A study of self-propagating high-temperature synthesis of NiAl in thermal explosion mode

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Abstract

Processing of NiAl in the thermal explosion mode of Self-propagating High-temperature Synthesis (SHS) was investigated at different heating rates varying between 5 and 60 °C/min. Three different Ni particle sizes were used and experiments were conducted in vacuum and argon atmospheres to arrive at an optimized processing window. On-line videography of the process provided the visual evidence of the different stages of thermal explosion. Evolution of the process was studied by on-line thermometry, optical and scanning electron microscopy, XRD and mercury intrusion porosimetry. The results showed that the combustion behaviour was independent of the atmosphere but strongly dependent on the rate of heating and hence on the extent of pre-combustion reaction. Process modelling was carried out to describe the effect of the rate of heating both on the pre-combustion reaction and the combustion in the case of thermal explosion. This model could successfully rationalize the experimental results.

Keywords: Self-propagating high-temperature synthesis (SHS); NiAl; Diffusion; Theory & modelling

1. Introduction

Chemical reactions that are sufficiently exothermic can transform spontaneously into products when initiated and propagate through the reactants’ mixture in the form of a combustion wave and this is the basis of Self-propagating High temperature Synthesis (SHS) or combustion synthesis [1]. Two variants of this process are recognized, namely the plane wave propagation mode and the thermal explosion mode. The plane wave propagation mode involves triggering the reaction by rapid heating of one end of the specimen. The reaction zone propagates as a wave front through the sample, driven by the exothermicity of the reaction. In the thermal explosion mode, the compacted reactant powders are heated up at a rapid rate in a furnace until the reaction is initiated uniformly throughout the sample. SHS is an efficient and attractive technique for the preparation of NiAl which has high heat of formation (118.4 kJ/mole) [2] and is one of the most promising intermetallic compounds for high temperature structural applications owing to the low density, high strength and
good corrosion resistance. Its low tensile ductility is one of the main reasons that severely restricts its use but can be averted to a great extent by keeping the composition very close to the stoichiometry and purity of the alloy very high [3]. Interestingly, the combustion synthesis technique can be judiciously employed to fulfill both. Therefore, there were many studies on the combustion synthesis of nickel aluminate in both plane wave propagation (PWP) [4] and thermal explosion mode [5], its mechanisms of structure formation [6], influence of initial conditions on combustion [7] and densification characteristics [5]. Dunand [8], in an exhaustive compilation, reviewed the different reactive synthesis techniques including combustion synthesis, used for the aluminides by different researchers with special emphasis to nickel aluminides. Earlier studies on SHS showed that a series of intermediate phases formed before the product of the desired composition and structure finally evolved in Ni–Al system [6,9]. Fig. 1 shows the various equilibrium phases present in Ni–Al system. The sequence of phase evolution which is most widely accepted is: Al + Ni + Al7Ni3 + Al3Ni2 + Ni3Al. This is equivalent to the sequence of phase evolution reported in binary bulk diffusion couples of Ni/Al [10]. In the case of a thin-film diffusion experiment also Al2Ni is reported to be the first phase to form in the Ni/Al system [11].

Li and Sekhar [12] surmised that the melting point of Al was the ignition temperature ($T_{ig}$) of Ni–Al combustion in the PWP mode and observed no evidence of the eutectic phase formation in the quenched microstructure possibly because of the high heating rate operative there. However, they reported the eutectic melting at 920 K in the thermal explosion mode and ascribed that to the relatively lower rate of heating. Effect of the particle size of the low melting constituent (Al) on the phase evolution was reported to be insignificant, but an interconnected network of it with minimal interfacial area was required for optimum densification [13]. Combustion temperature ($T_c$), propagation velocity, initial and final porosities, grain size of the reaction product and the microstructure evolution were found to be much influenced by the particle size of the high melting constituent, that is, Ni. Li et al. [12] reported that the product phase structure was independent of the variation of particle size of Ni (from 2.7 to 27.3 µm) and single phase NiAl always formed as per the stoichiometry. In the reactive sintering experiments of Ni3Al [5,7], variation of the heating rate played an important role in the transient liquid phase formation, value of $T_c$, melt fraction of the product and overall densification. This was also true for the fabrication of monolithic NiAl using a similar technique. Philpot et al. [7] reported the dependence of $T_{ig}$ on the rate of heating during thermal explosion of Ni–Al powder mixtures; the extent of the pre-combustion diffusion reactions during heating was found to influence the principal combustion reaction.

However, the question of the dependence of the product phase compositions on the reactant particle sizes has not been addressed with sufficient attention in the combustion of the Ni–Al system in the thermal explosion mode. Multiple phases can result when large particles of the reactants are used but the same particles could yield single phase NiAl by varying the heating rates. As will be seen in the following sections, a large variety of phase assemblages could be generated through the combinations of these two reaction parameters. Moreover, if the evolution of phases follows the path as described above, the occurrence of the intermediate phases in the final products signifies that the growth kinetics of the intermediate phase or phases

![Fig. 1. Binary phase diagram of Ni–Al system.](image-url)
is instrumental in deciding the final phase compositions of the product. The kinetics of growth can be either interface-controlled or diffusion-controlled depending on whether the thickness of the intermediate layer formed at the particle interfaces, is less or more than a critical thickness. Heating rate can be so chosen as not to allow a particular intermediate phase to grow to this thickness so as to achieve complete conversion to the desired final product. Thus, the present investigation aims at addressing the issues namely, the effect of particle size, rate of heating and atmosphere on thermal explosion of NiAl by detailed microstructural analysis and optimization of the process parameters to arrive at an effective processing window for the formation of dense single phase NiAl of homogeneous chemistry. Simple models are formulated to simulate the effect of heating rate on thermal explosion and explain the experimental results.

