

ROLE OF INTERFACIAL PHENOMENA IN PROCESSING METAL MATRIX COMPOSITE MATERIALS

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ABSTRACT

In the present paper the general algorithm to model interfacial energies, interfacial forces and complex interfacial phenomena is presented, which are relevant for producing metal matrix composites (MMCs). General equations that allow calculation of interfacial energies and interfacial forces are given. As an example of modeling complex interfacial phenomena, the problem of introducing solid ceramic particles into liquid metals is considered, as a first step to produce ceramic particle reinforced metal matrix composite materials.

Keywords: interfacial energies, interfacial forces, MMC, solid particles

1. INTRODUCTION

Interfacial phenomena play an increasing role in materials science and technology, as materials science is shifting from the requirement to control phenomena at the mm- and μm -level, towards the requirement to control the phenomena at the nm-level. The author recently summarized his results on complex physico-chemical modelling of interfacial energies, interfacial forces and complex interfacial phenomena in high-temperature systems, with special emphasis on the role of interfacial phenomena in the production of metal matrix composite materials [1]. This paper is a short summary of the results, presented in [1].

Modeling of interfacial phenomena is based on two basic elements (see Fig.1): on the modeling of interfacial energies and on the modeling of interfacial forces, acting on small phases. The equations for interfacial forces include different interfacial energies as parameters. When both of these elements are developed to study a given problem, the interfacial force should be

coupled with other forces, such as gravity, buoyancy, drag, etc., and in this way different interfacial phenomena can be modeled.

In the previous works of the author the following interfacial energies were modeled (for a review see [2]): surface tension of liquid metals, with special emphasis on the role of oxide layer of aluminium alloys [3], on its concentration dependence [4] and on the estimation of cohesion energy of liquid metals [5]; surface tension of molten salts [6], surface energies of refractories [2]; interfacial energies between liquid metals and solid metals of the same composition [7]; adhesion energy between liquid metals and ionic [8] or covalent [9] ceramics; interfacial energy between solid metals and solid ceramics [10-11]. The review paper has been written recently on a general algorithm to calculate interfacial energies in liquid metal / gas, solid metal / gas, solid monocarbide / gas, liquid metal / liquid metal, liquid metal / solid metal and solid monocarbide / liquid metal systems [39].

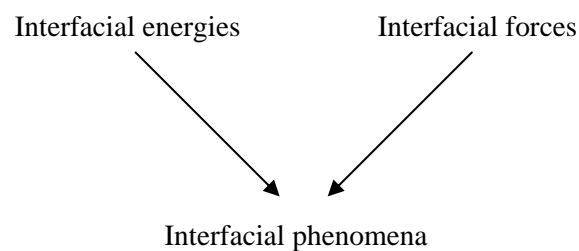


Fig. 1 - The general algorithm of modeling interfacial phenomena

Among interfacial forces the following models should be mentioned (for a review see [12]): the interfacial capillary force, acting on a solid sphere [13] or on a solid of any shape [14] at a liquid/gas interface; the interfacial adhesion force, acting between two solid phases, separated by a thin liquid layer [15, 11]; the interfacial gradient force, acting on a spherical particle or bubble in the interfacial energy gradient field, caused by a temperature or composition gradient [16, 17].

Among complex interfacial phenomena the following subjects were addressed (for reviews see [18-20]): feeding solidification cavities by liquid metals under microgravity [21-23]; stabilization of solid particles at a liquid/gas interface [13, 24]; incorporation of solid particles from a gas phase into a liquid phase [13, 25]; penetration and infiltration of liquid metals into porous solids [26-28], including the phenomenon of pre-penetration [29]; modeling of abrasive ability of particle reinforced amorphous metal matrix composites [30-31], coagulation of particles in liquid metals [32]; pushing and engulfment of solid particles by a growing solidification front [11, 33], including the effect of interfacial active solutes [34] and also dynamic effects [35]; and finally the stabilization of liquid metallic foams by solid particles [14, 36-38].

2. ON INTERFACIAL ENERGIES

Let us consider the interface between two, equilibrium phases, A and B. In the first approximation both phases A and B will consist of only one component, i.e. elements, or stoichiometric compounds. In other words, the solubility of A in B and B in A will be neglected. The interfacial energy ($\sigma_{A/B}$) will be modelled as the ratio of the excess Gibbs interfacial energy ($\Delta G_{A/B}$) (defined as always through the excess interfacial enthalpy ($\Delta H_{A/B}$) and excess interfacial entropy ($\Delta S_{A/B}$)) to the molar interface area ($\omega_{A/B}$):

$$\sigma_{A/B} = \frac{\Delta G_{A/B}}{\omega_{A/B}} = \frac{\Delta H_{A/B} - T \cdot \Delta S_{A/B}}{\omega_{A/B}} \quad (1)$$

