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Fabrication of laminated metal–intermetallic composites by interlayer *in-situ* reaction

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A simple and cost-effective method, interlayer *in-situ* reaction process, has been developed to produce laminated metal-intermetallic materials. Layered $NiAl_3$ and Ni_2Al_3/Ni composites have been fabricated successfully by using the process. It is shown that volume friction of the intermetallic layers can be well controlled by the thickness of the metals. It is difficult to produce high strength composites if the original metals are directly exposed at high temperature. This is rectified by a pre-treating processing in which a prefect interface is formed to prevent the metals from oxidation at high temperature. The pre-treated composites have an improvement in tensile strength and thermal stability. SEM observations show that the composites exhibit a mixing fracture mode suggesting that the composites would have high toughness.

1. Introduction

Laminated structures such as alternative metal and ceramic laminates have been proved to have great improvements in properties over the constituent elements [1–3]. Recently, there has been interest in laminated metal-intermetallic composites. Most intermetallic compounds have good properties such as high strength and exceptional oxidation resistance at elevated temperatures but they have their share of inherent low ductility and low fracture toughness at ambient temperature. The combination of intermetallic materials with metallic second phases can provide with promising room-temperature toughening and high-temperature strength and thermal stability [4, 5].

Several processing routes have been used to generate metal-intermetallic composites, including extrusion [6], vacuum plasma spraying [7], directional solidification [8], arc casting [9], and physical vapor deposition [10]. Each process provides characteristic microstructure with specific phase dimensions and has its processing limitations. For example, alternate layers of metal and intermetallic can be generated with sputter deposited composites, the laminate thickness and volume fraction of each can be controlled by time of exposure to the source and/or deposition rate [10], but it is an impractical process for economic airfoil manufacture when wall thicknesses are in the range of 0.5–1.5 mm [11]. Directional solidification can produce composites with laminated or fibrous intermetallics, but it suffers from compositional restrictions and low growth rate.

In the present study, a new method, interlayer *in-situ* reaction process, is developed to fabricate laminated nickel aluminide/nickel composites, in which regularly distributed intermetallic layers are formed through *in-situ* reaction between alternatively laminated metal sheets at high temperature. Effects of treating time and temperature on microstructures are studied. Mechanical tests are performed on the materials with different microstructures to provide a preliminary indication of composite properties.

2. Experimental procedures

2.1. Fabrication processing

If aluminum and nickel contact with each other at high temperature diffusion reaction occurs to produce nickel aluminide layers between them. In the experiment, pure aluminum (99.93 wt %) and nickel (99.98 wt %) sheets are used to fabricate laminated nickel aluminide/metal composites. The flow chart of the processing is shown in Fig. 1. In detail, the sheets were pre-cleaned in 15–20% hydrochloric acid for 10 min and then cleaned in water. After drying at room temperature, they were laminated alternately into aluminum/nickel multilayer samples which are pressed with a pressure of 220 MPa such that the metal sheets can keep close contact with each other. The pressed multilayers were then treated in a vacuum furnace with a vacuum of 10^{-2} Pa.

2.2. Microstructure determination

After fabrication, the specimens were cut and polished. Microstructures were examined in the optical microscope. The phase present was determined in a D/max-IIA X-ray diffractor (XRD). Quantitative energy

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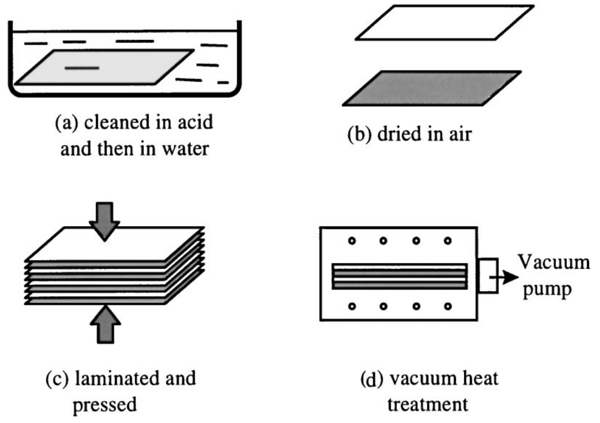


Figure 1 Flow chart of interlayer *in-situ* reaction process.

