Reaction synthesis and microstructures of NiAl/Ni micro-laminated composites

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Abstract

The effects of process parameters on reaction synthesis of NiAl/Ni micro-laminated composite from micro-foils of Ni and Al have been investigated. NiAl/Ni micro-laminated composites were fabricated through diffusion bonding, reaction synthesis and post-heat treatment of alternatively stacked Ni/Al multilayers. DTA analysis showed that the reaction between Ni and Al foils started from the nucleation and growth of NiAl, at Ni/Al interfaces followed by a diffusional growth of Ni2Al3 at Ni/NiAl interfaces. The volume fraction of un-reacted Al after reaction was thermodynamically calculated from the initial thickness ratio of Ni:Al and diffusion bonding time before the reaction. As the thickness ratio of Ni:Al increased, the adiabatic temperature and the volume fraction of pure liquid Al decreased. Experimentally measured adiabatic temperature, \( T_a \), was lower than the thermodynamically calculated value, decreased with increasing the thickness ratio of Ni-Al. As the diffusion bonding time increased, the volume fraction of pure liquid Al decreased gradually due to the consumption of Al forming intermetallic at interface of Ni-Al. When initial thickness ratio of Ni-Al during post-heat treatment increased, Al-rich nickel aluminide (Ni0.9 Al1.1) was transformed to Ni-rich nickel aluminide (NiAl) so that the final microstructures resulted in a formation of compositionally gradient series of intermetallic phases which consisted of NiAl and Ni3Al.

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1. Introduction

The intermetallic/metal micro-laminated composites were introduced by various researchers to overcome the brittleness of monolithic intermetallics at ambient temperature [1–4]. These composites offer an attractive combination of mechanical properties superior from the constituent phases, e.g. high toughness of the metal coupled with low density and high oxidation resistance of the intermetallics [5]. Although many micro-laminated composites using intermetallics phases such as silicides and aluminides have been researched, most of work conducted on intermetallics has focussed on the nickel aluminides [6]. NiAl/Ni micro-laminated composites are being considered as good candidate materials for high temperature structural or armor applications [7].

Reaction synthesis has been used for fabrication of intermetallic/metal micro-laminated composites, because it has many advantages such as near-net shaping, crucible-less processing, microscopic compositional homogeneity and low cost compared with the conventional processing consisted of melting and casting. Initially, Anselmi-Tamburini and Munir [1] showed that an SHS reaction could be initiated at the interface between elemental Ni and Al foils. Alman et al. [3] fabricated metal/metal aluminide micro-laminated composites using many metal foils such as Fe, Ni, Ti and Nb reacted with Al foils by hot pressing. Reaction synthesis technique involves both self-propagating high-temperature synthesis (SHS) mode and thermal explosion (TE) mode. In the SHS mode, one end of a reactant sample is heated with an igniter at a high heating rate (hundreds of degrees per sec-

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ond), and once ignited, the combustion wave self-propagates through the sample. In the TE mode, the whole reactant sample is heated in a furnace under low heating rate (tens of degrees per minute). Once heated to its ignition temperature, the combustion reaction becomes spontaneous and occurs place everywhere in the sample. It is obvious that the heating rate at which the reactants are heated prior to combustion is much lower in the TE mode than in the SHS mode, and this could lead to different mechanisms of the two reaction synthesis modes [7].

Most of the theoretical studies on reaction synthesis have been focused on the SHS mode, assuming a homogeneous reaction. In practice, the reaction synthesis of bulk aluminides have been usually achieved by TE mode which involves uniform heating of the sample accompanied by a certain degree of self-heating. Atzmon [8] introduced that the dependence of the ignition temperature for Ni–Al diffusion couples on the heating rate was a result of interfacial barriers. Farber et al. [9] extended the Atzmon’s model to describe the kinetics of reaction synthesis in consolidated blends of fine Ni and Al powders. Zhu et al. [10,11] studied reaction synthesis of multilayered Ni and Al foils in the TE mode and reported that the reaction started at the melting point of Al independent of the thickness of the Ni foil and analysed the reaction stage more precisely by measuring the temperature–time profile. Miura et al. [12,13] performed thermodynamic calculations to estimate the amount of liquid phase during the TE synthesis of several Ni–Al compositions and the theoretical results were found to be in good agreement with their experimental results.

