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Modeling self-sustaining waves of exothermic dissolution in nanometric Ni-Al multilayers

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ABSTRACT

The self-sustained propagating reaction occurring in nanometric metallic multilayers was studied by means of molecular dynamics (MD) and numerical modeling. We focused on the phenomenon of the exothermic dissolution of one metallic reactant into the less refractory one, such as Ni into liquid Al. The exothermic character is directly related to a negative enthalpy of mixing. An analytical model based on the diffusion-limited dissolution [1] coupled with heat transfer was derived to account for the main aspects of the process. Together, several microscopic simulations were carried out. The first series were set up to obtain all the parameters governing the process, including the heat release by dissolution. The second series of MD simulations was set up to detect the very possibility of self-sustaining propagation driven by exothermic dissolution. We aimed at developing a consistent multiscale description by numerically solving the model with the MD extracted parameters. The study proves that the exothermic intermixing of Ni and Al is a driving mechanism of self-sustaining propagation in reactive nanofoils.

1. Introduction

Self-propagating high-temperature synthesis (SHS) - also named combustion synthesis - is an attractive way of producing advanced materials [2]. Over the past decades, the SHS process has been investigated, amongst others, in the case of nanometric metallic multilayers[1] (N2M). N2Ms are made of alternated layers of metals A and B, whose thickness is nanometric (typically 4–100 nm) [3,4]. A N2M's sample contains hundreds, or even more, of superposed thin metallic films: A-B-A- … A reaction in an N2M can be initiated by a local heating at one edge of the sample, by means of spark or laser. Once ignited, the reaction propagates in a self-sustained way without any further supply of energy. The reactive front can be divided in three zones as shown in Fig. 1. In the direction of wave propagation, the first region is the after-burning zone, where the products of reaction are transformed into their final form. The central zone corresponds to the reaction zone itself, where the main exothermic process takes place. The heat produced in this region is sufficient to initiate the reaction and to sustain its propagation in the contiguous preheated zone (third region) [5].

An analytical model of gasless combustion in N2M, based on interdiffusion-control, was first proposed by Armstrong [6]. The model was further improved by including the effect of initial premixing at the interfaces [7]. Other models focused on the intermetallic product formation including the effect of reactant and product melting [8,9], two phase formation [10,11], radiative and conductive heat loses [12,13], influence of initial premixing [14] or vacancy concentration on diffusion coefficient [15]. It is important to note that most of these models are based on growth of an intermetallic phase between two solid reactants and ignore the influence of the dissolution of one component into another. And yet, the dissolution process plays a crucial role in binary systems in which one of the reactants has a lower melting temperature than the other (like Al-based N2M, for example Ni-Al or Ti-Al). Various experimental findings support this affirmation. Experiments on Al-based multilayers indicate that the reaction starts at a temperature

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[1] In the literature, N2M are also often referred as reactive multilayer nano-foils.

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Nomenclature

Subscripts

0	initial value
ad	adiabatic
ig	ignition
max	maximal value
mes	measured value
c	combustion
A	reactant A
A-B	A-B alloy
Al	aluminum
B	reactant B
cr	critical
dis	dissolution
inc	incubation
Ni	nickel
Ni-Al	nickel-aluminum alloy

Greek symbols

α	characteristic time scale of dissolution (s)
γ	reduced activation energy
κ	thermal diffusivity (m^2 s^{-1})
λ	thermal conductivity (J m^{-1} K^{-1} s^{-1})
Ω	atomic volume (m^3)
Φ	reaction heat release function (J m^{-3} s^{-1})
ρ	density (kg m^{-3})
τ	dimensionless time
θ	dimensionless temperature
φ	dissolution reaction rate function
ξ	dissolution variable, fraction of A (or Ni) in the liquid layer

Latin symbols

$\widehat{L}$	scaled sample length
$\widehat{l}$	scaled length
$\widehat{x}$	dimensionless *x* coordinate
$\widehat{x}_f$	front scaled position
$\mathscr{H}$	enthalpy (kJ mol^{-1})
$\mathbf{J}$	diffusion flux (m^{-2} s^{-1})
c_P	specific heat capacity (J kg^{-1} K^{-1})
D	diffusion coefficient (m^2 s^{-1})
D_0	Arrhenius prefactor (m^2 s^{-1})
D_{eff}	effective heat-mass diffusivity (m^2/s)
E	activation energy (J mol^{-1})
H	thickness of bilayer (m)
h	thickness of liquid inner layer (m)
L	sample length (m)
l	length (m)
M	molar mass (kg mol^{-1})
m	mass (kg)
m^0	atomic mass (kg)
N	number of atoms
n	mole fraction
n_s	solubility limit of A (Ni) in the liquid A-B (Ni-Al) alloy
Q	heat of reaction (J m^{-3})
q	reduced heat released by dissolution (K)
q_0	reduced heat released by dissolution at zero predissolution (K)
R	universal gas constant $R = 8.314$(J mol^{-1} K^{-1})
r	front coordinate $r = x - vt$ (m)
S	solid-liquid interface area (m^2)
T	temperature (K)
t	time (s)
u	dimensionless front velocity
V	volume (m^3)
v	front velocity (m/s)
w	thickness of predissolved layer (m)
x	*x* coordinate (m)
x_f	front position (m)
z	*z* coordinate (m)

Superscripts

ℓ	liquid
m	melting
s	solid

close to the melting temperature of aluminum. In some case, this temperature can be even lower, due to the melting point depression observed in nanometric layers [16]. The reaction thus occurs in a solid/liquid system. If the metallic reactants are miscible, the dissolution of the less refractory metal into the liquid leads to an intermixing with substantial heat release. Experiments show that intermixing produces up to 60% of total heat release. The efficiency of mixing at interfaces is directly related to the nature of the premixing layer. The nature of the premixing layer is of crucial importance in the development of the reactive processes. If the interfacial region consists of an intermetallic phase (see Fig. 1a), the dissolution is hindered by the thin product layer between the reactants. The existence of such a product layer between the reactants is, however, open to question. Indeed, XRD analysis of "as-deposited" N2M showed no intermetallic phase in the intermixed region between the reactants. The intermixed region probably contains a solid amorphous phase, which can easily be dissolved after the melting of the Al layer. Finally, the estimation of diffusion coefficients during reaction in N2M shows that their order of magnitude is typical of liquids or melts [17,18].

In this work, we focus on the exothermic dissolution of one reactant into another, when one reactant (let us say B) has a lower melting temperature than the other (let us say A). The main assumption is that the reaction starts at the melting temperature of B, and ends when all the A component is dissolved into B. Then, the solid reaction products are formed from the homogeneous liquid A-B alloy in the after-burning zone. The typical mechanism of a dissolution reaction wave is illustrated in Fig. 1b. In Section 2, we develop the phenomenological model of dissolution-controlled SHS wave propagation, based on heat transfer equations coupled with the dissolution rate equation, obtained in Ref. [1].

In addition, the process of dissolution-reaction can be investigated at the atomic level and then compared with the phenomenological approach. The work of Politano and Baras [19] reveals the possibility of studying reaction wave propagation in N2M by molecular dynamics (MD) simulations. MD has now proven to be an interesting tool in the study of N2M for at least two main reasons: the typical length scales (from nm to a fraction of μm) are accessible by means of large simulations and the microscopic approach does not presume any basic mechanism as compared to the