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Review

The wetting of solids by molten metals and its relation to the preparation of metal-matrix composites

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This review aims at making a bridge between the fundamentals of the wetting of solids by liquid metals and the practice of the preparation of metal-matrix composites. One recalls first the significance of concepts such as surface tension, work of adhesion, adsorption and the relation between these concepts, the phenomenon of wetting and the process of liquid metal infiltration. Thereafter, the wetting of various types of solids is considered: metals, oxides, carbon and carbides. In the light of this body of science, one proposes finally a critical evaluation of the literature concerning the preparation of metal-matrix composites by liquid metal infiltration techniques. Particular emphasis is devoted to reinforcements made of graphite, alumina or silicon carbide multifilament fibres; the use of coatings and the addition of alloying elements to the metal are successively discussed.

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1. Introduction

Metal-matrix composites have been the object of an intense research effort for more than twenty years [1]. Many metals have been considered as a possible matrix: lithium, magnesium, silicon, aluminium, titanium, copper, nickel, zinc, lead, etc. The light metals offer the greatest potential in terms of strength to density ratio. Owing to its low cost and ease of fabrication, the most studied metal matrix for applications at temperatures below 450° C is aluminium [2]. Titanium has been extensively studied in the perspective of higher-temperature applications [3]. Nickel and nickel-based superalloys are also possible candidates for high-temperature applications when weight limitation is not a primary objective [4–6].

The type of reinforcement that attracted the largest interest for structural applications has much varied over the years. Early studies were directed to the use of monofilaments of tungsten, boron (including SiC-coated boron), alumina and beryllium [1, 4, 7]. In the beginning of the 1970s, the interest shifted toward the relatively much cheaper carbon multifilament fibres [8, 9]. More recent work has been devoted to the newly developed alumina and silicon carbide multifilament fibres [10–13]. In parallel, the use of short-fibre reinforcements in the form of SiC or Al_2O_3 whiskers was also extensively investigated [14].

Many methods have been proposed for the preparation of metal-matrix composites [15]. Hot pressing and diffusion bonding at a temperature below the melting point of the metal proved successful when using monofilament fibres [3, 6, 16]. In the case of multifilament yarns of carbon, Al_2O_3 or SiC, the most satisfactory route is the infiltration of the reinforcing network by the metal in the molten state [9, 17]. As liquid metals usually do not wet the fibres, it is moreover generally necessary to force impregnation by applying an external pressure. Many methods based on this principle have been described: vacuum infiltration [10], squeeze casting [18], liquid metal pressing [12] and pressure-assisted network infiltration [11] (to cite only recent work).

However, owing to the poor wettability and small diameter of modern fibres, applying pressure does often not suffice to assure an optimum contact between matrix and fibre. Research has therefore been directed toward the design of wettability-enhancing procedures [19]. These procedures consist either in depositing a suitable overlayer on the surface of the reinforcing bodies, or in adding surface-active alloying elements to the metal. These recipes often appear rather empirical and the original articles (of patents) contain little discussion of the fundamental causes of successes or failures.

This paper aims at a comprehensive presentation of the physical chemistry underneath this empirism. Indeed, the literature on the wettability of solid surface by liquid metals is abundant but very scattered, and it is difficult to get a clear picture of the subject. Hence, it seems useful to propose a review which stresses the most recent advances without overwhelming the reader with the experimental details. We will

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start in Section 2 by outlining the thermodynamics of interfaces relevant to the understanding of wetting and liquid infiltration. Sections 3 and 4 will be devoted to the energetics of the interfaces between liquid metals and, successively, three classes of solids: metals, oxides and carbon and carbides. (It will appear that, indeed, the natures of the interface interactions with carbon and carbide are similar.) Finally, in Section 5, we will evaluate to what extent the recipes proposed for the preparation of metal-matrix composites (and cermets) using liquid infiltration methods may be rationalized on the basis of this body of knowledge.

This paper concentrates on the phenomenon of wetting. Only limited mention will be made of the other important interfacial properties, such as the strength and stability of the solid–solid interface between fibre and matrix. However, it will be shown that wetting is favoured by the formation of strong bonds across the solid–liquid interface. Enhanced wetting therefore usually induces enhanced strength of the interface, which is beneficial for the mechanical properties of the composite.

2. Thermodynamic principles

When discussing the properties of surfaces or interfaces, use is made of a series of concepts: surface energy, surface tension, adsorption and work of adhesion. This section aims at recalling the significance that is attributed by convention to such concepts and the relations between these concepts, the phenomenon of wetting and the process of liquid infiltration. For a more detailed discussion, the reader is referred to the book of Defay *et al.* [20] or to more succinct recent reviews [21, 22].