All excess energies are calculated as the sum of excess energies from the two sides of the interface:

$$\Delta G_{A/B} = \Delta G_{A/B}^A + \Delta G_{A/B}^B \quad (2)$$

If phase B is a gas (or vacuum or vapour), Esq. (2) can be simplified as: $\Delta G_{A/B}^B \cong 0$. For both sides of the interface the interface excess quantity is defined as the difference between the formation Gibbs energy of the component in the interface (i) and in the bulk (b) phase. For the A-side of the interface one can write:

$$\Delta G_{A/B}^A = \Delta_f G_{A/B}^{Ai} - \Delta_f G_A^b \quad (3)$$

Applying the formalism, described by Eq-s (1-3), five independent quantities should be modelled to describe any type of interfacial energies: the molar surface area, and the formation enthalpies and entropies at both sides of the interface (the enthalpy of formation and the entropy in the bulk of phases A and B are supposed to be known). For the condensed/gas interface, only three independent quantities should be modelled. This algorithm was applied to many systems, being relevant for the production of metal matrix composites [1-11, 39].

The above equations provide basis for estimating interfacial energies as function of the two types of phases on the both sides of the interface, and temperature. The composition dependence of the interfacial energies is classically modelled through the Gibbs formalism. However, it is more flexible to use the Butler formalism, according to which the partial interfacial energy of the two components A and B in the binary alloy A-B should be equal. Applying it for the alloy/gas interface the following equation is valid:

$$\sigma_{A(A-B)/g} = \sigma_{B(A-B)/g} \quad (4)$$

Eq.(4) is similar to the condition to avoid local Marangoni convection in the binary liquid alloy. The key to use Eq.(4) is the way how the excess thermodynamic functions are determined as function of the composition of the surface phase. This question will not be considered here in details (see [1, 4]).

3. ON INTERFACIAL FORCES

In many papers all different interfacial forces are being derived based on the Laplace equation. However, the Laplace equation is just one of the possible equations, which can be developed for microscopic phases, being in different situations. A more general equation of determining an interfacial force includes the derivation of a total interfacial energy of the system along a chosen direction (x), taken with a negative sign:

$$F_{\sigma,x} = -\frac{dG_{\sigma}(x)}{dx} \quad (5)$$

When $F_{\sigma,x}$ appears to be positive, its direction is the same as the direction of the x vector, along which the total interfacial energy is described. The later is written as the sum of all the interface area (A) in the system, multiplied by the appropriate interfacial energy:

$$G_{\sigma} = \sum_{A,B} A_{A/B} \cdot \sigma_{A/B} \quad (6)$$

Substituting Eq.(6) into Eq.(5), finally the interfacial force can be written as:

$$F_{\sigma,x} = -\sum_{A,B} \sigma_{A/B} \cdot \frac{dA_{A/B}}{dx} - \sum_{A,B} A_{A/B} \cdot \frac{d\sigma_{A/B}}{dx} \quad (7)$$

As follows from Eq.(7), an interfacial force will act on a phase, if at least one of the interface areas, or at least on of the interfacial energies of the system will change when the given phase is moved along direction x. If all $A_{A/B}$ -s and $\sigma_{A/B}$ -s are independent of x, there is no interfacial force, acting in the system.

According to the classification of the present author, six, significantly different interfacial forces can be defined, acting on a microscopic phase (such as a solid, reinforcing particle, used for producing metal-matrix composites):

- i. the 'curvature induced interfacial force', or Laplace force (pressure), which acts perpendicular to the curved interface, from outside to inside of the small phase,
- ii. the 'interfacial gradient force', which moves a small phase within a large bulk phase towards places with smaller interfacial energies, due to the effect of the composition- or temperature gradients in the larger phase (important in pushing / engulfment phenomena),

- iii. the ‘interfacial capillary force’, acting on a small phase, situated at the interface of two large (fluid) phases (important in introduction of particles from gas phase into liquid metals, and also in infiltration of ceramic preforms by liquid metals),
- iv. the ‘interfacial meniscus force’, acting between two small particles, situated at the same interface between two large fluid phases (important in coagulation of particles at the liquid metal surface),
- v. the ‘liquid bridge induced interfacial force’, acting between two, relatively large solid phases, connected with a liquid bridge of a relatively small volume (important in sintering processes),
- vi. the ‘interfacial adhesion force’, acting between two phases, being in the bulk of a large fluid, in absence of composition and temperature gradients (important for coagulation of particles).

The equations for the interfacial force in the abovementioned 6 situations are all significantly different, but all can be derived using the same equations (5-7). For the summary of equations see [12].

3. THE CONDITION OF INTRODUCING SOLID PARTICLES INTO LIQUID METALS

As an example of studying complex interfacial phenomena, let us consider one of the simplest cases, the static introduction of small spherical particles from the gas phase into liquid metals.

