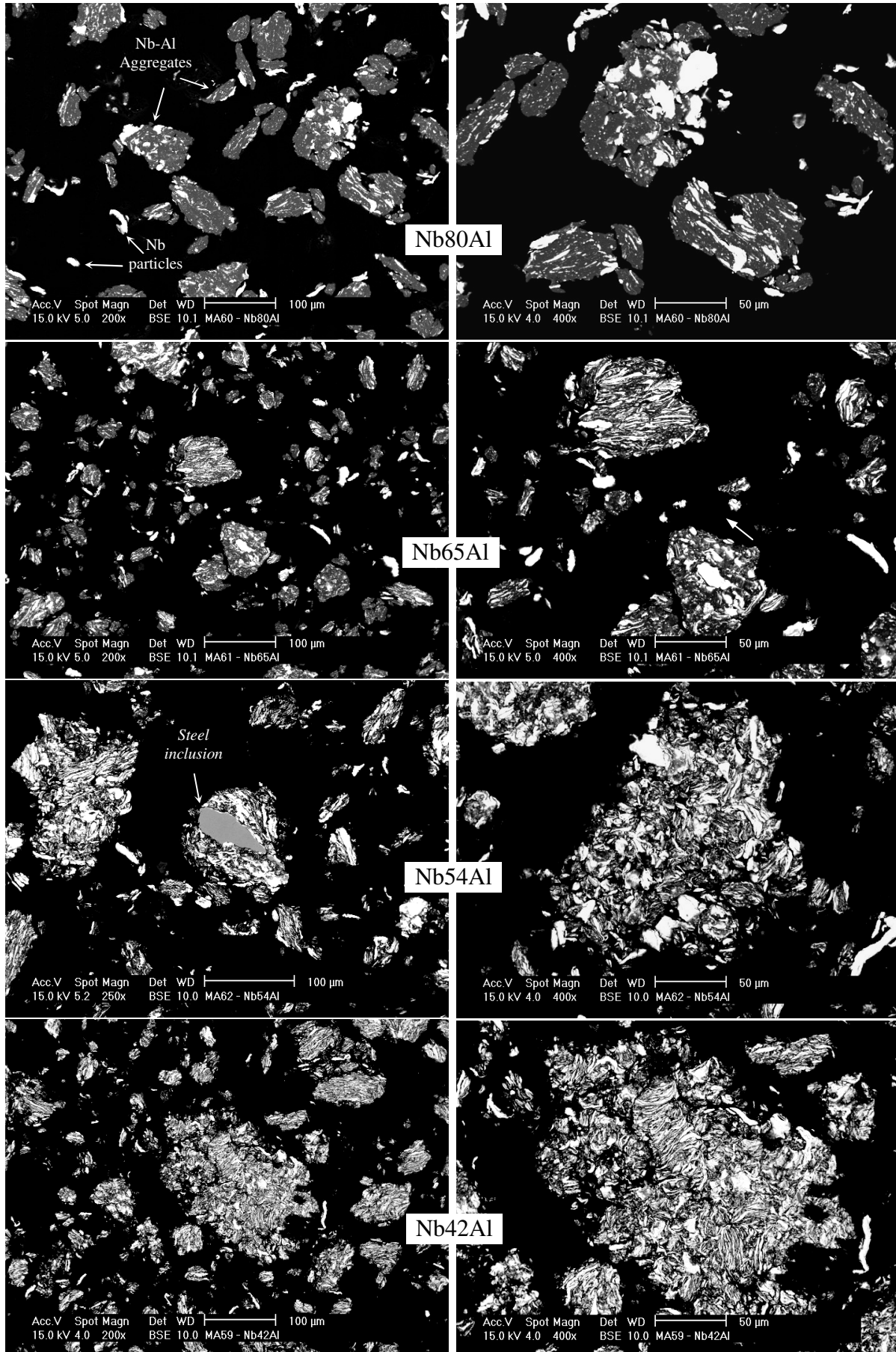


Fig. 1 – SEM micrographs (back-scattered electrons) of milled mixtures of different compositions: left column - lower magnification; right column - higher magnification.

Table 1 shows the ignition and combustion temperatures, as well as the densities (before and after the reaction) of pellets from various mixtures. Densification (D) was calculated assuming the completeness of the reaction (as theoretical densities), which was not always true. So its value can have some uncertainty.

