

## Reaction sintering of Nb–Ni–Al intermetallic alloys

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### Abstract

Homogeneous Nb–Ni–Al powder mixtures with nominal compositions Nb–10Ni–70Al, Nb–20Ni–65Al and Nb–30Ni–60Al (at.%) were pressed into compacts under an applied stress of 300 MPa and then reaction sintered. The resulting pellets were heat treated at 1140 °C for 6 h. Optical metallography, energy-dispersive spectroscopy and X-ray diffraction were used to characterize the microstructure of the as-reacted and heat treated pellets. Reaction sintering occurred for all the compositions investigated. The high nickel containing compacts (30 and 20 at.% Ni) reacted at a temperature of 500 °C and for the other compacts (10 at.% Ni) the reaction occurred at 850 °C. NbAl<sub>3</sub> and unreacted niobium were present, in different amounts, in the microstructure of all specimens containing nickel. NiAl and NbNiAl were only observed in the 30 at.% Ni containing pellet. Ni<sub>2</sub>Al<sub>3</sub> was formed in the other compositions. The results indicate that in 20 and 30 at.% Ni compacts the reaction is initiated at Ni–Al powder interfaces, whereas for 10 at.% Ni compacts the dominant reaction occurs at the Nb–Al interfaces. The heat treatment at 1140 °C for 6 h induces a decrease in the amount of unreacted niobium and NbNiAl, and the elimination of Ni<sub>2</sub>Al<sub>3</sub> with an increase in NbAl<sub>3</sub> and NiAl.

*Keywords:* Niobium; Nickel; Aluminium; Intermetallics; Alloys; Sintering

### 1. Introduction

Reaction or reactive sintering has increasingly been used to process intermetallic materials in bulk form [1,2]. It consists of heating a compacted mixture of powders until a self-sustaining exothermic reaction takes place. By this so-called simultaneous combustion [3] it is possible to attain not only the synthesis of the desired compound but also near full density materials. The advantages of this route include low processing temperatures, short processing times, relatively inexpensive equipment and a great flexibility for control of the composition and microstructure.

Among a number of intermetallic compounds prepared by this method, the aluminides have been the most investigated [2,4,5]. High aluminum content aluminides have received particular attention owing to their low density and high corrosion resistance, making them candidate materials for high temperature structural applications. The transition metal trialuminide NbAl<sub>3</sub> (4.54 mg m<sup>-3</sup>) [6] is further attractive owing to its high melting point (1680 °C) [7]. However, the intrinsic brittleness at room temperature, associated

with the D0<sub>22</sub> structure, has impaired the development of massive NbAl<sub>3</sub> for these uses.

Thus the addition of a third element to NbAl<sub>3</sub> is being investigated. One approach involves the partial replacement of Nb with other elements to induce a higher symmetry crystal structure. However, there is evidence that NbAl<sub>3</sub> unlike TiAl<sub>3</sub>, cannot be converted to cubic L1<sub>2</sub> by the addition of Cu, Fe, or Ni [8]. The stability of the D0<sub>22</sub> structure relative to L1<sub>2</sub> is strongly favored in NbAl<sub>3</sub> as demonstrated by quantum-mechanical total-energy calculations [9]. However, the multiphase approach seems to be promising. Sauthoff [10] has verified that alloying NbAl<sub>3</sub> with NiAl extends the range of deformability to significantly lower temperatures, compared with pure NbAl<sub>3</sub>, and the high temperature strength is only affected to a small degree. Furthermore, the primary creep strain of the NbAl<sub>3</sub>–NiAl alloys is lower than that of single-phase NbAl<sub>3</sub> [11]. These observations are encouraging for the processing of NbAl<sub>3</sub>–NiAl alloys.

Since NbAl<sub>3</sub> and NiAl can coexist in double-phase alloys and have been independently obtained by reactive sintering [12–15], the primary intention of this

research was to verify the reaction sintering behavior of the Nb, Ni and Al powder mixtures. The influence of initial compact composition on ignition temperature and phases formed in the reacted pellets was investigated.

