

Effect of the High-Energy Ball Milling on the Combustion Synthesis of NbAl₃

Ricardo Mendes Leal Neto^{1,2} and Cláudio José da Rocha^{1,2}

¹ Powder Processing Center CCP, Instituto de Pesquisas Energéticas e Nucleares, IPEN, CEP 05422-970 São Paulo, Brazil

² Department of Materials Engineering, Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Caixa Postal, CEP 05422-970 São Paulo SP, Brazil

Keywords: Aluminides, Combustion, Intermetallic, Milling

Abstract. For many years intermetallics and particularly aluminides have been synthesized by exothermal reactions. In this work, NbAl₃ was synthesized by simultaneous combustion from its elemental powders. A high-energy ball milling apparatus (SPEX mill) was used to accomplish the mixing of the powders promoting a highly refined dispersion. To get this, only the milling time was changed. For studying the influence of milling action on reaction synthesis, differential thermal analysis (DTA) was conducted on loose powders of the Nb75Al milled mixtures up to 1100 °C at a fixed heating rate under argon. In order to get some information about intermediate reactions observed small samples of the mixtures were heated in the DTA apparatus up to 750 °C. X-ray diffraction analysis was performed in as-milled and partially reacted samples for phase identification. Preliminary results showed that as milling time is increased, the ignition temperature is decreased to temperatures below the melting point of aluminum. Also a variation in the reaction evolution is observed, changing from two-stage to single stage reaction.

Introduction

Nb-Al intermetallic compounds have been considered for high temperature structural parts due to their high melting points and elevated strength [1-4]. Among them, niobium trialuminide (NbAl₃) has become attractive because of its high aluminum content resulting in a lower density [2,4,5]. Niobium aluminides have usually been prepared by the powder metallurgy route that commonly involves high temperature or pressure and therefore expensive equipment [4,6-8]. Combustion synthesis is an attractive alternative method. Starting from a mixture of their elemental powders which reacts exothermically, this is a simpler and relatively inexpensive process. The combustion can be performed in two modes, differing on the way the reaction is started [9,10]. In the self-propagating high temperature synthesis mode (SHS) the ignition is done locally and the reaction self-propagates through the mixture as a combustion wave until the reactants are consumed. In the simultaneous or volume combustion mode, the whole mixture is heated in a furnace to the ignition temperature. Various aspects of the combustion synthesis of NbAl₃ have been previously investigated, including the heating rate, particle size of both aluminum and niobium, green density of the mixture, degassing treatment, and mechanistic studies of the reaction [11-14]. Relating to the mixture variables, particle size or degree of dispersion is the most important, since it affects the connectivity of the reactants and mainly the kinetics of the reaction in a condensed system [9,11]. Fine particles are seen to reduce the diffusion distance and to enhance the number of contacts between the reactants. A very powerful way to obtain an intimate and fine mixture of the reactants is through high-energy ball milling. This

technique has extensively been used to promote what in general is called mechanical alloying [15,16]. This is accomplished by repeated events of welding, fracture and rewelding of the powder particles due to successive impacts of the balls. In the case of combustion synthesis, the chemical reaction can be started during the milling (reaction or reactive milling). Like other intermetallic compounds, NbAl_3 has been obtained by milling elemental powders to produce amorphous or nanocrystalline material [17-20]. In this paper, results of a preliminary investigation of the influence of ball milling on combustion synthesis of NbAl_3 are presented. Ball milling was not utilized here for *in situ* reaction but just as a previous treatment to the reactant mixture.

Experimental

Samples of elemental aluminum powder (99.7 % pure, -325 mesh) and niobium powder (99 % pure, -325 mesh) were individually weighted according to the nominal composition of NbAl_3 , i.e., Nb-75 at. % Al (Nb75Al). Each sample (10 g) was ball milled at room temperature in a SPEX 8000 mixer/mill with forced air-cooling. The milling was carried out in a stainless steel vial using 9/32-in. diameter stainless steel balls. The ball-to-powder weight ratio was 10:1. Loading was done in an argon-filled glove box. Stearic acid was added (1 wt. %) to prevent excessive welding. Samples were milled for 1, 2 and 3 hours. After milling, samples were analyzed by X-ray diffraction to determine possible phase formation. Metallographic specimens were also prepared from the as milled samples for microstructural observations.

