



Synthesis of niobium aluminides using mechanically activated self-propagating high-temperature synthesis and mechanically activated annealing process

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Abstract

The mechanically activated self-propagating high-temperature synthesis (MASHS) technique and the mechanically activated annealing process (M2AP) were used to produce NbAl₃ intermetallic compound. The MASHS process results from the combination of two steps: first, a mechanical activation of the Nb + 3Al powders mixture; second, a self-propagating high-temperature synthesis (SHS). The M2AP process also results from the combination of two steps: the first is the same; the second consists of the annealing of as-milled powders. Based on X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDXS), the as-milled powders, MASHS, and M2AP end-products were characterized. Various process controlling parameters such as mechanical activation milling conditions have been studied. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Intermetallic compounds occupy a prominent position among advanced materials owing to their exceptional properties. These include high melting point, ordered nature which imparts high specific strengths at high homologous temperature. These properties make them attractive candidates for many applications, especially, in the aerospace and chemical industries. In addition, many of these ordered intermetallic compounds have a positive temperature coefficient of yield strength, i.e. their strength increases with increasing temperature, at least over a wide temperature range which makes them more attractive for high temperature applications.

Niobium aluminides are of considerable interest as candidate materials exhibiting good resistance to both

high temperature sulfidation and oxidation, since they are expected to form protective scales such as niobium sulfide scales by sulfidation and alumina scales by oxidation [1]. Moreover, these aluminides appear to have the potential for high temperature structural applications because of their relatively high melting point, low density and large ductility or toughness. However, cold working of these materials is limited because they are brittle, will fracture and have low ductility at room temperature [2]. So, their processing is quite difficult and has restricted their commercial exploitation to a large extent. Nevertheless, in recent years, studies on nanocrystalline materials have shown that ceramics which are usually brittle, become ductile in nanocrystalline state. Thus the formability of intermetallic compounds is expected to improve greatly if they are produced in the nanocrystalline state.

Three methods are generally used to produce niobium aluminides: conventional melting/casting [3], powder metallurgy [4,5] and combustion synthesis [6]. The

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synthesis of intermetallic compounds by the conventional ingot metallurgy route, in many cases, has faced problems due to the large differences in the melting points and densities of their constituent elements and also due to the stoichiometry. Recent studies [4,5] have shown that these problems can be overcome by synthesizing these compounds using a mechanical alloying technique in which elemental or prealloyed powders are milled in high energy ball mills. This is a solid state process which is suitable for the production of segregation free materials with a very fine microstructure. Peng et al. [4] have successfully synthesized niobium aluminides using ball milling from elemental niobium and aluminum powders. However, such powders are quite abrasive materials and the long duration milling leads to contamination of the end-product by the mill and balls. Due to the limitations of these classical synthesis, some other methods have been investigated to produce Nb–Al intermetallic compounds.

Recently, an alternative method to synthesize molybdenum disilicide powders, named the mechanically activated annealing process (M2AP) was proposed by Gaffet et al. [7]. Such a solid state process combines a short duration high energy ball milling and a relatively low temperature isothermal annealing. Gaffet et al. [8] reported on the possibility to obtain pure nanocrystalline MoSi₂ after 2 h of mechanical treatment followed by an annealing of 2 h at 800°C. An other well known route to produce massive niobium aluminides [6] consists in using the exothermicity of their formation reaction ($-33 < \Delta H_{298} < -19$ kJ mol⁻¹ depending on the niobium aluminide concerned [4]). This technique has received a wide attention and is called self-propagating high-temperature synthesis (SHS). The exothermic reaction between reactant powders is initiated by an external heat source and becomes self-sustaining to yield the final product, without requiring additional energy. The SHS process saves time and energy since this processing time technique is in seconds or minutes compared with hours or days for conventional or powder metallurgy routes. Recently, a new variation of the SHS process was proposed by Gaffet et al. [9,10]: the mechanically activated self-propagating high-temperature synthesis (MASHS). This process is the combination of two steps: the first is a mechanical activation where pure elemental powders are co-milled for a short time at given energy and frequency of shocks; second is a SHS reaction. This process was firstly applied with success to elaborate nanocrystalline (30–35 nm) bulk FeAl intermetallic with a relative density close to 80% [10].

In this work, we have focused on the NbAl₃ compound synthesis. This intermetallic compound, with a melting point of 1680°C, might be suitable for use at temperatures around 1300°C and, its relatively low density (4.54 g cm⁻³) makes it advantageous over

superalloys and intermetallics of comparable melting temperatures. NbAl₃ is one of the three compounds in the Nb/Al system [11]. We have used both MASHS and M2AP processes to synthesize this niobium aluminide. The MASHS process leads to bulk, but porous NbAl₃, which might exhibit good mechanical properties due to the nanometric grain size resulting from the mechanical activation step. On the contrary, the M2AP process produces microcrystalline NbAl₃ powder. Various parameters of the MASHS process have been studied:

1. The mechanical activation effect: a comparison between Nb/Al powder just blended in a mixer or mechanically activated was performed.
2. The mechanical activation conditions: two milling conditions have been selected, the friction mode or direct shock mode.

The mechanical activation conditions were also studied for NbAl₃ synthesis by M2AP process and results were compared.

2. Experimental procedure

2.1. First step: mechanical activation

Two Nb + 3Al mixture preparation modes were performed to study the ball milling influence on the SHS process:

1. Nb + 3Al non-activated powder mixture, but just blended in a Turbula[®] mixer¹ for 4 h;
2. Nb + 3Al powder mechanically activated in the following conditions: pure elemental niobium (325 mesh) and aluminum (325 mesh) powders were sealed in 45 ml stainless steel vials with four stainless steel balls (15 mm in diameter, 14 g in weight) under enclosed air. The ball to powder mass ratio was 6:1. Mechanical activation treatment was performed using a specially designed planetary ball mill (called G5) which allows shock frequency and shock energy to be selected independently [12]. The physical parameters [13] of this machine are as follows: vials are fixed onto a rotating disc (rotation speed Ω) and rotate in the opposite direction to the disc with a speed ω . The Ω and ω values are checked and controlled by an ultrasonic tachometer. The milling duration process over the range 1–4 h was chosen to avoid the formation of some intermetallic fractions, but to allow the formation of a chemical gradient at a nanoscale. Hereafter, mechanically activated powders will be labeled G5/ Ω/ω /milling time. Two milling conditions were selected, the first one G5/150/200/4 h corresponding to direct shock mode and the other G5/150/400/4 h to a friction mode.

