JMEPEG (2012) 21:1912–1918
DOI: 10.1007/s11665-011-0114-y

Microstructural Characteristics of Accumulative Roll-Bonded Ni-Al-Based Metal-Intermetallic Laminate Composite

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(Submitted June 3, 2011; in revised form December 12, 2011)

The present investigation is an attempt to develop metal-intermetallic laminate composites based on Ni-Al system. In this study, Ni sheets and Al foils have been used for the development of Ni-Al laminate using accumulative roll-bonding technique at 773 K. The laminate composites were then subjected to the controlled annealing to affect reactive diffusion at the Ni/Al interface leading to intermetallic compound formation. The accumulative roll-bonded laminates showed good bonding of layers. Annealing treatment at 773 K led to formation of reaction product and maintained the interface integrity. A qualitative compositional analysis at the interfaces reflected the formation of Al-Ni compounds, and a gradual compositional gradient also across the interface. This process seems to be of promise so far as the continuous production of large scale metal-intermetallic laminate composites is concerned.

Keywords accumulative roll bonding, Al-Ni, annealing, metal intermetallic composite

1. Introduction

As the requirements for high performance and economically viable materials are becoming stringent, new processing techniques are developed to achieve the required microstructural features and mechanical properties. One of the structures which are considered to be of promise, in recent times, is the layered composite structures consisting of soft phase as matrix and a hard intermetallic phase as reinforcement (Ref 1, 2). These structural features are to mimic the naturally occurring shell structures. These metal-intermetallic laminate (MIL) composites are known to have high strength at elevated temperatures and high bending strength coupled with low density and oxidation resistance compared with constituent phases (Ref 3-5). Several MILs have been developed so far including Fe-Al (Ref 6, 7), Ni-Al (Ref 1, 5), Ti-Al (Ref 4, 8), Cu-Al (Ref 9), etc. However, Ni-Al-based laminate composites are considered to be economic and of paramount importance for high-temperature structural and armor applications. In general, these laminate composites are produced by employing constituent metallic foils stacked together, and affecting reactions between the individual metallic layers under high pressure (15-50 MPa) and high temperature (1073-1373 K) (Ref 1, 4, 5). This technique utilizes high temperature and pressure so as to establish close contacts between the individual layers and increased diffusion rate. There are several variants of this route employed to reduce the cost of processing as well as improve the properties of the composites. Recently, Mizuuchi et al. (Ref 1) have reported pulsed-current-hot-pressing technique to realize such laminate Ni-Al-based composites, where pulsed current is used to effect localized melting of the material and obtain pore-free intermetallic layers. Ding et al. (Ref 10) showed the possibility of hot pressing followed by cold rolling and annealing treatment to produce Ni-Ti multilayers. There are a number of studies on microstructural development in the Ni-Al system, but these studies are made mostly on the composites made by some variants of the above mentioned techniques. In one of the studies by Ren et al. (Ref 11), the affect of an applied magnetic field across the laminate shows the retardation of reaction at the Ni-Al interfaces.

Although such techniques have evolved and a good understanding of the reactions is already there, the product size and the cost involved in such techniques, using thin foils of the elemental materials, become prohibitive for their commercialization. A continuous process seems to be a more economically viable process. Therefore, an attempt has been made in the present study to employ accumulative roll-bonding technique (Ref 12), which involves repeated rolling and folding of stacked materials, to produce layered, bonded composites of individual metallic layers, followed by controlled heat treatment, to realize metal intermetallic composite (Ref 7). It is expected that the presence of high strain in the system due to repeated rolling would lead to a faster reaction at the interfaces. The evolution of microstructural features of the composites have been reported and discussed.