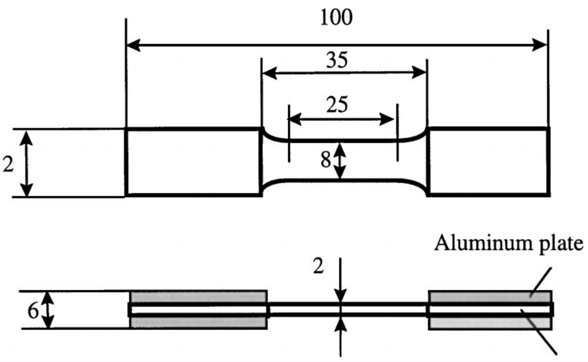


Figure 2 Sketch of the tensile specimens.

dispersive spectroscopy (EDS) of the polished cross-sectional surfaces was conducted in a S360 scanning electronic microscope (SEM) to determine individual phase compositions. Phases were determined by comparing EDS microprobe measurements with the Ni-Al binary phase diagram.

2.3. Mechanical testing

The as-fabricated specimens were machined for mechanical testing. Sketch of the specimens is shown in Fig. 2. The specimens were tested using a DL-1000B electronic tensile machine with a testing rate of 2 mm/min. After testing, the fracture surfaces were examined in the SEM.

3. Results and discussion

3.1. Microstructures of the laminates

Fig. 3 shows the typical microstructures of Al/Ni layers treated for different treating time at a temperature of 630 °C. Two intermetallic compounds are produced in the Ni/Al interface during the treatment. XRD results showed that the intermetallic layers are $NiAl_3$ and Ni_2Al_3. According to the phase compositions it is easy to determine in Fig. 3a that the bright layer adjacent to aluminum is $NiAl_3$ whereas the gray one is Ni_2Al_3 between $NiAl_3$ and Ni layers.

In principle, four intermetallic products would be produced during the reaction. However, only two compounds, Ni_2Al_3 and $NiAl_3$, are observed in the experiments. The reason is that the Gibbs free energy to produce Ni_2Al_3 and $NiAl_3$ is lower than NiAl and Ni_3Al at the reaction temperature. It is anticipated from the Al-Ni binary phase diagram [12] that if the temperature exceeds the decomposition point of $NiAl_3$, 854 °C, the products would be lack of $NiAl_3$ phase. Furthermore, at a treating temperature higher than the decomposition point of Ni_2Al_3, 1133 °C, laminated NiAl(or Ni_3Al)/Ni composites would be produced as only NiAl and Ni_3Al phases are stable over the point. Therefore, temperature is vital to the formation of different intermetallics. It would be possible to fabricate laminated composites with desired intermetallics by controlling the treating temperature in the process.

Several kinds of microstructures with regular layers are formed during the treatment, depending on the treating time and temperature. The initial microstructure produced at 630 °C is Al/$NiAl_3$/Ni_2Al_3/Ni layer, as shown in Fig. 3a. The two adjacent intermetallics uniformly grow towards the original metal layers to form a regularly layered structure through diffusion reaction. With an increase of the treating time the metal layers are consumed and the structure eventually becomes regular $NiAl_3$/Ni_2Al_3/Al or $NiAl_3$/Ni_2Al_3/Ni layers (Fig. 3b).