¹ Turbula[®], Schatz system made by W.A. Bachofen firm, Basel

2.2. Second step: reactive annealing or SHS reaction

2.2.1. Reactive annealing

The particles resulting from 2 and 4 h ball milling, both corresponding to friction and direct shock mode, were annealed at $T = 600^\circ\text{C}$ under vacuum ($P(\text{O}_2) = 4 \times 10^{-4}$ Pa), for one week. The annealing temperature is below the aluminum melting point allowing a solid–solid state reaction.

2.2.2. Self-propagating high-temperature synthesis reaction

After extraction from milling vials, powder mixtures have been cold-compacted into cylindrical vials using an uniaxial charge of 250 MPa for 30 s. After compaction, samples were brittle and measured 8 mm in diameter. Their density was evaluated from weight and geometric measurements. Then, these cylindrical green materials were placed on a heating sample holder to initiate the SHS intermetallic phase formation reaction. Depending on the sample milling conditions, the temperature of the heating substrate has been increased from 800 to 1050°C to initiate the SHS reaction. Thermal analyses were carried out using a chromel–alumel thermocouple which had been embedded during compaction of the Nb/Al samples.

2.3. Structural and morphological characterization

X-ray diffraction (XRD) analyses were performed using a diffractometer fitted out with a curve detector (INEL CPS 120). Monochromatic $\text{CuK}\alpha_1$ X-ray ($\lambda = 0.15406$ nm) was focused with a Ge monochromator. Pattern decomposition was carried out by means of the profile-fitting program PROFILE² to obtain parameters defining the position, height, area, integral breadth and shape of individual Bragg reflections.

Particles size and microstructure of as-milled powders and M2AP end-products were studied by scanning electron microscopy (SEM) and local phase composition was determined by energy dispersive X-ray spectrometry (EDXS). A back scattered electron (BSE) study has also been performed to determine the element distribution: the white areas corresponding to a high average atomic number were identified as niobium areas whereas the black ones were related to aluminum rich zones. These experiments were conducted using a JEOL 6400F scanning electron microscope fitted with LINK OXFORD energy dispersive X-ray analyzer. Moreover, a krypton BET method was used to determine the specific area of G5/150/200/1, 2, 4 h mechanically activated mixtures. The porosity of the different MASHS end-products has also been measured by He and Hg pycnometry.

3. Results and discussion

3.1. Characterization of non-activated and as-milled powder mixtures

The microstructure of as-milled powders in terms of crystallite size and morphology (size of a region over which the diffraction is coherent) and imperfections (microstrains, stacking faults, etc.) was studied using the XRD profile analysis described by Langford [14]. The procedure for carrying out this, by means of the Voigt function, is as follows: (i) check that the Voigt function is appropriate to analyse peak breadths, then examine the shape factor to determine the Lorentzian/Gaussian character, (ii) correct data from instrumental effects, (iii) make Williamson–Hall plot ($\beta^* = \beta \cos\theta/\lambda$ is plotted as a function of $d^* = 2\sin\theta/\lambda$) to be certain of the nature of the sample broadening and to precise the $[hkl]$ dependence of peak breadths, (iv) carry out a detailed analysis of peak breadths in accordance with the information from step (i).

From Williamson–Hall aluminum plots, it was evident that the peak broadening was essentially isotropic. On the contrary, the niobium integral breadths had a $[hkl]$ dependence of both size broadening (irregular shape and size distribution among crystallites) and strain broadening.

Concerning aluminum, profiles were modeled by the symmetric pseudo-Voigt function. For most of these profiles, the mixing factor was smaller than 1 (corresponding to the Lorentzian limit of the pseudo-Voigt function) indicating that the profile shape was mainly Voigtian. Therefore, Halder–Wagner plots [15] were used to determine the mean apparent crystallite size and lattice strains. The Turbula mixture exhibits an anisotropic size and strain broadening; moreover, the aluminum crystallite size is higher than the XRD detection limit (> 400 nm). Thus, neither strain level nor crystallite size evaluation were achieved by the Halder–Wagner method. Mechanically activated powders evidenced an isotropic behavior allowing to obtain the aluminum average crystallite size and distortion level by the Halder–Wagner method. Various short duration millings (1, 2, 4 h) were investigated both for friction and shock modes, to be sure there was no NbAl_3 formation by direct mechanical alloying. Whatever the mechanically activated conditions, milling time and activation mode, no intermetallic compound was detected. Fig. 1 shows the XRD pattern of the Nb + 3Al mixture milled in shock mode for different milling times. As it can be seen on Fig. 2a, the aluminum crystallite size is decreasing for the both milling modes, when the milling time increases from 1 to 4 h. After 4 h of milling, aluminum crystallite size is about 83 and 90 nm for shock and friction modes, respectively. Independent of the milling conditions, the aluminum strain level is very weak, about 6×10^{-4} .

² Available in the Socabim PC software package DIFFRACT-AT supplied by Siemens.

