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Reaction process during relative sintering of NiAl

L. PLAZANET, F. NARDOU
LMCTS, CNRS Université de Limoges, 123 Avenue Albert Thomas, 87060 Limoges, France

Nickel aluminide compounds were synthesized by the thermal explosion mode of the self-propagating high temperature synthesis (SHS). The effects of green density and heating rate on the combustion characteristics and the microstructure of the products were studied. It was found that the combustion can not be ignited with heating rates lower than 5 K min^{-1}. In this case, the formation of NiAl can be achieved by classic reactive sintering. At heating rates higher than 5 K min^{-1}, a precombustion stage exists for compacted samples allowing the ignition of the reaction at low temperature. Combustion temperature were found to be higher than thermodynamic predictions in argon and, moreover in air, because of the formation of aluminium oxide which triggers the NiAl synthesis reaction.

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1. Introduction

Nickel aluminide compounds display a number of attractive properties for developing new materials. The Ni–Al binary system [1] is composed of five ordered intermetallic phases (Fig. 1). Single phase NiAl is one of the most attractive compounds. It has a high melting point (1638 °C), a low density (5.91 g cm^{-3}), an excellent oxidation resistance and a good thermal conductivity (75 W m^{-1} K^{-1}). Because of these properties NiAl is a material with several potential engineering applications as corrosion-resistance coatings [2, 3], metallization of semiconductors [4] and surface catalysts [5]. It has also replaced Ni-based superalloys for the fabrication of high-temperature turbine blades and vanes [6]. However, like many intermetallics, NiAl is brittle at room temperature and has poor strength at high temperature, which limits the usefulness of this material.

The strengthening for high-temperature applications can be enhanced by alloying NiAl with refractory elements such as Hf, Ta and Nb [7–9]. The room-temperature ductility can be improved by microalloying with Fe, Mo and Ga [10] or Co and Cr [11]. NiAl composites are also being developed by dispersing a ceramic phase in the matrix. Ceramic phase can be formed by particles (TiB_2 [12, 13], HfC [14], AlN [15]) or fibres (Al_2O_3 [12]).

There are several routes for producing nickel aluminides, such as casting, rapid solidification, mechanical alloying or powder processing. In the case of NiAl, several studies have shown the interest of using a self-sustained reaction (so called self-propagation high temperature synthesis or SHS synthesis) [16–23]. This technique is concerned with the ignition of a composed powder mixture, in air or an inert atmosphere, producing a chemical reaction, with sufficient heat released (exothermic reaction) that it becomes self sustaining. There are two basic modes of combustion reaction differing by their means of ignition. In the propagating reaction mode, the powder reactants are ignited locally at one end of the sample using an external source of heat, and the combustion wave propagates through the reactant pellet converting it into product. The second method of producing SHS synthesis is thermal explosion: the powder reactants are heated up at a constant rate using a furnace until the reaction is initiated uniformly throughout the pellet at the ignition temperature T_{ig}. During the reaction, the combustion temperature T_c reaches a very high level in a very short time.

SHS processes offer a few advantages. The extremely high temperature vaporizes volatile contaminants, so products are of a high purity. High temperatures are not required and processing times are short, so energy savings are important. The major drawback of the products made by SHS reaction is the high level of remaining porosity. Typically, products are either powders or spongelike structures with up to 50% porosity. This results from intrinsic volume shrinkage, violent volatilization of reactants or outgassing of entrapped gases.

Concerning the nickel aluminium intermetallics, the reaction mechanisms occurring during the combustion synthesis have been studied principally in the case of Ni_3Al [24]. Parameters such as heating rate [25], particle size and atmosphere [26] are reported to have a great importance on the combustion processes, on the final densification and on the final composition. In the case of Ni_3Al, it is possible to obtain a dense product because the combustion reaction is not highly exothermic so the final porosity is about 3% with optimal sintering processes (high heating rates, vacuum atmosphere, boron addition) [27, 28].

In the case of NiAl, combustion reactions have been studied essentially with a local ignition. Works have also been done to produce fully dense NiAl and NiAl matrix composite using SHS combined with external pressure [15, 29, 30].

The present study attempts to explain the reaction mechanisms of the NiAl formation using the thermal

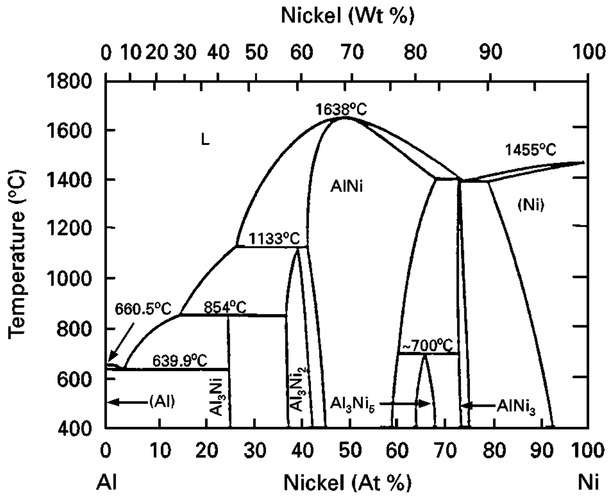

Figure 1 Phase diagram for Ni–Al system [1].