2. Experiments

2.1. Sample preparation

All the experiments were carried out with the equiatomic mixture of high purity (99.9%) Ni and Al powders. Three different varieties of Ni powders (referred to as Ni 1, Ni 2 and Ni 3 respectively) and one Al powder were used as the starting raw materials. Particle size and morphology were analyzed for each of them by a laser diffraction technique and scanning electron microscopy (SEM) respectively. The reactant powders were dry-mixed thoroughly in a tumbler ball mill and cold pressed at a pressure varying from 75 to 150 MPa into cylindrical specimens of 12 mm diameter and 6–8 mm height. The resultant variation in the green density was from 55 to 65% of theoretical.

2.2. Thermal explosion

Reactions of these three different (Ni+Al) green compacts (corresponding to the three different Ni powders) were carried out both under vacuum and in the argon atmosphere in the thermal explosion mode and at different heating rates which varied between 5 and 60 °C/min. A cylindrical transparent silica reactor was used for the reactions, details of which were given in an earlier publication [14]. The specimen, with an embedded thin B-type (Pt-6Rh/Pt-30Rh) thermocouple of 200 μm diameter, was put into the cold furnace and heated at a pre-programmed linear rate. Thermocouple output was collected online in a computer at a maximum acquisition speed of 100 Hz. The process of combustion was recorded by a CCD camera at a speed of 25 frames/s and stored online in a computer through a high speed frame grabber card. Thermal analysis was done to study the reaction sequence and determine the ignition point in a differential scanning calorimeter (DSC) in argon atmosphere and at a heating rate of 10 °C/min. A few samples were soaked at $T_{\text{liq}}$ to monitor the pre-combustion reactions and the microstructural changes accompanying the formation of the intermediate liquid phase.

2.3. Product characterization

Mercury intrusion porosimetry of the green compacts made of Ni 1, 2, 3 and of those reacted samples of Ni 2 and 3, in which cases the product did not undergo melting, was carried out to monitor the change in size distributions and amount of open pore volumes. Samples made of Ni 1 always resulted in complete melting on reaction and did not evidence the presence of open porosity. Microstructural evolution was studied by optical microscopy and SEM analysis of all the samples after combustion. Samples were etched by an electrolytic technique using a saturated oxalic acid solution bath kept at 10 V. Phase analysis was carried out by the X-ray diffraction (XRD) technique using Cu–Kα radiation. Elemental chemical analysis was carried out by using both electron probe microanalyzer (EPMA) and EDS attached to the SEM.

3. Results

3.1. Powder characteristics

The properties of the reactant powders are compiled in Table 1. Figs. 2 and 3 show the particle
Table 1
Properties of the initial reactant powders

<table>
<thead>
<tr>
<th>Powder Symbol</th>
<th>Nickel</th>
<th>Aluminium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni 1</td>
<td>Ni 2</td>
<td>Ni 3</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>99.9</td>
<td>99.9</td>
</tr>
<tr>
<td>Size ($d_{50}$) (µm)</td>
<td>10.94</td>
<td>110.83</td>
</tr>
<tr>
<td>Nature</td>
<td>Agglomerated</td>
<td>Agglomerated</td>
</tr>
<tr>
<td>Source</td>
<td>Aldrich</td>
<td>Indigenous</td>
</tr>
</tbody>
</table>

Fig. 2. Particle size distributions of the reactant powders.

Fig. 3. Morphologies of the reactant powders.

size distributions and the morphologies of the reactant powders respectively. All the Ni powders were spherical and agglomerated. Al was in single-particle form. The median particle diameters ($d_{50}$) of the powders were 10.94, 110.83, 129.57 and 41.94 µm for Ni 1, Ni 2, Ni 3 and Al respectively.

Fig. 4. (a) DSC plot of Ni+Al equiatomic mixture carried out in flowing argon at a rate of 10 °C/min. (b) Phase analysis of the specimen obtained at the end of the DSC experiment indicating the presence of Al₃Ni, Al₃Ni₂, NiAl and unreacted Ni.
3.2. Thermal analysis

Irrespective of the particle size of Ni, DSC experiments [Fig. 4(a)] showed two peaks, one endotherm at around 640 °C due to the melting of Al-rich eutectic followed immediately by a large exotherm corresponding to the main combustion reaction. However, it did not show any thermal effect for the pre-combustion solid state reaction. Fig. 4(b) shows the phase analysis of the specimen obtained at the end of the DSC experiment indicating the presence of Al₃Ni, Al₃Ni₂, NiAl and unreacted Ni. No free Al was detected.