Let us consider a small phase 3, situated at the interface of two fluid phases 1 and 2, and transferring with an infinitely small velocity from phase 2 into phase 1. Let us consider the situation when phase 3 is situated at the depth of immersion x into phase 1. During this process the three interfaces will gradually change, hence Eq.(6) will include three terms:

$$G_{\sigma} = A_{1/2} \cdot \sigma_{1/2} + A_{1/3} \cdot \sigma_{1/3} + A_{2/3} \cdot \sigma_{2/3} = (A_{1/2}^o - \Delta A_{1/2}(x)) \cdot \sigma_{1/2} + A_3 \cdot \sigma_{2/3} + A_{1/3}(x) \cdot (\sigma_{1/3} - \sigma_{2/3})$$

where $A_{1/2}^o$ is the initial fluid/fluid interface area, without phase 3, $\Delta A_{1/2}(x)$ is the x -dependent fluid/fluid interface area, covered by phase 3, A_3 is the total surface area of phase 3 and $A_{1/3}(x)$ is the x -dependent interfacial area between phases 1 and 3.

Substituting this equation into Eq.(5) and performing the derivation, the general equation can be derived for the “interfacial capillary force”, acting on phase 3, in a perpendicular direction to the fluid/fluid interface of phases 1/2:

$$F_{\sigma,x} = \sigma_{1/2} \cdot \frac{d\Delta A_{1/2}(x)}{dx} + (\sigma_{2/3} - \sigma_{1/3}) \cdot \frac{dA_{1/3}(x)}{dx} \quad (8)$$

Eq.(8) is generally valid for any shape of phase 3, neglecting the effect of curvature of the fluid/fluid interface along the surface of phase 3. When phase 3 has a spherical shape, the following geometrical relations are valid: $\Delta A_{1/2} = 2 \cdot r \cdot \pi \cdot x - \pi \cdot x^2$, $A_{1/3} = 2 \cdot r \cdot \pi \cdot x$. Substituting these equations into Eq.(8) and performing the derivation, the following general equation is obtained:

$$F_{\sigma,x} = 2 \cdot r \cdot \pi \cdot \sigma_{1/2} \cdot \left[1 + \frac{\sigma_{2/3} - \sigma_{1/3}}{\sigma_{1/2}} - \frac{x}{r} \right] \quad (9.a)$$

For the particular case when a solid particle 3 is situated at the liquid/gas interface, Eq.(9.a) becomes:

$$F_{\sigma,x} = 2 \cdot r \cdot \pi \cdot \sigma_{l/g} \cdot \left(1 + \cos \Theta - \frac{x}{r} \right) \quad (9.b)$$

where $\sigma_{l/g}$ is the surface tension of the liquid metal, Θ is the contact angle of the liquid metal on a solid ceramic particle in a gas atmosphere.

In the absence of other forces, the particle reaches its equilibrium at the liquid/gas interface when $F_{\sigma,x} = 0$. Substituting this condition into Eq.(9.b), the equilibrium depth of immersion of the particle equals:

$$x_{eq} = r \cdot (1 + \cos \Theta) \quad (10)$$

As follows from Eq.(10), the contact angle defines solely the equilibrium relative position of a small particle at the liquid/gas interface, if $0^\circ < \Theta < 180^\circ$. Substituting Eq.(10) into Eq.(9.b), one can write:

$$F_{\sigma,x} = 2 \cdot \pi \cdot \sigma_{l/g} \cdot (x_{eq} - x) \quad (9.c)$$

As follows from Eq.(9.c), the interfacial (capillary) force always tends to return the particle into its equilibrium position, if its actual position is different from that. Moreover, the interfacial force increases with the deviation of the actual position of the particle from its equilibrium position. In other words, the interfacial capillary force acts as an “elastic stabilizer”, or as a “spring”. This unique property of this force is what is behind the ability of small solid particles to stabilize liquid (metallic) foams [14, 36-38].

When a spherical solid particle of density ρ_s is situated at the liquid/gas interface of a liquid with lower density ($\rho_l < \rho_s$), the particle will be detached from the interface and sedimented in the liquid above a certain critical radius, r_{cr} . From the balance of the interfacial capillary force (9.b) at $x = 2r$ with the gravity and buoyancy forces this critical size can be found [13]:

$$r_{cr} = 1.22 \cdot \sqrt{\frac{\sigma_{l/g} \cdot (1 - \cos \Theta)}{(\rho_s - \rho_l) \cdot g}} \quad (11)$$

where $g = 9.81 \text{ m/s}^2$ (on Earth), the gravity constant. Eq.(11) describes the critical radius better than the earlier equations [40-41], as shown by comparison with experiments [42, 24].

As follows from Eq.(11), solid particles will be spontaneously introduced into liquid metals only, if they are perfectly wetted by the liquid metal, or if they are large enough (larger than several mm) and have higher density than a liquid metal. As a consequence, dynamic methods are needed to introduce small, not perfectly wetted particles into liquid metals. The dynamic conditions of penetration are considered in details in [25].

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