Differential thermal analysis (DTA) was performed on small as milled samples (100mg) under argon flux (5 ml/min). A 15°C/min heating rate was used in these experiments. This heating rate was chosen based on previous investigation [12]. In order to identify phase changes with temperature by XRD, heating was interrupted at 750°C during a DTA run.

Results and Discussion

X-ray diffraction patterns of Nb75Al samples milled for different times are shown in Fig. 1. The result of a non-milled mixture (or as-mixed powder) is added just for comparison purposes. At all milling times only peaks of Al and Nb elemental powders are observed. NbAl_3 phase was not formed, as desired. After milling for 1 hour, some broadening of the peaks was observed. Broadening occurred since an increase on defect density (plastic strain) and a decrease on crystallite (or grain) size are expected. A change (diminution) in the intensities of Al lines in relation to Nb lines is also seen. This can be clearly seen comparing the $(200)_{\text{Al}}$ and $(200)_{\text{Nb}}$ reflections from the patterns of the as-mixed powders and after milling for 1 hour. It may be attributed to a higher plastic strain in Al than in Nb particles, or to some formation of a solid solution of Al in Nb. Nevertheless, accurate measurements of the cell parameters and broadening are necessary to elucidate these observations. On further milling to 2 and 3 hours, no noticeable changes in broadening or in the relative intensities have been observed.

The effects of milling time on the mixing (dispersion), shape and size of reactants can be seen from SEM micrographs in Fig. 2. The light areas are from Nb particles while dark gray areas are from Al particles. At 1 hour of milling (Figs. 2a and 2b) a considerable welding and deformation of Al and Nb powders have been attained, forming alternated layer aggregates. Niobium layers can be used for monitoring the degree of mixing and plastic strain. At a less magnification (Fig. 2a), it can be observed that some elongated particles of Nb remain isolated (not joined with aluminum). Further milling decreases both thickness and length of the layers (Fig. 2c) and also the number of disjointed

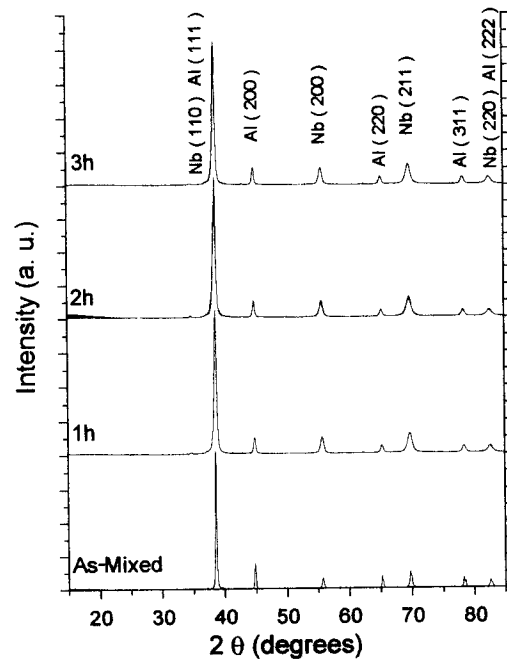


Figure 1 – XRD patterns of Nb75Al samples after milling for 0h (as-mixed) 1h, 2h and 3h.