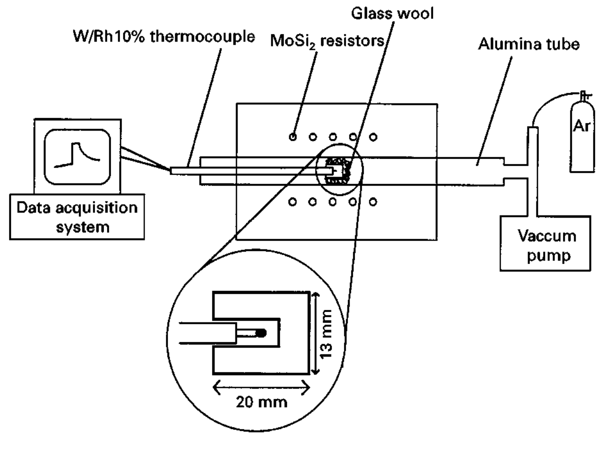

Figure 2 Experimental configuration for temperature measurement tests illustrating the thermocouple placement.

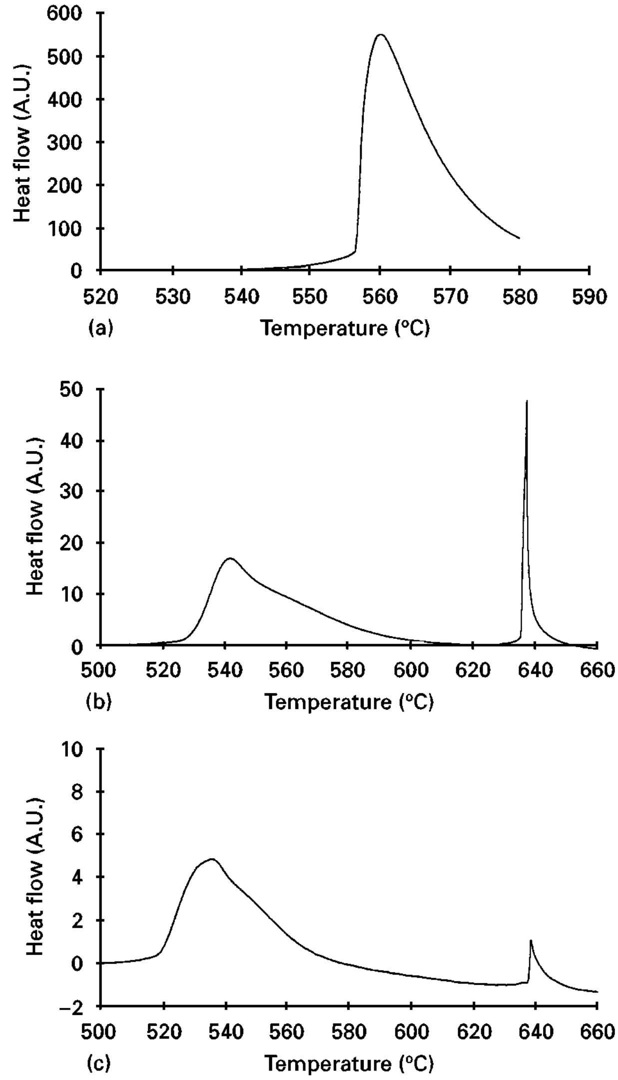

Figure 3 DTA curves of Ni–Al compacted mixtures heated in argon with different heating rates: (a) 20 K min^{-1}, (b) 3 K min^{-1} and (c) 1 K min^{-1}.

explosion mode. The objective was to determine the amount of heat released and the temperature reached during the combustion. Results were compared to thermodynamic predictions. The combustion reaction was studied as function of parameters such as green density or heating rate. The microstructure evolutions during reaction are also presented and discussed.

2. Experimental procedure

A Ni-123 powder from CERAC with an average particle size of about 5 μm and a purity of 99.9%, an aluminium powder from CERAC with an average particle size of 15 μm and a purity of 99.5% were used.

The powders were dry mixed in the molar ratio of 1 : 1 using a Turbulat type mixer for 2 h. The resulting mixture was cold pressed into green compacts with diameters of 13.1 mm with compacting pressure ranging 50 to 250 MPa, resulting in green density from 62 to 95% of theoretical density.

Natural sintering was performed in a horizontal tube furnace. The sintering atmosphere was argon or air with heating rates of 1 to 30 K min^{-1}. A 0.4 mm diameter hole was drilled from the bottom of the cylinder up to half of its height to accomodate a W/Rh 10% thermocouple to follow the temperature in the sample (Fig. 2).

Microstructures were characterized by X-ray diffraction (XRD), electron microprobe analysis (EDAX) and scanning electron microscopy (SEM). Differential thermal analysis (DTA) was used to determine the reaction temperatures and the amount of heat released. Dilatometric and thermogravimetric measurements were done in alumina crucibles to determine the dimensional and mass changes.

3. Results

Because of its exothermicity, following the reaction of formation of NiAl with differential thermal analysis is possible. Fig. 3 shows the DTA curves obtained by heating a blend of Ni and Al with heating rates of 20 K min^{-1} (Fig. 3a), 3 K min^{-1} (Fig. 3b) and 1 K min^{-1} (Fig. 3c) under argon. Samples pressed at 70% of the green density were used. When heating rate of 20 K min^{-1} is employed, only one strongly exothermic peak is detected, starting at 548 °C. With a heating rate of 3 and 1 K min^{-1}, there are two low peaks, the first one starting at 520 °C and the second at 638 °C. The transition for the two peaks to the one peak regime occurs for a heating rate of 5 K min^{-1}.