3.3. Combustion in thermal explosion mode

Under the present experimental conditions Ni 1 compacts underwent combustion at 5 °C/min. Samples made from Ni 2 and Ni 3 could be combusted at the minimum of 15 °C/min heating rate. No combustion was observed for any of the Ni particle size at a heating rate below 5 °C/min. Video output in Fig. 5 records the various steps of the thermal explosion. The sample remained unchanged till the temperature reached approximately 640 °C when a liquid phase formed and exuded and covered all surfaces rapidly. These liquid droplets were subsequently sucked back into the compact at the initiation of combustion and the whole compact turned red hot. Subsequently, the temperature increased rapidly to \( T_c \) and the whole sample became white hot leading to completion of the thermal explosion. This exuded liquid phase was analyzed to be an Al-rich eutectic that melted at 640 °C. This phenomenon occurred under nearly all conditions of the present investigation namely, atmosphere, rate of heating and Ni-particle sizes.

Thermal explosion of the Ni 1 samples resulted in the melting of the product and the resultant shape loss. Coarse Ni powders namely, Ni 2 and Ni 3 resulted in porous products up to a heating rate of approximately 35 °C/min and retained the shape of the preform on combustion. When the rate of heating was more than 35 °C/min they too gave rise to product melting and loss of shape of the preform.

![Fig. 5. Video output showing the various steps of thermal explosion.](image)

3.4. Temperature profile

Fig. 6(a) depicts the time–temperature profiles of compacts containing Ni 1 and Ni 2 at the linear heating rate of 25 °C/min. The behaviour of Ni 2 and Ni 3 were similar. This profile showed a plateau signifying the pre-ignition melting consistent with the results of DSC experiment, followed by initiation of ignition and a sharp rise to the peak of combustion (\( T_c \)) and a second arrest at the crystallization point of the product (\( T_{cr} \)) in case the \( T_c \) surpassed it. \( T_c \) was found to be maximum in the case of Ni 1. Whereas \( T_{ig} \) was minimum for the same. Moreover, appearance of the melt phase and the ignition point was nearly overlapping for Ni 1-compacts.

The temperature profiles of combustion for the different Ni powders changed with the variation in heating rate as well. This was especially the case for coarse Ni (Ni 2 and Ni 3) powders and Fig.
Fig. 6. (a) The time–temperature profiles of thermal explosion of compacts of Ni 1 and Ni 2 at a constant rate of heating (25 °C/min) showing the effect of Ni particle size. (b) Plot showing the effect of heating rate on the temperature profiles of coarse Ni powders. $T_m$, $T_c$ and $T_{cryst}$ are the temperature of pre-ignition melting, combustion temperature and the solidification point of the product respectively. (c) Plot showing the effect of rate of heating on $T_{ig}$.

6(b) depicts this effect. The temperature of appearance of initial liquid shifted from close to 640 to 675 °C when the rate of heating was higher than 15 °C/min. $T_{ig}$ and $T_c$ followed a similar trend and Fig. 6(c) shows the effect of the rate of heating on $T_{ig}$. When the rate was more than 35 °C/min, $T_c$ surpassed the melting point of the product. On the other hand Ni 1-compacts showed very little change except for the fact that at 60 °C/min the pre-ignition melting was not prominent in the temperature profile. However, both the plateau temperature and $T_{ig}$ shifted with increasing heating rate. Ni 1-compacts underwent melting of the product on thermal explosion in all the heating rates employed. Initial experiments showed that in the case of extreme slow heating rate (2 °C/min) the reaction occurred without any perceptible thermal explosion at all. However, the temperature profile did not show any change for any of the above Ni+Al systems with the atmosphere namely, argon or vacuum.

3.5. Porosity and pore structure

Fig. 7 shows the size distributions of the open porosity of the specimens made of Ni 2 powder before and after combustion together with their median pore diameters. It may be mentioned here that median pore diameters of the green compacts made from Ni 1, Ni 2 and Ni 3 were found to be 1.7, 4.01 and 3.03 µm respectively. After combustion the median pore diameters of Ni 2 increased
to 31.7 µm. Pore size distribution of the combusted Ni 1-compact was not carried out as melting of the product on combustion led to annihilation of open porosity.

3.6. Product phase analysis

Fig. 8 manifests the combined effect of Ni particle size and the heating rates on the product phase structure as revealed by XRD analyses. On combustion, the product of Ni 1 was always single-phase B2 NiAl and $T_c$ was higher than its melting point.

Ni 2 and Ni 3 yielded multiple phase products in the heating rates of up to approximately 35 °C/min which consisted of Al$_3$Ni, Al$_3$Ni$_2$, NiAl and unreacted Ni. No free Al was detected. While the product phase structure remained essentially the same for the reactions carried out under vacuum or in argon atmosphere for these powders, the relative proportions of the unreacted Ni and the phase Al$_3$Ni were found to decrease with increasing heating rates. The peak corresponding to the $d$-spacing of 1.76 angstrom (marked in Fig. 8) was used in ascertaining Ni concentrations as it is the only distinctive characteristic feature of elemental Ni as the other peaks are either common to a number of other possible binary phases or are too close to differentiate from other reflections. Interestingly, single phase B2 NiAl could be synthesized from Ni 2 and Ni 3 powders in both vacuum and argon atmospheres at heating rates above 35 °C/min and also resulted in the melting of the product.

