Effect of Al Content on Reaction Laser Sintering of Ni–Al Powder

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Abstract:
Laser reactive sintering, i.e., laser-induced self-propagating reaction sintering synthesis was used for the preparation of nickel aluminide intermetallic compounds. The experimental parameters controlling the ignition step such as ignition time and adiabatic temperature were calculated as a function of initial stoichiometry. Al mole ratio in initial powder mixture was varied from 25% to 50% for controlling adiabatic temperature. The increase in Al powder content resulted in the rise in adiabatic temperature and the morphology change of nickel aluminide compounds from needle-like to blocky.

Keywords: Reaction laser sintering; Nickel aluminide intermetallic compound; Adiabatic temperature; Ignition time; Morphology

1. Introduction

Because of high temperature structural and coating applications, nickel aluminide intermetallic compounds (NiAl and Ni$_3$Al) have received considerable attention. Many kinds of alloys based on Ni$_3$Al have been developed with broad utilizations, such as furnace rolls, radiant burner tubes for steel production, forging dies, and corrosion-resistant parts for chemical industries [1-4]. Morsi [5] reports many processes applied to the reaction synthesis of Ni–Al intermetallics in which combustion synthesis has been recognized as a promising method for producing advanced materials.

Powder compact laser sintering is a laser sintering process in which powder compacts are sintered by a laser. It was found that this method cannot sinter large materials because the input heat by the laser is not enough [6]. In order to overcome this weakness, reactive laser sintering is developed in this study, which uses reactive powders in substituted raw powder compacts [7, 8]. However, few articles have reported the laser reactive laser sintering of medium-enthalpy metallic powder systems such as Ni-Al and Ti-Al intermetallic materials. Therefore, this article studies the adiabatic temperatures affected by the powder content and the relation between the ignition delay time and laser processing parameters during laser-induced combustion synthesis of Ni-Al powder compacts.

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2. Experimental procedures

Commercial powders of aluminum (98.0% purity, 75 μm), nickel (99.5% purity, 15 μm) and graphite (98% purity, 150 μm) were used for experiments. Reactant powder mixtures with Al atomic ratios ranging from 25% to 50% were prepared. The powders were mixed in a ball mill for 1 h and then pressed into cylindrical samples with a diameter of 20mm and a height of 10mm. The compacts were ignited by laser irradiation using a Nd:YAG pulsed laser source (JHM-1GY-100B), which has a fundamental wavelength of 1062 nm with pulse duration of 6 ms, and repetition rate of 8 Hz. The output power was varied from 800W to 1600W. The 2 rectangle spot of the laser beam was adjusted to about 16mm × 22mm which nearly covering the surface on the compact. The surface of the compact was painted with a very thin layer of carbon black to increase the absorptivity for the laser beam. When the ignition was detected, the laser beam was turned off and the reaction could be self-sustaining. Temperature was measured using Ni-Cr/Ni-Si thermocouples.

3. Results and discussion

3.1 Adiabatic temperature \(T_{ad}\)

Adiabatic temperature can be calculated using simple thermodynamics and it represents the maximum temperature or the upper limit of the temperature achieved during a particular reaction. For the reaction synthesis of a nickel aluminate \(\text{Ni}_a\text{Al}_b\) the following equation is applicable for calculating the adiabatic temperature, [9]

\[
\Delta H(298) + \int_{T_{ad}}^{(298)} \sum n_j C_p(P_j) dT + \sum_{298-T_{ad}} n_j L(P_j) = 0
\]  

Where \(P_j\) refers to the appropriate products and \(n_j\) is the stoichiometric coefficient of products. \(C_p(P_j)\) and \(L(P_j)\) are the heat capacity and phase transformation enthalpy of the products, respectively. Assuming that adiabatic temperature is lower than the melting points of the products, the products do not go through a phase change the equation (1) can be transformed to,

\[
-\Delta H(298) = \int_{298}^{T_{ad}} \sum n_j C_p(P_j) dT
\]  

According to the Ni-Al system binary diagram and the results in Ref. [5], some of the reaction enthalpy parameters for the compound formation are listed in Tab. I, corresponding to the stoichiometric ratio.