3.1. One peak regime

3.1.1. Steps of the thermal explosion

In the case of a heating rate higher than 5 K min^{-1}, the synthesis of NiAl is caused by a thermal explosion, i.e. a SHS reaction because of the high amount of heat suddenly released at the reaction temperature.

The evolution of the temperature inside the sample has been followed by using a W/Rh thermocouple. A typical temperature–time curve was recorded during the thermal explosion of a sample precompacted at 70% of theoretical green density and heated with a rate of 20 K min^{-1} in argon atmosphere (Fig. 4a). Before T'_{ig}, the temperature in the sample raises at 20 K min^{-1} as the furnace temperature (1). T'_{ig} is the temperature from which an abnormal increase begins. This stage is called precombustion stage (2). When the sample reaches T''_{ig}, the SHS reaction proceeds explosively (3). Then, the combustion temperature T_c is seen to be approximatively 1680 °C, which is higher than the melting point of NiAl compound (1638 °C). The pellet keeps this temperature for 10 s (4) and then, it drops at the furnace temperature (5).

Another type of curve was obtained when heating a mixture not precompacted (Fig. 4b). The major difference with the heating of a compacted sample is the absence of the precombustion stage. The ignition temperature T_{ig} is higher than previously (635 °C). At this one, the sample reaches immediately the combustion temperature.

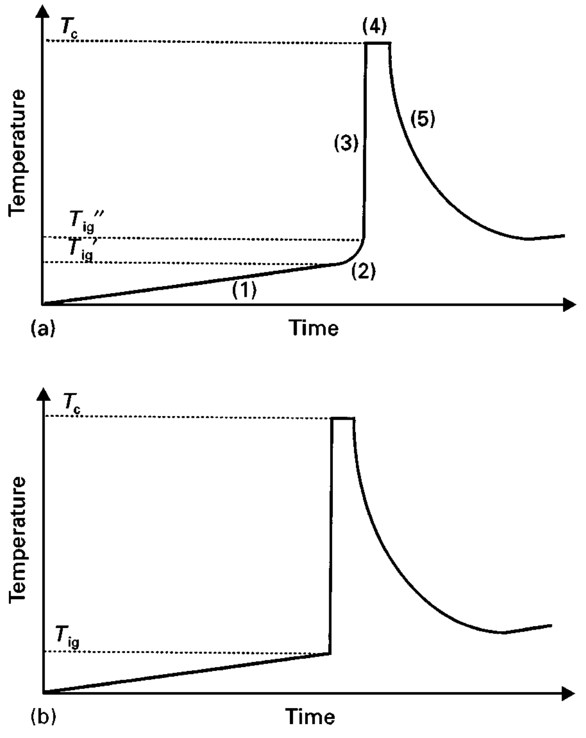

Figure 4 Typical exothermic peak in the thermal explosion mode of Ni + Al = NiAl for (a) compacted sample and (b) non-compacted sample.

3.1.2. Effects of green compaction and heating rate

The ignition temperature T'_{ig} and T''_{ig} were followed in the case of compacted samples from 50 to 250 MPa, i.e. green compaction from 62 to 95% of theoretical. The heating rate was 20 K min^{-1} and the atmosphere was argon. The influence of heating has been followed on samples which were green compacted at 70% and heated from 5 to 30 K min^{-1}. Results are given in Figs 5 and 6. Values of T'_{ig} and T''_{ig} obtained by thermocouple measurements where confirmed by DTA measurements.

When the powder is not precompacted, there is no precombustion stage. The ignition temperature is higher than for compacted samples (635 °C). When the green density is about 62%, precombustion stage begins at 548 °C and combustion occurs at 560 °C. Both T'_{ig} and T''_{ig} decrease when increasing the green density.

Concerning the influence of the heating rate, ignition temperatures are decreasing when increasing the heating rate. The combustion temperature remains constant at 1680 °C when increasing the heating rate.

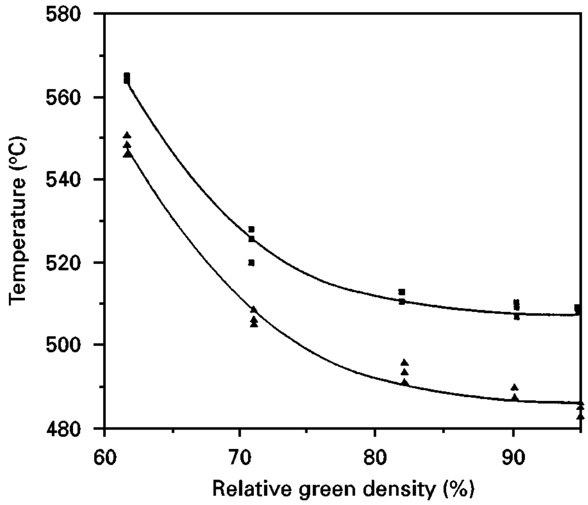

Figure 5 Effect of green density on the ignition temperatures, T'_{ig} (▲) and T''_{ig} (■), when combustion was conducted in argon.