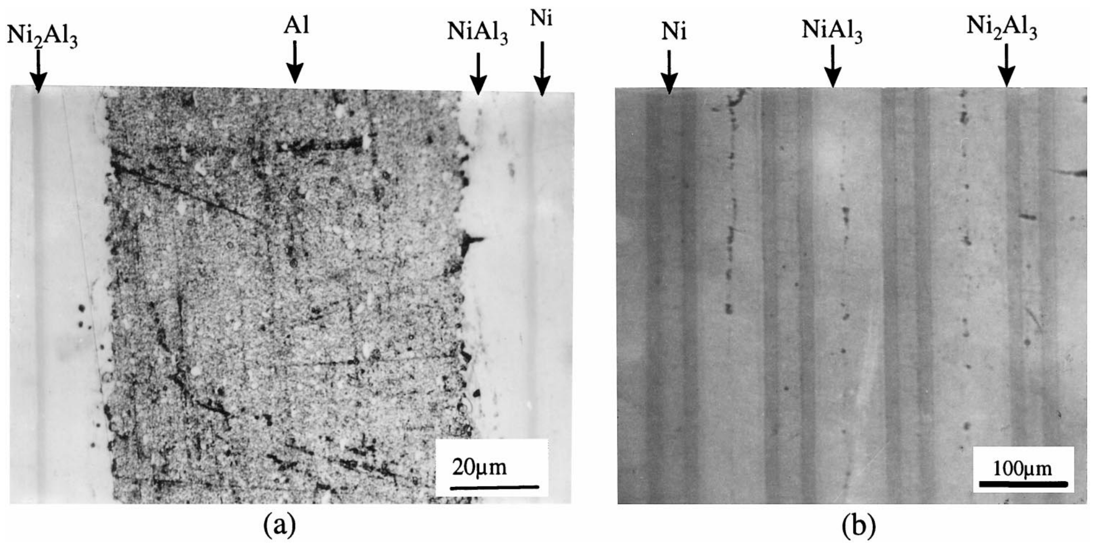


Figure 3 Microstructures of the layers treated at temperatures of 630 °C for (a) 30 min and (b) 150 min.

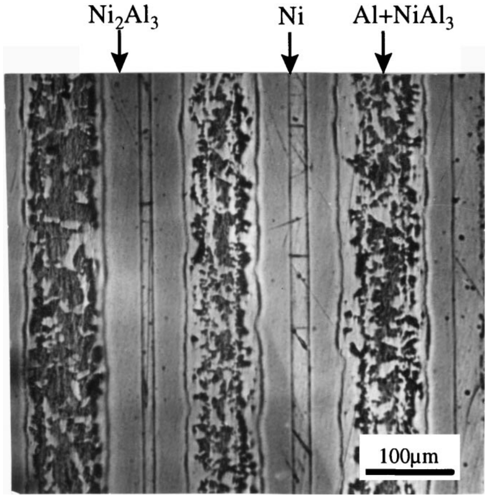


Figure 4 Microstructure of the layers treated at a temperature of 700 °C for 60 min.

However, if the treating temperature is higher than 640 °C, the Ni_2Al_3 keeps lamella shape but a eutectic-like structure forms in the aluminum layers, Fig. 4. This is due to the eutectic reaction above eutectic temperature. According to the Al-Ni binary phase diagram, nickel reacts with aluminum to form Al-$NiAl_3$ eutectic if treating temperature exceeds Al-$NiAl_3$ eutectic point (640 °C). In this case, liquid is expected to exist in eutectic area. It is therefore difficult to produce the structure with the regular $NiAl_3$ layers over 640 °C.

It is of interest to determine the thermal stable structures of the composites. Fig. 5 shows the thickness of intermetallic layers as a function of treating time at a temperature of 630 °C. There are three stages: intermetallic growth, transformation and stability. In the first stage where the treating time is less than 100 min, both $NiAl_3$ and Ni_2Al_3 layers grow but $NiAl_3$ layer grows more quickly. In this stage, diffusion reactions, $Ni + Al = NiAl_3$ and $Ni + Al = Ni_2Al_3$, occur at the interfaces. After 100 min the transformation stage follows, in which Ni_2Al_3 layer continues growing but the $NiAl_3$ begins to decrease because of the reaction, $Ni + NiAl_3 = Ni_2Al_3$, at the interface. At about 350 min when $NiAl_3$ layer is consumed completely the stable stage comes, in which the structure keeps unchanged. The final stable structure is Ni_2Al_3/Ni layers at the temperature of 630 °C.

