

Phase transformations during rapid heating of Al/Ni multilayer foils

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(Received 17 July 2008; accepted 4 August 2008; published online 25 August 2008)

We have used self-propagating exothermic reactions in Al/Ni multilayers as a means to explore the effect of rapid heating on phase transformations. Using time-resolved synchrotron x-ray microdiffraction with an extremely fast detector, we were able to examine the reaction sequence in detail at heating rates of $\sim 10^6$ K s⁻¹. We observed that the intermediate phases formed during the self-propagating reactions are different from those formed at lower heating rates, even though the final phases are the same. *In situ* characterization is essential, as other means of studying self-propagating reactions (such as quenching the reaction followed by *ex situ* analysis) provide different—and potentially misleading—results. © 2008 American Institute of Physics.

[DOI: 10.1063/1.2975830]

Metastable solid phases can be produced by rapid quenching from the liquid state, which limits the time available for diffusion and nucleation and growth of competing phases. Similar effects can be expected due to rapid heating, but most studies of phase transformations involving interdiffusion of chemical species have been performed either isothermally or at moderate heating rates (~ 1 K s⁻¹). In this letter, we show how phase transformations involving interdiffusion can be studied at much higher heating rates ($\sim 10^6$ K s⁻¹) by *in situ* observation of self-propagating reactions in metallic multilayers.

Self-propagating reactions can occur in materials consisting of two or more solid phases that liberate large amounts of heat upon mixing of their elemental components; the well-known thermite reaction is one example. Recently, self-propagating formation reactions have been studied in nanostructured multilayer foils comprising alternating 10–100 nm thick layers of elemental constituents (Fig. 1). Because the diffusion distances are small, exothermic reactions in multilayer foils propagate in localized fronts at velocities on the order of 1–100 m s⁻¹, reaching temperatures in excess of 1300 K in less than 10 μ s.¹ This makes reactive foils useful for a variety of applications, including joining of thermally sensitive materials.²

The steep thermal and chemical gradients that make self-propagating reactions scientifically interesting also make their investigation challenging. While prior *in situ* structural characterization of propagating reaction fronts (in powder compacts) involved temporal resolutions of milliseconds or greater,^{3,4} characterization of the reaction front in multilayer foils requires both spatial resolution better than ~ 100 μ m (the approximate width of the reaction zone) and temporal resolution better than ~ 100 μ s (the time for the front to pass a fixed location).

We recorded x-ray diffraction patterns in transmission through 30 μ m thick sputter-deposited reactive foils comprising 70 nm layers of Al 1100 alloy alternating with 30 nm

layers of Ni-7 wt % V (Fig. 1). Spatial resolution was achieved by using a glass capillary to focus the x-ray beam to a 60 μ m spot, and temporal resolution of 55 μ s was achieved by recording the diffraction patterns with an extremely fast pixel array detector⁵ capable of recording eight frames in rapid succession. The velocity of the reaction front in these foils is 2.8 ± 0.2 m s⁻¹; at this speed the reaction front passes the x-ray beam in about 57 μ s. The detector was triggered by sensing the light emitted from the reaction front as it approached the x-ray beam using a fiber optic coupled to a photodetector. Because the field of view of the fiber optic is larger than the x-ray beam size, triggering of the detector (which we define as $t=0$ in what follows) preceded the arrival of the reaction front at the beam position by 180 ± 20 μ s. By introducing suitable delays between triggering of the detector and frame capture and various exposure times, we were able to follow the entire course of the reaction in successive experiments. While single diffraction patterns were sufficient for phase identification even for the shortest exposure times, to achieve better signal-to-noise ratio, the results shown below represent sums of between two and six individual patterns. We also measured the tempera-

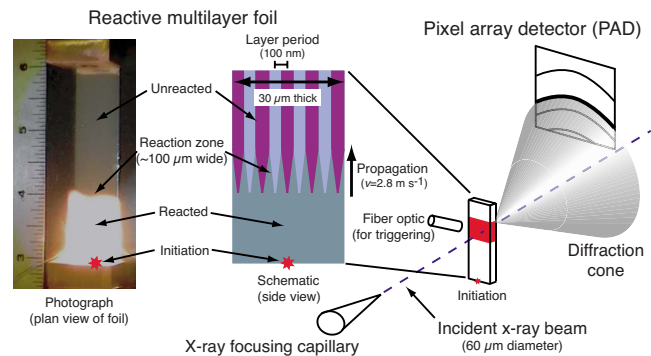


FIG. 1. (Color online) Specimens and x-ray scattering geometry. At left is a photograph of a propagating reaction front (in plan view) along with a schematic showing the reacting foil (in side view). X-ray diffraction patterns were recorded in transmission through the foils onto a pixel array detector.