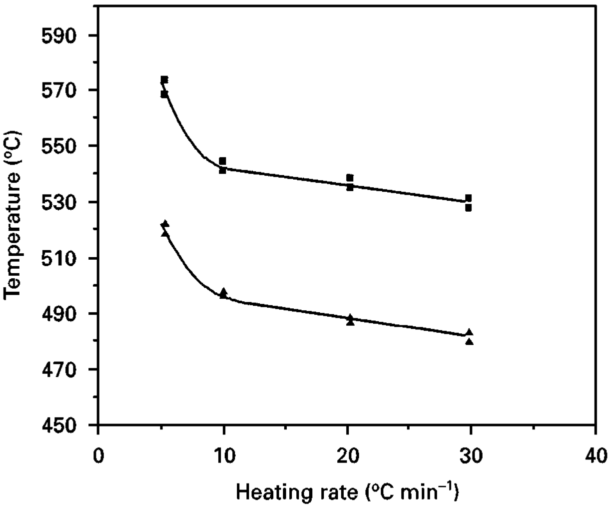

Figure 6 Effect of heating rate on the ignition temperatures, T'_{ig} (▲) and T''_{ig} (■), when combustion was conducted in argon.

Concerning the microstructure, for compacted samples, XRD patterns show that after the thermal explosion, all the powders have reacted to form NiAl (Fig. 7a). These results were confirmed by electron microprobe analyses. The final product is highly porous (about 50% of densification). Large voids are present because of the outgassing of entrapped gases (Fig. 8b).

3.2. Two peaks regime

When the heating rate is lower than 5 K min^{-1}. DTA curves show the presence of two weak exothermic peaks. The first one starts at 535 °C and the second one at 638 °C, at the Ni–Al eutectic temperature. This reaction is not a thermal explosion because no significant increase of temperature can be detected. Samples which have passed the first and the second peak were analysed by X-ray (Fig. 7b) and EDAX and observed by using SEM (Fig. 9).

XRD patterns show that after the first DTA peak, the mixture analysis contains nickel and aluminium but also reveals the presence of the $NiAl_3$ and Ni_2Al_3 phases. Concerning the microstructure, Ni_2Al_3 is localized between the grains of nickel and aluminium, forming a dense layer between these two phases (Fig. 9a). $NiAl_3$ is not visible by using SEM. It must be present in relatively low quantity because of the lowness of the X-ray signal concerning this phase. After the second reaction occurring at the eutectic temperature (638 °C), the same four phases remain present but the microstructure has changed. The barrier