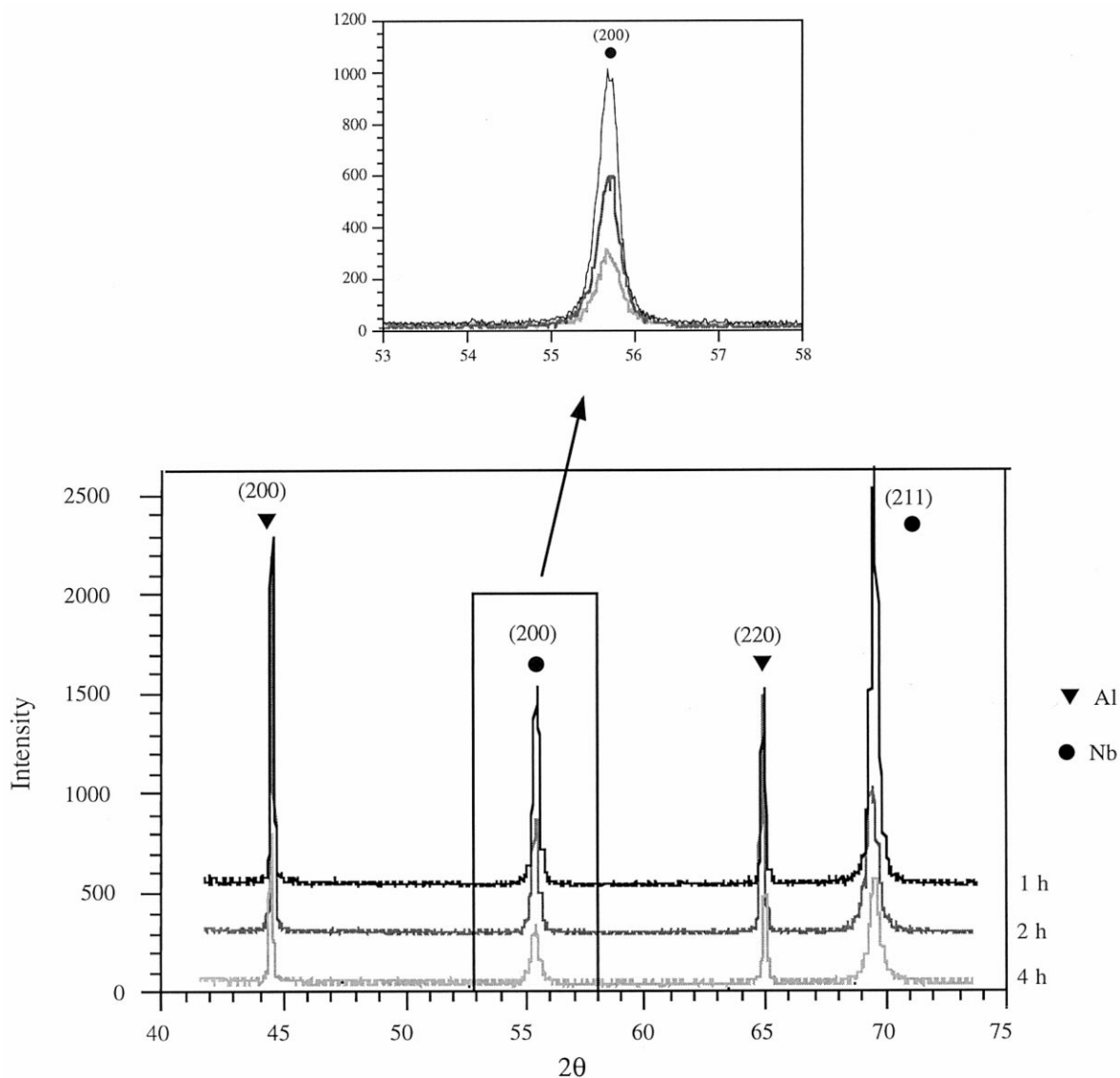
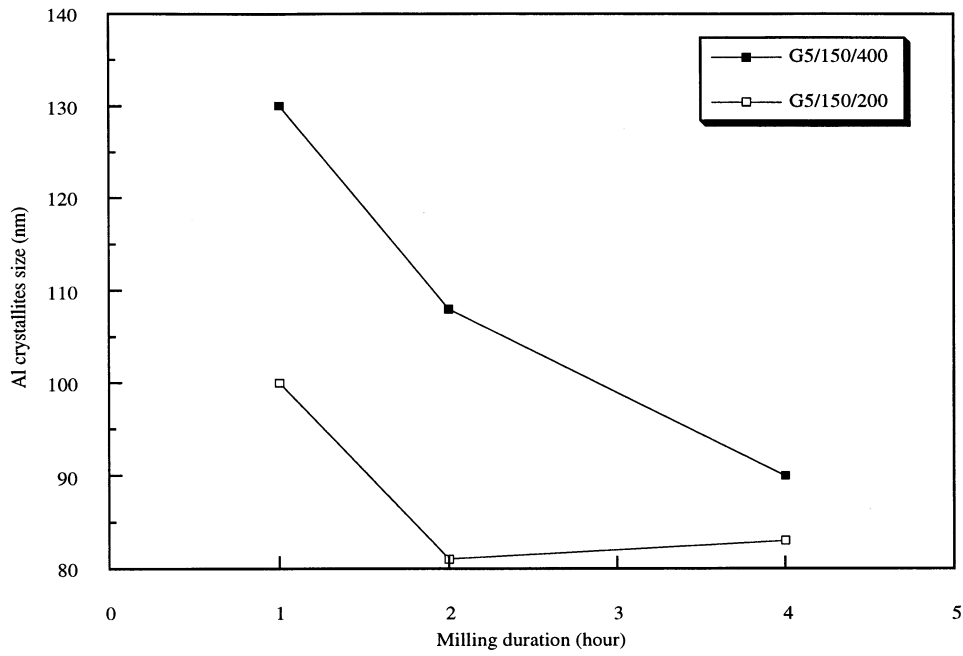


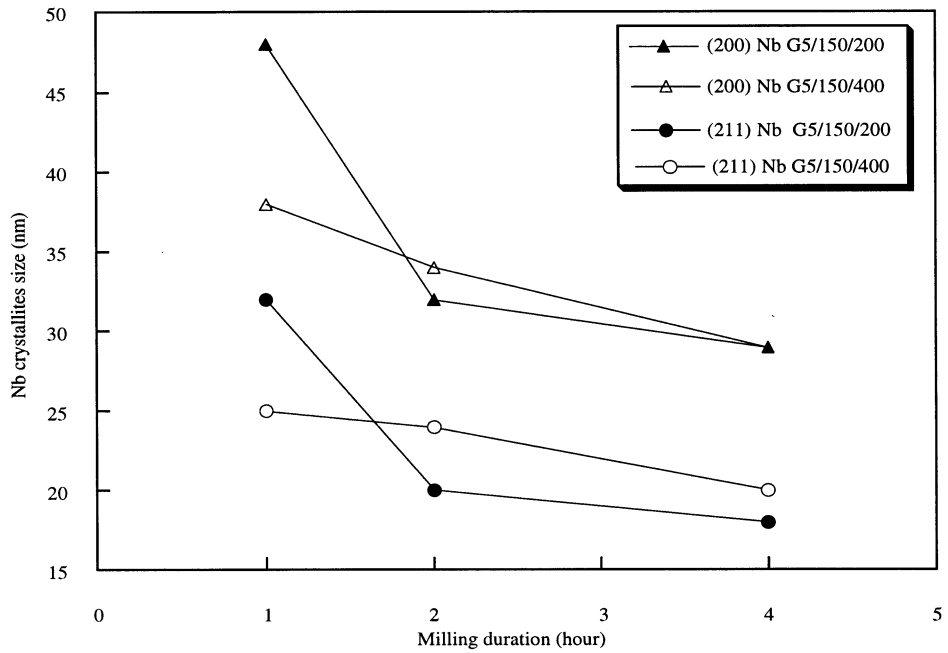
Fig. 1. XRD patterns of an Nb + 3Al mechanically activated mixture using shock mode for different milling times (1, 2 and 4 h).