## 2. Experimental approach

A gas-atomized aluminum powder (ALCOA, Brazil), a hydride-dehydride niobium powder obtained from FTI (Brazil), and a nickel powder (less than 10  $\mu\text{m}$ ) from Riedel-de Haën (Germany) were used. Al and Nb powders were initially sieved to  $-400\#$  (less than 33  $\mu\text{m}$ ) since this granulometric range was previously demonstrated to be optimum for  $\text{NbAl}_3$  synthesis and densification [13]. Nickel powder was used in the as-received condition.

Powder mixtures were made according to the following nominal compositions: Nb–10Ni–70Al, Nb–20Ni–65Al and Nb–30Ni–60Al (at.%). These proportions lie on a straight line connecting NiAl and  $\text{NbAl}_3$  compositions in the ternary phase diagram. The samples were individually mixed in air using a Turbula mixer at a speed of 35 rev  $\text{min}^{-1}$  for 10 min. After mixing, the samples were compacted by cold uniaxial pressing in a cylindrical steel die at 300 MPa. A solution containing stearic acid and acetone was used as die wall lubricant. The resulting green compacts have a diameter of 14 mm, a height of approximately 6 mm and densities from 88% to 92% of the theoretical mixture density. Reactive sintering of the green compacts was conducted in an evacuated quartz chamber placed within the cavity of a tubular furnace. At least five pellets of each composition were reacted for verification of reproducibility. 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 h for degassing, and further heating to the temperature required for self-ignition.

Heating rates before and after degassing were 15 °C  $\text{min}^{-1}$ . Ignition temperatures were measured with a thermocouple placed near the pellets. The reaction could be visually perceived by the lighting in the quartz chamber. After the reaction occurred, the furnace was turned off and the samples were cooled under vacuum by taking the quartz chamber off the furnace. The as-reacted pellets were heat treated at 1140 °C for 6 h under a vacuum of  $10^{-3}$  Pa. This temperature was chosen because it corresponds to the temperature of a published ternary diagram section [16]. Macro and microstructural characterizations were carried out on longitudinal polished sections of the as-reacted and heat treated pellets. Phase identification was accomplished by X-ray diffractometry (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS).

## 3. Results and discussion

Reaction occurred for all compact compositions investigated. Table 1 summarizes the results of ignition temperature, some visual aspects and phase identification of the as-reacted and heat treated pellets according to nominal compositions. Ignition temperatures varied significantly depending on the compact composition. Compacts containing 20 and 30 at.% Ni reacted at temperatures around 500 °C, whereas 10 at.% Ni reacted at a significantly higher temperature, 850 °C. Typically, the nickel-rich compacts (30 at.%) suffered strong reactions (visual observation). The shape of the resulting pellets denotes that some melting occurred. The pellets contain large voids as shown in Fig. 1(a). The Nb–20Ni–65Al pellets exhibited some deviation from the initial cylindrical compact shape as illustrated in the micrograph of Fig. 1(b). Shape variations of Nb–10Ni–70Al pellets were in general negligible (Fig. 1(c)).

Table 1  
Ignition temperatures, visual aspect and phases identified in both as-reacted and heat treated pellets for all compositions studied

Nominal composition (at.%)			$T_{\text{ignition}}$ (°C)	Visual aspect	Identified phases	
Nb	Ni	Al			As-reacted pellets	Heat treated pellets
10	30	60	500	Partial fusion, formation of large voids	NiAl (major), $\text{NbAl}_3$ , NbNiAl and Nb (minor)	$\text{NbAl}_3$ (major), NiAl, NbNiAl ( $\downarrow$ ), Nb ( $\downarrow$ )
15	20	65	500	Small shape distortion	$\text{NbAl}_3$ , $\text{Ni}_2\text{Al}_3$ , Nb (minor)	$\text{NbAl}_3$ ( $\uparrow$ ), NiAl, Nb ( $\downarrow$ )
20	10	70	850	Negligible distortion	$\text{NbAl}_3$ (major), $\text{Ni}_2\text{Al}_3$ , Nb (minor)	$\text{NbAl}_3$ (major), NiAl, Nb ( $\downarrow$ )

$\uparrow$  increased amount,  $\downarrow$  decreased amount.