As stated above, the mechanism of reaction synthesis of the NiAl compound is affected by various factors such as reaction synthesis mode (SHS or TE), size and shape of the reactant (particle or layer) and thermomechanical conditions. Most of the researches were mainly focussed on the reaction stage and the effect of thermomechanical processing conditions on microstructure before and after the reaction was not treated clearly. In this study, the effect of thickness ratio and diffusion bonding before reaction synthesis in Ni–Al microlaminated system was studied by thermodynamical calculation of the volume fraction of un-reacted Al after reaction.

The reaction synthesis was performed in thermal explosion mode by alternatively stacking the elemental Ni and Al foils and the microstructures at each step during the reaction were examined by quenching the sample during the reaction synthesis. The effects of processing parameters such as temperature and pressure during post-heat treatment were also investigated to describe the final microstructure of microlaminated composites.

2. Experimental procedures

2.1. Reaction synthesis of NiAl/Ni micro-laminated composites

Commercially pure (99.0% minimum) nickel (100 μm, Nilaco Co.) and aluminium (25, 50, 100 μm, Goodfellow Co.) foils with various thicknesses were used. These foils were cut into 20 mm × 20 mm squares and cleaned in the ultrasonic bath of acetone for 10 min. The specimens of three types with thickness ratio (Ni:Al) of 1:1, 2:1 and 4:1 were alternatively stacked to 2 mm thickness. Intermetallic/metal micro-laminated composites were produced by three steps: (a) diffusion bonding; (b) reaction; (c) post-heat treatment. Fig. 1 shows the typical thermomechanical processing profile for the preparation of intermetallic/metal micro-laminated composites. Thermocouples were embedded between Ni and Al foils to measure the initiation of reaction (T_i) and temperature increase (T_f) during the reaction. Both ends of the stacked pile were thermally insulated by zirconia felt (ZYF-100) to minimize the heat loss during reaction. Stacked pile was diffusion bonded for variable times at 600 °C to investigate the effect of diffusion bonding before reaction. Diffusion bonded specimens were heated to 750 °C and held at this temperature for 0.5–1 h depending on the initial thickness ratio. No pressure was applied to the specimens during reaction at 750 °C. Post-heat treatment under pressure was employed to close shrinkage cavity during solidification of the transient liquid phase and to remove any Kirkendall porosity during solid-state diffusion. During post-heat treatment, the effects of thermomechanical processing conditions such as temperature (900, 950 °C) and pressure (50, 100 MPa) were examined.

2.2. Differential thermal analysis and thermodynamic calculation

Alternatively stacked Ni and Al laminates were diffusion bonded for 60 min at 600 °C under 10 MPa of applied stress in the vacuum hot press (VHP) and were cut into
3 mm × 3 mm squares for DTA experiment. DTA (Mettler-Toledo TGA/SDTAS81e) was performed on samples placed in alumina crucibles. The heating was conducted in N2 at a constant rate of 5–100 °C/mim from 450 to 1000 °C. The temperature at which the exothermic peaks in the DTA curves occurred was a function of the heating rate, consistent with analysis of Kissinger [14]. In this analysis, the activation energies of the each reaction associated with observed exothermic DTA peaks were calculated according to the following:

\[
\frac{d \ln(h/T_p^2)}{d(1/T_p)} = \frac{Q}{R}
\]

where \(T_p\) is peak temperature, \(h\) is heating rate, \(R\) is gas constant, and \(Q\) is activation energy.

To investigate the effect of initial thickness ratio on the reaction, theoretical maximum temperatures during reaction were calculated by using the volume fraction of un-reacted Al as a parameter and compared to the measured values with respect to initial thickness ratio. In this calculation, the molar enthalpy of each phase was brought from the literatures [7,15]. Also, the volume fraction of un-reacted Al after reaction in terms of initial thickness ratio was calculated thermodynamically and compared to experimental values of specimens with and without diffusion bonding.

2.3. Characterization of microstructure

The microstructures of as-prepared specimens by DTA and VHP experiments were observed by optical microscope (Leica DMLM) and scanning electron microscope (Philips XL30FEG). The volume fractions of each phase in micro-laminated composite was analysed by image analyser. The crystal structure and chemical composition of each constituent phases were analysed by EDS and XRD. Phase evolution during reaction was analysed by neutron diffractometer (HRPD, Ge(331)) to prevent cracking of the brittle intermetallic layer which would occur by using abrasive cutting techniques. Microvickers hardness tester (Akashi, 25 g) was used to measure the hardness with the respect to the change of thermomechanical conditions during postheat treatment.