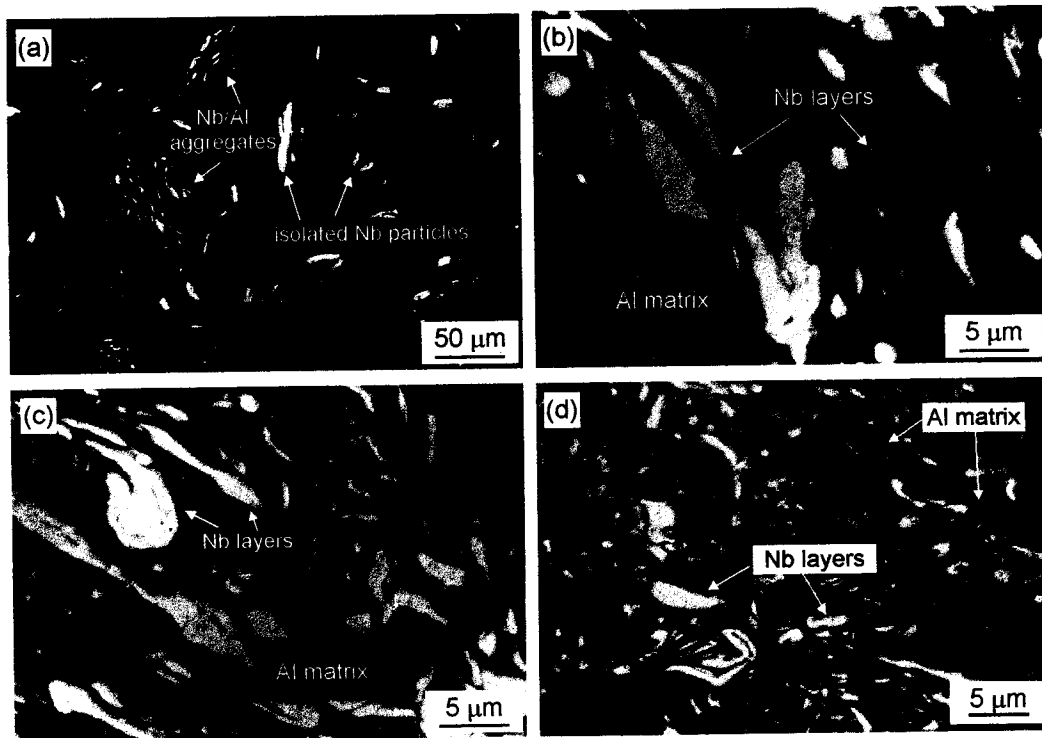


Figure 2 – SEM micrographs of samples after milling for (a) and (b) 1h, (c) 2h, (d) 3h.

particles of niobium (not shown). After 3 hours milling the degree of dispersion is higher (Fig. 2d) and isolated Nb particles have not been observed.

Fig. 3 shows baseline-corrected DTA curves for the as-mixed and milled samples. The Nb75Al as-mixed powder exhibited an endotherm at 660 °C (peak), followed by an exotherm at 950 °C (peak), which initiated at approximately 850 °C. The endothermic peak is due to the melting of aluminum powder and the exothermic peak resulted from the synthesis reaction of NbAl₃, as previously reported [11,12]. After 1 hour milling, two exotherms can be seen. One of them occurred just after the melting of aluminum and the other one started at about 800 °C. This second exotherm is not so well defined and seems to be formed by two events rather than a single one. Further milling to 2 hours caused the first exotherm to be more intense in relation to the endothermic melting, which was in turn changed to a lower temperature (~640 °C). Also, this exothermic event started just before the melting of aluminum (~600 °C). A very weak second exotherm can still be seen. After 3 hour milling a drastic change took place. The endotherm related to the melting of aluminum was lowered and changed to about 630 °C. Moreover, this endotherm seems to be superposed by an exotherm that initiated at around 500 °C.

Partial heating of the milled samples up to 750 °C was carried out in order to verify the result of the first exothermic events observed. X-ray diffraction patterns of these samples are shown in Fig. 4. A partial formation of NbAl₃ is seen to occur in the sample milled for 1 hour. In the pattern of the sample milled for 2 hours, almost all the peaks are related to NbAl₃ phase. It can be seen a small peak related to (111)_{Al} and (110)_{Nb} reflections. Semiheated sample milled for 3 hours exhibited no reflections related to Al or Nb, indicating a complete reaction. In the samples milled for 2 and 3 hours, some peaks of very low relative intensities remained unidentified.