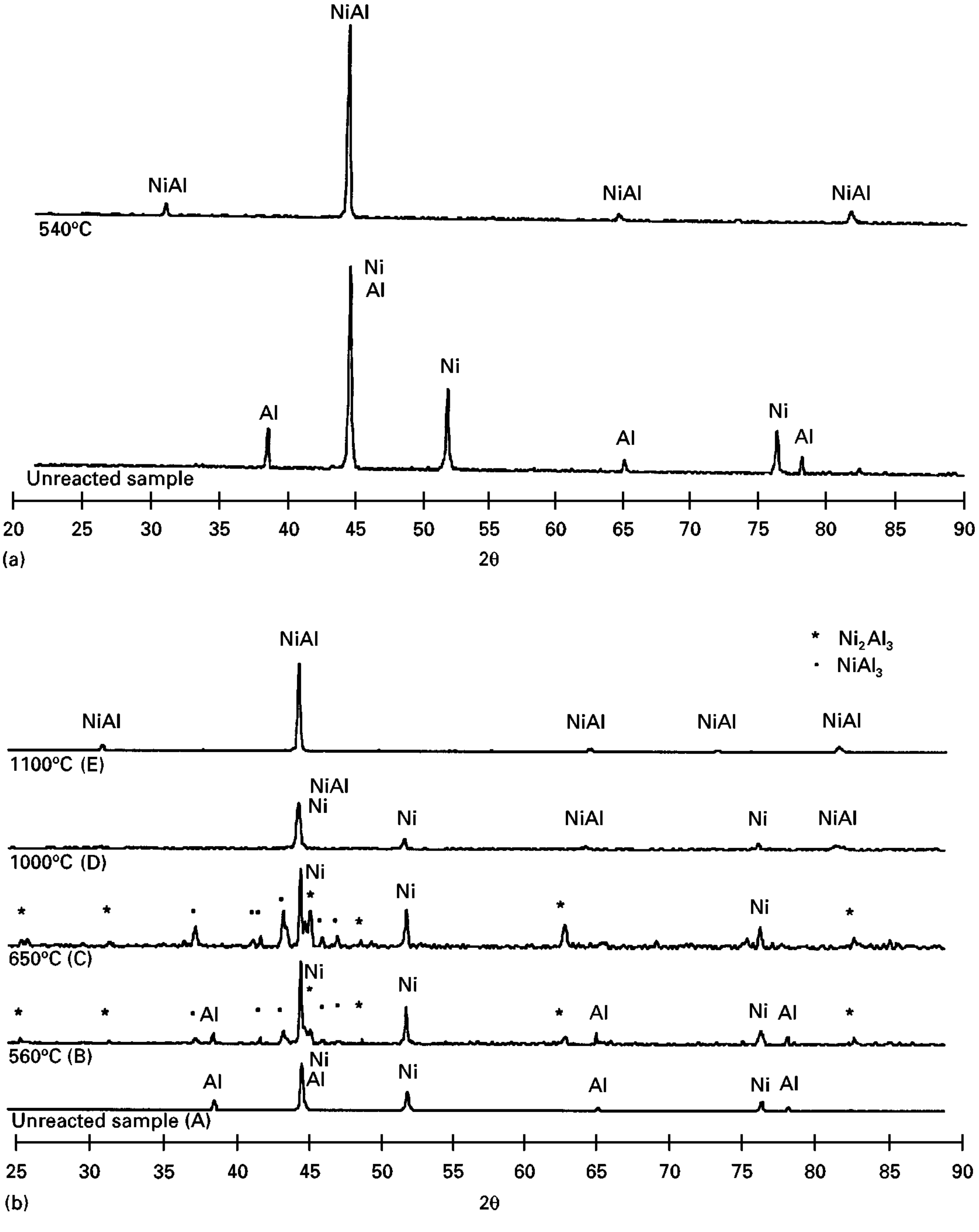

Figure 7 XRD patterns of unreacted and reacted samples (a) with a heating rate of 20 K min^{-1} and (b) with a heating rate of 3 K min^{-1}: A, before the first exothermic peak; B, after the first exothermic peak; C, after the second exothermic peak; D and E at higher temperatures.

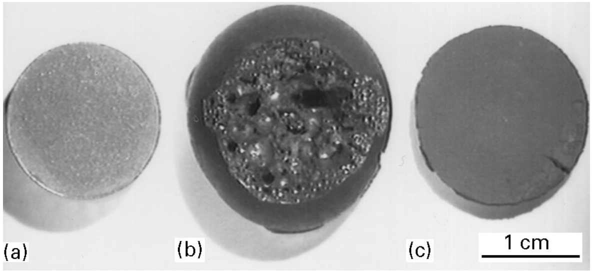

Figure 8 Photographs of (a) unreacted sample, (b) sample heated at 600 °C with a heating rate of 20 K min^{-1} in argon (presence of large voids because of the thermal explosion) and (c) sample heated at 600 °C with a heating rate of 3 K min^{-1} (no large voids but isotropic dedensification).

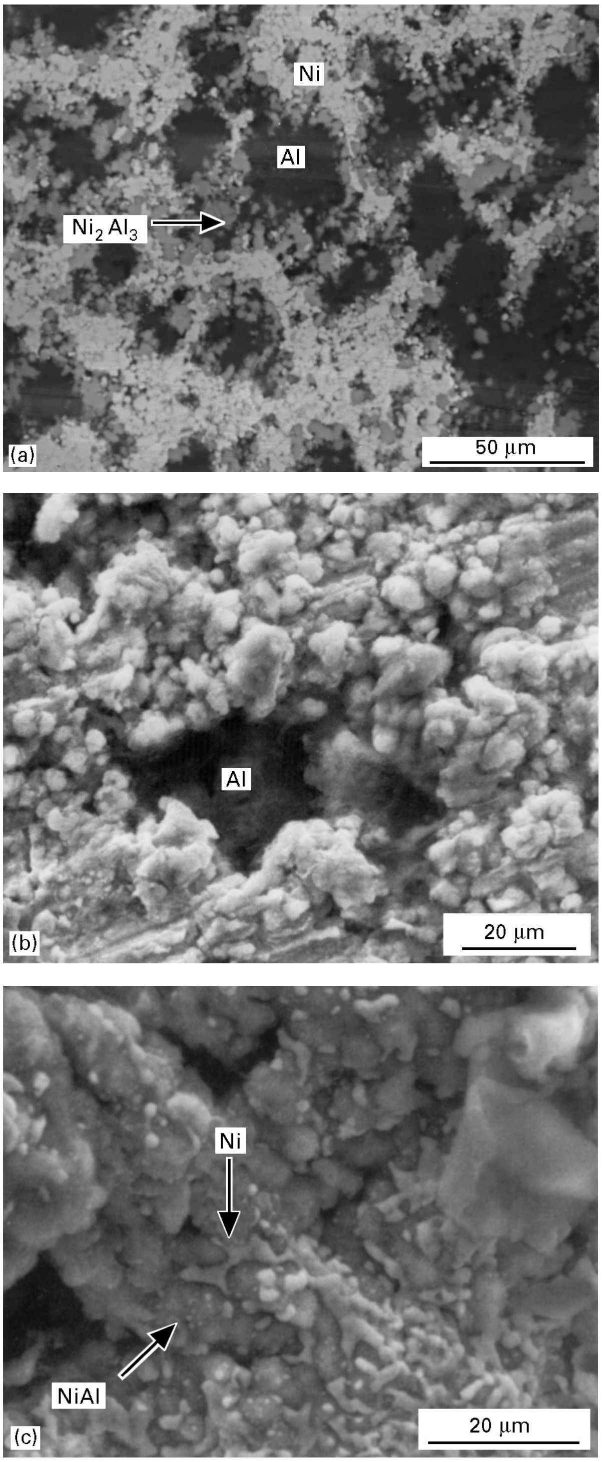

Figure 9 Backscattered electron micrograph of the microstructure of reacted Ni–Al sample heated at 3 K min^{-1} which have passed (a) the first exothermic peak, (b) the second one and (c) at 1000 °C.