<table>
<thead>
<tr>
<th>(x_{\text{Al}}) (atom%)</th>
<th>Specific heat capacity ((J \text{ mol}^{-1} \text{ K}^{-1}))</th>
<th>(-\Delta H_{298}^a) (kJ mol(^{-1}))</th>
<th>(T_{ad}) (°C) calculated</th>
<th>(T_{ad}) (°C) measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 Ni(_3)Al (C = 88.49 + 32.22 \times 10^{-3}T + 0.001 \times 10^{4}T^2)</td>
<td>153.13</td>
<td>1313</td>
<td>1203</td>
<td></td>
</tr>
<tr>
<td>0.30 NiAl (C = 41.93 + 13.6 \times 10^{-3}T - 0.033 \times 10^{4}T^2)</td>
<td>141.59</td>
<td>1449</td>
<td>1308</td>
<td></td>
</tr>
<tr>
<td>0.35</td>
<td>133.29</td>
<td>1590</td>
<td>1473</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>127.09</td>
<td>1622</td>
<td>1482</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>118.41</td>
<td>1639</td>
<td>1510</td>
<td></td>
</tr>
</tbody>
</table>
According to the atom ratio, the reaction equation for Ni-30at%Al, Ni-35at%Al and Ni-40at%Al are as follows.

\[
\begin{align*}
30.7 Ni + 0.3 Al & = 0.2 Ni_{3}Al + 0.1 NiAl \quad (3) \\
30.65 Ni + 0.35 Al & = 0.15 Ni_{3}Al + 0.2 NiAl \quad (4) \\
30.6 Ni + 0.4 Al & = 0.1 Ni_{3}Al + 0.3 NiAl \quad (5)
\end{align*}
\]

Thermodynamic calculations show that the adiabatic temperature \(T_{ad}\) increases with the increase of the Al powder content. Fig. 1 shows temperature-time plots of Ni-Al compacts with various Al contents under 1600W. The rise in the measured maximum temperature \(T_{max}\) of the SHS reaction confirmed the calculated results (Fig. 2).

![Fig. 1 Temperature-time plots of Ni-Al compacts with various Al contents under 1600W laser power.](image1)

![Fig. 2 Effect of Al content on the adiabatic temperature \(T_{ad}\) and maximum (measured) temperature of sintering](image2)

The measured temperature is 40–170 K lower than the calculated adiabatic temperatures, but the tendency is similar. The reaction become more intense with increasing Al powder content. This brings more heat loss and larger disparity between the calculated and the measured value.
3.2 Microstructure and XRD analysis of product

Fig.3 shows the X-ray diffraction pattern of the products for Ni-Al alloys with different compositions and Fig. 4 shows the microstructures for the samples with 25 at %Al, 35 at %Al and 50 at %Al. The predominant phase in the sample of 25 at %Al, as shown in Fig. 4(a), is Ni₃Al. The composite microstructures of Ni₃Al and NiAl formed in 35 at %Al sample are given in Fig. 4(b). The microstructure in Fig 4(b) had a needle morphology for Ni₃Al and the blackness substrate was characterized as NiAl, being in agreement with the XRD analysis showed in Fig.3. Fig. 4(c) shows the microstructures for the combustion synthesized NiAl revealed by the XRD analysis. In Fig.4, the product of NiAl and Ni₃Al present in the samples with 25 at %Al and 35 at %Al. Only NiAl is present in the sample with 50 at %Al.
3.3 Ignition delay time

A simple ignition model was proposed using the thermal theory together with the following assumptions: (1) The laser beam irradiation is the only source used to ignite sample reaction. (2) Propagation of the combustion wave inside the sample is regarded as continuous layer-by-layer ignition. The thickness of every layer is much less than the radius of the sample and body size, and the laser beam spot nearly covers the sample surface. (3) The thermophysical parameters of the material system are independent of temperature. (4) No convective or radiative heat loss is taken into account.

The ignition delay time was defined as the duration from the beginning of the laser irradiation to the time when the reactive flame was observed. Based on the thermal theory and the above assumptions, the governing equation for this 1-D model is follows [10],

\[ \rho_p C_p \frac{\partial T}{\partial t} = \lambda_p \frac{\partial^2 T}{\partial x^2} + q_0 \delta(x)H(t - \tau) \]

(6)

With the integral-transform and consideration of the initial and boundary conditions, equation (6) can be transformed to

\[ T(0,t) = \frac{q_0}{\lambda_p} (\frac{4 \lambda_p t}{\pi C_p \rho_p})^{1/2} + T_0 \]

(7)

The ignition delay time, \( \tau \), thus, can be written as

\[ \tau = \int_{T(0,t)=T_0}^{T(0,t)=T_0} \frac{\pi \lambda_p \rho_p C_p (T_{ig} - T_0)^2}{4q_0^2} \]

(8)

