

Synthesis of NbAl_3 and Nb-Ni-Al intermetallic alloys by self-propagating reaction sintering

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Abstract: In the present study, pressureless reaction sintering of Nb, Ni and Al elemental powder mixtures was investigated. Mixtures with nominal compositions Nb-75Al, Nb-10Ni-70Al, Nb-20Ni-65Al and Nb-30Ni-60Al (at. %) were prepared. The first composition has the stoichiometry of the NbAl_3 compound. The others pertain to the line connecting the NbAl_3 and NiAl points in the Nb-Ni-Al phase diagram. Processing variables were previously established for NbAl_3 in order to obtain simultaneous synthesis and densification. They were then fixed as much as possible for nickel additions. Compacts of the homogenized powder mixtures were vacuum reaction sintered. Observed ignition temperatures varied depending on composition. The Ni-rich compacts reacted at lower temperatures, between 480°C and 520°C. The others reacted at temperatures in the range of 840°C-860°C. NbAl_3 and unreacted niobium were present, in different amounts, in the microstructure of all specimens containing nickel. NiAl and NbNiAl were only observed in the highest Ni containing pellet. Ni_2Al_3 was formed in the others compositions.

1 INTRODUCTION

Intermetallic materials are currently recognized as potential candidates to replace nickel-base superalloys for high temperature applications [1]. Since Aoki and Izumi [2] discovered that polycrystalline NiAl could be ductilized by microalloying with boron, significative efforts have been made both on alloying design and processing of other intermetallic phases. Aluminides, specially those of high Al content, are receiving particular attention due to their low density and good oxidation resistance. Among these intermetallics are the transition-metal trialuminides such as NbAl_3 (4.54 Mg.m⁻³) [3] which is further attractive for high temperature use because of its high melting point (1680°C) [4]. However it is extremely brittle at room temperature as a consequence of DO_{22} crystal structure. In order to resolve this problem, attempts have been made on ternary additions. Sauthoff [5] has verified that alloying NbAl_3 with NiAl extends the range of deformability to significantly lower temperatures, compared to pure NbAl_3 , whereas the high temperature strength is affected only to a small degree. These observations encouraged us to processing NbAl_3 -NiAl alloys. Some efforts have been made to produce NbAl_3 and NiAl by reactive sintering [6-10]. Reactive sintering starts from mixed elemental powders using a self-sustaining synthesis reaction that provides sufficient heat for densification. By this way, costs are saved since the processing time is significantly shorter than with conventional techniques and a substantial amount of energy is provided by the exothermic reaction. The primary intention of this research is to verify what occurs when Nb, Al and Ni powder mixture is reacted. The influence of compact composition on ignition temperature, physical and microstructural characteristics of as reacted pellets was investigated. NbAl_3 synthesis is also performed to use as a reference for comparison of results.

2. EXPERIMENTAL APPROACH

A gas-atomized aluminum powder of -325# ($< 44\mu\text{m}$), obtained from ALCOA (Poços de Caldas, Minas Gerais, Brazil), a niobium powder of -325# ($< 44\mu\text{m}$), obtained from FTI (Lorena, São Paulo, Brazil) and a nickel powder ($< 10\mu\text{m}$), obtained from Riedel - de Haën (Germany), were used. First, Al and Nb powders were sieved to -400# ($< 33\mu\text{m}$). This granulometric range was previously demonstrated to be better for NbAl_3 synthesis and densification [7]. Nickel powder was used in the as received condition. Powder mixtures were prepared with nominal compositions Nb-75Al (NbAl_3), Nb-10Ni-70Al, Nb-20Ni-65Al and Nb-30Ni-60Al (at. %), pertaining to the line connecting NiAl and NbAl_3 compositions in the ternary phase diagram. The samples were individually mixed in air using a Turbula mixer at a speed of 35 rpm for 10 minutes. After mixing, the samples were compacted by cold uniaxial pressing in a cylindrical die at 300MPa. A solution containing stearic acid and acetone was used as die wall lubricant. The resulting green compacts have a diameter of 14mm, a height of approximately 6 mm and densities from 88 to 92% of theoretical. Reactive sintering of these compacts was conducted on an evacuated quartz chamber placed within the cavity of a horizontal resistance-heated furnace. Five pellets, at least, of each composition were reacted for reproducibility verification. Heating was carried out only after a vacuum of 10^{-3} Pa was attained in the quartz chamber. The treatment consisted of heating the compacts to 400°C , holding for 4 hours for degassing, and further heating to the temperature required for self-ignition (thermal explosion mode). Ignition temperatures were measured with a thermocouple located near the pellets. The reaction could be visually perceived by sample lightening through the quartz chamber. The heating rate before and after degassing was $15^\circ\text{C}/\text{min}$. After the reaction, the furnace was turned off and the samples were cooled under vacuum by taking the quartz chamber off the furnace. Reacted samples were longitudinally sectioned for metallographic observations. Macro and microstructural characterization were carried out on polished surfaces. Phase identification was accomplished by X-ray diffractometry (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS).

