Microstructural study of an oscillatory formation reaction in nanostructured reactive multilayer foils

J. C. Trenkle, J. Wang, T. P. Weihs, and T. C. Hufnagel

Citation: Appl. Phys. Lett. **87**, 153108 (2005); doi: 10.1063/1.2099544
View online: https://doi.org/10.1063/1.2099544
View Table of Contents: http://aip.scitation.org/toc/apl/87/15
Published by the American Institute of Physics

APPLIED PHYSICS LETTERS **87**, 153108 (2005)

Microstructural study of an oscillatory formation reaction in nanostructured reactive multilayer foils

J. C. Trenkle, J. Wang, T. P. Weihs, and T. C. Hufnagel[a)]
Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218

(Received 24 January 2005; accepted 16 August 2005; published online 6 October 2005)

We report evidence of an oscillatory formation reaction in nanostructured Zr/Al/(CuNi) reactive multilayer foils. The oscillations create periodic ripples on the surface of the foil as well as periodic variations in the length scale of the microstructure of the reacted foil. We describe the nature of the resulting microstructure, and relate this to superadiabatic temperature oscillations at the reaction front. We also examine the effect of ambient temperature on the magnitude and period of the oscillations, and compare the results to numerical predictions and to experimental data for other reactive systems. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2099544]

Nanostructured multilayer foils made of elements that react exothermically can sustain self-propagating reactions.[1–7] These reactive foils are made by vapor depositing many alternating nanoscale layers of materials with large negative heats of mixing. Application of a small thermal pulse initiates local atomic mixing, releasing a large quantity of heat. The heat is conducted primarily along the length of the foil, facilitating further atomic mixing (mostly perpendicular to the layers) and thus creating a self-propagating reaction (Fig. 1).[8] The reaction characteristics, including the maximum temperature and the velocity of the reaction front, can be tailored by precise control of foil parameters, such as the choice of reactants, the layer period, and thickness of the intermixed region (Fig. 1).[9] Although the reaction temperature can be quite high (>1500 °C),[8] the total heat evolved is small because the foil is thin. These features make reactive foils attractive heat sources for welding, brazing, and soldering temperature-sensitive materials.[10,11]

The reaction front in these reactive foils is predicted in some cases to propagate in an oscillatory fashion, causing a dynamic reaction temperature and velocity.[12] Similar oscillatory reactions have been predicted and observed in other solid-state systems including explosive crystallization of Sb and $In_{1-x}Ga_xSb$ amorphous films[13,14] and Ta/C powder compacts.[15–17] However, experimental observations of these oscillations have not yet been reported in formation reactions in reactive foils.

In this letter, we report evidence of oscillatory formation reactions in Zr/Al/(Cu,Ni) multilayer foils. We observe periodic ripples on the surface of the reacted foils, as well as periodic variations in the scale of the microstructure parallel to the reaction propagation direction. The temperature of the reaction at a given point affects the scale of the microstructure, with higher temperatures creating a coarser microstructure. Thus, using microstructural observations, we can examine the effect of reaction conditions, such as ambient temperature, on the magnitude and period of the oscillations.

We fabricated multilayer reactive foils of overall composition $Zr_{38.3}Al_{31.5}Cu_{15.1}Ni_{15.1}$ by dc magnetron sputtering sequential layers of Zr (99.8% pure), Al (>99% pure), and $Cu_{0.5}Ni_{0.5}$ (>99.95% pure). The chamber pressure prior to deposition was less than 6×10^{-7} Torr, and the pressure of Ar during deposition was 1.65 mTorr. The distance between the sputtering guns and the substrate was 8.9 cm. Foils with several hundred Zr/Al/(CuNi) trilayers with a period of 55 nm were deposited onto brass substrates; the foils were subsequently removed from the substrates to form ~40 μm thick free-standing multilayer foils.