2. Experimental details

The materials used in the present study were commercially available aluminum foils (0.09 × 30 × 90 mm) and pure Ni

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sheets (0.46 × 30 × 90 mm). The individual Ni sheets (460 μm) and Al foils (90 μm) were wire-brushed to remove the surface oxide layers and cleaned with acetone so as to induce proper metallic contact due to compressive loading during rolling. Initially, stack was made by placing four aluminum foils alternatively between five Nickel sheets. The stack was then

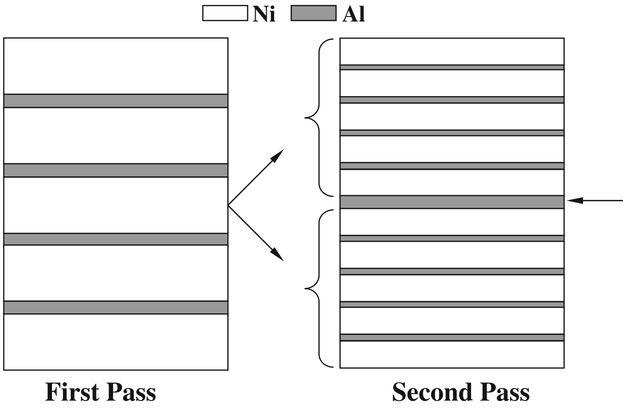

Fig. 1 Schematic diagram of the layer stack formation in the 1st and 2nd passes

Table 1 Stack thickness and percent reduction after the 1st and 2nd passes

	Layers		Stack thickness, mm			
Pass	Ni	Al	Initial	Final	% Reduction	Bonding
1st	5	4	2.66	1.19	55.26	Good
2nd	10	9	2.47	1.20	51.42	Good

Table 2 True strain values of individual layers after the 1st and 2nd passes (estimated from SEM images)

	Thickness, μm				True strain		Cumulative strain	
Pass	Ni initial	Al initial	Ni final	Al final	Ni	Al	Ni	Al
1st	460	90	206	30.99	0.80	1.17	0.80	1.17
2nd	206	30.99	97.8	12.09	0.74	0.94	1.54	2.11