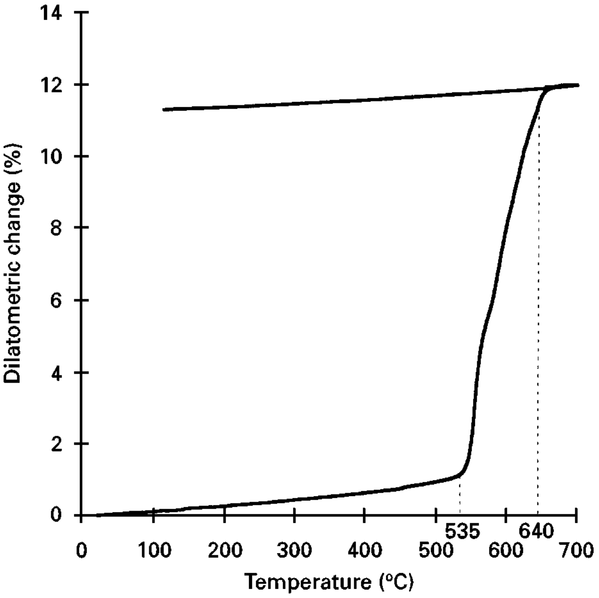

Figure 10 Dimensional changes of Ni–Al compact during heating at 3 K min^{-1}.

formed by Ni_2Al_3 have disappeared. The four phases are indistinguable except for some zones containing aluminium which have not reacted (Fig. 9b). The reaction occurring at 638 °C is liquid–solid reaction.

When heating this mixture at higher temperature, these phases are transformed in NiAl, the expected phase. At 1000 °C, Ni_2Al_3 and $NiAl_3$ are undetectable. Fig. 9c shows the formation of NiAl on the grains of nickel at this temperature. At 1100 °C, all the nickel have been consumed and the product is formed by pure NiAl.

The dimensional changes were observed by a dilatometric measurement (Fig. 10). An important dedensification occurs during the formation of the Ni_2Al_3 and $NiAl_3$ phases from 535 to 640 °C (corresponding to the two exothermic peaks).

The dedensification is isotropic and leads to a porous final product. No large void remains when using a heating rate lower than 5 K min^{-1} because of the absence of explosion (Fig. 8c).

4. Discussion

4.1. SHS reaction

The thermochemistry of the thermal explosion and generally of a SHS reaction can be explained by examining the enthalpy of both reactants and products as a function of temperature. If the combustion reaction is initiated at T_{ig}, the heat of the reaction is given by

$$\Delta H(T_{ig}) = -[H(R) + H(P)] \qquad (1)$$

where $H(R)$ is the amount of heat necessary to heat the reactants from T_0, the room temperature to T_{ig}, the ignition temperature. $H(P)$ is the amount of heat absorbed by the products under adiabatic conditions to raise the temperature of the products from T_{ig} to T_{ad}, the adiabatic temperature, i.e. the combustion temperature in adiabatic conditions. The amount of heat

$H(\mathrm{R})$ is given by Equation 2

$$H(\mathrm{R}) = \int_{T_0}^{T_{\mathrm{ig}}} \sum n_i C_{\mathrm{p}}(R_i)\mathrm{d}T + \sum_{T_0 - T_{\mathrm{ig}}} n_i L(R_i) \quad (2)$$

where n_i, $C_{\mathrm{p}}(R_i)$, and $L(R_i)$ are the reaction stochiometric coefficients, heat capacities and the phase transformation enthalpies (melting) of the reactants R_i.

The amount of heat absorbed by the products during the explosion is given by the Equation 3

$$H(\mathrm{P}) = \int_{T_{\mathrm{ig}}}^{T_{\mathrm{ad}}} \sum n_j C_{\mathrm{p}}(P_j)\mathrm{d}T + \sum_{T_{\mathrm{ig}} - T_{\mathrm{ad}}} n_j L(P_j) \quad (3)$$

where n_j, $C_{\mathrm{p}}(P_j)$, and $L(P_j)$ are the reaction stochiometric coefficients, heat capacities and the phase transformation enthalpies (melting) of the products P_j.

Considering the reaction given NiAl from Ni and Al

$$\mathrm{Ni} + \mathrm{Al} \rightarrow \mathrm{NiAl} \quad (4)$$

The heat of formation is given by Equation 5

$$-\Delta H(T_{\mathrm{ig}}) = \left[\int_{T_0}^{T_{\mathrm{ig}}} (C_{\mathrm{p_s}}(\mathrm{Ni}) + C_{\mathrm{p_s}}(\mathrm{Al}))\mathrm{d}T \right] + \left[\int_{T_{\mathrm{ig}}}^{T_{\mathrm{m}}} C_{\mathrm{p_s}}(\mathrm{NiAl})\mathrm{d}T + L(\mathrm{NiAl}) + \int_{T_{\mathrm{m}}}^{T_{\mathrm{ad}}} C_{\mathrm{p_l}}(\mathrm{NiAl})\mathrm{d}T \right] \quad (5)$$

where T_{m} is the melting temperature of NiAl.

No phase transformation for the reactants is taken in account because the ignition temperature is lower than the melting temperature of aluminium (933 K) and nickel (1726 K). A schematic representation of this process is determined and shown in Fig. 11 in which the thermodynamic data are taken from Barin *et al.* [31].

For a reaction ignited at room temperature (SHS mode with local ignition), the adiabatic temperature is found to be the melting temperature of NiAl (1912 K) [32]. Increasing the initial temperature by preheating usually results in an increase of the adiabatic temperature. In the case of NiAl, because of the high phase transformation enthalpies, the adiabatic temperature remains constant and equal to the melting temperature of NiAl in a range of ignition temperature from 293 to 913 K. Under these conditions, the adiabatic temperature should be 1912 K for an ignition temperature of 540 °C (813 K). The combustion temperature of our case is higher of 40° than the predicted temperature. This exothermic phenomenon is supposed to originate from the oxidation of aluminium and/or nickel during the preheating, which imputs an extra-heat to the system and triggers the combustion reaction.