3. RESULTS

Table I summarizes the results of ignition temperature range, present phases and some macroscopic aspects of the reacted pellets for each composition. Ignition temperatures varied significantly depending on composition. Two distinct groups can be envisaged: the first group reacted at higher temperatures and includes Nb-Al and nickel-poorer pellets: the second group reacted at lower temperatures and comprehends nickel-rich pellets. Typically, nickel-richest pellets (30 at. %) suffered a strong reaction, resulting in a spherical shape which denotes that some melting occurred. The pellets contain large voids as shown in Fig. 1a. The majority of the pellets of Nb-20Ni-65Al composition presented some shape distortion as shown in (Fig. 1b). Pellets of the first group showed smaller distortion and their general aspect is similar to the pellet of Fig. 1b. XRD and EDS analysis allowed phase determination to be performed unambiguously in most cases. NbAl_3 was always formed (light gray areas in Fig. 2a and 2b). For non-nickel containing pellets NbAl_3 is the major phase. SEM analysis revealed at some triple grain boundaries an Nb_2Al - NbAl_3 eutectic. Small aluminum losses can explain its formation as observed previously [7,8]. XRD analysis exhibited unreacted niobium in all Ni containing pellets, shown as light areas (islands) involved by light gray NbAl_3 grains in the SEM micrograph of Fig. 2b. These light areas seem to be fragmented in the

TABLE I- Results of reacted pellets for all compositions studied

Nominal Composition (at %)			T_{ignition} ($^\circ\text{C}$)	Identified Phases	Macroscopic Observations
Nb	Ni	Al			
25	---	75	840-860	NbAl_3 (major), Nb_2Al - NbAl_3 eutectic (minor)	small distortion
20	10	70	840-860	NbAl_3 (major), Ni_2Al_3 , Nb (minor)	small distortion
15	20	65	480-520	Ni_2Al_3 , NbAl_3 , Nb (minor)	Some shape distortion
10	30	60	480-520	NiAl (major), NbAl_3 , NbNiAl and Nb (minor)	Partial Fusion (large voids)

Ni-richest pellets (Fig. 2a). Punctual EDS analysis on these areas was unsuccessful in finding unreacted niobium probably due to their small size. The large ones have the composition Nb-16Ni-51Al. NbNiAl phase detected by XRD may correspond to this measurement. This phase can be better described by the formula $\text{Nb}(\text{Ni}_{1-x}\text{Al}_x)_2$, where x varies from 0.19 to 0.83 [11]. Here, $x = 0.76$. Dark gray areas in Fig. 2a and 2b are different phases. In the Ni-richest pellets, NiAl was formed with composition varying from 50 to 60 at.% Ni. XRD revealed that very small amount of Ni_2Al_3 is present. However, SEM failed to detect this phase. These gray areas in another Ni containing pellets have 43.5 at.% Ni, corresponding to hyperstoichiometric Ni_2Al_3 . XRD support this result.

4. DISCUSSION

Published ignition temperatures for Nb-75Al powder mixtures range from 750°C [8] to 1000°C [6]. Processing variables like powder particle size, heating rate or green density can change this temperature. Thus, the observed ignition temperature (~850°C) for NbAl₃ is consistent with reported values.

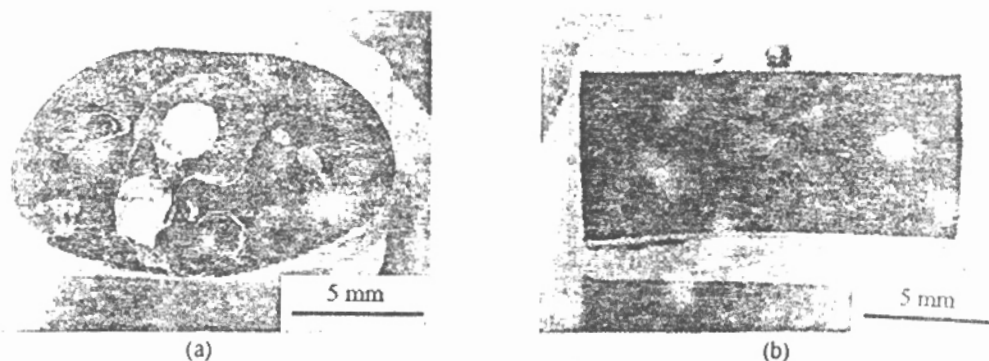


Figure 1 - Macrographs of representative reacted pellets: (a) Nb-30Ni-60Al; (b) Nb-20Ni-65Al (longitudinal sections).