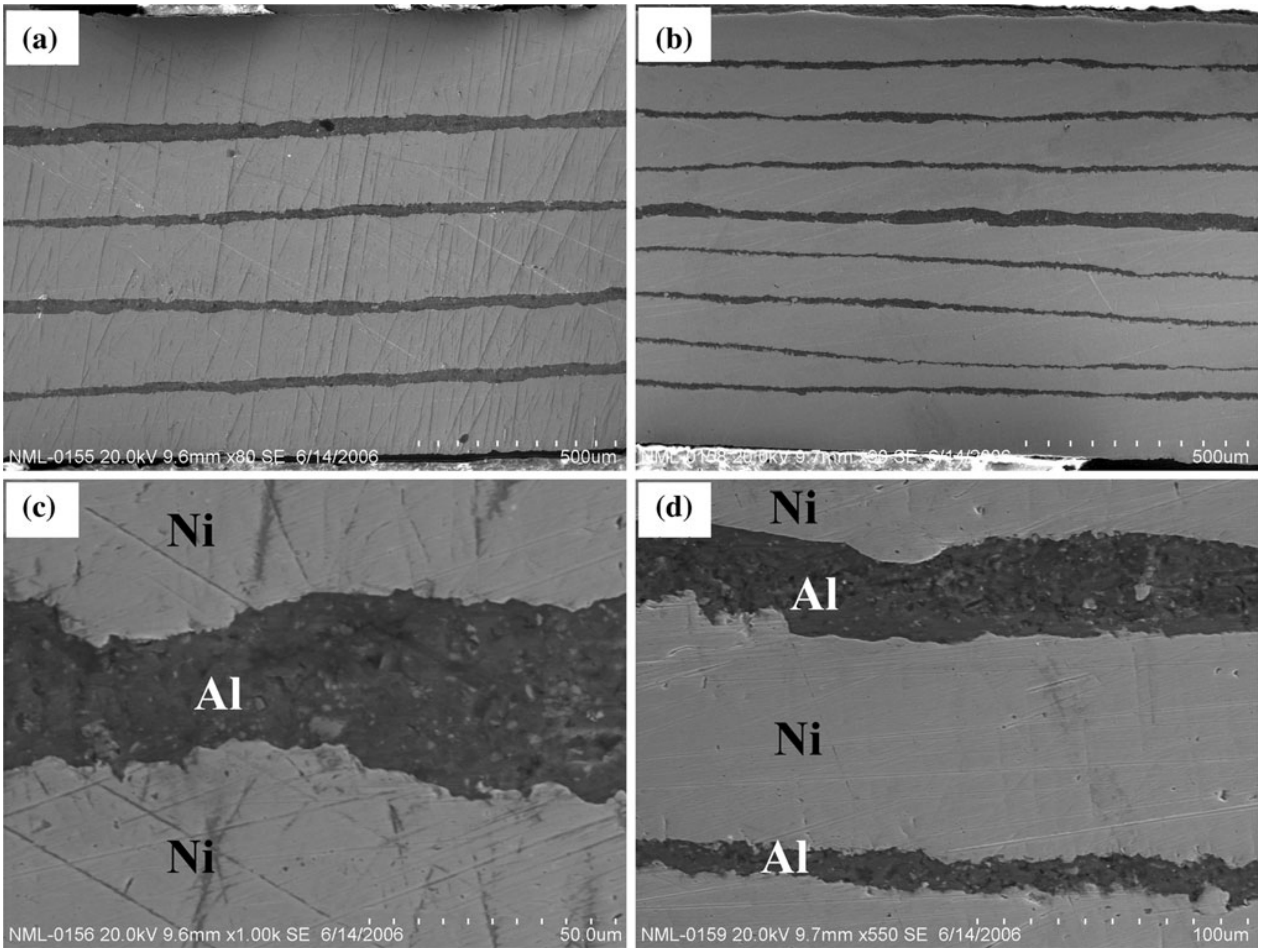

Fig. 2 (a, b) Layered structure after the 1st and 2nd passes, respectively, and (c, d) high magnification micrographs showing good bonding after the 1st and 2nd passes, respectively

fastened together by using thin steel wires (0.5-mm diameter) to prevent slipping of individual layers during the rolling process. Before the rolling experiment, the layered stack was soaked at 773 K for 5 min. It was then immediately rolled dry (the rolls were thoroughly cleaned to avoid slipping during roll pass) at a tangential speed of 7.9 m min^{-1}. The diameter of rolls was 300 mm. It was observed that, after the rolling passes, a small amount of Al layer protruded from the stack. This may be because, for an applied rolling load, the deformation of Al layer was larger compared to that of the Ni layer. The rolled sample was then cut into two halves and stacked again by placing an aluminum foil of the same dimension, after proper surface cleaning. The whole process of rolling was repeated again. A schematic of the stack sequence is shown in Fig. 1. This shows the Al layers used in the 1st pass along with Al layer used in the 2nd pass. The details of the sample characteristics and individual layer characteristics are shown in Table 1 and 2, respectively. Table 1 shows that a single pass deformation of around 50-55% in thickness gives rise to good bonding between Ni-Al layers. Table 2 shows that cumulative strains for Ni layers are 0.93 and 1.79, respectively, for 1st and 2nd passes. This is in contrast to the strains experienced by Al layers, which are 1.35 and 2.44 in the 1st and 2nd passes, respectively.

The samples from both the 1st and 2nd pass laminates were taken for annealing treatment to form intermetallic layers at Ni-Al interfaces by reactive diffusion. The samples were kept in a resistance heating furnace at a temperature of 773 K for three different time durations of 1, 2, and 4 h.

Samples of suitable size from the 1st and 2nd passes were cut in the transverse direction from the center of each specimen. All samples were mounted in a hot mounting press using a conductive-type mounting compound (Black Carbon). Mounted samples were then polished using standard metallographic technique. The samples were studied under scanning electron microscope (HITACHI S-3400N) attached with compositional line scan facility. Qualitative elemental variation was recorded across the Ni-Al interfaces, and quantitative compositional analysis of the phases formed was studied by the energy dispersive x-ray (EDX) analysis.

3. Results

3.1 Microstructural Observations

The procedure of manufacturing layered Ni-Al composites was successfully utilized in this study. Layered structure could be obtained with no trace of debonding at the Ni-Al interfaces. Roll-bonding experiments were carried out at room temperature and 573 K, and it resulted in poor bonding at the interface; however, a high temperature of 773 K led to a good bonding. On the other hand, at the temperature of 873 K, Al layer deformed extensively which was not required and not considered in the present study. Therefore, 773 K was chosen as optimized temperature for further processing. Figure 2(a)-(d) show the structure of the laminates in as-rolled condition, i.e., before annealing treatments. Figure 2(a) and (b) show the structure after 1st and 2nd passes, respectively. High magnification micrographs in Fig. 2(c) and (d) show a good bonding between Ni and Al layers, both after the 1st and 2nd rolling passes, respectively. It is also worth mentioning that there was not any reaction product at the interface during soaking and rolling stages of processing.