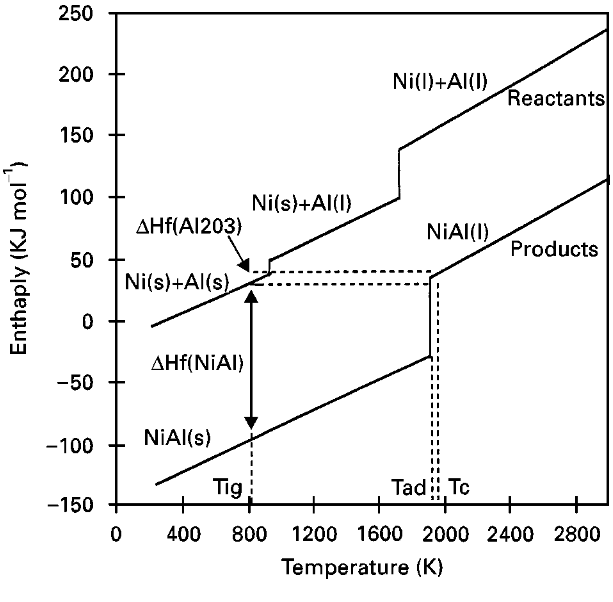

Figure 11 Enthalphy–temperature curves of reactants (Ni + Al) and product (NiAl). At $T_{\mathrm{ig}} = 813$ K, heat produced by $\mathrm{Al_2O_3}$ formation is used to trigger the NiAl combustion synthesis reaction (under argon).

To confirm this hypothesis, the thermal explosion of a sample has been done in air. The combustion temperature reaches a value of 1795 °C, which is 115 °C higher than in argon and 155 °C higher than thermodynamical predictions. The X-ray analysis of the sample after reaction shows the presence of aluminium oxide (Fig. 12). Thermogravimetric analysis were done in order to understand the origin of this oxide (Fig. 13).

During the heating in air, only the nickel oxide NiO is produced. There is no alumina appearing between 20 and 500 °C. Indeed, aluminium grains are naturally covered of a protective layer of alumina avoiding their oxidation at low temperature. The mass gain of a mixture of Ni–Al follows the mass gain of pure nickel. It is then possible to conclude that alumina appearing in the X-ray analysis is formed not before but during the thermal explosion because of the very high temperature reached during the combustion. The difference between the calculated and the experimental combustion temperature is due to the strong exothermicity of the aluminium oxidation which imputs extra-heat to the system and triggers the combustion reaction.

Unfortunately, it is not possible to follow the gain of mass during the thermal explosion because the important amount of dissipated heat causes cracking of the alumina nacel containing the sample. For the same reason, the measurement of the heat released by differential thermal analysis is not possible.

When heating under argon, alumina is undetectable by X-ray analysis but should exist because the combustion temperature is 40 °C higher than predictions. In order to obtain a pure product after the explosion, an efficient vaccum system and a high purity argon must be used.

Concerning the combustion reaction, when a Ni–Al cold compacted mixture is rapidly heated, the thermal explosion leading to the formation of NiAl occurs in two steps. Indeed, as for the Ti–Ni system [33], there is a precombustion stage prior to the thermal explosion. When the furnace temperature reaches T'_{ig}, the grains of Ni react with those of Al at their boundaries to form a layer of NiAl. Because of the cold compaction, contacts between Ni and Al are numerous so there is enough heat released by the reaction to induce the increase of the temperature in the sample from T'_{ig} because of the high exothermicity of the