Concerning niobium, non-activated and mechanically activated Nb + 3Al powder mixtures showed an anisotropic size and a strain broadening. Consequently, it was not possible to determine the average crystallite size and strain level using the Halder–Wagner method. Thus, to overcome this anisotropy problem, we used the single-line method proposed by De Keijsers et al. [14]: this approach is applied to each line separately in order to extract information on crystallite size and microstrain. It is assumed that the Lorentzian contribution in the pseudo-Voigtian breadth is only due to the size effect whereas the Gaussian one is attributed to the strain effect. Niobium anisotropic behavior mentioned above brings us to investigate each line profile separately. In this study, we were interested on the 200 and 211 Bragg reflections. Fig. 2b shows the niobium crystallite sizes resulting from the 200 and 211 peaks using

De Keijsers's method, for both milling modes at different milling times. Firstly, it can be seen that whatever the milling mode and the Bragg reflection, the longer the milling time, the smaller the crystallite size; this is in agreement with the rise of the 200 niobium peak full width at half maximum (FWHM) as shown on Fig. 1, observed when the mechanical activation time increases relative to the shock mode; second, for a definite milling mode, the crystallite sizes resulting from the 200 reflection is higher than for the 211 and they both decrease as the milling time increases; third for a definite Bragg reflection (200 or 211), crystallite size is higher after 1 h milling with the shock mode activation than with friction activation. After 4 h of milling, it becomes equivalent: 30 and 20 nm for the 200 and 211 Bragg reflections, respectively. In the same time, whatever the milling mode, the strain level increases versus milling



a



b

Fig. 2. (a) Aluminum crystallite sizes from Halder–Wagner analysis of the XRD patterns: comparison between the mechanical activation modes for different milling times. (b) Niobium crystallite sizes from 200 and 211 De Keijser analysis of the XRD patterns: comparison between the mechanical activation modes for different milling times.

time and is about 3×10^{-3} (instead of 1.5×10^{-3} for a non-activated powder) after 4 h of milling. Fig. 3 which compares an XRD pattern of an activated powder (G5/150/200/4 h) with an XRD pattern of a non-activated powder, displays a modification of the peak

intensity and shape in the case of as-milled powders. This is due to the decrease in crystallite size and the increase in residual lattice distortion during the mechanical activation process. The niobium crystallite sizes obtained after the Turbula process are about 123

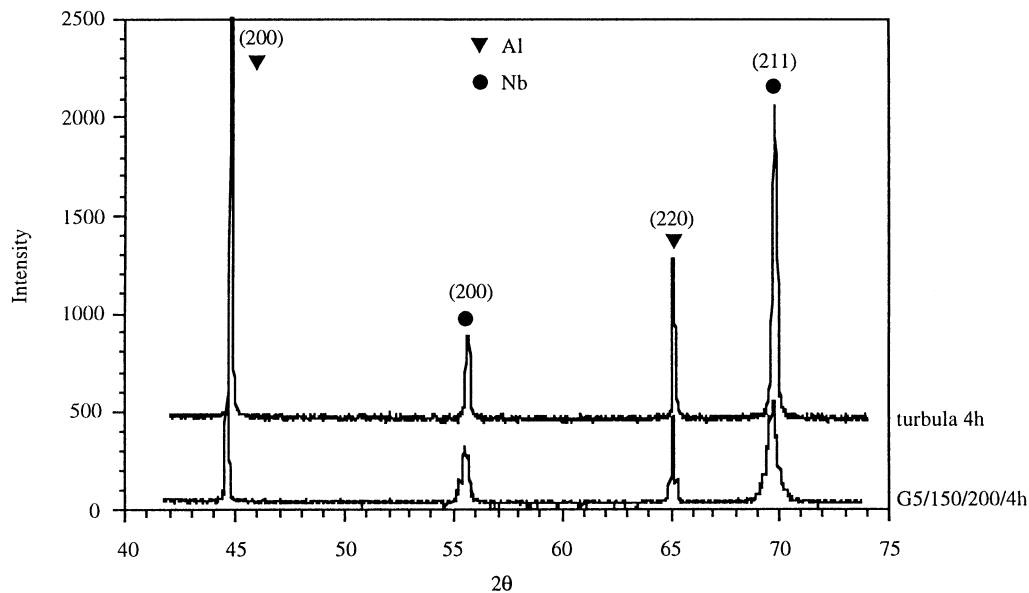


Fig. 3. Nb + 3Al mixture XRD patterns: comparison between mechanically activated mixture and Turbula.

and 71 nm for the 200 and 211 Bragg reflections, respectively.

Contamination by the milling vials or by the stainless steel balls used during the mechanical activation process, was evaluated by EDX micro-analysis. There was no contamination since neither chromium nor iron was detected. Indeed, in the case of such powders which are quite abrasive materials, the short duration of milling avoids the contamination of the end-product by the milling vials and balls.

SEM observations show that ball milling induces the formation of aggregates because a fracture-welding mechanism occurs during the mechanical activation process. A BSE study was performed on G5/150/200/1, 2, 4 h mixtures (Fig. 4): after 1 h milling (Fig. 4a), we can observe 50 μm individual niobium and aluminum particles; the last ones contain small amounts of niobium. After 2 and 4 h milling (Fig. 4b and c, respectively), there are no more elemental niobium and aluminum particles: niobium particles seem to be located as inclusions, inside aluminum aggregates to form agglomerates including both niobium and aluminum. This agglomerate size is respectively about 100–200 μm and 500–600 μm after 2 and 4 h milling. These observations are in agreement with BET measurements for which specific surface decreases from 0.111 to 0.036 $\text{m}^2 \text{g}^{-1}$ as the milling time increases from 2 to 4 h. Moreover, after 4 h milling, the agglomerates size is higher for the shock mode (Fig. 4c) than for the friction one (Fig. 5) and niobium is much more well-distributed with the shock mode, promoting larger Nb–Al interface areas.

In summary, on the basis of the SEM and XRD investigations, the structure of as-milled powders may

be considered micrometric agglomerates composed of niobium and aluminum nanometric crystallites, without NbAl₃ intermetallic compounds formation.

3.2. Characterization of the mechanically activated annealing process end-products

The end-products relative to the isothermal annealing corresponding both to the friction and direct shock modes have been studied by XRD. Concerning G5/150/400/2 h and G5/150/200/2 h ball-milling conditions, the annealing treatment induces the formation of NbAl₃ traces together with many oxides (niobium and aluminum oxides) and it remains unreacted niobium and aluminum. The annealing time (one week) and temperature (600°C) lead to nearly complete reaction in the case of G5/150/200/4 h since the main phase detected is NbAl₃. On the contrary, the annealing treatment is less efficient for the G5/150/400/4 h condition since unreacted niobium and aluminum remains beside the NbAl₃ phase (Fig. 6).

In order to determine the microstructure of the NbAl₃ obtained by M2AP (in the case of G5/150/200/4 h ball milling condition), the XRD profile analysis previously described was carried out. Profiles were modeled by symmetric pseudo-Voigt function and the Voigt approach was consequently applied for these compounds. The Halder–Wagner plots indicate that the size of the coherent diffraction domain is close to 150–200 nm and no significant microstrains were observed.