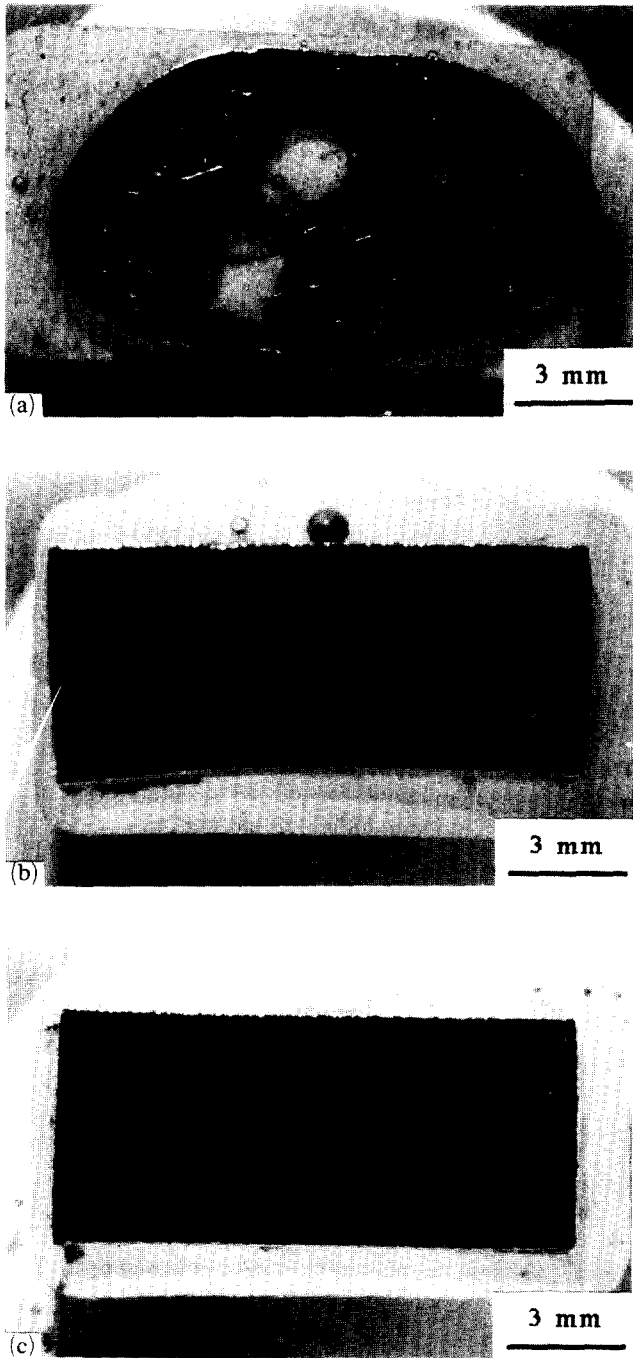


Fig. 1. Micrographs of the longitudinal section of the as-reacted pellets: (a) Nb-30Ni-60Al, (b) Nb-20Ni-65Al, and (c) Nb-10Ni-70Al (at.%).

XRD data included in Fig. 2 clearly show that NbAl<sub>3</sub> and unreacted Nb are present for all pellet compositions investigated (most intense reflection peak (112) of NbAl<sub>3</sub> at  $2\theta = 39.4^\circ$  and (110) peak of Nb at  $2\theta = 38.5^\circ$ ). The NbAl<sub>3</sub> phase is revealed by polarized light in the optical micrographs and appears as light gray areas in the SEM images, as illustrated in Fig. 3