We initiated a self-propagating formation reaction in the foils, clamped between two copper blocks in air, by applying a 30 V spark directly to the foils. After completion of the reaction, the surface of the foils (which had been smooth and mirrorlike) showed periodic, concentric ripples, centered on the point of initiation (Fig. 2). These ripples are similar in appearance to those reported in oscillatory reactions of powder compacts,[15,17] two-layer self-propagating systems,[18] and explosive crystallization of amorphous films.[14]

To examine the microstructure of the reacted foils, we sectioned the specimens in a direction perpendicular to the surface ripples (parallel to the reaction propagation direction). Scanning electron microscopy (SEM) reveals a two-phase microstructure with a periodic variation in the size of the phases [Fig. 3(a)]. The period of the variation in microstructure is consistent with that of the surface ripples (Fig. 4). Electron microprobe analysis of the bands indicates that the composition of the dark and light phases in Fig. 3(a) are $Zr_{35}Al_{29}Cu_{14}Ni_{22}$ and $Zr_{41}Al_{25}Cu_{17}Ni_{17}$, respectively. X-ray diffraction scans of the reacted foils show that these phases are crystalline. We were unable, however, to conclusively identify the phases using these data, presumably because they are nonequilibrium phases that are not present in the ICDD Powder Diffraction File.[19] Wickersham and coworkers found similar periodic regions composed of large grains that correlated with the surface ripples in amorphous films following explosive crystallization.[14]

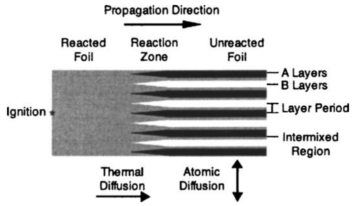

FIG. 1. A schematic of a self-propagating reaction in a binary reactive foil with the constituents (A,B) and foil parameters labeled.

[a)] Electronic mail: hufnagel@jhu.edu

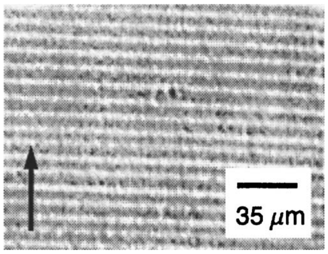

FIG. 2. Optical micrograph showing the periodic, concentric ripples that develop on the surface of a reacted foil. The arrow indicates the reaction propagation direction.

To interpret the microstructure and, in particular, the size of the grains in terms of the local temperature of the reaction, we first calculated the adiabatic temperature of a steady-state reaction from the enthalpy of reaction and a weighted average of the temperature-dependent heat capacities of the elements in the foil. The enthalpy of reaction (638 J g^{-1}) was measured by performing differential scanning calorimetry on unreacted foil using a Perkin–Elmer Pyris 1 DSC. The calculated adiabatic temperature of the reaction (1275 °C) is higher than the melting point of Al (660 °C), but not that of Zr (1855 °C) or the CuNi alloy (1320 °C).

In an oscillating reaction front, the reaction temperature can temporarily exceed the adiabatic reaction temperature by several hundred degrees.[12] Such a "superadiabatic" oscillation occurs when a temperature perturbation increases the temperature in the reaction front,[12,15–17,20,21] which causes the local rate of atomic diffusion to increase. The perturbation is amplified by increased mixing, resulting in an increase in the local temperature. Once the reactants are consumed, the oscillation is damped and the reaction front returns to steady-state propagation until a new cycle is initiated.