3.7. Evolution of microstructure

3.7.1. Intermediate liquid phase

Fig. 9 shows the microstructural analysis of the specimen which was heated to 640 °C to allow the liquid to form. The figure shows the liquid droplet on the surface of the compact and the fracture surface with evidence of participation of the liquid phase.

3.7.2. Multiple phase microstructure

Compacts of coarse Ni powders (Ni 2 and Ni 3) led to porous and multiple phase microstructures at slower heating rates (up to approximately 25 °C/min) and is shown in Fig. 10. In general, the microstructure consisted of three phases, namely, the central Ni-rich phase encircled by a rim of intermediate phase and embedded within a matrix of a third phase. Phase analysis of such a product is given in Fig. 8(b). Chemical analyses with EPMA established that the central Ni-rich phases were essentially unreacted Ni (99.98 at.% Ni) which were surrounded by a rim of Al$_3$Ni$_2$ (40.86 at.% Ni). The matrix phase was found to be Al$_3$Ni with a chemical composition of 25.8 at.% Ni and 74.2 at.% Al. Apparently, the central Ni-rich phase inherited the locations of the reactant Ni particles of the green compact.

Depending on the rate of heating and the particle size of Ni, a different degree of structural conversion was observed in the microstructure. Fig. 11 shows the microstructure of the multiple phase samples which had undergone increased conversion and as a result does not show any significant elemental Ni peak in the XRD plot [Fig. 8(c)].
shape of the globules bore the sign of the participation of a liquid phase which must have engulfed the solid hitherto unreacted Ni particle during the course of combustion. The interglobular matrix region is composed of equiaxed grains of NiAl (43.66 at.% Ni) and Ni-rich (46.54 at.% Ni) martensite. The core of the globules contained a mixture of Ni<sub>3</sub>Al and Ni(Al) solid solution with a composition of 73.17 at.% Ni. In some portions of the samples unreacted nickel surrounded by Al<sub>3</sub>Ni<sub>2</sub> was also noticed. The microstructures remained essentially the same for both Ni 2 and Ni 3 powders irrespective of the atmosphere.

3.7.3. Single phase microstructure
Under the conditions of the present experiments, Ni 1 always formed molten B2 NiAl and as a result the microstructure of the product of thermal explosion was essentially fully dendritic in nature [Fig. 12(a)].

Heating rates above 35 °C/min also yielded single phase NiAl and gave rise to the melting of the product for both Ni 2 and Ni 3 powders. Both of them showed similar dendritic cast microstructures [Fig. 12(b)] which were coarser compared to those of Ni 1 product.

3.8. Summary of results

For clarity, the effects of Ni particle size and the heating rate on combustion behaviour, phase evolution and microstructure in equiatomic Ni–Al system are summarized in Table 2.
Fig. 9. Microstructural analysis of the sample showing the liquid droplet on the surface of the compact and the fracture surface shows the change in the surface morphology of the Ni particles.

4. Modelling the effect of heating rate

The results of the parametric variation of thermal explosion were modelled in two parts. The first part dealt with the formation of the intermediate phase before melting of the Al-rich eutectic through solid state reactive diffusion. The second part addressed the problem of chemical conversion of Ni particles once they are engulfed in liquid Al or Al-rich eutectic.

4.1. Part I

We consider a sphere of Ni embedded in an Al matrix and a compound layer of Al₃Ni grows at the interface. This is assumed since the average particle sizes of the coarse Ni powders i.e., Ni 2 and Ni 3 are 2.5–3 times higher than Al powder and Al is the more ductile phase.

For a steady rate of diffusion across the compound layer (Fig. 13)

\[
\frac{dc}{dr} = \frac{1}{r^2 dr} \left[ D r^2 \frac{dc}{dr} \right] = 0
\]

(1)

With boundary conditions given by: \(c(r = r_{ab}) = c_{\beta\alpha}\) and \(c(r = r_{bg}) = c_{\beta\gamma}\)
developed the basic formulation and Go¨ done by Go¨ for a spherical particle. In binary diffusion couples. A similar analysis has used that for the growth kinetics of planar structure respectively. the pure phases A and B. Kidson [16] and Kidson [16], the (a) the fine and (b) the coarse dendritic Fig. 12. The cast microstructure of the product. Fine and coarse Ni gave rise to (a) the fine and (b) the coarse dendritic Now, following the general scheme of analysis done by Gösele et al. [15] and Kidson [16], the case of a compound layer AβB of thickness rβ growing between two saturated phases AαB and AγB where α > β > γ, is examined. When α and γ are ≈ and 0, respectively, AαB and AγB represent the pure phases A and B. Kidson [16] first developed the basic formulation and Gösele et al. [15] used that for the growth kinetics of planar binary diffusion couples. A similar analysis has been carried out here for a spherical particle. In Fig. 13 the concentration profile of the component A in the absence of interfacial reaction barriers is indicated by a dashed line. The concentrations of A at the interfaces are given by its corresponding equilibrium values cβeq A and cβeq B. In the presence of interfacial reaction barriers, the concentration gradient across the AβB layer is smaller and the actual concentrations at the interfaces are cβeq A < cβeq A and cβeq B > cβeq B. The chemical interdiffusion coefficient of AβB phase ˜Dβ is assumed to be constant.