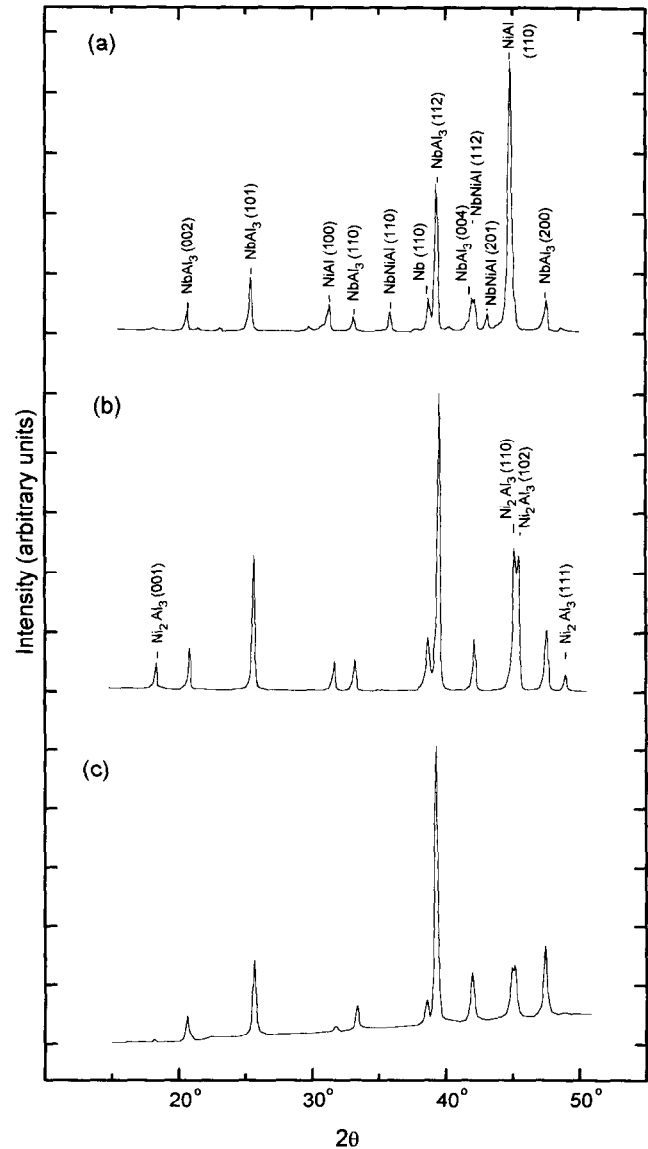


Fig. 2. X-ray diffraction diagrams from as-reacted samples: (a) Nb-30Ni-60Al, (b) Nb-20Ni-65Al, and (c) Nb-10Ni-70Al (at.%).

Unreacted niobium is better visualized in the SEM images as irregularly shaped white areas surrounded by light gray NbAl<sub>3</sub> grains. The white areas in the SEM images of pellets containing 30 at.% Ni (Fig. 3(b)) are fragmented and contain, in addition to unreacted Nb, another phase with composition Nb-16Ni-51Al that corresponds to the Laves phase Nb(Ni<sub>1-x</sub>Al<sub>x</sub>)<sub>2</sub>, with  $x$  varying from 0.19 to 0.83 as reported by Benjamin et al. [16]. The value of  $x$  in this case is 0.76.

The dark gray areas in the SEM images were identified as being NiAl containing 50–60 at.% Ni for the Nb-30Ni-60Al pellet (Fig. 3(b)), and Ni<sub>2</sub>Al<sub>3</sub> (43.5 at.% Ni) for the other two pellet compositions (Figs.

3(d) and 3(f)). This phase is indicated in the diffraction diagrams of Fig. 2 as NiAl, with strongest reflection (100) at  $2\theta = 44.8^\circ$  (Fig. 2(a)), and  $\text{Ni}_2\text{Al}_3$  which has two strong reflections at  $2\theta = 44.7^\circ$  (110) and  $45.1^\circ$  (102).

The micrographs of Fig. 3 clearly show that the amount of each phase present in the microstructure

depends on the compact composition. The decrease in nickel content leads to a decrease in NiAl and  $\text{Ni}_2\text{Al}_3$  and an increase in  $\text{NbAl}_3$  contents. Also, the  $\text{NbAl}_3$  grain size observed for Nb–20Ni–65Al is much finer than that observed for the two other compositions. Low magnification observations (not included) show that the volume fraction of unreacted Nb increases when the amount of Ni in the compact is increased.