If the aluminum layer is transformed completely into Ni_2Al_3 the thickness of intermetallic layer can be expressed as

$$L_{\mathrm{i}} = \frac{\rho_{\mathrm{Al}}}{\rho_{\mathrm{i}}} \cdot \frac{L_{\mathrm{Al}}}{1-m} \tag{1}$$

where m is nickel weight percent in the intermetallic product, L_{Al} and ρ_{Al}, and L_{i} and ρ_{i} are the thickness and density of the aluminum and intermetallic layers, respectively. Intermetallic volume fraction, V_{i}, is then expressed as

$$V_{\mathrm{i}} = \frac{R}{(1-m) \cdot \dfrac{\rho_{\mathrm{i}}}{\rho_{\mathrm{Al}}} + \left(1 - m \cdot \dfrac{\rho_{\mathrm{i}}}{\rho_{\mathrm{Ni}}}\right) \cdot R} \tag{2}$$

where R is ratio of the original aluminum to nickel thickness($R = L_{\mathrm{Al}}/L_{\mathrm{Ni}}$), ρ_{Ni} is the density of aluminum and L_{Ni} is the thickness of the nickel.

The intermetallic volume fraction as a function of ratio of aluminum to nickel is plotted in Fig. 6. Experimental results are also plotted in Fig. 6. It is shown that there is a criterion, $R_{\mathrm{c}} = 2.25$. When $R < R_{\mathrm{c}}$, the laminates with residual nickel occur. When $R > R_{\mathrm{c}}$, the final structure becomes nickel-aluminum compounds with the residual aluminum. This indicated that the final stable structures with different intermetallic volume fraction depend on the original metal thickness ratio.

3.2. Mechanical properties

Fig. 7 shows the tensile strength of the layered composites treated at a temperature of 630 °C for different time. At the initial treatment, the tensile strength is 250 MPa that is equal to the results from the rule of mixture. With

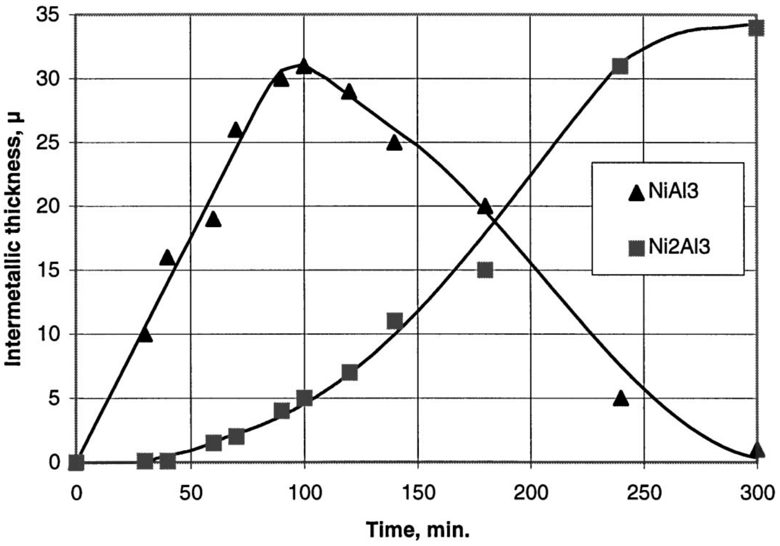


Figure 5 The thicknesses of the intermetallic layers as a function of time.

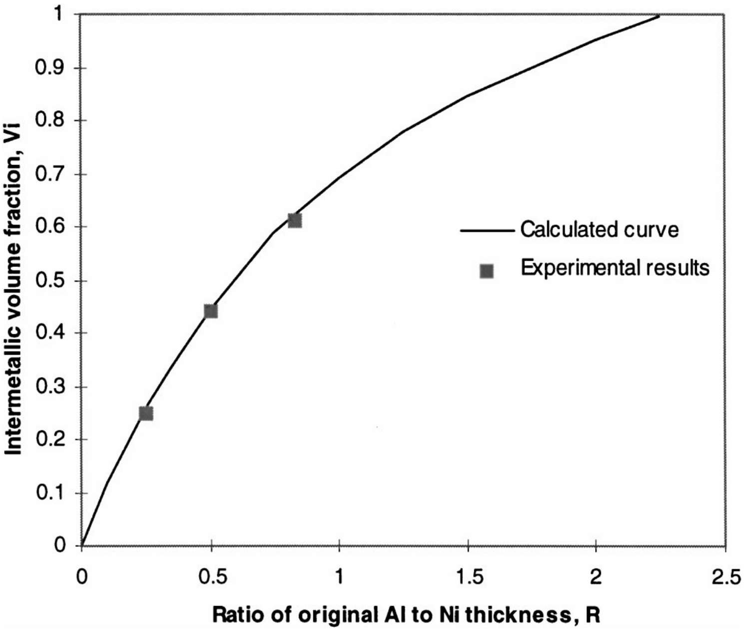


Figure 6 Relation between intermetallic volume fraction, V_i, and ratio of aluminum to nickel thickness, *R*.