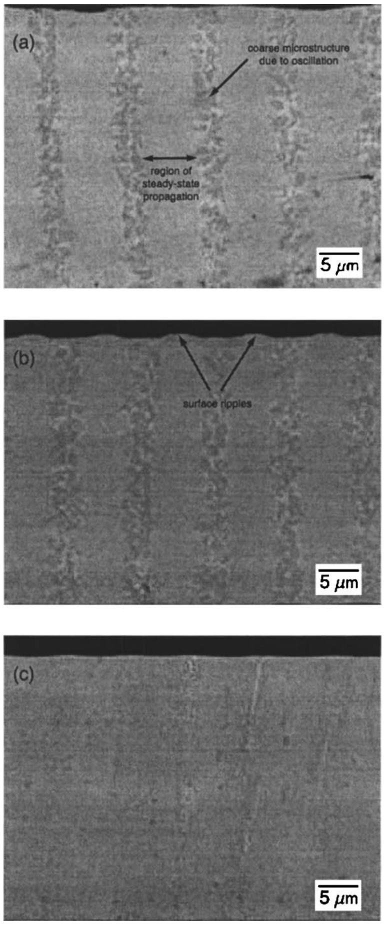

FIG. 3. SEM micrographes of Zr–Al–Cu–Ni multilayer foils reacted at (a) 25 °C, (b) −20 °C, and (c) 93 °C. Similar microstructural features are clearly seen in all three conditions. The reaction propagation direction is from the left-hand side to right for all samples.

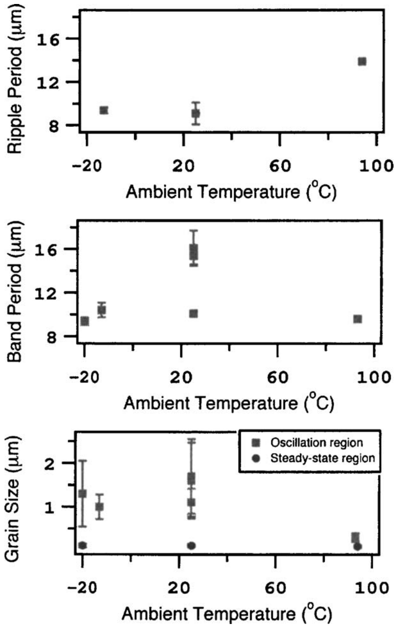

FIG. 4. Surface ripple period, microstructure (band) period, and grain size as a function of ambient temperature. The grain size refers to the single-grained darker phase.

The representative microstructure shown in Fig. 3(a) consists of relatively broad bands of fine-grained material alternating with narrow bands of coarse-grained material, which would be consistent with steady-state propagation (producing the fine-grained material) punctuated by superadiabatic oscillations that produce the coarse-grained material. The presence of the same two phases throughout the microstructure (albeit with varying length scales) suggests that the two regions experience similar transformations. Presumably, the oscillations produce a coarser microstructure because at the higher temperature the growth rate of the new phases is higher, the nucleation rate is lower, or both. Assuming that this is true, we can use the correlation between grain size and temperature to compare the magnitude of the superadiabatic oscillations in different samples.

In order to examine the effect of ambient temperature on the oscillations, we placed the reactive foils between copper blocks at temperatures ranging from −20 °C to 94 °C before initiating the reaction. All of the reacted foils show periodic bands of coarser microstructure (Fig. 3). The period of these bands and the surface ripples change little with ambient temperature. Because the darker phase is separated into distinct single grains, we measured this phase exclusively in order to record a "grain size." The grain size in the oscillation regions is smallest for the foils reacted at the highest ambient temperatures (Fig. 4). However, we observe no change in this grain size for foils reacted at lower temperatures (from −20 °C to 25 °C). Thus, the variations in grain size suggests that the magnitude of the oscillations decreases as the ambient temperature increases above room temperature. The changes in ambient temperature also had little effect on the grain size in the steady-state regions (~100 nm).

When investigating similar oscillations, Van Saarloos and co-workers developed a general one-dimensional nonlinear heat flow and stability analysis that predicts oscillation magnitude during explosive crystallization will decrease with increasing ambient temperature.[13] This was confirmed experimentally in the crystallization of Sb and $In_{1-x}Ga$ films.[14] It was also seen for Ta/C powder compacts[22] and predicted numerically for formation reactions in Al/Ni multilayer foils.[12] These earlier results and predictions all agree with the current observations. However, the period of the oscillations does not decrease with ambient temperature as seen for the Ta/C powder compacts and as predicted numerically. The reason for these disagreements with our results (particularly with regard to the numerical modeling[12]) is under investigation.