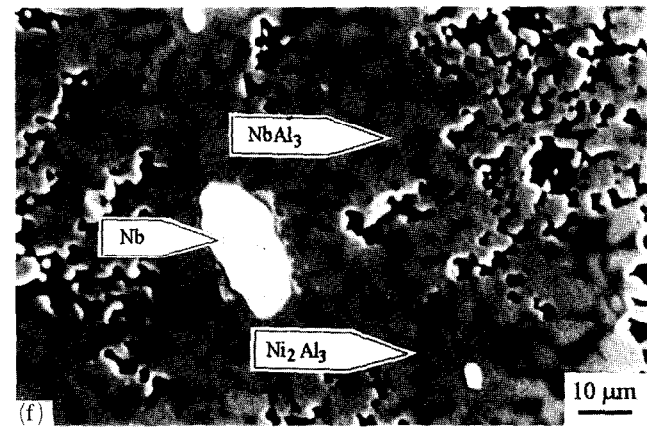
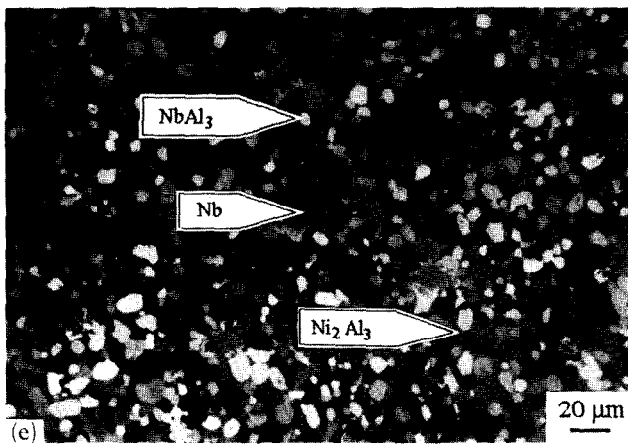
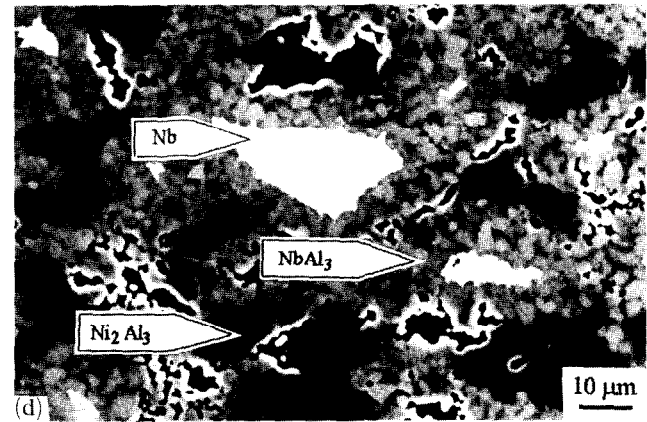