From the previous results, it was found that the shaker mill action caused strong changes in the microstructure and in the thermal behaviour of Nb75Al powder mixtures. Although this is a preliminary investigation, some important aspects can be figured out. The first one is the change from a single step reaction to two step reaction, which occurred after milling for 1 and 2 hours. It is obvious from XRD analysis of semiheated samples that the first exothermic peak (about 670 °C) is related to the synthesis of NbAl₃. This lowering of ignition temperature can be explained by the intimate contact (mixture) obtained with the milling action. This fact contributes to the reduction of the diffusion distance, and probably also to the enhancement of the wetting of molten Al over Nb layered particles. The latter can be supported by previous investigations on simultaneous combustion synthesis of NbAl₃. It was reported that after the melting of aluminum, a nonwetting phenomenon occurs [11,13,14]. Kachelmyer *et al.* [13] observed a dependence of contact angle with temperature and suggested that the initial nonwetting characteristic of molten Al over Nb may be responsible for an ignition temperature as high as 880 °C, well above the melting point of Al. At this temperature, they observed a spreading of Al over Nb, increasing the contact between the reactants and so initiating the reaction. In the present investigation, the reaction at 670 °C was not completed in the sample milled for 1 hour so a second step at a higher temperature took place. This behaviour is believed to be associated to the isolated Nb particles observed in this sample (Fig. 2a). In the sample milled for 2 hours, the first exothermic peak started just before the melting of aluminum as a result of an increased milling action. This reaction was seen to be more intense, consuming almost all the reactants, as seen in the XRD patterns (Fig. 4). That is the reason for the very low intensity of the second exothermic peak. In the sample milled for 3 hours, the exotherm initiated at about 500 °C is associated to a complete NbAl₃ synthesis, as shown by XRD analysis conducted on semiheated samples to 750 °C, indicating the increased effect of the milling action. The observed small endothermic peak (Fig. 3) could be explained by a previous consumption of Al, before its melting. A

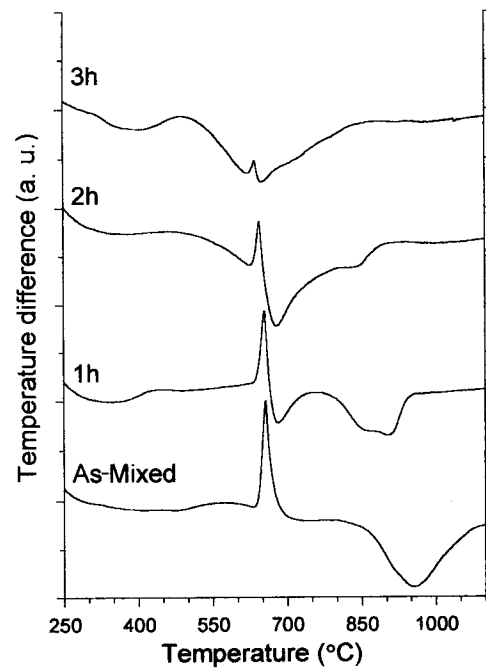


Figure 3 – DTA of Nb75Al samples after milling for 0h (as-mixed) 1h, 2h and 3h.

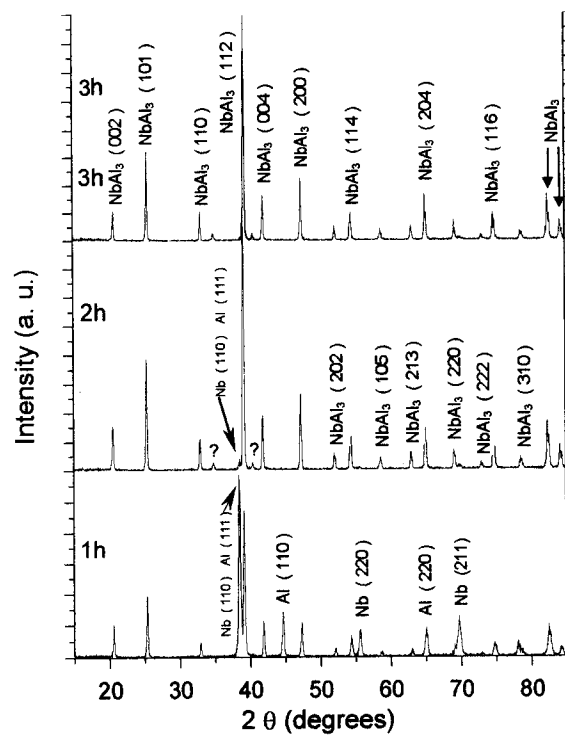


Figure 4 – XRD patterns of Nb75Al samples milled for 1h, 2h and 3h after heating to 750 °C.

less intense lowering of the endothermic peak associated to the melting of aluminum can also be observed in the sample milled for 2 hours, as synthesis reaction started just before.

