



Dissolution process at solid/liquid interface in nanometric metallic multilayers: Molecular dynamics simulations versus diffusion modeling



V. Turlo, O. Politano, F. Baras*

Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université Bourgogne Franche-Comté, 9 Avenue A. Savary, BP 47 870, F-21078 DIJON Cedex, France

ARTICLE INFO

Article history:

Received 20 April 2015

Revised 28 July 2015

Accepted 30 July 2015

Available online 26 August 2015

Keywords:

Ni dissolution in liquid Al

Multilayer thin films

Molecular dynamics simulations

Theory and modeling

Diffusion

ABSTRACT

The dissolution process of Ni into liquid Al in a layered Ni–Al–Ni system is here studied by means of molecular dynamics simulations, using an embedded-atom method type potential. Molecular dynamics simulations allow us to describe the underlying microscopic mechanisms associated with the dissolution process and prove that the number of Ni dissolved is the key variable in following the progress of the reaction occurring in NiAl nanofoils. A diffusion-limited dissolution model has also been developed. This model is tractable enough to use simulation data to extract kinetic and thermodynamic parameters such as solubility, melting temperature and diffusion coefficients. The comparison with experimental data is satisfactory. The present work assesses the predominant role played by diffusion in the dissolution process at the nanoscale in layered systems.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Nanometric metallic multilayers (N2M) are made of thin layers of metals deposited alternately. The thickness of each layer may be as small as a few nanometers. The number of layers may vary from tens to thousands. The technique of deposition to produce N2M in the form of coating or free standing foils is now well developed. Since the patent of Barbee Jr. and Weihs [1,2], interest in these nanomaterials has been continuously growing [3]. A very peculiar property of N2M is that a reaction between the pure metals initiated at one edge of the sample will propagate throughout the system in a self-sustained way (SHS). The heat released locally allows the reaction to move forward without any supply of energy. N2M are used in various applications either for joining, brazing or soldering without damaging the materials that have to be joined or as a heat delivery source. The NiAl multilayer is often used as a model system and as such it has been widely investigated. The SHS reaction at the nanoscale can be triggered at low temperature (near ambient temperature) and the propagation speed is high compared to the process in micrometric metallic powders. The elemental mechanisms responsible for these properties are not completely understood. For miscible metals such as Ni and Al, the energy released during the reaction is either associated with the mixing (positive enthalpy of mixing) or to the formation of

intermetallic compounds. Exothermicity is essential in the self-sustained propagation of the reactive front.

The structure of the N2M material is a succession of interfaces separated by a few nanometers. These many areas of contact should promote the mixing between the pure metals. The liquid or solid character of the metal in question certainly plays a predominant role in the mixing process. In most cases, the ignition temperature coincides with the melting temperature of one of the two metals. For $T > T_m$, the N2M is composed of the superposition of liquid and solid metals. The mixing is then associated with the dissolution of one phase into the other. This paper is concerned with the elemental mechanisms underlying the dissolution of solid metal into liquid metal in the case of thin layered films. The Ni–Al reactive foil has been chosen as the representative material.

The dissolution process goes well beyond the specific case of metals. The beginnings of dissolution research date from the late XIX century ([4], for a review see [5]). The goal was to obtain a mathematical expression of the rate of dissolution for comparison with experimental data. The general expression gives the rate as a linear function of the saturation degree of the solution.

$$\frac{dC}{dt} = k(C_s - C) \quad (1)$$

where C and C_s are the concentration of the substance and its solubility, respectively. The explicit form of the factor k depends on the surface of contact and other parameters such as the diffusion coefficient in the case of the diffusion layer model introduced by Nernst and Brunner. In pharmaceuticals, the equation translates the fact that

* Corresponding author.

E-mail addresses: vladyslav.turlo@u-bourgogne.fr (V. Turlo), olivier.politano@u-bourgogne.fr (O. Politano), florence.baras@u-bourgogne.fr (F. Baras).

the drug release is efficient for a while but then slows down until saturation is reached. This very general form is also commonly used to describe the dissolution of Ni micrometric particles into Al liquid [6]. In the model proposed by Nernst and Brunner, the dissolution is supposed to be controlled by diffusion across an interfacial layer without any influence of diffusion into the liquid phase. In other words, the diffusion is supposed to be much slower in the layer than into the liquid itself. This assumption becomes invalid or at least questionable when a concentration gradient exists in the liquid layer, as is the case in the thin liquid layers of N2M.

Dissolution is an important phenomenon in the SHS process, especially in nanofoils. It plays a central role in the progress of the reaction due to the heat release during mixing and to the subsequent possibility of phase transformation. More than sixty percent of heat production is due to dissolution. At nanoscale, the dissolution process may interfere with other elemental processes such as melting, interdiffusion, or phase transformation. In this respect, molecular dynamics simulations offer a good approach in understanding the development of basic mechanisms that occur in nanofoils. Several studies dealing with the case of NiAl foils and have focused on well defined problems. Molecular dynamics has been successfully used to study the demixing phenomena in NiAl nanosized particles [7], the melting and crystallization in the Al₅₀Ni₅₀ system [8,9], the sintering process and the alloying between Al and Ni nanoparticles [10], the exothermic alloying of Ni/Al multilayers induced by shock loading [11,12], to determine the pressure dependent melting temperature of Al and Ni [13] and to evaluate the role of relative melting temperatures [14], to prove the very possibility of reaction at relatively low temperatures for a solid/solid system [15] and to evaluate the role of the nanostructure on reaction and transport in NiAl nanolaminates [16]. Molecular dynamics has also been used to investigate the interfacial mixing behavior in transition metals (Fe, Co, Ni)–Al multilayer systems during deposition [17] or to study the atomic scale structure of sputtered metal multilayers [18]. Of direct relevance to this work, a continuum and MD study by Xu et al. [19] reveals different pathways in the interdiffusion of Ni and Al in reactive foils depending on the temperature. In that work and related ones [20,21], the interdiffusion is described in terms of a scalar quantity, the mixing measure which obeys Eq. (1).