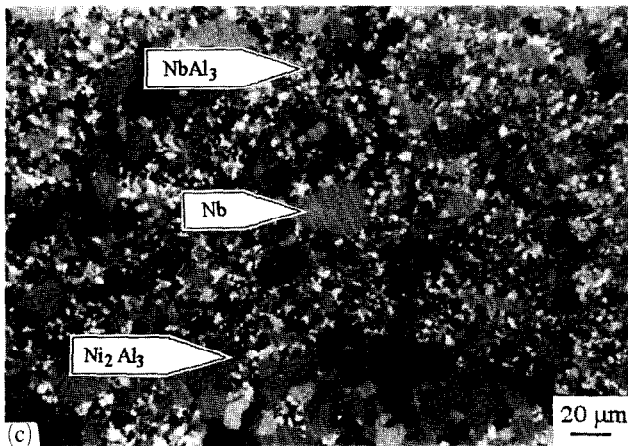
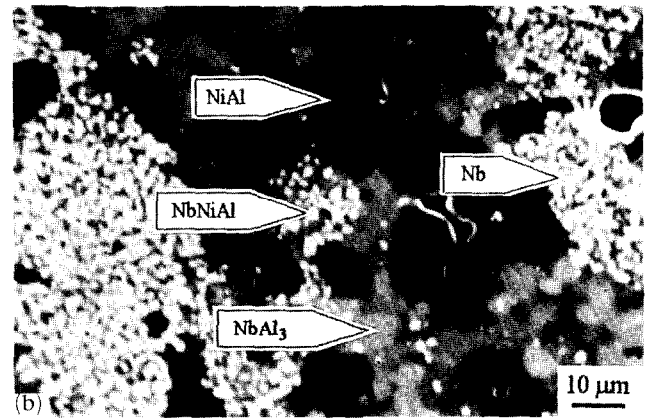
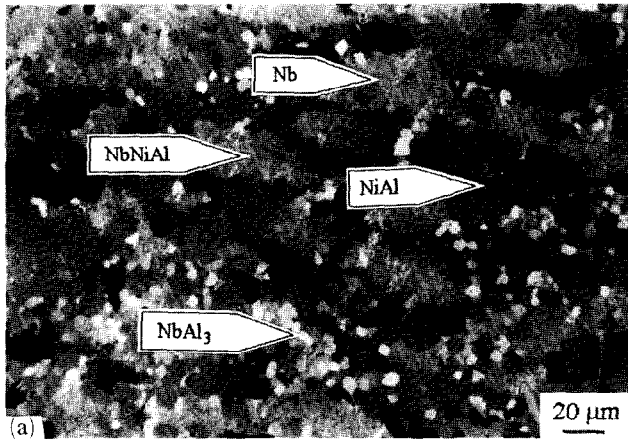