In summary, we have observed evidence of oscillatory formation reactions in nanostructured Zr/Al/(CuNi) reactive multilayer foils. The presence of periodic surface ripples and a periodic internal microstructure are both evidence for superadiabatic temperature oscillations during propagation of the reaction front. The trends of magnitude and period of the oscillations are in partial agreement with predictions based on numerical modeling (of a different multilayer system). We expect that the characteristics of the oscillatory combustion reaction can be tailored through a suitable control of the foil architecture.

The authors gratefully acknowledge financial support from the National Science Foundation through Grant No. DMI-0300396, with Howmet Research Corporation as our industrial partner. The views expressed are those of the authors, and not necessarily those of the National Science Foundation.

[1] J. A. Floro, J. Vac. Sci. Technol. A **4**, 631 (1986).
[2] C. E. Wichersham and J. E. Poole, J. Vac. Sci. Technol. A **6**, 1699 (1988).
[3] L. A. Clevenger, C. V. Thompson, R. C. Cammarata, and K. N. Tu, Appl. Phys. Lett. **52**, 795 (1988).
[4] L. A. Clevenger, C. V. Thompson, and K. N. Tu, J. Appl. Phys. **67**, 2894 (1990).
[5] E. Ma, C. V. Thompson, L. A. Clevenger, and K. N. Tu, Appl. Phys. Lett. **57**, 1262 (1990).
[6] T. S. Dryer, Z. A. Munier, and V. Ruth, Scr. Mater. **30**, 1281 (1994).
[7] T. P. Weihs, A. Gavens, M. E. Reiss, D. VanHeerden, A. Draffin, and D. Stanfield, in *TMS Proceedings*, Orlando, FL (TMS, Warrendale, PA, 1997).
[8] T. P. Weihs, *Self-Propagating Reactions in Multilayer Materials* (IOP, Bristol, 1997), Chap. F7, p. F7.1.
[9] A. J. Gavens, D. VanHeerden, A. B. Mann, M. E. Reiss, and T. P. Weihs, J. Appl. Phys. **87**, 1255 (2000).
[10] J. Wang, E. Besnoin, A. Duckham, S. J. Spey, M. E. Reiss, O. M. Knio, M. Powers, M. Whitener, and T. P. Weihs, Appl. Phys. Lett. **83**, 3987 (2003).
[11] A. J. Swiston, T. C. Hufnagel, and T. P. Weihs, Scr. Mater. **48**, 1575 (2003).
[12] S. Jayaraman, O. M. Knio, A. B. Mann, and T. P. Weihs, J. Appl. Phys. **86**, 800 (1999).
[13] W. van Saarloos and J. Weeks, Phys. Rev. Lett. **51**, 1046 (1983).
[14] C. Wickersham, G. Bajor, and J. Greene, J. Vac. Sci. Technol. A **3**, 336 (1985).
[15] A. G. Merzhanov, A. K. Filonenko, and I. P. Borovinskaya, Dokl. Akad. Nauk SSSR **208**, 892 (1973).
[16] V. M. Shkiro and I. P. Borovinskaya, in *Combustion Processes in Chemical Technology and Metallurgy* (OlKhF, Chernogolovka, Russia, 1975), p. 253.
[17] I. P. Borovinskaya, A. G. Merzhanov, N. P. Novikov, and A. K. Filonenko, Fiz. Goreniya Vzryva **10**, 4 (1974).
[18] V. G. Myagkov, L. E. Bykova, and V. A. Seredkin, Dokl. Akad. Nauk SSSR **363**, 762 (1998).
[19] Powder Diffraction File Software (PDF-2), International Center for Diffraction Data, Newton Square, PA (2002).
[20] K. G. Shkadinskii, B. I. Khaikin, and A. G. Merzhanov, Fiz. Goreniya Vzryva **1**, 19 (1971).
[21] A. P. Aldushin, T. M. Martem'yanova, A. G. Merzhanov, B. I. Khaikin, and K. G. Shkadinskii, Fiz. Goreniya Vzryva **9**, 613 (1973).
[22] V. M. Shkiro, G. A. Nersisyan, and I. P. Borovinkskaya, Fiz. Goreniya Vzryva **14**, 58 (1978).