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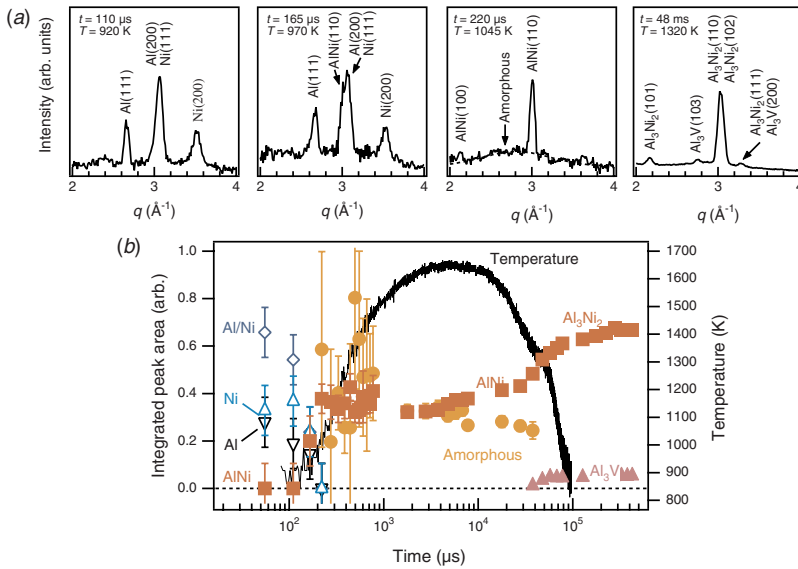


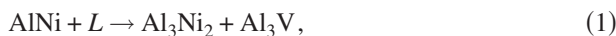
FIG. 2. (Color online) (a) Diffraction patterns recorded at various times t during the reaction and through cooling. Note that the reaction front arrives at the x-ray beam at $t = 180 \pm 20 \mu\text{s}$, so the first pattern is from the unreacted foil. (b) Normalized integrated peak area and reaction temperature. Because two overlapping peaks from Al_3Ni_2 cannot be resolved from the AlNi(110) peak over the interval where Al_3Ni_2 forms ($t = 30\text{--}50 \text{ ms}$), these peaks from both phases are represented by a single symbol.

ture of the reaction front with a ratio pyrometer⁶ in a separate series of experiments.

The diffraction patterns in Fig. 2(a) illustrate the sequence of phase transformations during the reaction and through cooling. At $t = 55$ and $110 \mu\text{s}$, prior to the arrival of the reaction front at the x-ray beam position, only diffraction peaks from the original microstructure (fcc Al and Ni) were observed. The first obvious changes occurred at $t = 165 \mu\text{s}$ when a peak from the cubic intermetallic AlNi appeared as a shoulder on the Al(200)/Ni(111) peak, the background increased (which we attribute to the formation of an amorphous phase) and the intensity of the fcc Al and Ni peaks decreased. By the next frame ($t = 220 \mu\text{s}$) all the peaks from fcc Al and Ni disappeared, leaving only the AlNi peak and the amorphous scattering maximum.

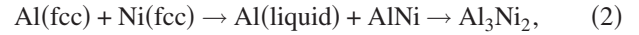
The amorphous phase we observed was most likely an Al-rich liquid; at $t = 165 \mu\text{s}$ the temperature exceeded the melting point of pure Al (933 K), and the position of the amorphous peak ($q_{\text{max}} \approx 2.8\text{--}2.9 \text{\AA}^{-1}$) was consistent with that of an Al-rich liquid Al-Ni alloy.^{7,8} The apparent coexistence of liquid and crystalline Al while the reaction front was crossing the x-ray beam (patterns taken at $t = 165$ and $220 \mu\text{s}$) is most likely an artifact resulting from the limited spatial resolution of the experiment. Over this interval the scattering had contributions both from the reaction zone (where we believe the Al was largely molten) and the region ahead of the front (where crystalline Al remained).

The only other phase transformation we observed occurred much later, well after the reaction front passed the x-ray beam. Over the period $t = 30\text{--}50 \text{ ms}$, peaks from hexagonal Al_3Ni_2 and tetragonal Al_3V developed, the amorphous halo disappeared, and an inflection point in the temperature data indicative of an exothermic reaction occurred at $T \approx 1350 \text{ K}$ [Fig. 2(b)]. These observations correspond to the peritectic reaction

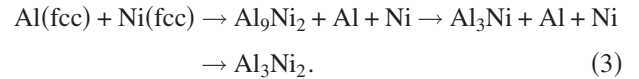


which appears on the Al-Ni-V ternary phase diagram at $T = 1373 \text{ K}$.⁹ The final phases (Al_3Ni_2 and Al_3V) are the equilibrium phases for an Al-Ni-V alloy of the overall composition of these multilayers.