Conclusions

The reaction synthesis of NbAl_3 was seen to be drastically affected by high-energy ball milling of the reactants. The major changes revealed by differential thermal analysis were on the ignition temperature and on the reaction evolution. As milling time is increased, the ignition temperature is decreased, going from 850 °C (non-milled sample) to 500 °C, well below the melting point of aluminum. In the same direction, the single reaction at higher temperature observed in the as mixed sample changed to a two-step reaction and over to one step reaction at lower temperature. For better understanding of the various aspects of combustion reaction conducted on milled samples, additional experiments are currently in progress.

Acknowledgements

The authors would like to acknowledge the Thermal Analysis Laboratory (Ceramic Materials Division) supported by FAPESP and the XRD Laboratory (Physical Characterization Division). We also thank CTMSP from Marinha do Brasil, for the permission of use of some of its facilities.

References

- [1] E. A. Loria, in International Symposium on Tantalum and Niobium, Tantalum-Niobium International Study Center, Brussels (1989), p. 631.
- [2] G. Sauthoff, *Z. Metallkde.* 81 (1990), p. 855.
- [3] E. P. Barth, J. K. Tien, S. Uejo and S. Kambara, *Mat. Sci. Eng. A* 153 (1992), p. 398.
- [4] C. -P. Reip and G. Sauthoff, *Intermetallics* 1 (1993), p. 159.
- [5] K. S. Kumar, *Intern. Mater. Rev.* 35 (1990), p.293.
- [6] J. H. Schneibel; P. F. Becher; J. A. Horton, *J. Mater. Res.* 3 (1988), p. 1272.
- [7] M. G. Hebsur; I. E. Locci; S. V. Raj and M. V. Nathal, *J. Mater. Res.* 7 (1992), p 1696.
- [8] R. Ray and R. Ayer, *J. Mater. Sci.* 27 (1992), p. 1642.
- [9] Z. A. Munir, *Am. Ceram. Soc. Bull.* 67 (1988), p. 342.
- [10] J. J Moore and H. J. Feng, *Prog. Mater. Sci.* 39 (1995), p. 243.
- [11] J. C. Murray and R. M German, *Metall. Trans. A* 23 (1992), p. 2357.
- [12] P. I. Ferreira and R. M. Leal Neto, *Int. J. Powder Metall.* 30 (1994), p. 313.
- [13] C. R. Kachelmyer; A. S. Rogachev and A. Varma, *J. Mater. Res.* 10 (1995), p. 2260.
- [14] R. M. Leal Neto and P. I. Ferreira, *J. Mater. Synth. Process* 7 (1999), p. 245.
- [15] J. S. Benjamin, *Metall. Trans.* 1 (1970), p. 2943.
- [16] J. S. Benjamin, *Mater. Sci. Forum* 88-90 (1992), p. 1.
- [17] Z. Peng, C. Suryanarayana and F. H. Froes, *Scripta Metall. Mater.* 27 (1992), p. 475.
- [18] K. Isonishi and K. Okazaki, *J. Mat. Sci.* 28 (1993), p. 3829.
- [19] Z. Peng, C. Suryanarayana and F. H. Froes, *Metall. Trans.* 27A (1996), p. 41.
- [20] K. M. Lee, H. U. Yang and I. S. Ahn, in 1998 PM World Congress, EPMA (1998), p.390.

Advanced Powder Technology II

doi:10.4028/www.scientific.net/KEM.189-191

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doi:10.4028/www.scientific.net/KEM.189-191.567