2.1. The Gibbs model

As sketched in Fig. 1a, the interface between two bulk phases consists of a layer of finite thickness where the characteristics (such as for example the concentration C_i of component i in moles per unit volume) vary continuously. At the boundaries of the layer, all characteristics merge into the characteristics of the bulk phases. Fig. 1b represents the model of the interface introduced by Gibbs in order to allow a simple expression of the thermodynamics of the system. In this model, both bulk phases are assumed to remain homogeneous up to a dividing surface of zero thickness. If C_i' is the mole fraction of component i in one of the phases, far from the interface, and V' is the volume of this phase in the model representation, the number of moles n_i' of i in this phase is

$$n_i' = C_i' V'$$

Similarly, for the other phase,

$$n_i'' = C_i'' V''$$

For the model to be stoichiometrically equivalent to the real system, a certain number of moles n_i^s must then be attributed to the dividing surface such that

$$n_i^s = n_i - n_i' - n_i''$$

where n_i is the total number of moles of component i in the whole system. (The total number of moles in the system will be denoted $n = \Sigma n_i$.) Note that n_i^s may be positive or negative. Dividing n_i^s by the area A of the dividing surface, one defines the "adsorption" Γ_i of component i as

$$\Gamma_i = n_i^s / A$$

In a similar way, an "excess" value at the dividing surface may be attributed to all extensive properties of the system. In particular, one can define the surface entropy S^s as $S^s = S - S' - S''$ and the (Helmholtz) "surface free energy" F^s as $F^s = F - F' - F''$.

It must be realized that the values of the extensive quantities that are attributed to the dividing surface following the approach of Gibbs vary when the position of this surface changes. This difficulty, which gives the Gibbs model an apparently unphysical character, can be alleviated in some circumstances by locating the surface in such a way that some quantity becomes equal to zero (see next section for an example).

2.2. Interface tension and interface free energy

The occurrence of a tension at the interface between a pure liquid and a gas may be explained qualitatively in the following way. The molecules at or near the surface are attracted inwards and in directions parallel to the surface by their neighbours. This force is not balanced by a corresponding force outwards because of the lower density (and possibly the different nature) of the molecules in the vapour phase. This means that work has to be done in order to bring a molecule from the bulk to the surface. This additional energy possessed by the molecules near the surface may thus be expressed as amount of energy per unit surface area.

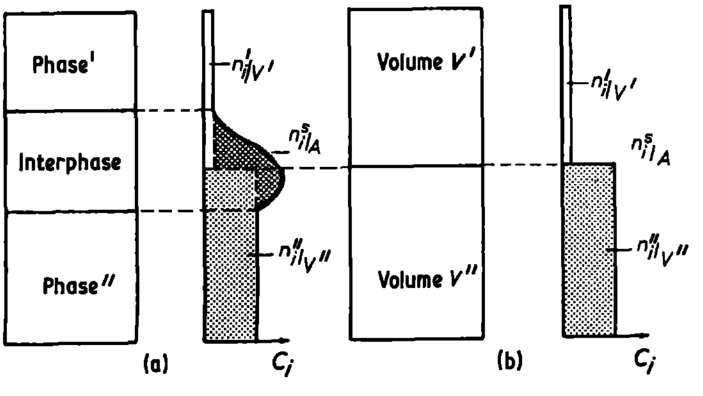

Figure 1 (a) Real interface distribution of component i. (b) The Gibbs model of this interface.

In the case of liquids, the molecules are mobile enough as to be able to respond to the imbalance of forces acting on them in the surface layer. For mechanical equilibrium, this manifests itself macroscopically by the surface behaving as a membrane stretched under a tension – the "surface tension" γ – which has the dimensions of a force per unit length (or a work per unit surface area). This surface tension is the same at all points and for all directions on the surface. It is a value directly accessible experimentally: $\gamma \, \mathrm{d}A$ is the mechanical work required to create an additional surface area $\mathrm{d}A$.

The total differential of the free energy of a system consisting of two fluid phases separated by an interface having a surface tension γ may be expressed in the framework of the Gibbs model [20] as

$$\mathrm{d}F = -P'\mathrm{d}V' - P''\mathrm{d}V'' - S\mathrm{d}T + \gamma\mathrm{d}A + \sum \mu_i'\mathrm{d}n_i' + \sum \mu_i''\mathrm{d}n_i'' + \sum \mu_i^{\mathrm{s}}\mathrm{d}n_i^{\mathrm{s}} \quad (1)$$

P' and P'' are the pressures of the two phases; S and T are the entropy and temperature of the system, respectively; μ_i' and μ_i'' are the chemical potentials of component i in the bulk phases; the chemical potential μ_i^{s} of i at the dividing surface is defined as

$$\mu_i^{\mathrm{s}} = \frac{\partial F^{\mathrm{s}}}{\partial n_i^{\mathrm{s}}} = \frac{1}{A}\frac{\partial F^{\mathrm{s}}}{\partial \Gamma_i} \quad (2)$$