The steady state flow rate iβ of A atoms in the AβB phase will be as follows: from diffusion:

\[
i_{\beta}^{A} = 4\pi\bar{D}_{\beta}\mathcal{r}_{eq}^{2}\frac{dc_{\beta\alpha}}{dr}\bigg|_{\beta\alpha} = -4\pi\bar{D}_{\beta}\mathcal{r}_{eq}^{2}\frac{dc_{\beta\gamma}}{dr}\bigg|_{\beta\gamma} \tag{3}
\]

from interfacial reaction:

\[
i_{\beta}^{A} = 4\pi\bar{r}_{\beta\gamma}\mathcal{r}_{eq}^{2}\kappa_{\beta\alpha}(c_{\beta\alpha}^{eq} - c_{\beta\alpha}) \tag{4}
\]

where \(\kappa_{\beta\alpha}\) and \(\kappa_{\beta\gamma}\) are the two reaction constants. In this case the flux will not be constant because \(r_{\beta\gamma}\) and \(r_{\beta\gamma}\) are not equal. So, we obtain

\[
c_{\beta\gamma}^{eq} - c_{\beta\alpha}^{eq} = \bar{D}_{\beta}\frac{1}{\kappa_{\beta\alpha}\mathcal{r}_{eq}^{2}\mathcal{r}_{\beta\gamma}}(c_{\beta\alpha}^{eq} - c_{\beta\gamma}) \tag{5}
\]

\[
c_{\beta\gamma}^{eq} - c_{\beta\gamma}^{eq} = \bar{D}_{\beta}\frac{1}{\kappa_{\beta\gamma}\mathcal{r}_{eq}^{2}\mathcal{r}_{\beta\gamma}}(c_{\beta\alpha}^{eq} - c_{\beta\gamma}) \tag{6}
\]

\[
c_{\beta\alpha}^{eq} - c_{\beta\gamma}^{eq} = \left[1 + \bar{D}_{\beta}\frac{1}{\kappa_{\beta\alpha}\mathcal{r}_{eq}^{2}\mathcal{r}_{\beta\gamma}} + \bar{D}_{\beta}\frac{1}{\kappa_{\beta\gamma}\mathcal{r}_{eq}^{2}\mathcal{r}_{\beta\gamma}}\right](c_{\beta\alpha}^{eq} - c_{\beta\gamma}) \tag{7}
\]

where \(r_{\beta} = r_{\beta\gamma} - r_{\alpha\beta}\) and \(1 - \kappa_{\beta\alpha}\mathcal{r}_{eq}^{2}\mathcal{r}_{\beta\gamma} = \frac{1}{\kappa_{\beta\gamma}\mathcal{r}_{eq}^{2}\mathcal{r}_{\beta\gamma}} + \frac{1}{\kappa_{\beta\alpha}\mathcal{r}_{eq}^{2}\mathcal{r}_{\beta\gamma}}\).

Combining the above, the expression for flow rate is obtained as

\[
i_{\beta}^{A} = 4\pi\bar{D}_{\beta}\mathcal{r}_{eq}^{2}\frac{r_{\beta\gamma}\mathcal{r}_{eq}^{2}}{r_{\beta}}\left[1 + \bar{D}_{\beta}\frac{1}{\kappa_{\beta\gamma}\mathcal{r}_{eq}^{2}\mathcal{r}_{\beta\gamma}}\right]^{-1}(c_{\beta\gamma}^{eq} - c_{\beta\alpha}^{eq}) \tag{8}
\]

Now, the change of position of the two interfaces \(r_{\alpha\beta}\) and \(r_{\beta\gamma}\) with time \(t\) will be:

\[
(c_{\alpha\beta}^{eq} - c_{\beta\alpha})\frac{dr_{\alpha\beta}}{dt} = \bar{D} \frac{dc_{\beta\alpha}^{eq}}{dr}\bigg|_{\beta\alpha} \tag{9}
\]
Table 2
Summary of results

<table>
<thead>
<tr>
<th>Particle Diameter of Nickel (µm)</th>
<th>Effect on combustion and the product phase microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>129.57</td>
<td>Multiple phase porous product, poor conversion, large amount of unreacted nickel and Al₃Ni, Low Tᵢₑ, Tₑ&lt; m.p.t. of NiAl</td>
</tr>
<tr>
<td>110.83</td>
<td>No combustion</td>
</tr>
<tr>
<td>10.94</td>
<td>Single phase NiAl; Cast microstructure, fine dendrites; Low Tᵢₑ, high Tₑ, Tₑ&gt; m.p.t. of NiAl</td>
</tr>
<tr>
<td>5-10</td>
<td>15-25</td>
</tr>
<tr>
<td></td>
<td>Rate of heating (°C/min)</td>
</tr>
</tbody>
</table>

\[
\frac{dr_B}{dt} = \bar{D} \left( \frac{dc_B}{dr} \right)_{\beta γ} \tag{10}
\]