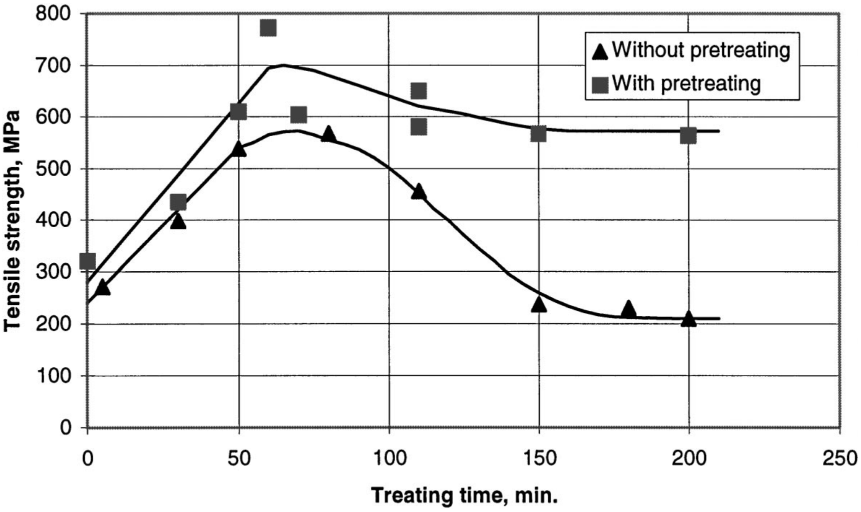


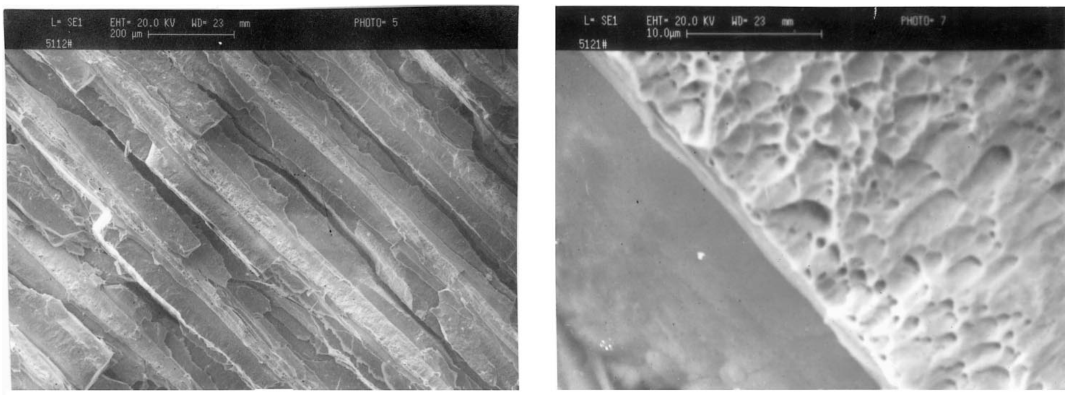
Figure 7 Tensile strength of the layered materials as a function of heat-treating time.

increasing the treating time, the strength curve exhibits two regimes, a strength-increasing regime followed by a strength-decreasing one. The tensile strength increases up to a maximum value of 580 MPa and then drops to a minimum value of about 220 MPa.