The three chemical potentials in the two phases and at the surface may be different as the system may not be in equilibrium. The surface tension may thus be defined thermodynamically as

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{T,V,n_i',n_i'',n_i^{\mathrm{s}}} \quad (3)$$

Using further the Gibbs model, it can be shown that Equation 1 gives [20]

$$\gamma = \frac{F^{\mathrm{s}}}{A} - \sum_i \Gamma_i \mu_i^{\mathrm{s}} \quad (4)$$

When the position of the dividing interface is chosen in such a way that $\Sigma_i \, \Gamma_i\mu_i^{\mathrm{s}} = 0$, γ becomes equal to the surface free energy per unit surface area. This explains why the concepts of surface tension and surface free energy are not always clearly distinguished in the literature. Surface tension and surface free energy are related but distinct concepts: the surface tension of a liquid is a well defined and measurable property, whereas the surface free energy is an abstract quantity which depends upon the choice of the dividing surface in which it is defined.

As in the case of liquids, atoms in the surface layer of a solid experience an imbalance of forces due to their asymmetrical environment. This gives rise to a phenomenon analogous to the surface tension of liquids. However, owing to the limited mobility of the atoms in solids, this tension is usually not isotropic and not uniform (differing for example for the different faces of a single crystal). The major difference with liquids is that, in the case of solids, this tension is not directly accessible experimentally by measuring the amount of work necessary to stretch the surface by an amount $\mathrm{d}A$ (except in some limiting cases). The tension of an interface involving a solid phase remains an abstract concept that can be defined exactly only by reference to the thermodynamics of the system. In order that the theory established for liquids remains applicable to such interfaces, this tension will be merely defined with reference to the free energy of the system by use of Equations 3 or 4. For the sake of simplicity, it will be considered, whenever possible, in what follows that the dividing interface is chosen such that $\Sigma \, \Gamma_i\mu_i^{\mathrm{s}} = 0$; this will make unnecessary the distinction between interface tension and interface energy.

In the case of solid–liquid interfaces, it may sometimes be helpful to think of the interface tension γ_{sl} with reference to the tensions γ_{sv} and γ_{lv} of the surfaces of the solid and liquid phases in vacuum. For this purpose, one can follow Dupre [23] in defining the "work of adhesion" W_{a} as

$$W_{\mathrm{a}} = \gamma_{\mathrm{sv}} + \gamma_{\mathrm{lv}} - \gamma_{\mathrm{sl}} \quad (5)$$

W_{a} has thus the dimensions of an energy per unit surface area. It is equal to the work that must be performed in order to separate one unit surface area of the two phases in vacuum. It is therefore a measure of the strength of the binding between the two phases. The concept of work of adhesion will be especially useful in the following as an aid for understanding qualitatively the energetics of the interfaces liquid metal–non-metallic solid.

2.3. Interface tension and adsorption

At equilibrium, $\mu_i' = \mu_i'' = \mu_i^{\mathrm{s}} = \mu_i$ and the differential of the surface tension may be written

$$\mathrm{d}\gamma = -(S^{\mathrm{s}}/A)\,\mathrm{d}T - \sum \Gamma_i \mathrm{d}\mu_i \quad (6)$$

This is the well-known Gibbs adsorption equation.

Consider a phase containing only two Components 1 and 2 with mole fractions X_1 and X_2. At constant temperature,

$$\mathrm{d}\gamma = -\Gamma_1\mathrm{d}\mu_1 - \Gamma_2\mathrm{d}\mu_2 \quad (7)$$

Using the Gibbs–Duhem equation

$$\mathrm{d}\mu_1 = -(X_2/X_1)\,\mathrm{d}\mu_2 \quad (8)$$

Equation 7 becomes

$$\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_2} = -\left[\Gamma_2 - \left(\frac{X_2}{X_1}\right)\Gamma_1\right] = -\Gamma_{2,1} \quad (9)$$

$\Gamma_{2,1}$ is called the relative adsorption of Component 2 with respect to Component 1. ($\Gamma_{2,1} > 0$ means that $\Gamma_2/\Gamma_1 > X_2/X_1$ or that Component 2 is more surface-active than Component 1.) The chemical potential μ_2 of Component 2 in the mixture may be expressed as

$$\mu_2 = \mu_2^* + RT\ln a_2 \quad (10)$$

where μ_2^* is the chemical potential of pure Component 2 and a_2 is the activity of Component 2 in the mixture. This leads to

$$\Gamma_{2,1} = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}(\ln a_2)} \quad (11)$$

This last relation is very important: it expresses that if the addition of Component 2 to the mixture causes a