So, the change of the layer thickness \( r_B = (r_{βγ} - r_{αβ}) \) with time is given by

\[
\frac{dr_B}{dt} = \bar{D} \left( \frac{1}{r_{βγ}^2 - c_{βγ}^γ} \left( r_{αβ}^2 c_{αβ}^α - c_{βα}^γ \right) \right) \left( \frac{1}{r_{βγ}^2 c_{βγ}^γ - c_{βα}^γ} \right)
\]

\[
= \left( \frac{r_B}{\bar{D}} + \frac{1}{\kappa_{βγ}^α} \right)^{-1} \Delta c_{βγ}^γ \tag{11}
\]

\[
= G \Delta c_{βγ}^γ \kappa_{βγ}^α \left( \frac{r_B \kappa_{βγ}^α}{\bar{D}} + 1 \right)^{-1}
\]
Fig. 13. Schematic representation of the reaction–diffusion model along with the concentration profile of A atoms across an A\(_b\)B/A\(_b\)B/A\(_b\)B diffusion couple with or without interfacial barrier. The phases are assumed to be saturated (\(a/\beta H_{11022} c_{\beta a}/H_{11022} c_{\beta b}\)).

\[
D_{\beta}G\Delta c_{\beta}^{\text{eff}} = \frac{dr_{\beta}}{dt} = \frac{0.66e^{-1.49}}{kT} \text{ cm}^2/\text{s} \quad (13)
\]

where \(k\) is the Boltzmann constant in eV/K and \(T\) is the absolute temperature. Atzmon [17] applied this to study the effect of interfacial diffusion barrier on the ignition using computed temperature profiles. Instead of that, an experimentally obtained time–temperature profile up to a temperature of 640 °C is used here to solve the above equation and the value of the thickness of Al\(_3\)Ni at different times and temperatures is computed numerically. An advantage of the experimentally obtained temperature profiles is that they contain information about the externally applied heating and the chemical heating at the same time as they happen in the actual experiments. Fig. 14(a,b) show the variation of thickness with temperature and time at different rates of heating. The thickness of Al\(_3\)Ni is found to be more at slower rates of heating as compared to the faster rates of heating.

Now, supposing the diameters of the Ni particle at room temperature and at 640 °C are \(d_1\) and \(d_3\) respectively, the thickness of the Al\(_3\)Ni film is \(\delta\) and the diameter of the Ni particle together with the film is \(d_2\), the following equation can be arrived at:
Fig. 14. (a) The variation of thickness of Al₃Ni with temperature at different rates of heating. (b) The variation of thickness of Al₃Ni with time at different rates of heating. (c) Plot showing increasing consumption of Ni particle due to the formation of Al₃Ni with decreasing rate of heating.

\[ V_0 = \frac{\pi}{6} d_1^3 \quad \text{and} \quad W_0 = \frac{V_0 \rho_{\text{Ni}}}{M_{\text{Ni}}} \]

\[ V_2 = \frac{\pi}{6} d_2^3 \quad \text{and} \quad W_2 = \frac{V_2 \rho_{\text{Ni}}}{M_{\text{Ni}}} \]

\[ V_1 = \frac{\pi}{6} (6d_3^3 + 12d_3^2 + 8d_3^2) \quad \text{and} \]

\[ W_1 = \frac{V_1 \rho_{\text{Al₃Ni}}}{M_{\text{Al₃Ni}}} \]

respectively. \( M \) and \( \rho \) refer to the molecular weight and density respectively. The number of moles of Ni consumed is also \( W_1 \) and that corresponds to the reduction in weight of Ni. This cubic equation can be solved analytically to obtain the value of \( d_3 \) that is the diameter of the unreacted Ni particle after reduction due to the formation of Al₃Ni.

Fig. 14(c) displays the plot of the diameter of the unreacted Ni particles after heating up to 640 °C versus the rate of heating. This plot reveals that beyond a certain threshold rate of heating the growth of Al₃Ni film saturates and becomes quite insignificant. This matches well with the experimental results where the temperature profiles for the higher rates of heating showed [Fig. 6(b)] the melting of elemental Al instead of the Al-rich eutectic. Moreover, the product-phase analyses showed [Fig. 8(c)] that the amount of Al₃Ni decreased with increasing rate of heating and there was no Al₃Ni present when the rate of heating was above 35 °C/min.

4.2. Part II

Based on the model originally proposed by Aleksandrov et al. [18], refined further by Kanury [19] and applied in PWP mode by Li et al. [12], it is assumed that as soon as the temperature 640 °C is reached the Al-rich eutectic melts and engulfs the Ni spheres and an intermediate complex layer of a composition of NiAl forms around it instantaneously. Further diffusion across this complex leads to the formation of NiAl by precipitation from the saturated liquid whereas the thickness of the layer remains constant as the rate of growth at the complex–Ni interface is equal to rate of dissolution at the Al–complex interface.
Under steady-state condition, the rate of Al diffusion is equal to the rate of Ni particle consumption if the interfacial reaction barriers are ignored and this will lead to the following equation [12]:

\[
\frac{M_{Ni}D_0}{\rho_{Ni} r_0^3} \exp \left[ - \frac{E}{RT(t)} \right] dt = \frac{M_{Al} r^3}{\rho_{Al}} \frac{M_{NiAl}(r_0^3 - r^3) - M_{Ni}(3r^2 \delta)}{\rho_{Ni}} \left( r + \delta \right) dr
\]

if the radius of Ni particle is \( r_0 \) at time \( t = 0 \) and \( r \) at time \( t = t \) (where \( t > 0 \)) and the thickness of the complex layer is \( \delta \). Here \( 4.8 \times 10^{-6} \text{ m}^2/\text{s} \) is used as the value for \( D_0 \), the reference diffusion coefficient [12]. \( E \) is the activation energy for combustion synthesis of NiAl which was experimentally determined to be 170.99 kJ/mole. The details of this is reported elsewhere [20]. The above equation is then solved numerically using the experimentally obtained time–temperature profile from 640 °C onward. The diameters of the unreacted Ni particles after being heated to 640 °C were calculated in the first stage of the model and the same were used as the starting diameters here. We further assumed that the diameter remained unchanged till the temperature reached \( T_{ig} \).