The XRD phase identifications are in agreement with previous SEM observations (Fig. 4c and Fig. 5) exhibiting larger Nb–Al interfaces areas with the shock mode

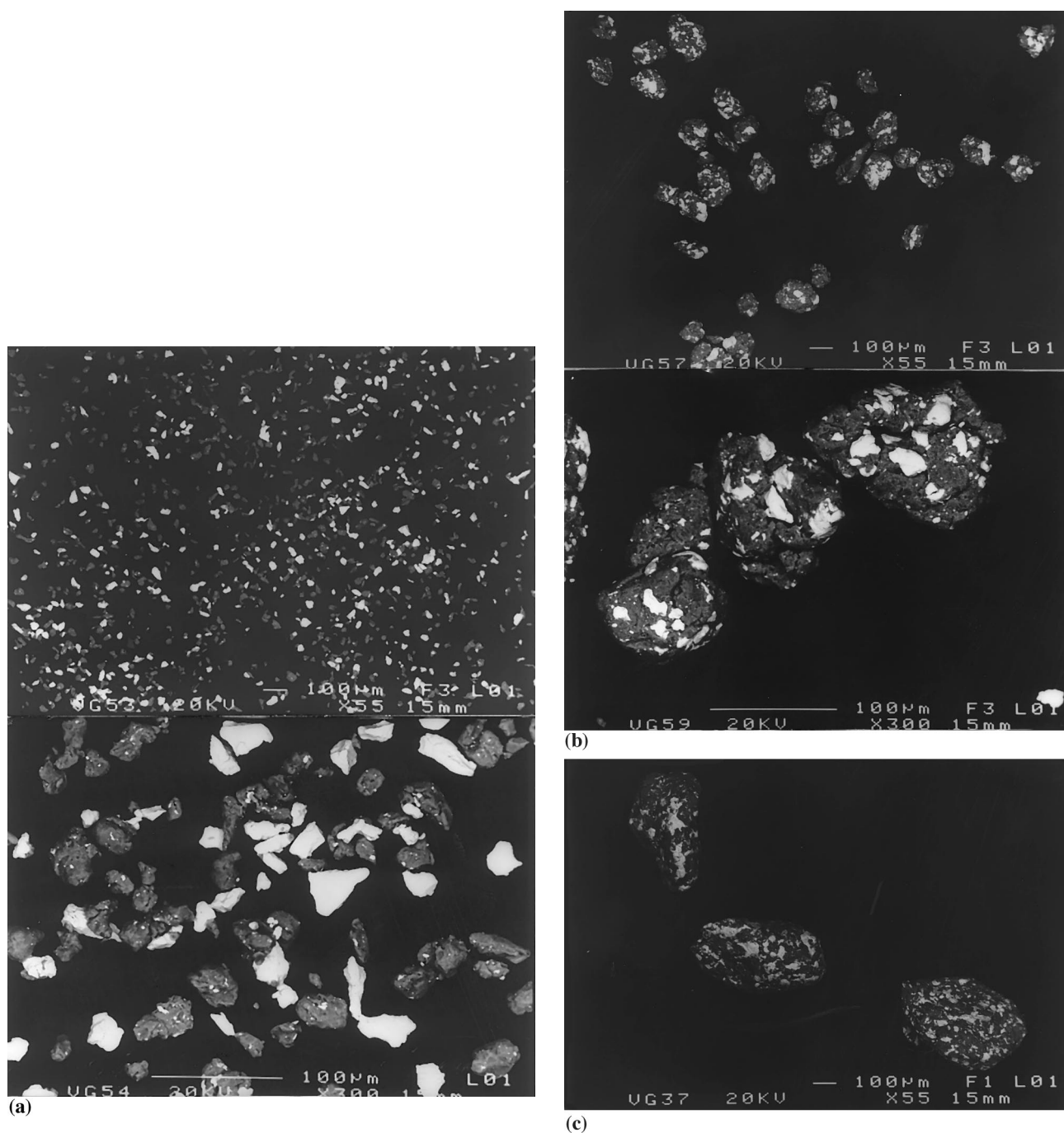


Fig. 4. BSE images of as-milled powders for G5/150/200 activation conditions for different milling times: (a) 1 h; (b) 2 h; and (c) 4 h.

and consequently an easier NbAl_3 formation. Annealed particles have been observed by SEM on their surface and also on their cross-section after embedding in resin and polishing (Fig. 7). For both milling modes, SEM observations are in agreement with XRD investigations: for G5/150/400/4 h annealed particles (Fig. 7a), BSE images reveal the presence of black, white and gray areas corresponding respectively to aluminum, niobium and NbAl_3 phases. For G5/150/200/4 h annealed parti-

cles (Fig. 7b), it can be mainly seen gray zones corresponding to the NbAl_3 phase. Thus, it can be concluded that milling conditions, specifically milling time and mode, are important parameters controlling the annealing treatment efficiency. Indeed, a mechanical activation applied to a $\text{Nb} + 3\text{Al}$ powder mixture using the direct shock mode for 4 h seems to define the best condition to obtain the NbAl_3 single phase after an isothermal annealing treatment.

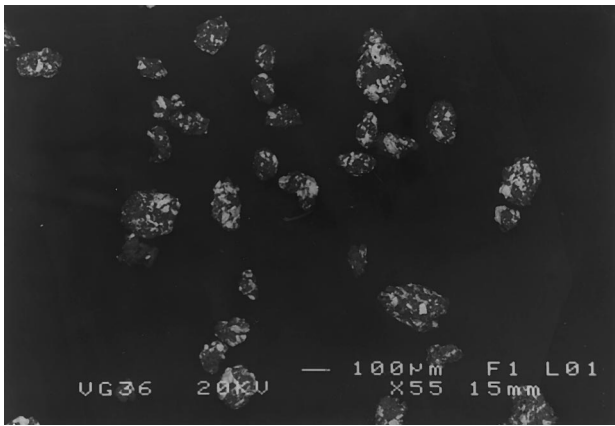


Fig. 5. BSE images of as-milled powders for G5/150/400/4 h activation conditions.