We can therefore summarize the sequence of phase formation during the self-propagating reaction as follows:



where the role of V has been neglected for clarity. This reaction sequence is quite different from that observed when the reaction occurs at slower heating and cooling rates. For comparison, we heated identical foils in a differential scanning calorimeter (DSC) at 0.7 K s^{-1} , stopping the reaction after each exothermic peak and performing *ex situ* x-ray diffraction to identify the phases present. For the DSC experiments, the phase formation sequence was



Other studies of Al/Ni multilayers at similar heating rates have shown a variety of phase formation sequences, depending on the overall composition of the multilayer foil and the thicknesses of the individual layers.¹⁰⁻¹⁹ The wide range of observed behaviors results from the kinetic and chemical constraints particular to each experiment. One reasonable explanation for the phase formation sequence considers whether a critical nucleus with the proper composition can form, given the concentration gradient resulting from interdiffusion.²⁰ If not, another phase must form instead. In our DSC experiments Al_9Ni_2 nucleated first in the intermixed region on the Al side of the original Al/Ni interfaces because the composition gradient was less steep there.¹⁵ The competing intermetallic phases (such as Al_3Ni) were richer in Ni and thus would have had to nucleate closer to the Ni layer, but could not due to the steeper concentration gradient there. (We note that it may also be possible to develop an alternative explanation for the phase formation sequence based on interfacial reaction barriers²¹ and the effect of heating rate on interdiffusion.)

In a self-propagating reaction, rapid heating ($\sim 10^6 \text{ K s}^{-1}$ in this experiment) and high temperatures result in rapid diffusion, but the time available for nucleation of intermetallic phases is much shorter than in the DSC experiments. Indeed, in our experiments on self-propagating reactions, the formation of the Al_9Ni_2 and Al_3Ni intermetallic phases by solid-state reaction was suppressed. It appears that AlNi nucleated preferentially over other possible phases because its high melting point (1911 K) provided a consis-

tently large driving force for nucleation; in contrast, the maximum temperatures of stability of other intermetallics (such as Al_3Ni_2 at 1406 K) were rapidly exceeded. Nucleation of AlNi was also promoted by its stability over a wide composition range (~ 20 at. %) and the simplicity of its crystal structure.

Even halting a self-propagating reaction (by imposing a negative thermal gradient to quench the reaction) and examining the resulting microstructure *ex situ* does not yield the same results as *in situ* observations. Such quenching experiments have been performed on multilayers similar to those studied here.²² As in the case of slow heating described above, nucleation of Al_9Ni_2 was observed upon quenching the propagating reaction and the formation of AlNi was not. In contrast, our *in situ* diffraction experiments provided no evidence that Al_9Ni_2 ever formed, and we see clear evidence for the formation of AlNi and its participation in a peritectic reaction to form Al_3Ni_2 during the late stages of the reaction. These differences indicate that the quenching process itself influences self-propagating reactions and alters the phase formation sequence. Thus, the results of quenching experiments followed by *ex situ* analysis must be interpreted with caution.

Finally, we note that improvements in the *in situ* x-ray diffraction techniques described here can be expected. Synchrotron beamlines with greater flux would enable better spatial and temporal resolution. Pixel array detectors are potentially capable of ≤ 1 μs resolution; the temporal resolution of the experiments described here was limited by the available flux needed to acquire data with sufficient signal-to-noise ratio for analysis. Future developments may include larger format detectors that would allow either collection of data over a larger range of reciprocal space or higher resolution data over a more limited range. Such improvements are likely to lead to new insights into a variety of phenomena in materials that have characteristic time scales on the order of microseconds.

We gratefully acknowledge Alexander Kazimirov, Darol Chamberlain, Daniel Schuette, Darren Southworth, and Harish Nathani for their assistance with the *in situ* experiments and Sterling Cornaby and Don Bilderback for providing the x-ray capillary. Financial support for this work was provided by the National Science Foundation (Grant No. DMI-0300396, with Howmet Research Corporation as our indus-

trial partner), the Department of Energy (Grant No. FG02-97ER62443), and the Office of Naval Research (Grant No. N00014-07-1-0740). Portions of this research were conducted at the Cornell High Energy Synchrotron Source (CHESS), which is supported by the National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences under award DMR-0225180.

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