Figure 3(a)-(f) show the microstructural features after annealing treatment at 773 K for different durations. These micrographs indicate a gradual growth of intermetallic layers at the Ni-Al interfaces. Figure 3(a)-(c) are the micrographs of the laminate after 1st pass annealed for 1, 2, and 4 h, respectively. It clearly indicates that the initial reaction (i.e., after 1 h) does

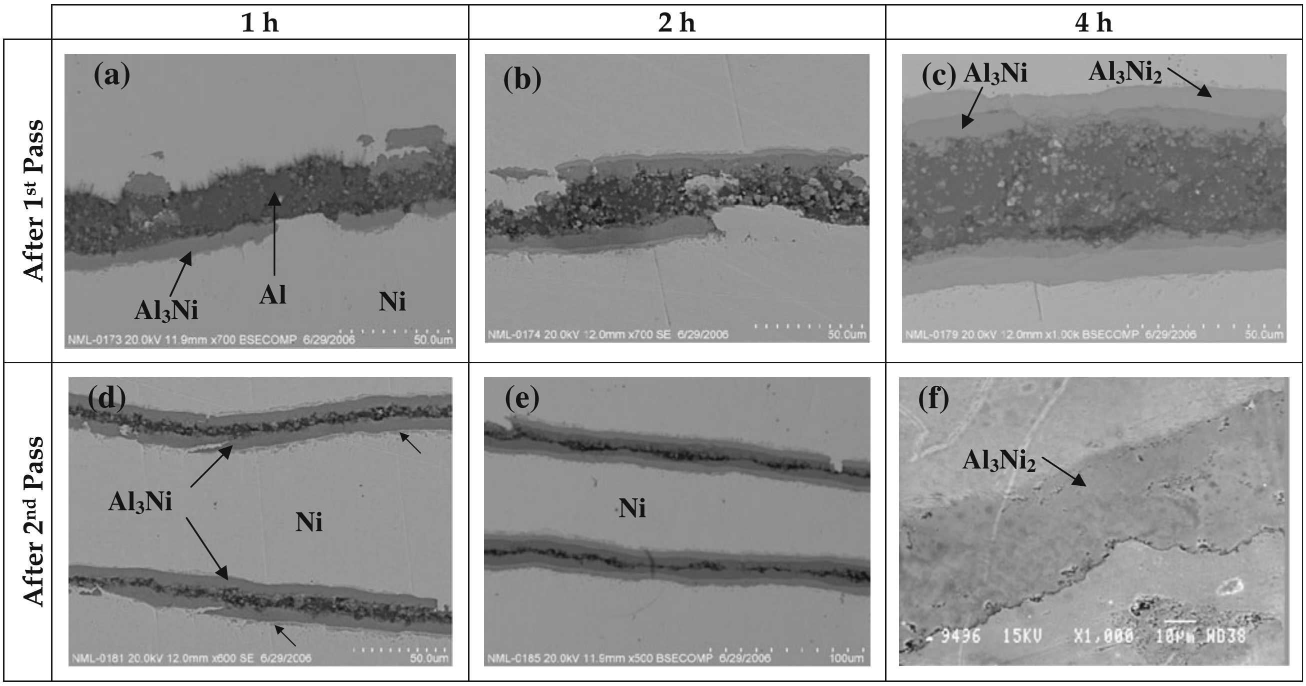

Fig. 3 Micrographs of (a-c) 1st pass laminate annealed for 1, 2, and 4 h, respectively, and (d-f) 2nd pass laminate annealed for 1, 2, and 4 h, respectively

not take place throughout the interface. However, there are some spikes or blurred interfaces indicating diffusion of Al into Ni at the interface. This may be due to the high dislocation density generated at the interfaces, and because dislocations act as easy path for diffusion. This is also manifested in the fact that the growth takes place from the interface into the Ni matrix (Fig. 3a) and Al has better diffusivity in Nickel compared with Ni in Al. The gray particles in the Al layer have been identified as an intermetallic of Al and Ni, to be discussed later. As the time of annealing increased, more interfacial area was covered with the reaction product. Moreover, it is observed in Fig. 3(b) that there are two layers growing at the interface having