The increase of the tensile strength is due to the presence of the high-strength intermetallic layers. As shown in Fig. 5, with an increase of the time, the intermetallics grow, leading to an increase in volume friction of the intermetallics. As a result, the strength of the composites increases with increasing the treating time. Fracture surface observation in the SEM reveals many fracture planes that have different height (Fig. 8a). Each fracture plane is a mixture of brittle fracture of the intermetallic layers and ductile one of the residual metals (Fig. 8b). Though the experiments on toughness of the materials are not made in this study, according to the fracture mode, it is reasonable to say that the materials would have high toughness compared with the mono-intermetallic meterials.

The strength decrease after long heat treatment is attributable to a degradation of the intermetallic layers due to the presence of oxides. EDS results show a high oxygen content at the interface, suggesting that serious oxidation would occur at the interface. In fact, the vacuum in the experiments is not high (only 10^{-2} Pa) enough to prevent aluminum from oxidation at high temperature. Before a perfect interface is established between nickel and aluminum layers through interfacial reaction, oxygen diffuses along the interface to react with the metals to produce oxides at the interface. At the initial stage the oxides would have no significant influence on the strength of the layers because the oxides exist at the interface. With the growth of intermetallic layers the oxides would be pushed at the growing interface, some of which would captured in the growing intermetallic layers to form inclusions or voids, especially in the final reaction stage (Fig. 9). This results in the formation of weak points in the intermetallic layers, from which cracks would initiate easily, leading to premature failure of the layers during loading. As a result, the tensile strength drops.

To solve the problem a pre-treating process is employed before the high temperature treatment. Instead



(a) (b)

Figure 8 SEM Photographs of fracture surfaces of the layered composites showing (a) different fracture planes and (b) the mixture of brittle intermettalic fracture and ductile metal fracture.

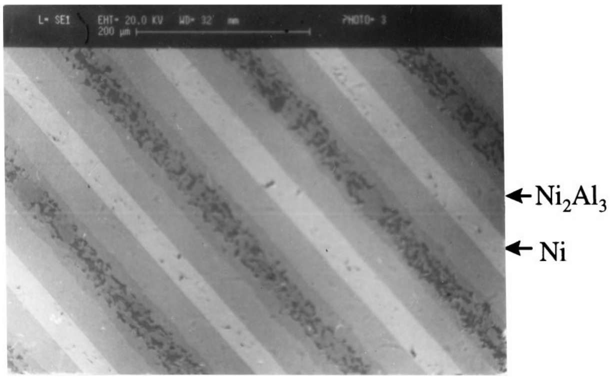


Figure 9 SEM photograph of layered composite showing the presence of inclusions and voids in the intermetallic layers after heat treatment at 630 °C for 200 min.

of directly exposed at high temperature, the samples are firstly pre-treated at a low temperature of 350 °C for 30–60 min, and then exposed at a treating temperature of 630 °C. The results of the processing are also plotted in Fig. 6. Compared with the former process, the pre-treated samples exhibit an increased tensile strength that remains about 580 MPa for a long time, the maximum of which reaches a value of 722 MPa.

The increase of the tensile strength is beneficial from a decrease of oxides in the intermetallic layer. In the pre-treating processing, metals react with each other to form an intermetallic layer that bonds the interface before serious oxidation takes place. The bonded interface prevents the metals from further oxidation during the high temperature treatment. Consequently, both the intermetallic layers and interfaces still keep 'clean' after long treatment so that the composite can keep its high strength as well as the intermetallic layers. Therefore, to obtain a thermal stable composite, it is important to prevent metals from oxidation in treating. The pre-treating process is successful in solving the problem.

4. Conclusions

1. The layered nickel aluminide ($NiAl_3$ and Ni_2Al_3)/nickel composites with different volume fractions can be produced with the interlayer *in-situ* reaction process at a temperature of 630 °C. The stable structures of the composites depend only on the ratio of the original metal layer thickness and temperature.

2. The tensile strength of the layered composites increases with an increase of the volume fraction of intermetallic products. However, it decreases after long heat treatment due to oxidation of the reacted metals at the interface. This can be rectified by a low temperature pre-treating process, in which a prefect interface is formed to prevent the further oxidation of the metals at high temperature.

3. The fracture surface of the layered composites exhibits a mixture fracture mode in which each plane with different fracture height is a mixture of brittle fracture of intermetallic and ductile one of residual metal layers.

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