3. Results and discussion

3.1. Phase evolution during reaction synthesis of micro-laminated composite

Fig. 2a shows the DTA thermograms of diffusion bonded specimens. It is seen that the two exothermic peaks appear after Al foils melts. In the specimen with 1:1 initial thickness ratio, there is an endothermic peak of NiAl3 decomposition due to thicker Al. Fig. 2b shows the microstructures of specimens quenched from the temperatures marked A, B, C and D of the specimen with 1:1 initial thickness ratio. According to composition analysis by EDS, the reaction paths are as follows and these results are well matched with the previously reported [9–11].

First : \(\text{Ni} + 3\text{Al} \rightarrow \text{NiAl}_3 + \Delta H_1\)  
Second : \(\text{NiAl}_3 + \text{Ni} \rightarrow \text{Ni}_2\text{Al}_3 + \Delta H_2\)

Therefore, \(\text{NiAl}_3\) nucleates (B) and grows (C) in the transient liquid Al as Ni dissolves into the molten Al and \(\text{Ni}_2\text{Al}_3\) is formed by diffusional transformation of \(\text{NiAl}_3\) (D). The activation energies of each reaction were analysed by Kissinger method which considered the shift of exothermic peak with respect to heating rate in DTA curves. Fig. 3 shows that the activation energies for first and second peak are 142 and 106 kJ/mol, respectively, and these values are related to the formation of \(\text{NiAl}_3\) and \(\text{Ni}_2\text{Al}_3\). The activation energy of \(\text{NiAl}_3\) formation is relatively similar to the literature values (140–170 kJ/mol) but the value of \(\text{Ni}_2\text{Al}_3\) formation is much smaller than the previously reported values (~200 kJ/mol) [16–18]. This may be due to the pre-formation of \(\text{Ni}_2\text{Al}_3\) during diffusion bonding before reaction because most of reaction synthesis is performed in powders without diffusion bonding.

As seen in the microstructures of Fig. 6, the reaction product in \(\text{NiAl}_3\) and \(\text{Ni}_2\text{Al}_3\), which is very brittle at room temperature. Post-heat treatment is required to convert from these phases to \(\text{NiAl}\) and \(\text{Ni}_2\text{Al}_3\) having better strength at high temperature. Final intermetallic/metal micro-laminated composites are manufactured by VHP through the thermomechanical condition shown in Fig. 1. Microstructures of each laminates are summarized quantitatively in Table 1. Volume fractions of intermetallic in the laminates with 1:1, 2:1, and 4:1 initial thickness ratios are measured to 80, 60, and 40%, respectively.

3.2. Effect of initial thickness ratio of Ni and Al on microstructure of micro-laminated composite

The important parameters in the reaction synthesis are the ignition temperature \(T_i\) and adiabatic temperature \(T_a\). The adiabatic temperature can be calculated using simple thermodynamics and it represents the maximum temperature or the upper limit of the temperatures achieved during a particular reaction. Miura et al. [12,13] calculated thermodynamically the liquid phase during reaction synthesis of Ni–Al powder mixtures having arbitrary compositions. In this paper, the theoretical maximum temperature of Ni–Al laminates having various initial thickness ratios is calculated thermodynamically by using the volume fraction of un-reacted Al as a parameter. Assuming that the laminates of Ni and Al are at \(T_i\) (923 K) before ignition based on previous result [10], i.e., no intermediate phases are formed before reaction synthesis starts. Molar fractions of each phase obtained are used to deduce volume fractions of each phase by using theoretical density data assuming no volume change during reaction. Molar enthalpies \(\Delta H\) of each phase found in the literature [15] are used in this calculation. In an adiabatic condition,
molar enthalpy of sample at $T_i$ ($Q(T_i)$) equals to molar enthalpy at any arbitrary temperature attained, $T_a$ ($Q(T_a)$), as follows:

$$Q(T_i) = Q(T_a)$$

$$Q(T_i) = \alpha H_{sNi}(T_i) + (1 - \alpha) H_{sAl}(T_i)$$

$$Q(T_a) = \beta H_{sNi}(T_a) + \gamma H_{lAl}(T_a) + \delta H_{sNiAl}(T_a)$$

where $\alpha$, $\beta$, $\gamma$, $\delta$ are molar fraction of pure Ni, residual pure Ni, liquid Al, formed intermetallic, respectively, and $H_{sNi}$, $H_{sAl}$, and $H_{sNiAl}$ is molar enthalpy of solid Ni, liquid Al, formed intermetallic, respectively. The above equations provide a way to estimate volume fraction of liquid phase as a function of initial temperature, temperature attained, $T_a$, sample composition and the kinds of intermetallic formed.