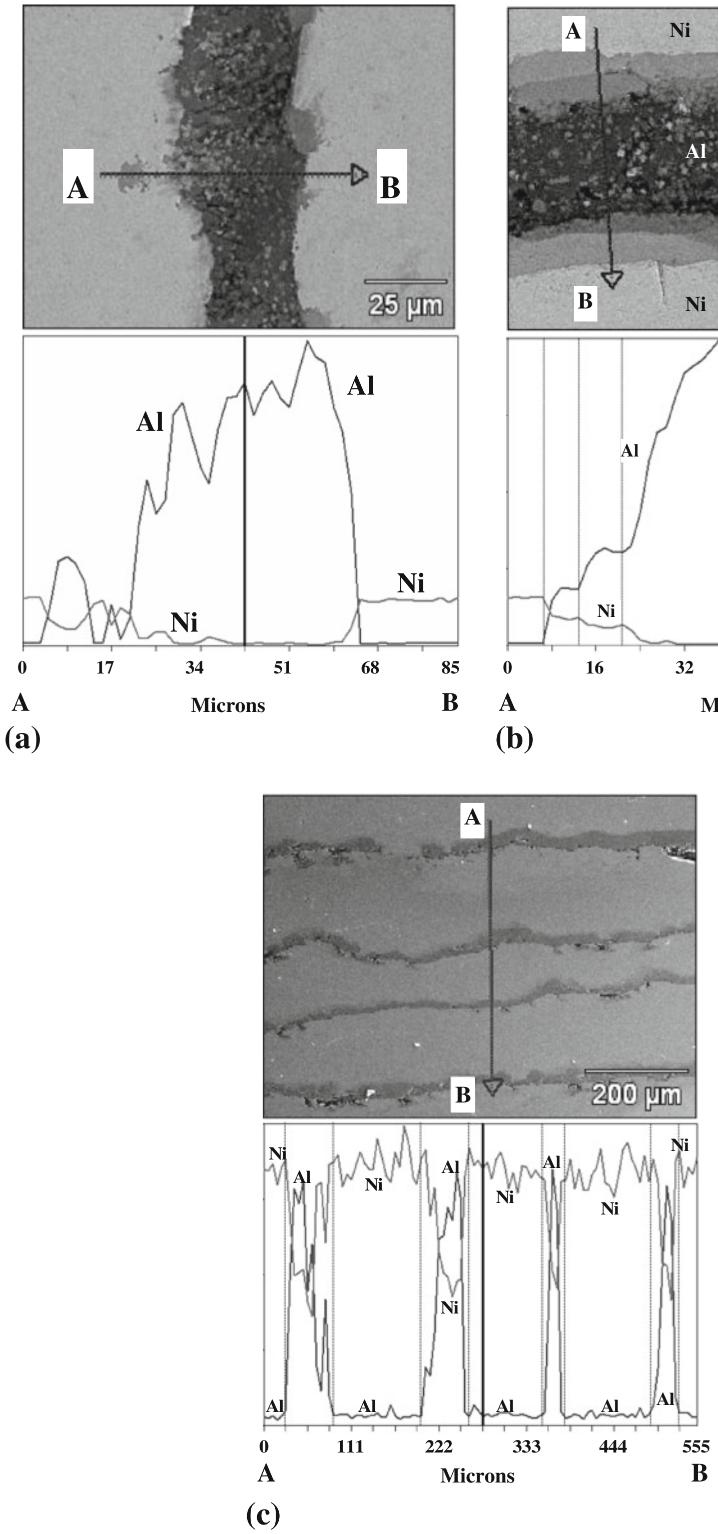

Fig. 4 Compositional line scans across the interfaces for the conditions: (a) the 1st pass, 773 K, 1 h; (b) the 1st pass, 773 K, 4 h; (c) the 2nd pass, 773 K, 4 h

different compositions. After the completion of 4 h, almost the whole interface is delineated with two reaction products. In contrast, after the 2nd pass, the interface was covered with a single product layer just after 1 h of annealing (Fig. 3d). This is a prominent observation, after annealing of the 2nd pass samples, compared to that of the 1st pass where a discontinuous and non-uniform layer of Al_3Ni was formed, which relates to the high strain incorporated in the 2nd pass. The gray particles in this figure (shown by small arrows), away from the interface, in the Ni matrix indicates rapid diffusion of Al in the matrix. After 2 h, only a thin layer of Al remains (Fig. 3e), which fully transforms to a single phase after 4 h of annealing.

