

Experimental evidence of two-stage formation of Al_3Ni in reactive Ni/Al multilayer foils

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This paper reports a two-stage process for the formation of Al_3Ni via igniting and quenching Ni/Al multilayer foils. The first stage involved lateral growth of Al_3Ni from isolated nucleation sites and subsequent coalescence into a continuous layer. The second stage was the growth of such Al_3Ni layers in the direction normal to the layering until the entire Al was consumed, as suggested in Coffey's model. Al_3Ni subsequently reacted with the remaining Ni to form AlNi .
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Self-propagating exothermic formation reactions have been intensively studied in a variety of reactive multilayer foils, e.g. Ni/Al, Ni/Si and Nb/Si [1,2]. These foils contain numerous alternating nanoscale layers of elements with large negative heats of mixing. A small thermal pulse causes atoms to diffuse normal to the layering and results in a rapid exothermic reaction. The heat produced is conducted down the foil and facilitates more atomic mixing and compound formation, thus establishing a self-propagating reaction.

Previous studies [3–6] of phase formation during annealing in metal/Al multilayer thin films, e.g. Nb/Al and Ni/Al, indicated that the generation of the Al-rich phases, such as Al_3Nb and Al_3Ni , is a two-stage process that can be described by the model of Coffey et al. [7]. The first stage is interpreted as the growth of the product phase from isolated nucleation sites in the direction parallel to the interface and its subsequent coalescence into a continuous layer. The second stage is the growth of such layers in the direction perpendicular to the interface until one or both reactants are consumed. This two-stage process has been used to explain the two exothermic peaks that were observed in the formation of a single phase in differential scanning calorimetry (DSC) runs of reactive multilayer thin films.

However, this two-stage formation process has not been directly observed in multilayer thin films during

self-propagating reactions. The layer thicknesses of multilayer thin films are of the order of tens of nanometers. The reaction occurs very rapidly and the whole reaction is completed in only several milliseconds. In this study, Ni/Al multilayer foils were fabricated by a cold-rolling method [8,9]. The cold-rolled foils contained alternating layers of Ni and Al with thicknesses of the order of micrometers. These foils reacted much more slowly than multilayer thin films with layer thicknesses of the order of nanometers, and thus could reveal details of the exothermic formation process.

Ni/Al multilayer foils were fabricated by cold rolling. Thin sheets of elemental Ni and Al with a Ni/Al thickness ratio of 2:3 were stacked alternately together, in order to obtain a Ni/Al atomic ratio of 1:1. The stacked sheets were placed in between a folded stainless steel sheet, which had previously been hardened by repeated rolling. This assembly was cold rolled a few times using a laboratory rolling mill to reduce its thickness to half of the original thickness. The Ni/Al sheets were then taken out of the stainless steel sheet and cut into halves; these halves were then stacked together to recover their original thickness, and then cold rolled without changing the distance between the rollers (this is defined as a rolling cycle). After several rolling cycles, a uniform Ni/Al multilayer foil was achieved. The total thickness of the foil was around 200 μm . The details of the cold-rolling process for the fabrication of Ni/Al multilayer foils have been described elsewhere [10].

The cold-rolled Ni/Al multilayer foils were ignited by a flame. After heating for several seconds, a

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self-propagating reaction started in the foil and two distinct reaction steps were observed. First, the reaction front spread along the foil at a relatively slow rate and the foil surface became darker. Then, a second reaction followed, where the reaction front spread very rapidly along the entire foil, emitting a visible red light. To characterize the reaction products, reacted Al/Ni foils were ground into powders for symmetric X-ray diffraction (XRD) examination using Cu K_{α} radiation. As-cold-rolled Al/Ni foils were also examined by XRD for comparison. XRD traces for as-cold-rolled and as-reacted Ni/Al multilayer foils are plotted in Figure 1. For the as-cold-rolled foils, all the peaks in the XRD scan correspond to Al and Ni, as shown in the upper scan in Figure 1. After reaction, all major peaks correspond to the ordered B2 AlNi compound, which is the equilibrium compound for this composition, as shown in the lower scan in Figure 1.