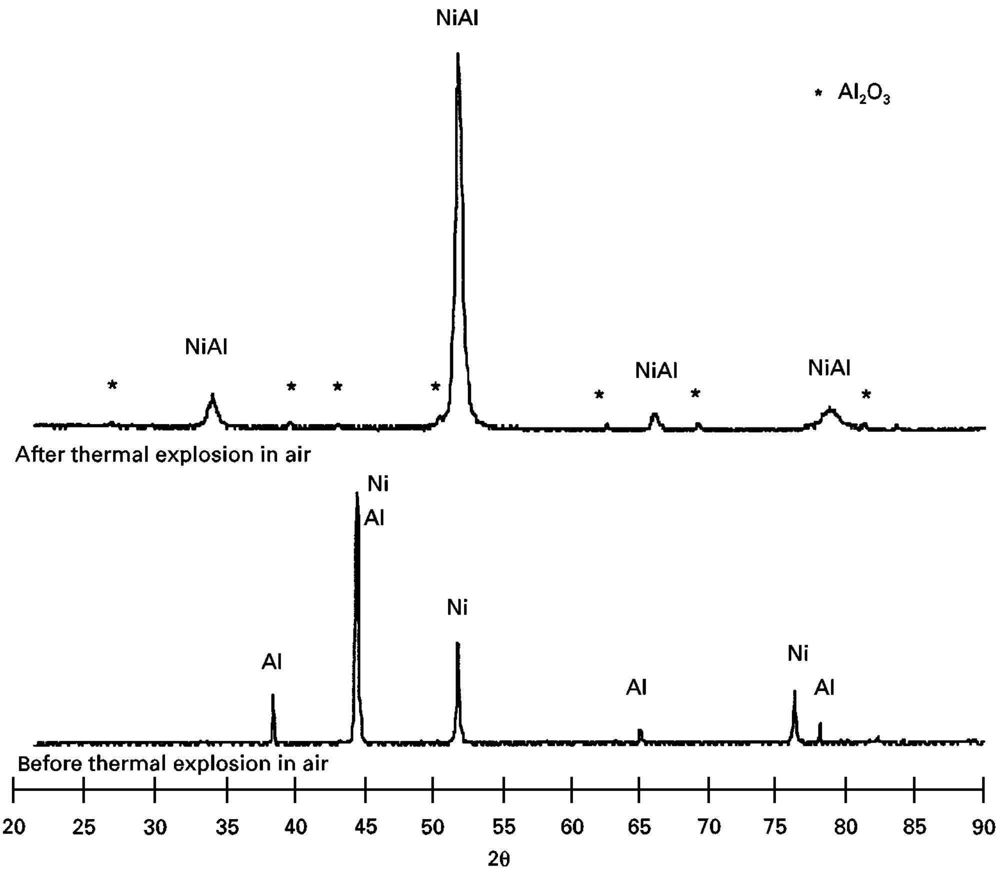

Figure 12 XRD patterns of Ni–Al mixture heated in air (a) before the combustion reaction and (b) after the combustion reaction.

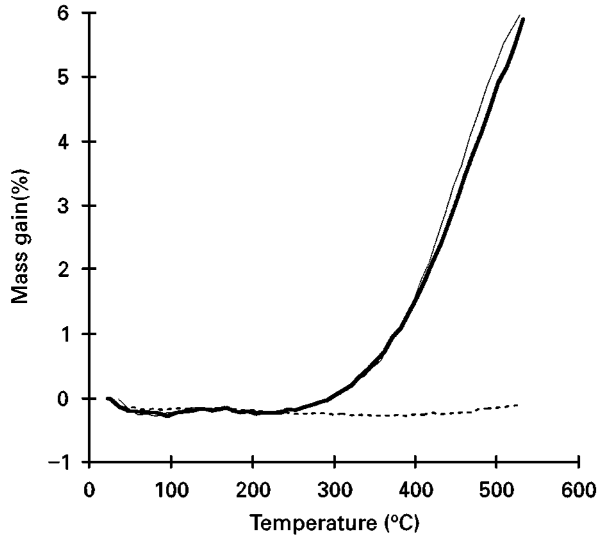

Figure 13 Thermogravimetric analysis of Al (– – –), Ni (——) and NiAl (▬) heated in air with a heating rate of 20 K min^{-1}.

reaction. This increase of the temperature, in turn, leads to more reaction releasing more heat, and so on. At T''_{ig}, the dramatic increase in the reaction rate results in the thermal explosion of the mixture.

In the case of a non-precompacted mixture, there is no precombustion stage. The number of contacts between Ni and Al grains is lower than for a compacted sample. The zones of formation of NiAl are not numerous so the amount of heat released is too weak to be detected at T'_{ig} and to allow the beginning of the self-sustained reaction. The combustion occurs because the amount of heat necessary to ignite the reaction is provided only by the furnace. It explains that the combustion begins at higher temperature than for a compacted sample.

When the green density increases, the ignition temperature is decreasing. It stresses the hypothesis that a high level of compaction provides a high number of contacts between the grains of Ni and Al. The more the number of contacts, the more heat is released, so the thermal explosion begins earlier than for a less cold compacted sample.

4.2. Classical reactive sintering

For low heating rates, the NiAl formation can be divided into several steps. At first, the phases $NiAl_3$ and Ni_2Al_3 appear at 520 °C. Ni_2Al_3 is developing as a dense layer at the interface of the grains of nickel and aluminium making difficult the reaction between the two elements because of the lack of contacts. Then, the system can not produce enough heat to reach the eutectic temperature so there is no melting. The reaction of formation of $NiAl_3$ and Ni_2Al_3 is a solid–solid reaction. The system remains the same until the furnace reaches the eutectic temperature at 640 °C. The liquid which forms spreads the Ni_2Al_3 layer allowing more nickel and aluminium grains to react. The weakness of the exothermic peak shows that the reaction is not important. Pictures have shown that some Al rich zones have not reacted.

When the temperature becomes higher, the $NiAl_3$ and Ni_2Al_3 phases react with the remaining nickel and the aluminium and this reaction induces the apparition of the expected NiAl phase. The nickel is totally consumed from 1100 °C.

5. Conclusion

The heating rate is a very important parameter for the combustion synthesis of NiAl intermetallic by using the thermal explosion mode. At heating rate higher than $5\ K\ min^{-1}$, the combustion can be induced by preheating the sample at 538 °C. Combustion temperatures of 1680 °C in argon and 1795 °C in air have been reached which is higher than the melting point of NiAl phase. The oxidation reaction of aluminium into alumina is able to trigger the thermal explosion because of the high exothermicity of this reaction, so synthesis of NiAl must be conducted in ultrapure argon to obtain a pure product. With lower heating rate, thermal explosion can not be ignited. The intermediate $NiAl_3$ and Ni_2Al_3 phases are present before the formation of the NiAl phase at 1100 °C.

In all cases, products are very porous. In order to obtain a dense intermetallic which could be used for structural applications, it is necessary to add a step including an external applied pressure at the process of fabrication.

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