3.3. Characterization of the mechanically activated self-propagating high-temperature synthesis end-products

The SHS reaction carried out on the Nb + 3Al Turbula mixture, formed NbAl₃ together with many oxides because the exothermic reaction between powder reactants took place in air and was long and difficult to initiate. SHS reaction applied to the G5/150/400/4 h (Fig. 8) and G5/150/200/4 h (Fig. 9) as-milled powders leads to the formation of a majority of NbAl₃ and a small amount of Nb₂Al. Nevertheless, it is difficult to estimate the amount of NbAl₃ in comparison with the amount of Nb₂Al because of the preferential orientation existence. The NbAl₃ microstructure characterized in terms of size and microstrains by XRD according to the previous procedure shows that the integral breadth of NbAl₃ had a $[hkl]$ dependence of the size broadening. In a first approximation, the De Keijsjer method

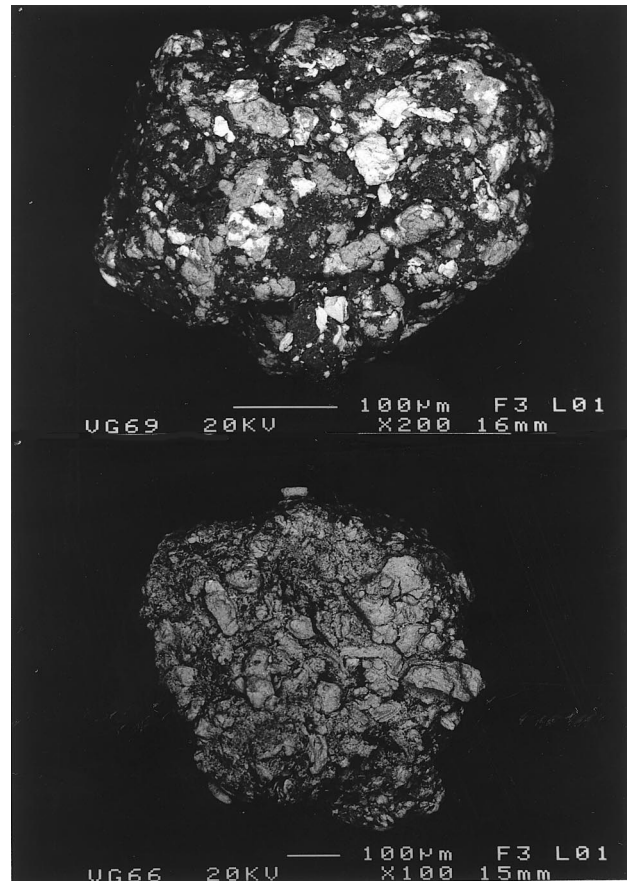


Fig. 7. BSE images of M2AP end-products for different mechanical activation conditions: (a) G5/150/400/4 h; (b) G5/150/200/4 h.

shows three main groups of reflection, namely $[00l]$, $[h00]$ and $[h0l]$, having different nanometric crystallite sizes. This suggests a crystallite shape which could be prismatic since the following order is observed: size $[h00] >$ size $[00l] >$ size $[h0l]$. According to the symme-

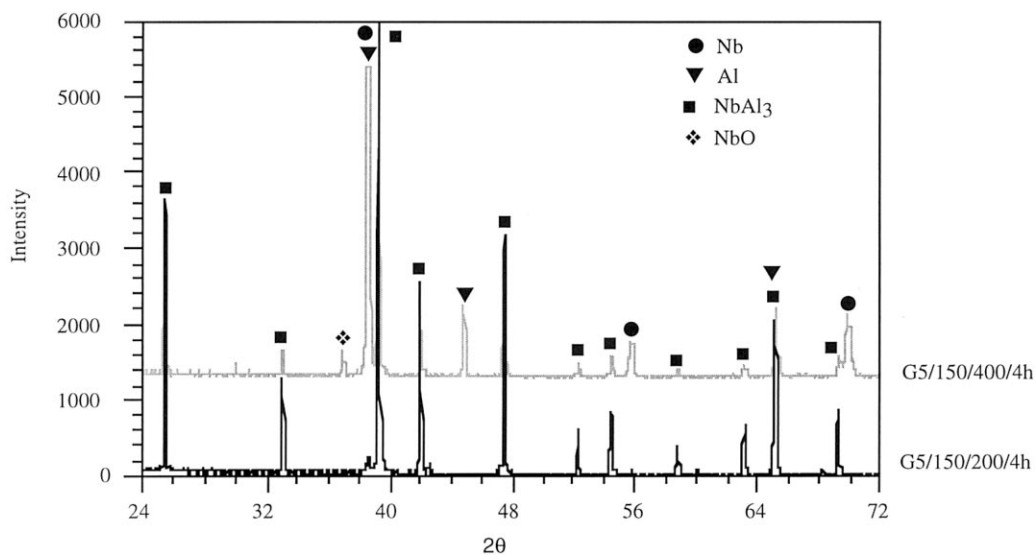


Fig. 6. Activation mode effect on the M2AP end-products in the same annealing conditions.

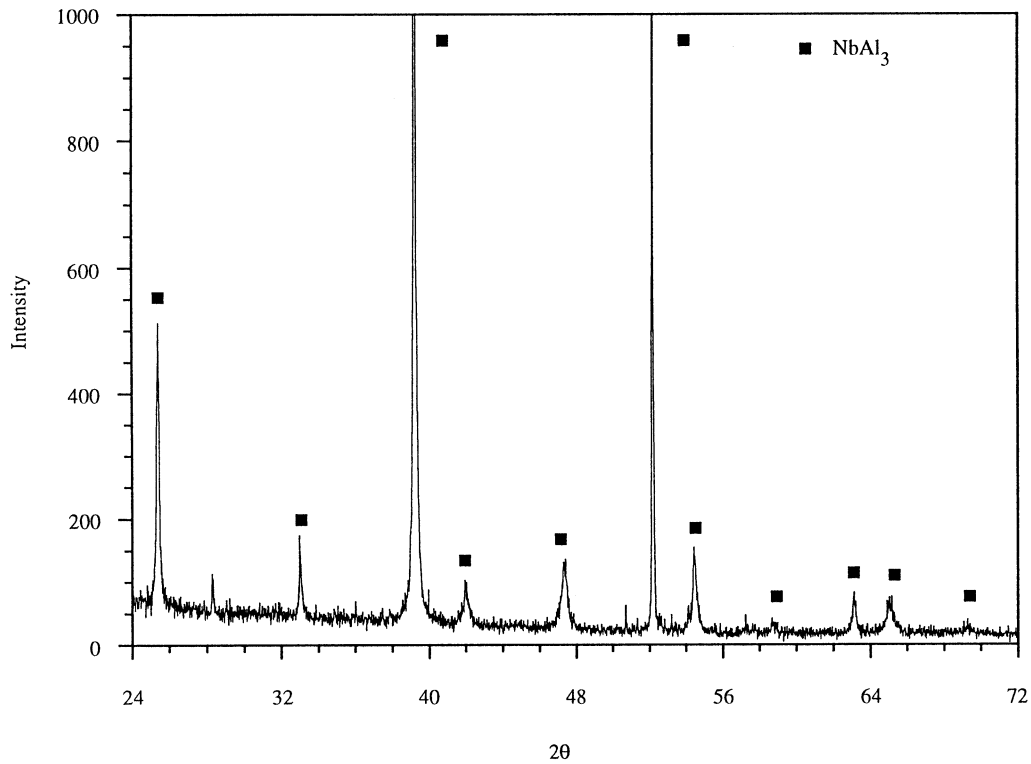


Fig. 8. MASHS end-product XRD pattern relative to an Nb + 3Al mixture mechanically activated in friction mode.

try of NbAl₃, an average cylindrical shape can reasonably be assumed. So, to confirm this result, it will be essential to determine microstructural parameters using the Fourier analysis in reference with Louër et al. works [16].