In order to identify the two distinct reaction steps, some Ni/Al multilayer foils were quenched so that the first reaction step terminated in the middle of the foils. The microstructures of Ni/Al multilayer foils were observed by scanning electron microscopy (SEM) using a Hitachi S-3600N with energy-dispersive X-ray analysis (EDX). Figure 2 shows the SEM images of a quenched Ni/Al multilayer foil. At one end of the foil, necked Ni particles were embedded in the Al matrix, showing that no reaction occurred (Fig. 2(a)). At the middle of the foil, where the reaction was quenched, a thin layer of

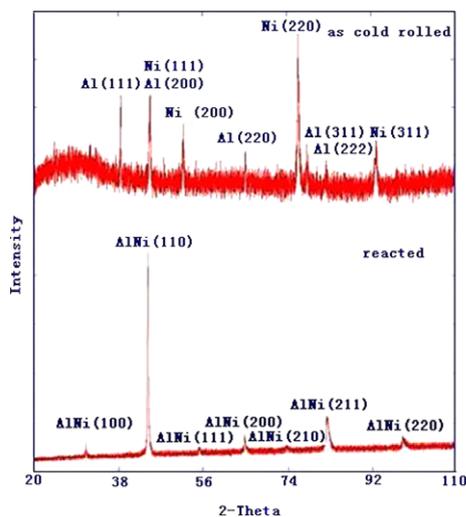


Figure 1. XRD patterns of Ni/Al multilayer foils before and after reaction.

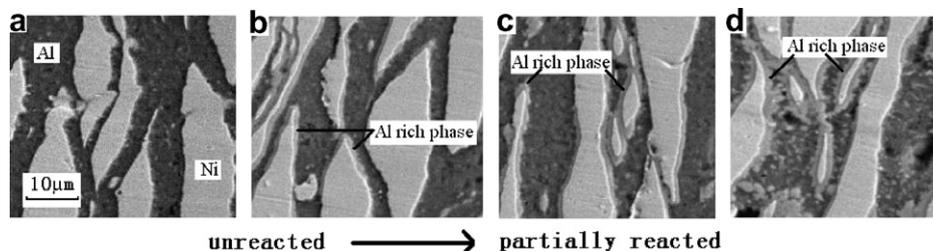


Figure 2. SEM images of a quenched Ni/Al multilayer foil.

Al-rich phase (the Ni/Al atomic ratio obtained by EDX is $\sim 1:3$) was seen to grow around the necked Ni particles. Such Al-rich layers were distributed at isolated sites and did not fully cover the Ni particles (Fig. 2(b)). Figure 2(c) shows the part of Ni/Al foil that completed the first reaction step, where the Al-rich layers continued to grow and fully encircled the Ni particles. In this paper, this kind of foil is defined as partially reacted foil. In Figure 2(d), these Al-rich layers began to grow in thickness and spread to the neighboring Ni particles. According to the model of Coffey et al., the generation of the Al-rich phase in metal/Al multilayer thin films during annealing is a two-stage process [7]. The first stage is the growth of the Al-rich phase from isolated nucleation sites in the direction parallel to the interface and the subsequent coalescence into a continuous layer. The second stage is the growth of such layers in the direction perpendicular to the interface until one or both reactants are consumed. According to Coffey's model and the microstructures at various positions of the quenched foil, Figure 2(b) and (c) show the parts of the foil that experienced the growth of the Al-rich phase from isolated nucleation sites and its subsequent coalescence into a continuous layer, which represents the first formation stage of the Al-rich phase. Figure 2(d) shows the growth of the Al-rich layers in the direction perpendicular to the interface, which represents the second formation stage of the Al-rich phase.

The phase formation and heat of reaction were characterized for these foils using a Perkin Elmer DSC. In each DSC run, about 10 mg of as-cold-rolled foil was heated from 200 to 725 °C at a rate of 40 °C min^{-1} in flowing nitrogen. A baseline was obtained by repeating the heating cycle, which was then subtracted from the heat flow in the first run. By integrating the net heat flow with respect to time, the heat of reaction was obtained. DSC curves for the as-cold-rolled and partially reacted Ni/Al multilayer foil are shown in Figure 3. Three exothermic peaks can be identified for both the as-cold-rolled and partially reacted Ni/Al multilayer foils. In the DSC curves, peak A is much broader than peaks B and C. It extends from 430 to 630 °C for the as-cold-rolled foil. Previous numerical simulations and theoretical calculations suggested that a burst of nucleation occurring heterogeneously at boundaries in the interface plane rather than randomly over the whole interface area during the formation process in reactive thin films can result in broad peaks in DSC curves [11,12]. For the as-cold-rolled Ni/Al multilayer foils with non-uniform interface area, the broad peak A in the DSC scan is due to the spatial bias (the deviation from spatial