The limitations of the classic dissolution model (1) have prompted us to propose an alternative model for systems such as N2M in which dissolution is not controlled only by interfacial aspects. The model is presented in Section 2 in a general way. In Section 3, we describe the details of the MD simulations for the Ni–Al reactive foil. Results and discussions are found in Section 4. After a detailed analysis of the simulations data, the comparison with modeling is used to extract parameters such as solubility and activation energy.

2. Diffusion-limited dissolution modeling

The dissolution of a phase *A* into another phase *B* seems to be a simple problem. It is a transient phenomenon that occurs until the concentration of *A* in *B* reaches the solubility limit. Solubility is sensitive to the temperature of the system. If *A* is in the solid state (*A*_{sol}) and *B* is liquid (*B*_{liq}), the dissolution must take place through the interface. In the case of a nanometric multilayer, the system is made up of interfaces that are separated by a few nanometers only. Despite the large number of interfaces, the dissolution may be hindered by the microscopic processes which are predominant at nanoscale. The kinetics associated with the phase transformation *A*_{sol} → *A*_{liq} at the interface *A*_{sol}/*B*_{liq} can be controlled by the interface itself since the *A* atoms have to cross an atomic barrier. In other situations, the kinetics is limited by the diffusion of the *A*

atoms into the *B* liquid. The effective rate of dissolution depends on the microscopic mechanism.

In this section, we derive the effective rate of the dissolution of *A* solid into *B* liquid for the specific geometry of a liquid slab stuck between two solid layers in the case of a diffusion-controlled dissolution (see Fig. 1). The rate of dissolution is obtained from the time-dependent concentration profile of *A* into *B*. For this purpose, we consider a simple model in which a liquid *B* layer of thickness *h* is located between two semi-infinite *A* solid layers. The system contains two *A*_{sol}/*B*_{liq} interfaces which the *A* atoms have to cross to mix with the *B* atoms. Diffusion currents of *A* from the left *J*_{left} and from the right *J*_{right} feed the central liquid region. In addition, besides the specific geometry, the model relies on a set of assumptions:

- Due to the symmetry of the system, a one-dimensional description has been adopted.
- The dissolution process is controlled only by the diffusion in the liquid layer.
- The thickness *h* of the liquid layer remains constant during the dissolution process.
- The diffusion coefficient *D* is associated with the diffusion of *A* in *B* and does not depend on the concentration.
- The solubility limit is constant at a given temperature.

The hypothesis that may seem inappropriate is that which assumes the constant size of the liquid layer during the dissolution process. We will show later that the volume *V*_ℓ = *S* × *h* where *S* is the surface of the interface is in fact constant during the process. The diffusion equation for the mole fraction¹, *n*, of *A* atoms diffusing into the liquid layer needs to be solved with an initial condition corresponding to a step function. This corresponds to the absence of *A* dissolved atoms in the liquid layer

$$n(z, t = 0) = 0 \quad \text{for } -h/2 < z < h/2 \quad (2a)$$

$$n(z, t = 0) = n_s \quad \text{for } z < -h/2 \text{ and } z > h/2 \quad (2b)$$

The boundary conditions are given by

$$n(z, t) = n_s \quad \text{for } z \rightarrow \pm\infty \quad (3)$$

where the solubility, *n*_s, is the maximum mole fraction of *A* soluble in *B* liquid. The boundary conditions at *z* = ±∞ correspond to the maximum mole fraction, *n*_s, of *A* in *B* that can be reached in equilibrium conditions. Although the one dimensional diffusion problem is defined from −∞ to +∞, the solution of the diffusion equation will only describe in an appropriate way the profile of *A* liquid atoms in the inner layer. The mole fraction *n* profile inside the liquid layer reads

$$n = n_s + \frac{n_s}{2} \cdot \left[\operatorname{erf}\left(\frac{z-h/2}{2\sqrt{Dt}}\right) - \operatorname{erf}\left(\frac{z+h/2}{2\sqrt{Dt}}\right) \right] \quad (4)$$

The concentration gradient is easily obtained

$$\frac{dn}{dz} = \frac{n_s}{2\sqrt{\pi Dt}} \cdot \left[\exp\left(-\frac{(z-h/2)^2}{4Dt}\right) - \exp\left(-\frac{(z+h/2)^2}{4Dt}\right) \right] \quad (5)$$

Using the thermodynamic formulation of diffusion, we express the diffusion current in terms of the gradient of the mole fraction. The diffusion current of *A* through the left interface *z* = −*h*/*2* in the direction *z* > 0 is given by

$$J_{\text{left}} = -\frac{D}{\Omega} \cdot \frac{dn}{dz} \Big|_{z=-\frac{h}{2}} = \frac{D}{\Omega} \cdot \frac{n_s}{2\sqrt{\pi Dt}} \cdot \left[1 - \exp\left(-\frac{h^2}{4Dt}\right) \right] \quad (6a)$$

¹ The mole fraction *n* stands for the ratio between the number of *A* atoms and the total number of atoms in the liquid layer *n*_{A,ℓ}/(*n*_{A,ℓ} + *n*_{B,ℓ}).

Download English Version:

<https://daneshyari.com/en/article/7879620>

Download Persian Version:

<https://daneshyari.com/article/7879620>

[Daneshyari.com](https://daneshyari.com)