Fig. 3. Optical micrographs (polarized light) and SEM images of the as-reacted pellets: (a) and (b) Nb–30Ni–60Al, (c) and (d) Nb–20Ni–65Al, (e) and (f) Nb–10Ni–70Al (at.%).

Fig. 4 illustrates typical optical micrographs and SEM images of the pellets after the heat treatment at 1140 °C for 6 h. XRD data obtained for these samples are presented in Fig. 5. As a consequence of the heat treatment, noticeable changes occur in the microstructure, as can be perceived by comparison of Fig. 3 and Fig. 4. The initial irregular shape of the unreacted

niobium particles in the as-reacted pellets is modified to a well rounded shape in the heat treated situation. The round particles now contain fine  $\text{NbAl}_3$  grains in the center. A decrease in the amount of unreacted niobium is observed for all compositions, concomitantly with the disappearance of  $\text{Ni}_2\text{Al}_3$  and the increase in  $\text{NbAl}_3$  and  $\text{NiAl}$ .

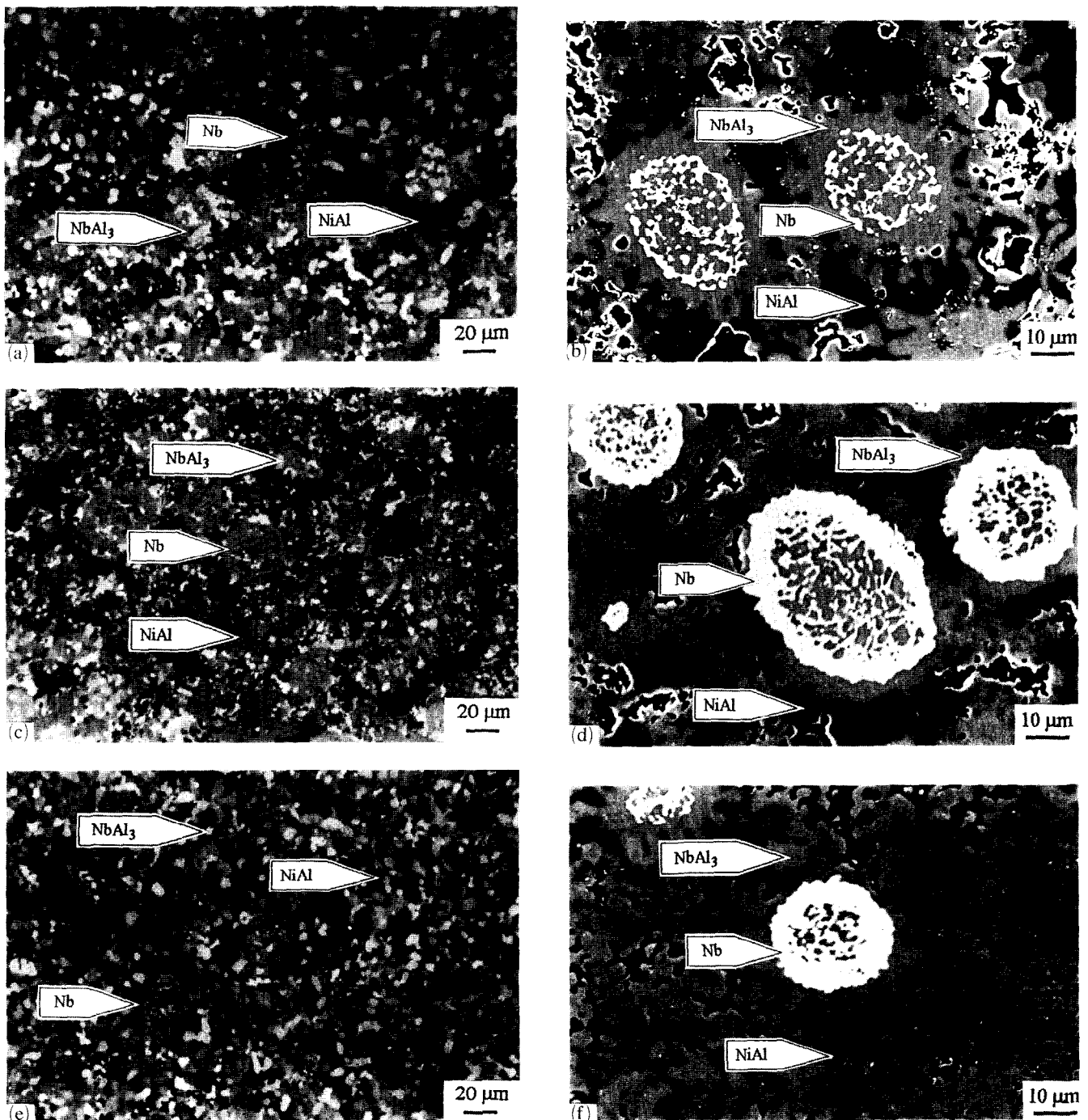


Fig. 4. Optical micrographs (polarized light) and SEM images of heat treated pellets: (a) and (b) Nb-30Ni-60Al, (c) and (d) Nb-20Ni-65Al, (e) and (f) Nb-10Ni-70Al (at.%).