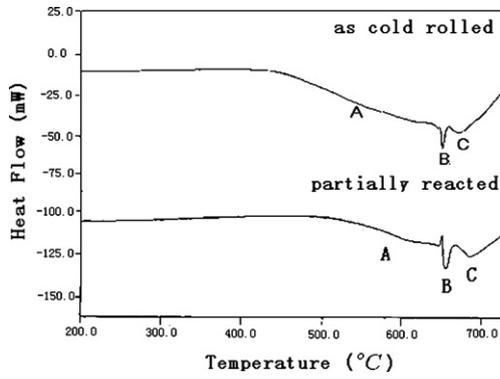


Figure 3. DSC curves of as-cold-rolled and partially reacted Ni/Al multilayer foils.

randomness) in the nucleation of product phase. Peak A of the partially reacted multilayer foils (which starts at about 500 °C) is much smaller than that of the as-cold-rolled foils (which starts at about 430 °C), suggesting that the first stage reaction has already occurred in the partially reacted multilayer foils. The three peak temperatures for the partially reacted multilayer foils are higher compared with the as-cold-rolled foils, meaning that more energy input from DSC is needed to complete the same phase formation process. The reason for the peak temperature shift is that the first stage formation reaction has already occurred before the DSC experiment in the partially reacted foils, and thus less energy can be released from the foils during the DSC scan.

To identify the reaction products at different reaction stages, some of the cold-rolled Ni/Al multilayer foils were heated to 530 and 640 °C, which are the peak temperatures of A and B in the DSC curve for the as-cold-rolled foils, using the same heating rate as in the previous DSC runs. Figure 4 shows the XRD patterns and SEM images for these annealed foils. The peaks in the XRD scans correspond to Al, Ni and Al₃Ni, suggesting that Al₃Ni was generated at these stages (Fig. 4(a) and (b)). For the foil annealed to 530 °C (the temperature of peak A), Al₃Ni appeared at isolated sites along the Ni/Al interface (Fig. 4(c)), which is evidence for the first stage formation process of Al₃Ni. This also suggests that peak A in the DSC curve is associated with the growth of Al₃Ni at isolated nucleation sites. The foil annealed to 640 °C (the temperature of peak B) has some extra Al₃Ni peaks in the XRD scan (Fig. 4(b)) compared with the foil annealed at lower temperatures (Fig. 4(a)). The Al₃Ni layers became continuous, fully covered Ni particles, and grew in thickness towards the neighboring Ni particles (Fig. 4(d)), which is the evidence for the second stage formation process of Al₃Ni. This is in agreement with Coffey et al.'s interpretation of the two exothermic peaks observed for the formation of a single phase. These results prove our explanation for the two-stage formation process of the Al-rich phase (Al₃Ni) in the cold-rolled Ni/Al multilayer foils. Therefore, in the DSC scans, the first two peaks (A and B) correspond to the two exothermic formation stages of Al₃Ni. To identify the final product of the

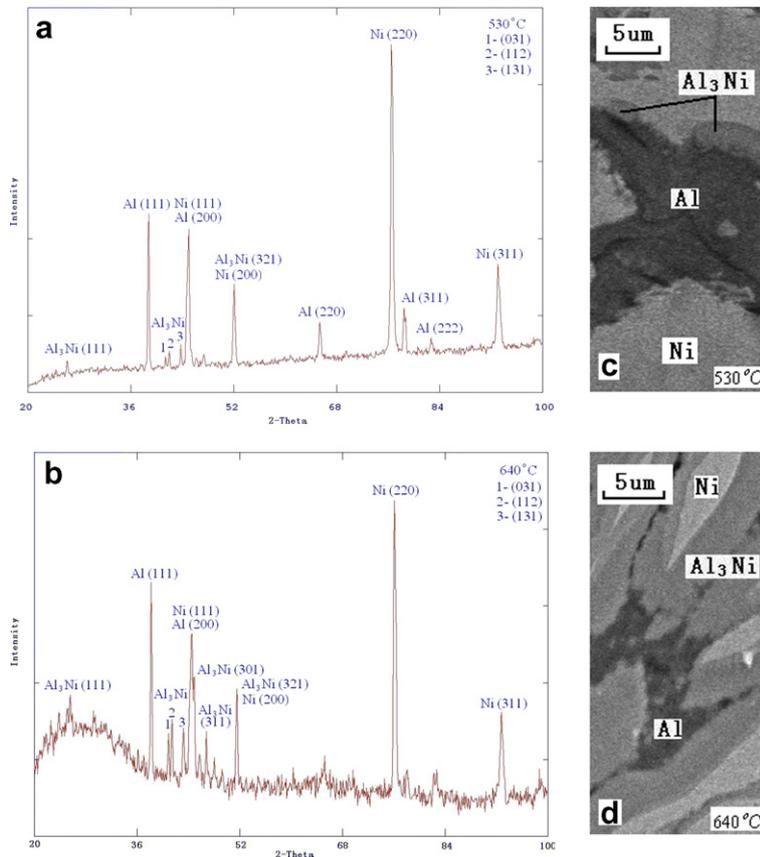


Figure 4. XRD patterns and SEM images of the Ni/Al multilayer foils heated to 530 and 640 °C.