Table 1
Summary of microstructures in intermetallic/metal micro-laminated composites

<table>
<thead>
<tr>
<th>Initial thickness ratio (Ni:Al)</th>
<th>Final thickness ($\mu$m)</th>
<th>Volume percent (%)</th>
<th>Intermetallic phases formed from reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal</td>
<td>Intermetallic</td>
<td>Metal</td>
</tr>
<tr>
<td>1:1</td>
<td>30</td>
<td>140</td>
<td>18</td>
</tr>
<tr>
<td>2:1</td>
<td>48</td>
<td>68</td>
<td>40</td>
</tr>
<tr>
<td>4:1</td>
<td>72</td>
<td>45</td>
<td>60</td>
</tr>
</tbody>
</table>
during the reaction. In the present study, formed intermetallic during reaction is assumed to be NiAl in this calculation. Fig. 4 shows the temperature dependence of the amount of pure liquid Al with various Al concentrations. The amount of liquid Al decreases with increasing temperature attained because Al is used to form intermetallic generating heat for further increase in temperature attained. Fig. 5 shows the temperature-time plots measured at the center of reaction pile for different initial thickness ratio of laminates. There is plateau at about 650 °C corresponding to the melting point of the Al. So, the ignition temperature is the melting point of Al independent of the initial thickness ratio. The microstructures of quenched specimens after reaction shows that un-reacted Al exists only in the specimen with 1:1 initial thickness ratio as shown in Fig. 6 a. 

$T_a$ is calculated by Eq. (4) from the quantitative analysis of microstructures shown in Fig. 6 and compared with experimental values of Fig. 5. As shown in Fig. 7, experimental values of $T_a$ have very similar tendency with calculated values and decreases as initial thickness ratio increases. Difference between calculated and measured values can be explained by low rate of data acquisition from thermocouples. Calculated $T_a$ (1325 °C) of specimens with 1:1 initial thickness ratio matches very well with Zhu’s result (1350 °C) [10]. Therefore, the effect of initial thickness ratio on reaction synthesis can be explained qualitatively by thermodynamic approach.

3.3. Effect of diffusion bonding condition on microstructure of micro-laminated composite

The initiation of reaction synthesis highly depends on the interface condition. In case of powder mixtures, reduction process is required to remove surface oxide but thermomechanical process such as diffusion bonding under pressure is usually performed in laminates. Janssen and Rieck [19] reported the penetration plot of Ni–Al binary couples with each surface oxide removed. Fig. 8 shows that the penetration curves of our Ni–Al binary couples diffusion bonded under pressure without surface treatment are shifted to longer time compared to previously reported Janssen’ results in which NiAl3 is formed by the fast grain-boundary diffusion in the beginning of the diffusion process (A region). This means that the surface oxides at interface act as an important barrier for the reaction of Ni and Al. It is also seen that the rate-limiting step in the beginning of the Ni2Al3 formation (B region) is the reaction of Ni and NiAl3 as addressed by van Loos [20]. When the diffusion bonding before reaction occurs, intermetallic formed at interface could be considered in the thermodynamic calculation because some of elemental metal foils can be consumed and therefore some of heat expected to be generated during reaction synthesis can be wasted. In this case, Eq. (4) is rewritten as follows:

$$Q(T_i) = Q(T_a)$$

$$Q(T_i) = \alpha H^s_{Ni}(T_i) + \beta H^s_{Al}(T_i) + \gamma H^s_{NiAl3}(T_i)$$

$$Q(T_a) = \varepsilon H^s_{Ni}(T_a) + \zeta H^s_{Al}(T_a) + \eta H^s_{NiAl3}(T_a)$$

$$\alpha + \beta + \gamma = 1$$
Fig. 6. Microstructures of reacted specimen with Ni:Al initial thickness ratio of (a) 1:1 ($V_{f,Al}$ ≈ 4), (b) 2:1 ($V_{f,Al}$ = 0), (c) 4:1 ($V_{f,Al}$ = 0).