Temperature profiles corresponding to the different milling conditions and obtained during NbAl₃ formation are shown in Fig. 10. These thermograms monitored during NbAl₃ synthesis are in agreement with those which were observed by Kachelmyer et al. [6]. As the sample is heated, the temperature increases up to the aluminum melting point (647–650°C). That is indicated by a plateau in the temperature profile. During this time of melting, heating is continued. After the aluminum melting completion, samples continue to heat up to the ignition temperature (793, 842 and 1044°C for 150/400/4 h, 150/200/4 h ball milling conditions, and non-activated powders, respectively), where the temperature increases sharply to the combustion temperature. Combustion temperature could not be evaluated because chromel–alumel thermocouples melt above 1350°C. Heating is shut off once the samples ignite. The results related to the different temperature profiles are summarized in Table 1. From it, different features can be shown: the mechanical activation step introduced to the SHS process for both modes significantly decreases the melting time, the ignition time and the ignition temperature (about 200°C) and increases the heating speed from melting to ignition temperature

in comparison with the classical SHS process (Turbula). The time between the end of aluminum melting and the ignition temperature is labelled ‘ignition time’ and is shown along with the melting time in Fig. 10.

According to Kachelmyer et al. [6], it was found that the fraction of molten aluminum in the sample after the melting (i.e. at the end of the temperature plateau) was approximated by a heat balance given as follows:

$$\frac{dT}{dt} m C_p t_m = L_m m_{Al} x \quad (1)$$

where dT/dt is the heating rate, m is the mass of mixture, C_p is the effective heat capacity of the mixture, t_m is the melting time, L_m is the latent heat of fusion of Al, m_{Al} is the mass of Al, and x is the fraction of molten Al. Thus, the shorter melting time, associated to the mechanically activated (Nb + 3Al) pellets can be attributed to a modification of the thermodynamic situation by changing the energy in the system before combustion synthesis. Indeed, some authors [17] reported that the stored enthalpy during ball milling of iron elemental powders can reach 5–10 kJ mol⁻¹ (15–20% of ΔH fusion) due to the increase of interface area during mechanical activation. Thus, the latent heat of fusion is decreased by mechanical activation and therefore the melting time must decrease to respect the balance of Eq. (1).

Since the melting time decreased with the mechanical activation, the subsequent time required to reach the

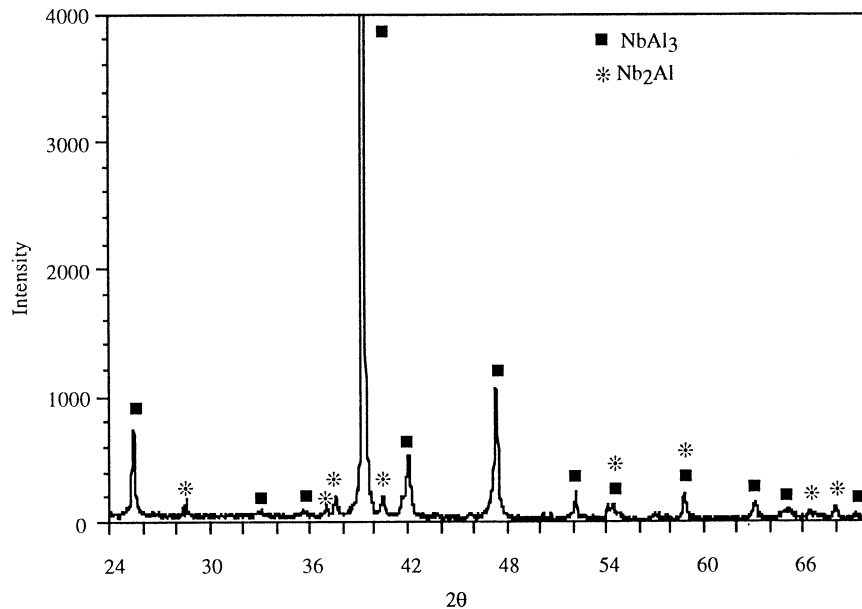


Fig. 9. MASHS end-product XRD pattern relative to an Nb + 3Al mixture mechanically activated in shock mode.

ignition temperature decreased. Finally, the effect of milling conditions on grain size and residual stress were reported to modify the phase transformation kinetics induced by the final SHS process. Indeed, this lower ignition time may be interpreted by the reduction of diffusion length after ball-milling due to the existence of three dimensional polyinterfaces on a nanometric scale [18]. Cardellini et al. [19] have observed similar phenomenon in NiAl systems.

The first MASHS milling step significantly decreases the ignition temperature (about 200°C) in comparison with the classical SHS process (Turbula). Same observations were given by Charlot et al. [10,20] concerning the synthesis of the FeAl intermetallic by MASHS. As reported in recent literature [21,22], short duration ball-milling before SHS is able to change the powder behavior during subsequent heat treatment. The niobium aluminides exothermic formation reaction is easier than that of a simple Turbula mix, due to the formation of three dimensional polyinterfaces between small crystallites of niobium and aluminum. This mechanical treatment before sample heating is able to destroy surface oxide layers on grains from commercial powders which

results in good contact between the surface of niobium and aluminum small crystallites inside as-milled powders. This finding leads us to believe that atom distribution inside as-milled powders is very close from niobium aluminide compounds like NbAl₃ and that the diffusion path is easier than for the Turbula mix. Moreover, it seems that the friction mode is more effective to activate the MASHS process. Indeed, such a mode has been shown to lower the ignition temperature.

After compaction, the green sample density evaluated from weight and geometric measurements was 80% of the theoretical density. The MASHS end-product density measured by He and Hg pycnometry was 60% of the theoretical density. This effect is due to the expansion of adsorbed gases in the sample. In relatively high density pellets, as the sample is heated, the passage of expanding contaminant gases is restricted due to the lower porosity. This leads to a lower density pellet. The similar experiment performed by Kachelmyer [6] showed that the pellet reacted under vacuum resulted in a higher product density than that reacted in an argon atmosphere. Thus, the vacuum aided in the evacuation of the gases both prior and during reaction.