Fig. 15(a) shows a typical plot of the diameter of the Ni particle versus time along with the corresponding temperature profile. It shows the initial rapid rate of conversion of the Ni particle which decreases subsequently. Since the time lag between the initiation of the melting plateau and the actual ignition varied with the rate of heating, the comparison of the conversion profiles at different heating rates could be done only if their starting points were the same. Fig. 15(b) illustrates such a comparison among different rates of heating. Higher the rate faster is the reaction though initial rapid rate of conversion is common to all. Further, it shows that the reaction proceeds well after the combustion is over.

5. Discussions

This study aimed at exploring the combustion behaviour of NiAl in the thermal explosion mode in relation to a few specific reaction variables and by modelling the reaction characteristics. These parameters included variations in Ni particle size, heating rates and reaction atmosphere. In all these experiments, it was observed that the combustion behaviour of powder compacts of stoichiometric NiAl composition was similar both under vacuum and in argon essentially signifying the gasless nature of the reaction and corroborating the observations of Naiborodenko et al. [4,21]. Coarse Ni powders namely, Ni 2 and Ni 3 showed remarkable similarity in their response to various synthesis experiments. Fine Ni powder or Ni 1 was approximately one order of magnitude smaller than the coarse Ni powders and exhibited different combustion behaviour.

DSC analysis confirmed that the combustion was preceded by the melting of the Al-rich eutectic at around 640 °C. Earlier, Gasparyan et al. [9] car-
ried out a series of thermal analysis experiments of equiatomic NiAl in a specially designed high-temperature DTA using a range of heating rates from 2.4 to 13 °C/min. They reported another exothermic peak due to formation of Al₃Ni by solid state reaction at a lower temperature when the rate of heating was low (6.6 °C/min and less); at a higher heating rate, for example, at 13 °C/min, this feature could not be noticed. The result of DSC showed concurrence both in terms of the nature of the thermograph and the phase analysis of the product of thermal analysis.

The videograph provided probably the first ever visual evidence of various stages of thermal explosion including the pre-ignition melting as anticipated from the thermal analysis. It also manifested the considerable lag between the initiation of melting and the ignition point (2 s for the one demonstrated), the extremely fast reaction (0.44 s in the current example) and the uniformity of volume combustion where typically the entire sample reacted simultaneously.

The effect of particle size of Ni on the thermal response could be rationalized in terms of the available reacting surface areas for these varieties. Lower surface area of coarse Ni powders (Ni 2 and Ni 3) led to the sluggish reaction. Philpot et al. [7] reported similar effect of increased T_{ig} with increasing particle size of Ni in Ni–Al system containing 10, 17.5 and 25 at.% Al. Increase in the T_c with decreasing reactant particle size is also widely reported in the literature. The effect of the thermal schedule on the temperature profile can be explained in terms of the extent of a pre-ignition solid-state diffusive reaction. This is because the experimental rate of heating is considerably low and as rightly pointed out by Munir et al. [1], can cause, possible reactions between the reactants before combustion. So, formation of Al₃Ni during pre-ignition heating is favoured if the rate of heating is low [Fig. 14(c)]. Since melting of the eutectic phase between Al(Ni) and Al₃Ni is dependent on the formation of Al₃Ni, pre-ignition melting, in turn, is governed by the rate of heating. This appears as a more prominent plateau for the eutectic melting at lower heating rates, irrespective of Ni particle size. Higher rates of heating, kinetically disallows formation of Al₃Ni and results in a lesser amount of eutectic. Because of a lesser residence time at any temperature during rapid heating, the melting plateau as well as T_{ig} shifted towards a higher temperature, i.e. the melting point of Al. Earlier, Philpot et al. [7] studied the effect of heating rates on thermal explosion of Ni–Al system containing 10 and 25 at.% Al and observed two peaks for heating rates up to 2 °C/min and only one peak for higher rates and nevertheless reported an increase in T_{ig} with increasing heating rates in every case. On the other hand, T_c increased with increasing heating rate because higher heating rates ensured completion of the highly exothermic reaction of NiAl formation by reducing the extent of a pre-combustion diffusive reaction. These were again true irrespective of the particle size of Ni. Besides, when the heating rate was very high, such as 60 °C/min or more, the melting plateau became almost imperceptible especially in the case of the fine Ni powder. This is an effect that can be compared with the absence of any perceptible indication of melting in the temperature profile of NiAl in PWP mode in spite of the fact that melting of Al or Al-rich eutectic is a well proven phenomenon in this system. A data acquisition frequency of 100 Hz also proved inadequate to seize the melting event. In view of this, it seems rational that the rate of temperature rise must have been too fast for the acquisition system to cope with. Thus, in the event of a very fast rate of temperature rise, the melting plateau may also not be noticed in the thermal explosion mode.