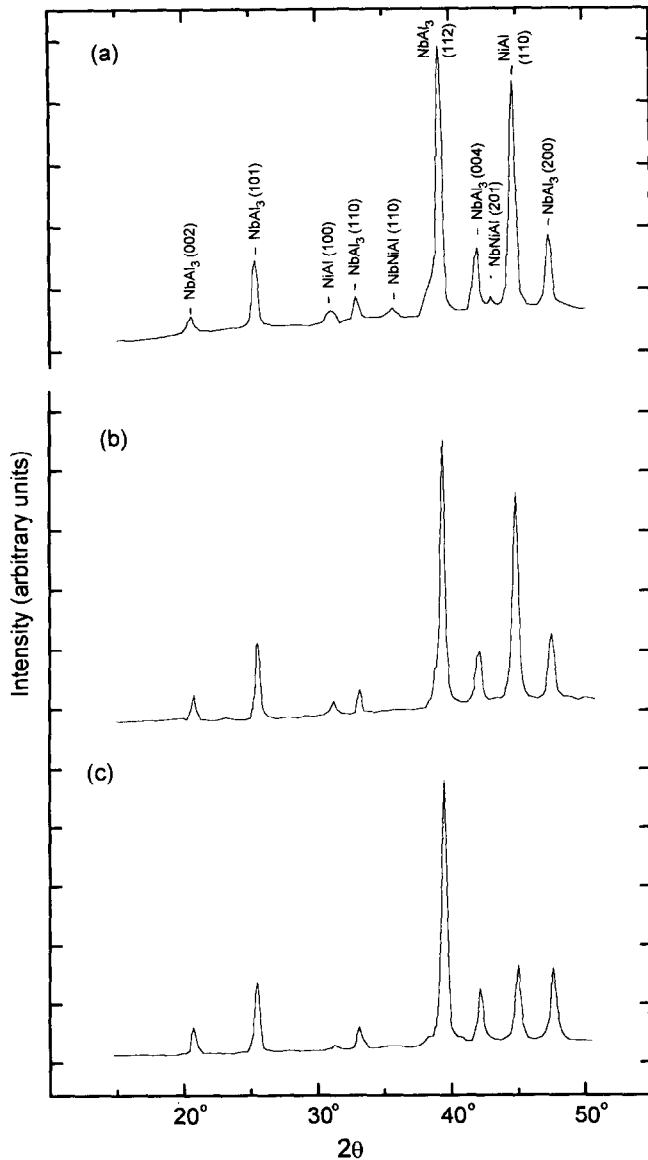


Fig. 5. X-ray diffraction diagrams from heat treated samples: (a) Nb-30Ni-60Al, (b) Nb-20Ni-65Al, and (c) Nb-10Ni-70Al (at.%).

The ignition temperature of 500 °C verified for the Nb-30Ni-60Al and Nb-20Ni-65Al compacts is of the same order of magnitude of those reported by Rhein et al. [15] for NiAl synthesis when very fine Ni powder (less than 10  $\mu\text{m}$ ) is used, suggesting that the reaction is initiated at Ni-Al interfaces. In contrast, the ignition temperature measured for Nb-10Ni-Al compacts, 850 °C, is comparable with that obtained previously by the present authors [13] and others [12,17] for NbAl<sub>3</sub> synthesis, indicating that for this composition the reaction is started at Nb-Al interfaces.

The previous observations when associated with the phases identified in the microstructure of the as-

reacted pellets may indicate the reaction sequence. Ignition temperatures observed for 30 and 20 at.% Ni compacts can be associated with Ni<sub>2</sub>Al<sub>3</sub> or NiAl initial synthesis (heats of formation of 56.48 kJ mol<sup>-1</sup> and 58.79 kJ mol<sup>-1</sup> [18] respectively). The heat released by these low temperature reactions was enough to raise the bulk temperature to the onset of the reaction at Nb-Al interfaces. In the Nb-10Ni-70Al compacts, the lesser number of contacts between Ni and Al, providing the Ni concentration is low, was probably not sufficient to generate the heat necessary for starting the bulk reaction, which occurred only after the reaction was started at Nb-Al interfaces at higher temperature.

The available section of the equilibrium phase diagram of the Nb-Ni-Al system at 1140 °C [16], indicates only the presence of the phases NbAl<sub>3</sub> and NiAl, in amounts that depend on alloy composition. The results obtained for the heat treated pellets show that the 6 h heat treatment was insufficient to complete the transformations since unreacted niobium is still observed. However, this time was enough to transform Ni<sub>2</sub>Al<sub>3</sub> into NiAl completely, and substantial amounts of unreacted niobium into NbAl<sub>3</sub>.

#### 4. Conclusions

The preliminary investigation conducted in this work on reaction sintering of Nb-Ni-Al compacted powder mixtures revealed that the reaction occurs for all compositions studied. The ignition temperatures are affected by composition indicating a change in reaction mechanisms. Compacts containing 20 at.% or more Ni reacted at 500 °C whereas for low Ni content compacts the reaction is initiated at 850 °C. The phases NbAl<sub>3</sub> and unreacted niobium were present in all pellets containing nickel. NiAl and NbNiAl occurred only in 30 at.% Ni containing pellets whereas Ni<sub>2</sub>Al<sub>3</sub> was formed for the other compositions. Although the heat treatment of as-reacted pellets at 1140 °C for 6 h introduced noticeable changes in the phases present, it was insufficient to promote final equilibrium.

The low ignition temperature observed for some mixtures plays an important economical role, especially when the synthesis of higher ignition phases is concerned.

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