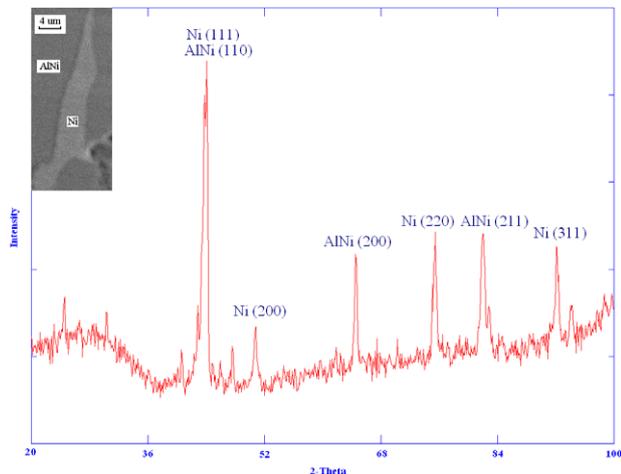


Figure 5. XRD pattern and SEM image of a Ni/Al multilayer foil heated to 725 °C.

reaction, a cold-rolled Ni/Al multilayer foil was heated to 725 °C (the maximum temperature for DSC runs) at the same heating rate. The XRD pattern and SEM image for this foil are shown in Figure 5. Two phases can be identified: the reaction product, i.e. AlNi, and the remaining Ni. Thus the last peak (peak C) in the DSC scan is associated with the formation of the final product, AlNi.

Using the DSC curves, SEM observation and XRD scans of the Ni/Al multilayer foils at various formation stages, the entire reaction process for the cold-rolled Ni/Al multilayer foils can be identified. The first reaction stage with slow reaction front propagation is the lateral growth of Al₃Ni phase from isolated nucleation sites and its subsequent coalescence into a continuous layer. This stage is associated with the broad peak A in the DSC curve and is defined as the first stage of the formation process of Al₃Ni. The next reaction stage, with fast reaction front propagation, is the growth of the Al₃Ni layers in the direction normal to the interface until all the Al is consumed. This stage is related to peak B in the DSC curve and is defined as the second stage of the formation process of Al₃Ni. Afterwards, Al₃Ni reacts with the remaining Ni to form the final reaction product, AlNi, corresponding to peak C in the DSC scan. The entire formation process is schematically illustrated in Figure 6.

By integrating the net heat flow with respect to time from the DSC curve of the as-cold-rolled Ni/Al multilayer foil, the heat of the reaction was calculated to be $-57.5 \text{ kJ mol}^{-1}$. This is slightly smaller than the formation enthalpy of AlNi (-59 kJ mol^{-1}) [13]. This is due to the incomplete reaction of the foil. As shown previously, some Ni remained after the foil was heated to the maximum temperature for the DSC runs, 725 °C (Fig. 5).

In conclusion, a two-stage formation process of Al₃Ni was observed in cold-rolled Ni/Al reactive multilayer foils. The first stage was the lateral growth of Al₃Ni phase from isolated nucleation sites and its subse-

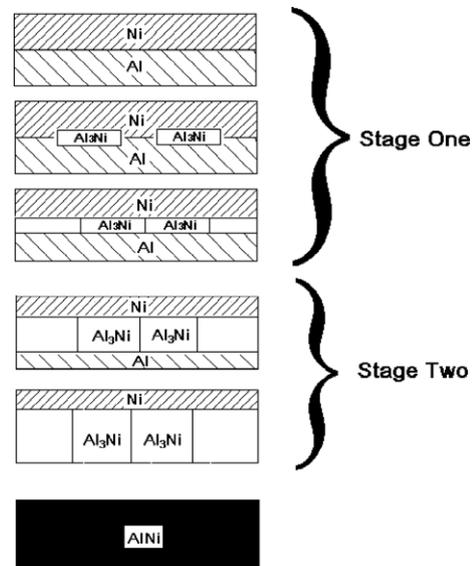


Figure 6. Schematic illustration of the formation process of Al₃Ni and AlNi.

quent coalescence into a continuous layer. The second stage was the growth of such Al₃Ni layers in the direction normal to the interface until all Al was consumed. Afterwards, Al₃Ni reacted with the remaining Ni to form the final reaction product, ordered B2 AlNi compound.

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