Post-combustion porosimetry of the samples of both Ni 2 and Ni 3 heated at low heating rates showed increased pore volumes and pore diameters. This is in spite of the involvement of a liquid phase during combustion. There is not much reported in the literature on the evolution of porosity and pore structure during thermal explosion. Some conflicting reports on increase of porosity during reactive sintering of NiTi have been forwarded by Igharo et al. [22] and Li et al. [23]. Li et al. [24,25] showed that the porosity increased in NiTi only in the PWP mode. As discussed by Munir et al. [26] in detail, the genesis of porosity is dependent on the following four factors: (1) initial porosity; (2) higher product density; (3) evolution of volatiles and gases and (4) thermal
migration of pores. However, it leads to a dense product if the reaction yields large quantities of a liquid phase.

Like porosity and pore structure, phase distribution and microstructure too conformed closely to the thermal responses of different reactant mixtures under varying experimental conditions. The product of the fine Ni powder always gave rise to single-phase B2 NiAl with a dendritic microstructure. The bigger Ni 2 and Ni 3 particles underwent varying degrees of incomplete conversion at lower heating rates. The corresponding $T_c$ was also always below the melting point of NiAl. This was, as discussed earlier, essentially because of the pre-combustion solid state reactions (formation of Al$_3$Ni in the current case) that occurred to a significant extent when the heating rate was slow. That the amount of Al$_3$Ni would increase with decreasing rate of heating was demonstrated in the Part I of the process modelling presented earlier. This extensive pre-combustion solid state reaction reduced the exothermicity of the successive combustion reaction primarily by reducing the availability of fresh reaction surfaces and increasing the diffusion distances. Moreover, preferential formation of Al$_3$Ni involved higher consumption of Al (three times that of Ni atom) and might lead to incomplete chemical conversion at the end especially if the reaction temperature was not high enough to allow homogenization. Gasparyan et al. [9] reported similar results where increased Al$_3$Ni formation led to a reduction in the extent of the subsequent combustion reaction. They observed this effect both in the case of varying heating rate and green density of the specimen. Observations by Philpot et al. [7] also corroborate the effect. Thus, the final product microstructure contained Al$_3$Ni and Al$_3$Ni$_2$ along with unreacted Ni when the conversion was minimum. As suggested by Gasparyan et al. [9], only the following two reaction stages were likely to have been completed:

$$\text{Ni} + 3\text{Al} \rightarrow \text{Al}_3\text{Ni}$$

$$\text{Ni} + \text{Al}_3\text{Ni} \rightarrow \text{Al}_3\text{Ni}_2$$

Thus, the DSC-treated sample contained multiple phases where the heating rate was 10 °C/min and the reaction temperature was much below the melting point of NiAl.

There are some striking resemblances of this microstructure to the one obtained by Dunand et al. [27] by reactive infiltration of preforms of Ni powder or Ni/Al$_2$O$_3$ powder blends with molten Al at temperatures in the range 685–760 °C. They obtained similar microstructures containing unreacted Ni powders encircled by a film of Al$_3$Ni$_2$ within a matrix of Al$_3$Ni/Al(Ni)–Al$_3$Ni eutectic, (1) irrespective of the preform temperature and the content of Al$_2$O$_3$ for coarse Ni powders (150–220 µm), and (2) only in case of low preform temperature (285 °C) and high Al$_2$O$_3$ content (31 vol. %) for fine Ni powders (5–15 µm). This similarity of microstructure lends further credence to the idea that the elemental Ni particles got engulfed by the molten Al or Al-rich eutectic and further reaction proceeded by diffusion through the reaction product formed thereupon.

A little higher heating rate (30–35 °C/min) caused further conversion and so the microstructure showed the evidence of more Ni-rich phases including the intended product NiAl. The amount of unreacted Ni decreased and no Al$_3$Ni was seen. Ni–Ni$_3$Al eutectic appeared as the diffusion of Al was not sufficient to ensure complete conversion to NiAl. Interestingly, Dunand et al. [27] too observed the presence of Ni$_3$Al when infiltration was incomplete and non uniform.

The situation changed in the case of still higher heating rates (>35 °C/min) where $T_c$ surpassed the melting point of the intended product, namely NiAl, as the extent of pre-combustion reaction was insignificant. This ensured complete conversion to B2 NiAl as the XRD showed. The product was no longer porous because of the melting. Part II of the model successfully simulated this effect of the rate of heating on the completion of the reaction and showed that the Kanury model [19] could be applied to the thermal explosion mode with little alteration.

6. Conclusions

Pre-combustion solid-state reactions play a major role in the thermal explosion of NiAl, especially in case of large Ni particles and low rates of heating and are instrumental in yielding
products of varying extent of incomplete conversion. Increasing the heating rate can minimize this effect and achieve complete conversion to single phase B2 NiAl even when the particle size of Ni is as large as 130 µm. Simple models based on a solid-state reactive diffusion scheme and Kanury mechanism can effectively explain and rationalize different aspects of the process.

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References