3.2 Compositional and Phase Analysis

The qualitative variation in elemental content at and near the interface has been characterized by line scan. Figure 4(a) shows the elemental profiles across the interface formed after annealing 1st pass sample for 1 h at 773 K. It seems that Al diffuses to Ni matrix leaving some areas unaffected. It is to be noted that the Al layer shows black contrast in the right, whereas, it reveals small gray particles in the left part of the layer. The Al and Ni layers are clearly distinguishable from the line plot. The presence of Ni is negligible in the Al layer. A gradual decrease of the Ni concentration at the interface indicates that there is no sharp boundary. The presence of phases, in gray contrast, away from the interface indicates diffusion of Al into Ni layer through an easy diffusion path. After 4 h of annealing at the above condition, continuous layers are formed at the interfaces. However, a backscattered image (as shown in Fig. 4b) shows two distinct layers indicating the presence of Ni rich and Ni lean layers. If Fig. 4(a) and (b) are compared, then it is clearly visible that, in the latter case, the Al layer profile does not change sharply as seen in the former. This indicates that Ni diffuses to Al layer with increasing annealing time. As discussed by Mizuuchi et al. (Ref 1), the compositional gradient may lead to a better bonding between Ni and Al layers and also between the Ni and nickel aluminide in the later stages of annealing. The line scans for samples from the 2nd pass, annealed for 4 h, are shown in Fig. 4(c). These line profiles across the four layers show that the amounts of Ni and Al in all the layers are the same. This is indicated by the same height of Al and Ni lines in all the transition zones as indicated in the figure.

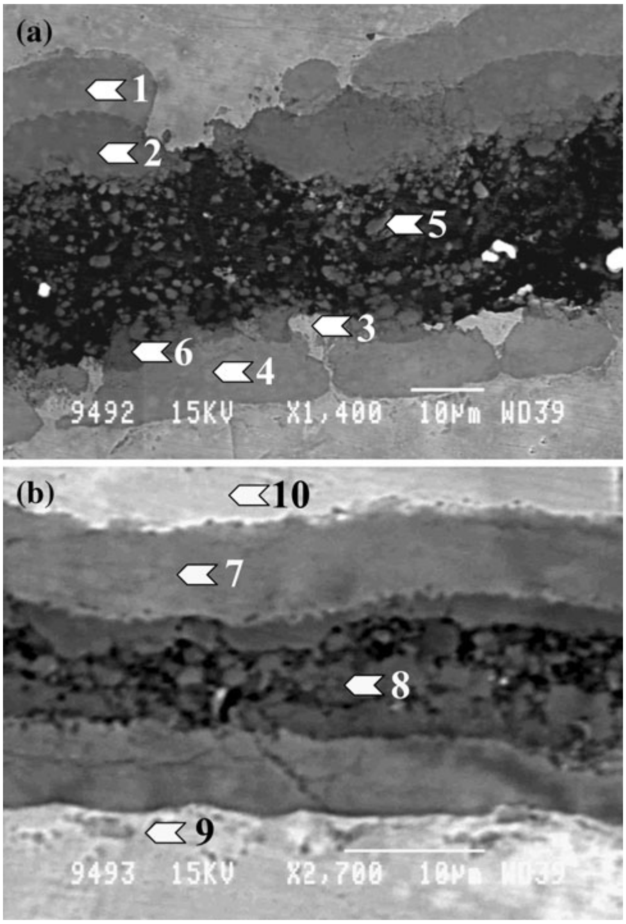

Fig. 5 Composition and phase analysis across the interfaces for the conditions: (a) 1st pass, 773 K, 4 h; (b) 2nd pass, 773 K, 2 h