There is a slow decrease of the ignition temperatures as aluminum content is changed to lower values. Nb65Al, Nb54Al and Nb42Al mixtures were ignited temperatures lower than the melting point of aluminum. This can be explained based on microstructure of milled powders. Lower the aluminum content, higher the homogeneity degree and the interfacial area between niobium and aluminum layers, making ignition to start earlier. This effect is similar to the increase of the milling time at a fixed composition, as discussed in a previous paper [7]. Combustion temperatures also decreased in the same sense. For comparison purposes, Nb75Al mixtures were processed in a similar manner, igniting at 670°C and reaching about 1520°C. So, in spite of the same ignition temperature of the Nb80Al mixture, the combustion temperature was higher. The reason is that the Nb80Al sample has aluminum in excess for the reaction of NbAl₃ (Nb75Al), extracting heat from the reaction and impairing the rise of the overall pellet temperature. The decrease then observed as aluminum content is lowered up to 42 at.% is mainly due to an incomplete reaction as can be seen in micrographs of Figure 2.

Table 1- Green and after reaction densities, ignition and combustion temperatures (T_{ig} and T_c), and densification (D) of reacted pellets from investigated mixtures.

Composition	Theoretical Density (ρ_t) (g/cm ³)		Green Density (ρ_g)		T_{ig} range (°C)	T_c range (°C)	After Reaction Density (ρ_r)		$D = \left(\frac{\rho_r - \rho_g}{\rho_t - \rho_g} \right)$
	Mixture	Alloy	(g/cm ³)	% ρ_t			(g/cm ³)	% ρ_t	
Nb80Al	3,96	4,16	3,11 ± 0,02	78,5 ± 0,3	660 680	1150 1170	3,98 ± 0,01	95,7 ± 0,3	82,9 ± 1,7
Nb65Al	4,88	5,12	3,58 ± 0,04	73,2 ± 0,7	570 590	1090 1110	4,81 ± 0,11	93,9 ± 2,2	80,0 ± 6,9
Nb54Al	5,53	5,74	3,89 ± 0,01	70,4 ± 0,2	535 545	1030 1050	4,05 ± 0,02	70,5 ± 0,4	8,4 ± 1,9
Nb42Al	6,23	6,38	4,18 ± 0,02	67,0 ± 0,3	525 535	660 675	3,95 ± 0,05	61,8 ± 0,8	-10,4 ± 3,3

Complete or near-complete reaction was observed only at Nb80Al (this work) and Nb75Al compositions (see ref. 7). At Nb80Al pellet small niobium-rich phase can be found inside NbAl₃ grains. Despite the aluminum excess, the growth of NbAl₃ at the surface of niobium particle impaired the contact with liquid aluminum. The aluminum diffusion was slowed due to the low combustion temperature. Pellets from the other compositions show non-reacted niobium regions. Non-reacted niobium was seen to increase with niobium content, so it is the major phase at Nb42Al composition, as verified by X-ray analysis (Table 2). The microstructure of the Nb65Al pellet clearly evidences a liquid phase formation (Nb₂Al- NbAl₃ eutectic) around NbAl₃ globular grains. As combustion temperature was about 1100°C, this eutectic phase was formed below the eutectic

reaction temperature indicated in the Nb-Al equilibrium phase diagram [11]. So, despite the reaction has been started by solid-state diffusion of aluminum into niobium particles (layers), exothermal heat from NbAl_3 growing nucleus was high enough in this case to rise the temperature in the neighborhoods and melts the remaining aluminum, not initially consumed by the reaction. The mechanism that explains the presence of a eutectic phase, knowing the combustion temperature is 1100°C , is not clear. Nb_2Al was also formed by solid-state diffusion between NbAl_3 and Nb particles in the absence of free aluminum, as evidenced in the microstructures of Nb54Al and Nb42Al samples. In both of them one can see the lamellar structure that characterizes the as-milled state.