Table 1

Temperature profiles parameters of the Nb+3Al mixtures: comparison between mechanically activated mixtures and Turbula

| | SHS | | |
|---|---------|----------------|----------------|
| | Turbula | G5/150/200/4 h | G5/150/400/4 h |
| Melting time (s) | 7 | 4.5 | 2.5 |
| Ignition time (s) | 8.5 | 2 | 1.5 |
| Ignition temperature (°C) | 1044 | 842 | 793 |
| Heating speed from melting to ignition temperatures (°C s ⁻¹) | 46.4 | 97.5 | 95.3 |

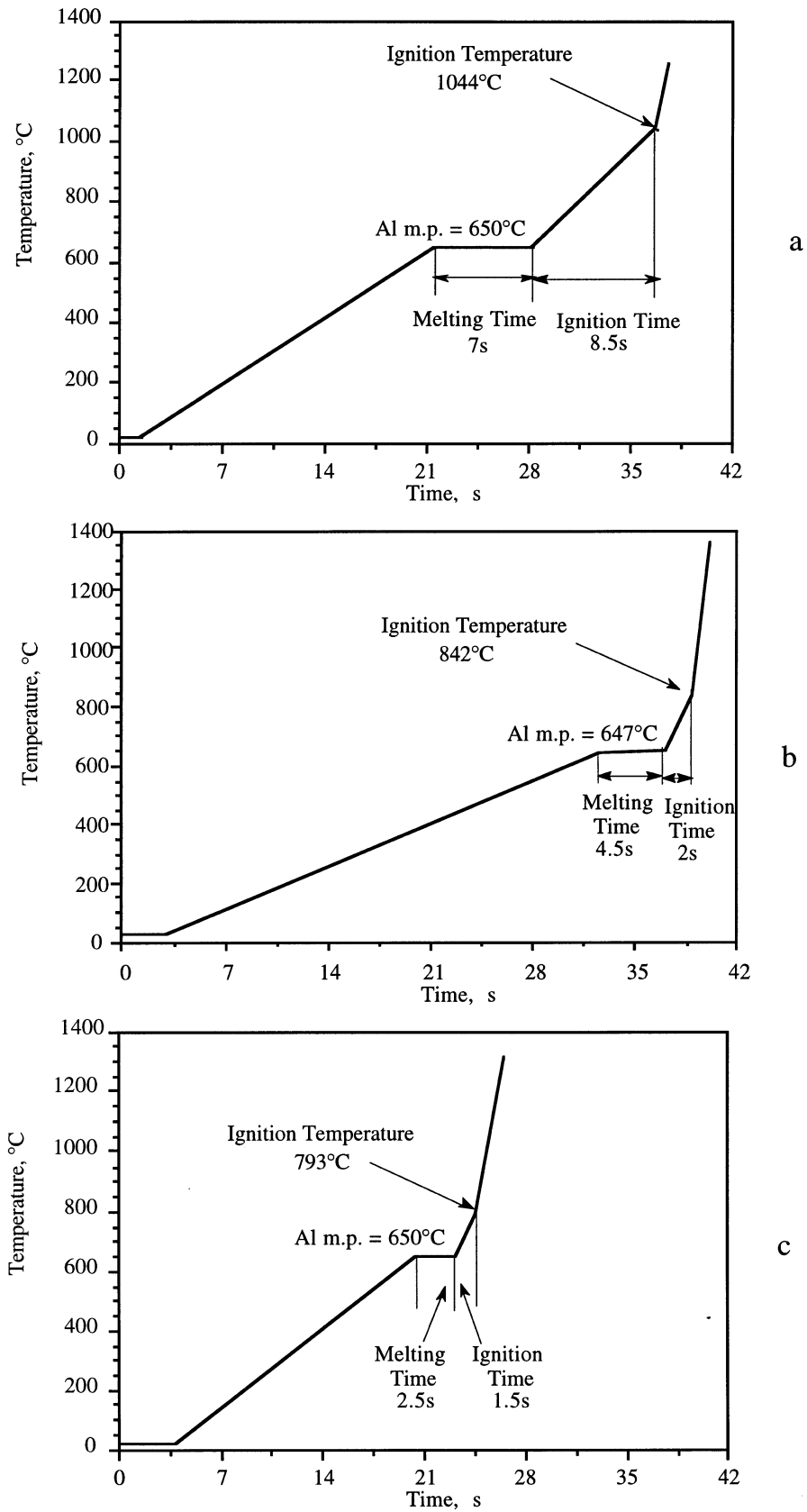


Fig. 10. SHS temperature profiles for different Nb + 3Al powder mixtures: (a) Turbula; (b) shock mode; (c) friction mode.

4. Conclusion

This paper clearly shows the influence of the mechanical activation on the isothermal annealing treatment and SHS process. Starting from a mixture of elemental pure powders, the first step M2AP or MASHS milling process leads to the formation of nanostructured powders in which nanoscale three dimensional polyinterfaces between the initial elemental niobium and aluminum powders are formed. The reaction which forms the target phase occurs only during the subsequent annealing or SHS step. The M2AP process produces microcrystalline NbAl₃ powder. The MASHS process enables to produce submicronic bulk materials, but the weakness of the relative density (60%) need some future development to obtain a fully dense bulk materials.

The quality of the mechanical activation depends on the mode of transfer of mechanical energy to grains of powders. Using the G5 particular planetary ball-mill, it is possible to select a friction or a direct shock mode to activate powders during the initial step of the M2AP or MASHS process.

Concerning the M2AP process, it seems that the shock mode activation is more efficient since it produces single phase NbAl₃.

Concerning the MASHS process, the mechanical activation allows the melting time, the ignition time and the ignition temperature to be decreased compared with the classical SHS process. The decrease in the melting time can be attributed to a modification of the aluminum latent heat of fusion due to the increase in the interfacial area during mechanical activation. The lower ignition time may be interpreted by the reduction in the diffusion length after ball-milling due to the existence of three dimensional polyinterfaces at nanometric scale. On the other hand, the existence of three dimensional polyinterfaces between small crystallites of niobium and aluminum make it easier to form niobium aluminide as compared with the simple Turbula mix, lowering the ignition temperature of about 200°C. These thermal analyses demonstrate that the friction mode is more efficient in decreasing the ignition temperature than the direct shock one. Therefore, we can conclude that the mechanical activation depends on the mode of transfer of mechanical energy to ground powders. It constitutes

thus a very flexible way of influencing phase transformations.

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