The quantitative idea of the phases formed during the annealing process was confirmed by EDX analysis. Figure 5(a) and (b) show the locations of the EDX measurement for the samples of the 1st pass annealed for 4 h and those of the 2nd pass annealed for 2 h, respectively. The compositions of the respective locations have been summarized in Table 3. This analysis implies that the sequence of phases present in Fig. 5(a) is as follows: Ni-rich phase (outer most layer in light contrast, i.e., locations 3 and 10)/Al_3Ni_2 (locations 1 and 4)/Al_3Ni (locations 2 and 6)/Al-rich phase (middle layer in dark contrast). As the annealing time increases, all Al is consumed giving rise to Al_3Ni (location 8), and further increase in annealing time (2nd pass, 4 h) leads to complete transformation of Al layer into Ni_2Al_3 layer.

4. Discussion

4.1 Prediction of Formation of First Intermetallics During Annealing at 773 K Temperature

In the phase diagram of an Al-Ni system, there are several nickel aluminide intermetallic compounds, such as Al_3Ni, Ni_2Al_3, NiAl, Ni_5Al_3, and Ni_3Al (Ref 13). First phase to form under this kind of solid-solid interaction can be predicted by

Table 3 Composition and phase analysis

	Locations as shown in the Fig. 5									
	1	2	3	4	5	6	7	8	9	10
Al, at.%	59.15	75.08	4.16	58.63	64.59	76.34	61.29	76.14	38.87	2.06
Ni, at.%	37.76	24.92	95.74	39.67	35.41	23.66	38.71	23.86	61.13	97.94
Phase	Ni_2Al_3	$NiAl_3$	Ni rich	Ni_2Al_3	Ni_2Al_3	$NiAl_3$	Ni_2Al_3	$NiAl_3$	Ni rich	Ni rich