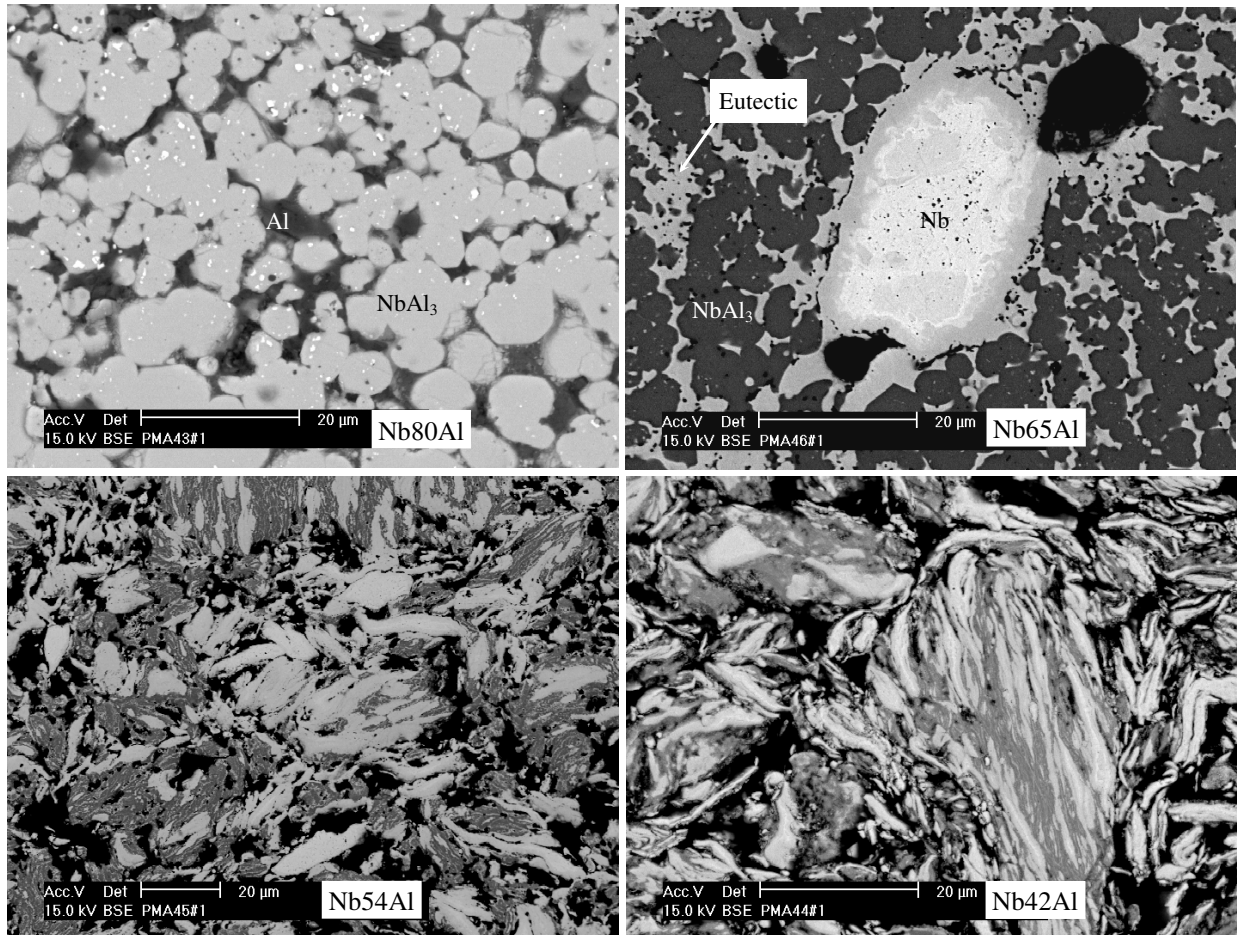


Figure 2 – SEM micrographs (backscattered electrons) of polished sections of the reacted pellets. Starting mixture compositions are indicated on the micrographs.

Table 2 – Results from X-ray diffraction analysis

Composition	Detected Phases		
	Major Phase	Secondary Phase	Minor Phase
Nb80Al	NbAl_3	Al	----
Nb65Al	NbAl_3	Nb_2Al	Nb
Nb54Al	NbAl_3	Nb_2Al , Nb	----
Nb42Al	Nb	NbAl_3 and Nb_2Al	----

Densification is relatively high at Nb80Al and Nb65Al compositions, decreasing drastically in the cases that there is no evidence of liquid formation, as in Nb54Al and Nb42Al pellets. In the later the pellets swelled (negative densification), as a result of solid-state diffusion combined with very low combustion temperature.

Final Comments

As previously observed for Nb75Al mixtures, mechanical activation caused a decrease of ignition temperatures of the mixtures from Nb80Al to Nb42Al. This decrease was seen however to be higher as aluminum content was lowered, which is a consequence of the refinement and homogeneity degree attained during milling. Reaction mechanism depends on the ignition temperature (higher or lower than aluminum melting) and very probably on the heating rate not varied here. More work is needed in order to understand this mechanism, which will be covered by future papers.

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