# Combustion in reactive multilayer Ni/Al nanofoils: Experiments and molecular dynamic simulation

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## ABSTRACT

A comparative study, including experiments and molecular dynamic simulation, of the combustion waves in the Ni/Al multilayer reactive nanofoils reveals unknown mechanisms of the process. High speed macro-video recording, brightness pyrometry and thermal imaging proved that the combustion wave consists of two stages; the first stage can propagate independently with the same velocity as the complete wave. Products of the first stage of combustion are nano-grains of NiAl separated by liquid gaps of the Al-Ni melt. SEM and TEM study of the intermediate and final products of combustion allow us to suggest a new mechanism of "mosaic" dissolution-precipitation describing nano-heterogeneous reaction at the first stage of the process, which explains dynamics of the combustion wave and resultant microstructure. It was shown also that most of the heat released in the second stage of combustion is generated by grain coarsening. Thus, a conclusion is made that the combustion wave in the Ni/Al reactive multilayer nanofoil is proposed to be a sequential, two stage process involving chemical (first stage) and physical (second stage) exothermic transformations.

## 1. Introduction

Reactive multilayer nano-foils (RMNFs) are pore-free reactive materials, which consist of alternating layers of different metals, e.g., Ni/Al, Ti/Al, Pt/Al, with the thickness in the range 4–100 nm, and total number of layers up to several thousand [1–10]. After their invention in 1996 [1], RMNFs have found valuable applications, primarily in the joining of heat-sensitive materials [3–6]. In particular, the Ni/Al composition remains the focus of numerous experimental and theoretical works. Local heating of the foil initiates a self-sustained propagating wave of exothermic reaction that is typically considered to be a gasless combustion wave, or the so-called solid flame. The combustion of Ni/Al RMNFs possesses some unique features including: extremely high heating rates ($10^5$–$10^6$ K/s), combustion front propagation velocities of up to 10 m/s, and an uncharacteristically low onset reaction temperature (400–500 K) which is well below the melting points of both reactants [7–9]. It was experimentally found that the value of the

combustion front propagation velocity strongly depends on the composition of the foil and the bilayer thickness [7]. The specifics of RMNF combustion are discussed further in some reviews [2,8–10].

In spite of the active research, many features of the self-sustained reaction waves in the Ni/Al multilayer nanofoils remain puzzling. For example, it was experimentally shown that the combustion wave involves two stages [11,12], but existing interpretations of this fact are diverse. One explanation is based on the assumption that the first stage is formation of $Ni_2Al_3$ followed by the second stage in which NiAl appears. A numerical model was recently developed to support this hypothesis [13]. However, in situ experimental investigations of the phase transformations by using of time-resolved transmitting electron microscopy [14,15] and diffraction of synchrotron radiation [16–18] show that B2-NiAl is the only phase that appears in the reaction wave. Another explanation is that reactive dissolution of solid Ni into the Al melt leads the first combustion front, followed by precipitation of NiAl grains from the saturated liquid Al(Ni) solution [12]. The third hypothesis is that the first front is attributed to formation of the intermetallic phase, while the secondary combustion reaction is postulated to be oxidation, which transforms a portion

**Nomenclature**

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| $U$ | linear propagation velocity of combustion |
| $L$ | distance along the combustion propagation direction ($L = 0$ indicates the position of combustion front, $L < 0$ corresponds to initial material, $L > 0$ to products) |
| $T$ | temperature |
| $t$ | time |
| $a$ | thermal diffusivity |
| $D$ | mass diffusivity |
| $D_{ad}$ | mass diffusivity at adiabatic (theoretical) temperature of combustion |
| $D_{max}$ | mass diffusivity at maximal experimentally measured combustion temperature |
| $E$ | activation energy |
| $\varepsilon$ | surface energy of NiAl phase |
| $M$ | molecular mass |
| $\rho$ | density |
| $d_0$ | diameter of NiAl grains in primary product |
| $d_F$ | diameter of NiAl grains in final product. |

of the hot intermetallic compound into metal oxide [10]. Clearly, this explanation cannot be applied for combustion in vacuum or inert gas.

The relationship between propagation of the combustion front and the mechanism of exothermic intermixing of Ni and Al atoms also raises questions. Two basic mechanisms of the reaction between the nano-layers can be outlined. First is a well-known reaction diffusion model based on an assumption that diffusion of the reactants through a continuous layer of solid product, which is formed on the boundary between the layers, controls the combustion wave propagation. Resent modifications of this model, developed specially for the RMNFs, assume only formation of continuous intermixed layer, without specification of the phase constitution of this layer: it may be liquid or solid solution, or intermetallic compound [7,19–23]. The second mechanism suggests that macrokinetics of the combustion process is limited by the rate of solid Ni dissolution in liquid Al [24].