where $\alpha$, $\beta$, $\gamma$, $\epsilon$, $\zeta$, $\eta$ are molar fraction of pure Ni, pure Al, formed intermetallic during diffusion bonding, residual Ni, residual liquid Al and reaction formed intermetallic, respectively. $\gamma$ is used as a variable in this calculation. Fig. 9 shows that the amount of liquid Al decreases with increasing amount of NiAl$_3$ intermetallic formed before ignition in the specimen of 1:1 initial thickness ratio. Experimentally measured values follow well the decreasing tendency within 1300–1350 °C of $T_a$. It means that diffusion bonded speci-
mens which contains the proper amount of intermetallic is thought to have less liquid phase during reaction synthesis. However, the effect of diffusion bonding on the amount of liquid phase is so little that the reaction temperature needs to be raised for completion of the reaction.

3.4. Effect of post-heat treatment on microstructure of micro-laminated composite

Fig. 10 shows the final microstructures with various thermomechanical conditions in the specimens of 1:1 initial thickness ratio. Longer time at reaction temperature (750 °C) and higher post-heat treatment temperature are required to acquire the Ni₃Al and Ni₅Al intermetallics. The crystal structures of laminates at each step are analysed by neutron diffractometer as shown in Fig. 11. It shows that Al exists at the diffusion bonded specimen and is transformed to Ni₃Al (γ) after reaction and NiAl (δ) after post-heat treatment. Fig. 12 shows the hardness change at each position marked A, B, C, D and E of the specimens shown in Fig. 10. The hardness at the center of intermetallic is lower than other positions due to shrinkage cavity and becomes more uniform through the entire intermetallic layer as the applied pressure increases. For final microstructures of the laminates post-heat treated to the same condition as Fig. 11, EDS (Fig. 13) and XRD (Fig. 14) analysis shows that every laminates has the stack sequences of Ni/Ni₃Al/NiAl/Ni₃Al/Ni. Also there are Ni₁₈Al₄₂ (lattice...
parameter, \(a = 2.871 \, \text{Å} \) between NiAl and Ni\(_3\)Al. When the initial thickness ratio increases, the crystal structure is transformed from Ni\(_{0.9}\)Al\(_{1.1}\) (\(a = 2.867 \, \text{Å}\)) which is Al-rich NiAl phase to NiAl (\(a = 2.888 \, \text{Å}\)) which is Ni-rich NiAl phase due to the decrease of diffusion distance of Ni into intermetallic layer. The chemical composition and layer width of Ni\(_3\)Al phase is nearly constant due to narrow compositional region in Ni–Al phase diagram.

4. Conclusions

The microstructure changes during reaction synthesis in Ni–Al systems using micro-foils were analysed experimentally and theoretically. The effects of thickness ratio, diffusion bonding, and post-heat treatment on microstructures of NiAl/Ni micro-laminated composites were discussed. The conclusions are summarized as follows:

1. The reaction between Ni and Al micro-foils started with a nucleation and growth of NiAl followed by a diffusional growth of Ni\(_3\)Al between Ni and NiAl. By post-heat treatment with applied pressure, the reaction products were converted to NiAl and Ni\(_3\)Al having higher strength at elevated temperature.
2. The effect of initial thickness ratio (Ni/Al) and diffusion bonding on microstructure was thermodynamically calculated by using the volume fraction of un-reacted liquid Al as a parameter. Experimentally measured adiabatic temperature, \(T_a\), was lower than the thermodynamically calculated value and decreased with increasing the thickness ratio. The theoretical amount of un-reacted liquid Al decreased as the amount of NiAl intermetallic formed before reaction increased in the specimen of 1:1 initial thickness ratio. \(T_a\) was calculated to 1300–1350 °C from experimentally measured amount of un-reacted liquid Al.
3. The post-heat treatment at high temperature (900–950 °C) under pressure (50–100 MPa) were required to obtain pore-free NiAl and Ni\(_3\)Al intermetallics after reaction. When the initial thickness ratio of Ni/Al increased, the crystal structure of reaction product was transformed from Al-rich Ni\(_{0.9}\)Al\(_{1.1}\) to Ni-rich NiAl. The hardness at the center of intermetallic was lower than that of edge due to shrinkage cavities and became uniform through the entire intermetallic layer as the applied pressure increased.

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