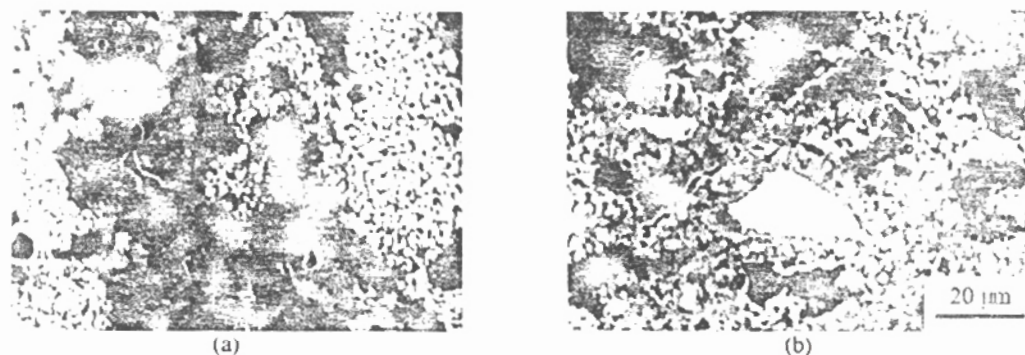


Figure 2 - Backscattered electron micrographs of (a) Nb-30Ni-60Al and (b) Nb-20Ni-65Al reacted pellets.

This temperature cannot be compared with ignition temperatures of the second group. It indicates that in the latter case the reactions have not initiated between Nb and Al particles. However, these temperatures can be well associated with reactions in the Ni-Al system. In fact, the extremely fine nickel powder ($< 10\mu\text{m}$) could be responsible for such a low temperature as demonstrated theoretically and experimentally by Rein et Al. [10]. Furthermore, the formation of NbAl_3 compound in these pellets is an evidence that the magnitude of the heat released by low temperature reaction was enough to raise the bulk temperature to that required for the reaction at Nb-Al interfaces. NiAl synthesis may justify the strong reactions in the Ni-richest pellets. The heat of formation of NiAl is 58.79 kJmol^{-1} [12], higher than NbAl_3 (32.63 kJmol^{-1}) [13] and comparable to Ni_2Al_3 (56.48 kJmol^{-1}) [12]. Reported adiabatic temperature for NiAl has a value of 1650°C [9], higher than the melting point of itself (1638°C) [14] and near to NbAl_3 (1680°C) [4]. These features and the highest nickel concentration (30 at.%) can explain the partial melting observed. At lower nickel content (20 at. %), the formation of Ni_2Al_3 could provide NbAl_3 ignition, though with less heat release. In contrast, this was not true for the Ni-poorest pellets (10 at.%). Probably, the lesser number of contacts between Ni and Al, providing that Ni concentration is lower, was not sufficient to generate necessary heat to start bulk reaction. Visible reaction was only observed at about 850°C with NbAl_3 synthesis. Ni_2Al_3 and unreacted Nb cannot be justified by reported isothermal section of Nb-Ni-Al equilibrium diagram at 1140°C [11]. Nominal compositions studied here lie between NiAl - NbAl_3 and NiAl - NbAl_3 -liquid phase fields. Of course, the equilibrium was not attained in the reacted pellets. Probably, the maximum temperature reached by pellets containing 20 and 10 at.% Ni was inferior to the melting point of Ni_2Al_3 , i.e., 1133°C [14]. For Ni-richest pellets the temperature rise during reaction was probably higher than 1140°C , allowing NbNiAl formation in the nickel-richest pellets. The observed Ni_2Al_3 and NbNiAl formation may explain unreacted Nb by the consumption of the aluminum needed for NbAl_3 reaction completion. Further work (e.g., heat treatment in the as reacted pellets, nominal composition variations, etc.) must be done for better understanding of these results.

5. CONCLUSIONS

This work shows that the combustion synthesis of a ternary mixture of Nb, Al and Ni powders is possible. The phases NbAl_3 , NiAl , Ni_2Al_3 , NbNiAl and unreacted Nb were observed in the reacted pellets in amounts that depends on initial composition. The low ignition temperature verified at some mixtures is an interesting result concerning economical aspects.

6. REFERENCES

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