In our previous works, which involved high-resolution TEM studies and molecular dynamic simulations, we shed light on the mechanisms of dissolution, precipitation, and grain growth [25,26]. The molecular dynamics (MD) employed in those studies is a valuable tool for examining mixing and reactions in Ni/Al nanofoils, as their typical length scale (a few nanometers) corresponds precisely to the scale accessible in simulations. Concerning the nanolayered Ni–Al system, MD has been used to study some specific aspects of the Ni–Al nanofoils: the possibility of a reaction at a relatively low temperature and the development of intermetallic phases [27], the effects of the as-deposited microstructure on the initiation of the Ni–Al reactive multilayer [28], the interdiffusion of Ni and Al at interfaces [29,30], the role of pressure on the initiation of the reaction [31], the nucleation and growth of the B2-NiAl phase at interfaces in RMNF [25] and shock-induced alloying reactions in NiAl nanolaminates [32]. In all of these studies, the simulated systems were limited in size to a few nanometers, which was nevertheless adequate for their purpose. Recently, molecular dynamics were used to simulate larger systems of about 1 μm. High-temperature, self-propagating reactions were investigated in nanolayered Ni/Al foils [33], and reaction mechanisms were studied in thermally ignited core/shell Ni/Al wires [34].

In the present paper new experimental results on the thermal structure of the combustion wave in the Ni/Al RMNF are reported and are related to the mechanisms of nano-heterogeneous exothermic reactions. We also apply molecular dynamic simulations to reveal intrinsic features of the nucleation and growth of NiAl grains so as to validate the suggested mechanism of gasless combustion wave propagation.

## 2. Materials and methods

In the experimental studies we used two types of Ni/Al RMNFs. Type I foils were purchased from Indium Corp. with bilayer thicknesses of 50 nm and overall foil thickness of 60 μm. Thinner foils that were used in quenching experiments, type II foils, were fabricated by dc magnetron sputtering of Al 1100 (99 wt% Al, 0.87 wt% (Si, Fe), 0.12 wt% Cu) and Ni/V (93 wt% Ni, 7 wt% V) targets with a bilayer period of 90 nm and an overall thickness of only 8 μm. Ni/V was used in place of pure Ni because it is nonmagnetic. Note that commercially purchased foils also use Ni/V for the same reason. For the depositions, substrates are mounted on a rotating carousel positioned between the targets, resulting in a multilayer structure. The chemistry and bilayer spacing of the multilayers were controlled by varying the sputtering power and carousel rotation rate. The depositions were performed in a vacuum chamber evacuated below $2 \times 10^{-6}$ Torr and then backfilled to 1 mTorr with Ar (99.999% pure).

Two types of experiments were carried out: free-suspended foil combustion (Fig. 1a), and combustion of foil under intense heat losses (Fig. 1b). For the former scheme a small weight (1 g) was attached to the bottom end of the foil strip not only to prevent bending of the foil during combustion, but also to monitor possible change of the sample's length. For the experiments with intense heat losses, the foil strip was tightly clamped between copper and quartz disks (Fig. 1b). The experiments were conducted in vacuum ~$10^{-4}$ Pa, with the foil strips about 3 cm long and 0.5–1 cm wide. A high speed color video camera, MIRO M310, with macro- and micro-lenses was used for recording the combustion process. Frame-by-frame computer analysis provided time dependences of the combustion front position, while the velocity of the front propagation was obtained by differentiating those dependences. Also, the reaction front brightness profile was monitored using a high-frequency photo-diode sensor pointed at the surface of the foil through steel capillaries with an inner diameter of either 0.2 or 0.4 mm. A high speed infrared camera, FLIR system (SC6000, MA, USA), was used to record the dynamic thermal pattern and to measure characteristic temperature points of the combustion front. Reactions were ignited locally at the top of the foils using three different methods: spark from a 14 V battery, heat from a thin (∅200 μm) heated tungsten wire, and heat from a relatively thick (∅1 mm) W-coil

The combustion under high heat losses (Fig. 1b) was carried out in order to extinguish the combustion wave, to suppress all post-combustion processes, to quench intermediate products, and thereby to obtain a "frozen" combustion wave in the foil. This "frozen" combustion process is called a *quenched combustion wave*. Crystalline products formed in the quenched combustion wave are *primary* combustion products, while products of combustion of the free-suspended foil (Fig. 1a) will be referred to as the *final product*. The structure and composition of the primary and final combustion products were studied using field emission scanning electron microscope "Zeiss Ultra Plus" (Germany) and transmitting electron microscope "Titan" (FEI, USA). Specimens for the TEM studies were prepared using a double beam Nanolab system "Helios" 600 (FEI, USA), and the preparation procedure is described in detail elsewhere [26]. XRD analysis was performed using a DRON-3 goniometer.

Molecular dynamics simulations (MDS) were performed to reveal intrinsic mechanisms of reactive atomic intermixing, and