In the above equations, \( \lambda_p \), \( C_p \) and \( \rho_p \) are, respectively, thermal conductivity, specific heat and density of the porous compact, \( q_0 \) is the effective laser power density, \( t \) is the time, \( \tau \) is the total interaction time of the laser beam with the compact, that is, the ignition delay time, and \( T_0 \) is the ambient temperature. The value of these parameters can be obtained by the following equations,

\[ \lambda_p = \lambda_{Ni} \left[ 1 + 2 \psi - 2 \phi (\psi - 1) \right] \left[ \frac{1 - p}{1 + p / 2} \right] \]

(9)

\[ C_p = (C_{Ni} \times x_{Ni} + C_{Al} \times x_{Al}) \left( 1 - p \right) \]

(10)

\[ p = \left( 1 - \rho_p / \rho_{Al} \right) \times 100\% \]

(11)

Where \( \lambda_{Ni} \), \( \lambda_{Al} \), \( C_{Ni} \), \( C_{Al} \), \( \rho_{Ni} \), \( \rho_{Al} \) and \( x_{Ni} \), \( x_{Al} \) are the thermal conductivity, specific heat, density and weight percent of elemental Ni and Al powders, respectively. \( \psi \) is a constant, equaling to \( \lambda_{Ni} / \lambda_{Al} \) and \( \phi \) is the volume percent of Al powder.

Fig. 5 Effect of Al content on the ignition delay time of Ni-Al compacts under various laser powers.
Tab. II Parameters used for the calculation of laser ignition delay time

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{\text{Ni-25 at.%Al}}$</td>
<td>Kg m$^{-3}$</td>
<td>6826</td>
</tr>
<tr>
<td>$\rho_{\text{Ni-30 at.%Al}}$</td>
<td>Kg m$^{-3}$</td>
<td>6567</td>
</tr>
<tr>
<td>$\rho_{\text{Ni-35 at.%Al}}$</td>
<td>Kg m$^{-3}$</td>
<td>6230</td>
</tr>
<tr>
<td>$\rho_{\text{Ni-40 at.%Al}}$</td>
<td>Kg m$^{-3}$</td>
<td>5790</td>
</tr>
<tr>
<td>$\rho_{\text{Ni-50 at.%Al}}$</td>
<td>Kg m$^{-3}$</td>
<td>5170</td>
</tr>
<tr>
<td>$P$</td>
<td>W</td>
<td>800-1600</td>
</tr>
<tr>
<td>$A$</td>
<td></td>
<td>$0.8^{[11]}$</td>
</tr>
<tr>
<td>$S$</td>
<td>m$^2$</td>
<td>$3.52 \times 10^{-4}$</td>
</tr>
<tr>
<td>$T_g$</td>
<td>K</td>
<td>933</td>
</tr>
<tr>
<td>$T_0$</td>
<td>K</td>
<td>303</td>
</tr>
</tbody>
</table>

For the Ni-Al alloys, all the necessary values of the parameters for the calculation are listed in Tab. II. A comparison between computational and experimental data of ignition delay time under various laser powers is given in Fig. 5. It can be seen, despite some deviations, that the calculated values agree well with the experimental results obtained at laser output power 800W. The ignition delay time becomes long with the decrease in the aluminum component.

4. Conclusions

(1) A model based on the thermodynamic theory about laser-induced ignition has been proposed. This model reveals the relation between the ignition delay time, laser processing parameters and material characteristics. Experimental results demonstrate that the theoretical analysis is reasonable.

(2) Reactive laser sintering of Ni–Al compacts is automatically maintained by chemical reaction heat. With the increase in the Al content, $T_{ad}$ rises and the delay time of the reaction reduces.

(3) Ni$_3$Al was obtained when the Al content is at 25 at.%; while the Al content is at 30 at.% and 35 at.%, both Ni$_3$Al and NiAl can be formed. Microstructure observations are in agreement with the result of X-ray analysis.

Reference

Садржај: Синтеза помоћу ласерског реакцијивног синтеровања, т.ј. реакцијно синтеровање ласерски изазваном самопропагирајућом реакцијом је коришћено за припрему једињења никл алуминида. Експериментални параметри који контролишу корак паљења као што су време паљења и адјабатска temperatura су израчунате као функција почетне стехиометрије. За контролу адјабатске temperature моларни однос алумнијума у почетној смеси праха је варирао од 25 до 50%. Повећање садржаја праха алумнијума је довело до повећања адјабатске temperature и морфолошких промена једињења никл алуминида од игличастих до коцкастих.

Кључне речи: Рекционо лазерско синтеровање, једињење никл алуминида, адјабатска temperatura, време паљења, морфологија.