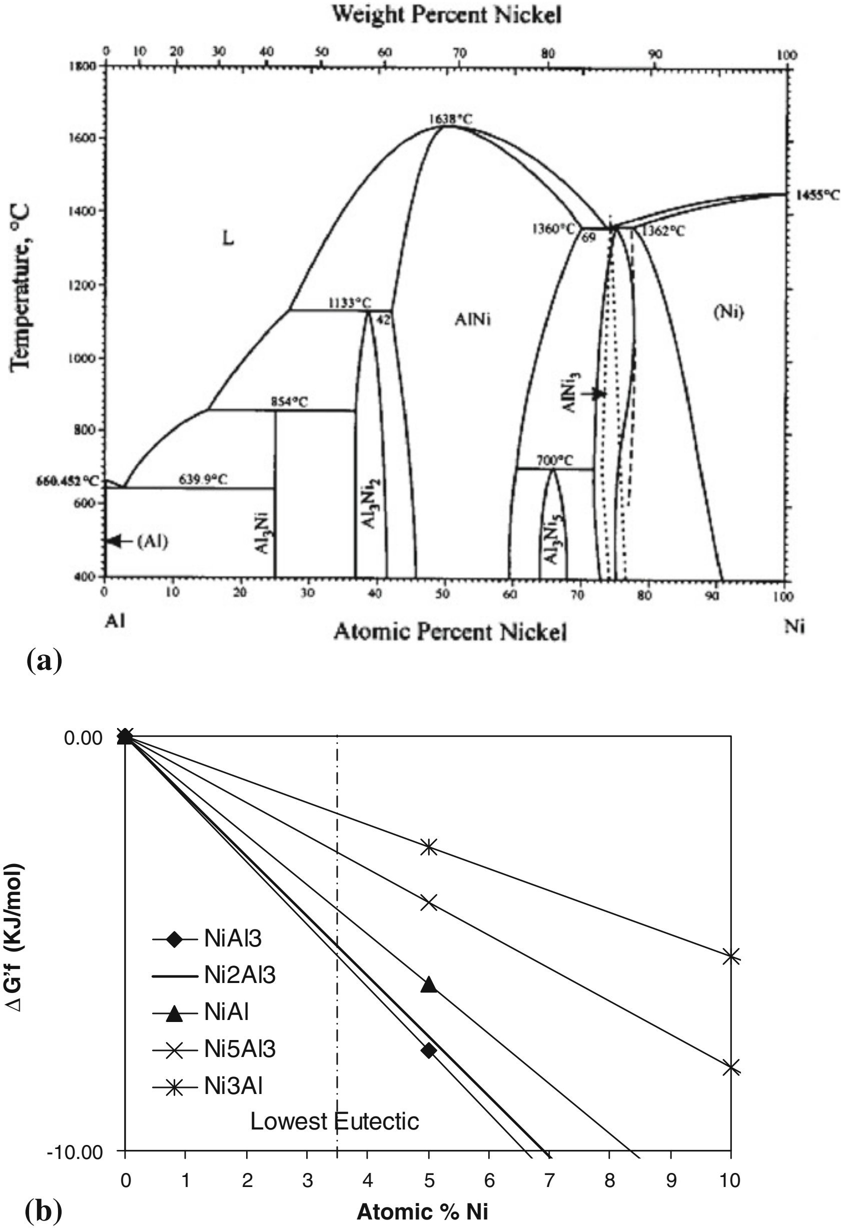

Fig. 6 (a) Schematic diagram of the equilibrium binary alloy phase diagram (Ref 13) and (b) effective free energy of formation diagram for Al-Ni at 773 K

EHF (effective heat of formation) theory proposed by Pretorius and coworkers (Ref 14, 15). According to EHF theory, first phase to form during metal-metal interaction is the phase with the most negative heat of formation at the concentration of the lowest temperature eutectic of the binary system. Figure 6 shows the calculated values of effective free energy of formation for various possible phases at lowest eutectic composition (Ni = 3.5 at.%). This shows that the formation of $NiAl_3$ phase is kinetically favored. Further, phases ($NiAl_3$ and Pure Ni) will react with each other to form a phase (Al_3Ni_2) with a composition between that of the interacting phases and closest to that of the lowest eutectic composition (Ref 13). However, transformation to NiAl and Ni_3Al requires a high annealing temperature and longer duration. Therefore, it is expected that the formation of latter two phases would not have taken place in the present case.

4.2 Effect of Strain on the Intermetallic Growth Rate

Effect of strain on the nature and growth of intermetallics phase can be studied by comparing samples going through the 1st pass ($\varepsilon_{Ni} = 0.93$ and $\varepsilon_{Al} = 1.35$) and the 2nd pass ($\varepsilon_{Ni} = 1.79$ and $\varepsilon_{Al} = 2.44$). If we look at the growth morphology after the 2nd pass in Fig. 3(d), it is readily seen that most of the Al layer is transformed just after 1 h. After 2 h at 773 K (Fig. 3e), samples from the 2nd pass are almost transformed to intermetallic phase leaving a hairline Al layer. This is further confirmed by EDX analysis done on the 2nd pass sample as shown in Fig. 5(b), where the middle layer (i.e., location 8) is completely transformed into Al_3Ni phase and is followed by a thick and continuous Al_3Ni_2 layer. The enhanced transformation kinetics can be attributed to the high accumulative strain experienced by both the Ni and Al layers during rolling passes. This is in contrast to the MILs made by thin foils using hot-pressing technique, where a high temperature of approximately 1273-1373 K is required. In the present investigation, the Al layer utilized is thicker than that employed in the former processing route (Ref 1, 2).

The present study, therefore, dealt with the development of Ni-based Ni-aluminide laminate composites. The effect of high strain accumulation during rolling was made use of to affect complete reaction at lower temperatures and short annealing duration. Though the grain refinement study has not been carried out in this investigation, it is well known that this kind of high strain processing leads to grain refinement of the matrix phase giving rise to improved properties. The qualitative compositional analysis indicated that the diffusion across the interface is a function of temperature as well as time of annealing.

5. Conclusions

The present investigation is the first attempt to develop economically viable production route for the MIL composites. Thick foils have been used for making laminates of Ni-Al by accumulative roll bonding followed by controlled annealing at 773 K to affect consumption of Al foils to form intermetallic compound. It was observed that the reaction after the 2nd pass of roll bonding was faster compared to that after the 1st pass. The high strain accumulation during rolling has been concluded to effect the faster reaction at the interface. Low temperature of 773 K and longer duration of annealing are more effective to avoid de-lamination of individual layers and ensure a good adherence of intermetallic compounds.

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