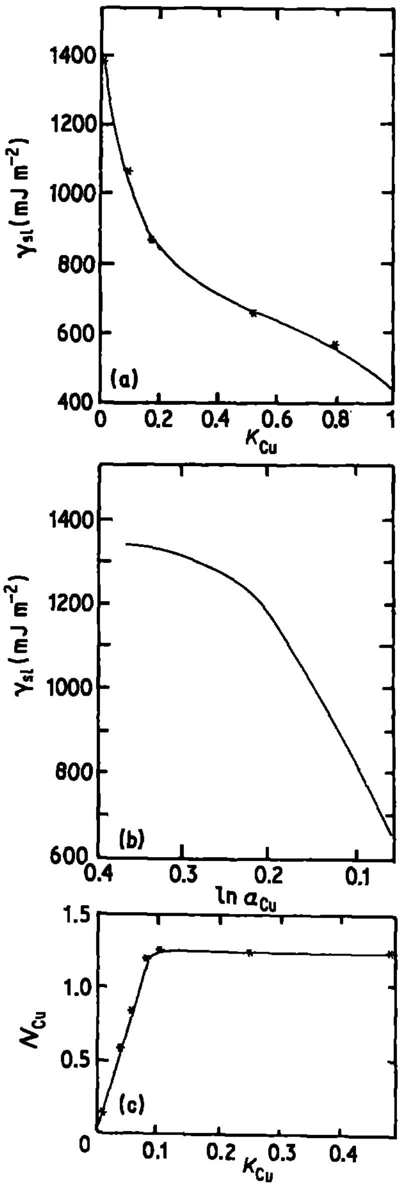

Figure 2 (a) Interface tension γ_{sl} in the system solid Fe–liquid Ag–Cu alloy as a function of alloy composition. (b) Same as in (a) expressed as a function of the logarithm of the activity of copper in the liquid. (c) Equivalent number of copper monolayers at the interface as a function of alloy composition. (After Pique *et al.* [24], with permission).

decrease of the surface tension, the more it does so, the more Component 2 segregates to the surface. In practice, Equation 11 makes possible the calculation of the amount of adsorption of a component on the surface when the variation of γ as a function of the bulk activity of this component has been measured. Such an approach, which has often been practised in the literature, can be carried out for any type of interface.

A recent example is the calculation by Pique *et al.* [24] of the adsorption of copper at the interface solid Fe–liquid Ag–Cu solution. Fig. 2a presents the experimental variation of γ_{sl} as a function of $K_{Cu} = X_{Cu}/(X_{Cu} + X_{Ag})$. Fig. 2b gives the same variation expressed as a function of ln a_{Cu}. Fig. 2c shows the equivalent number of copper monolayers N_{Cu} at the interface (as a function of K_{Cu}) calculated, from the experimental results, using a relation analogous to Equation 11: the adsorption of copper increases quickly to reach saturation at $N_{Cu} = 1.25$ as soon as $K_{Cu} = 0.08$. This indicates that copper is much more interface-active than silver in this system. (The origin of this phenomenon will be discussed in Section 3.)

When $X_2 \ll X_1$, γ is often very non-linear with respect to a_2 and the evaluation of $\Gamma_{2,1}$ from Equation 11 may be inaccurate. A solution for this difficulty has been proposed by Belton [25] who, introducing the adsorption model of Langmuir in Equation 11, obtains, after integration

$$\gamma = \gamma_l - RT\Gamma_{20} \ln (1 + ka_2) \qquad (12)$$

where γ_l is the surface tension of pure Component 1, Γ_{20} is the adsorption of Component 2 at full coverage and k is the equilibrium constant in the Langmuir adsorption. Belton shows that this expression fits accurately many literature data on the variation of γ as a function of the concentration of a diluted solute.

Rather than calculating the amount of interface adsorption from experimental data, it would be more useful, for practical purposes, to be able to predict *a priori* the values of γ or Γ from a knowledge of the molecular properties of the system. Such a prediction cannot be made in the framework of classical thermodynamics: it involves the treatment by statistical thermodynamics of a simplified model of the system. The most popular approach is the monolayer model of Guggenheim [20, 26]. This model allows one to express the surface tension of a regular mixture of two Components 1 and 2 by a set of two symmetrical equations:

$$\begin{aligned} \gamma_a &= \gamma_1 a + RT \ln (X_1^s/X_1) + l\alpha X_2^{s^2} + m\alpha X_2^2 - \alpha X_2^2 \\ \gamma_a &= \gamma_2 a + RT \ln (X_2^s/X_2) + l\alpha X_1^{s^2} + m\alpha X_1^2 - \alpha X_2^2 \end{aligned} \qquad (13)$$

a is the surface area per mole ($a = A/n^s$) assumed to be the same for the two components; X_1^s and X_2^s are the molar fractions of Components 1 and 2 in the surface monolayer; l and m are the fractions of the total number of bonds formed by one component with one other component lying either in the same layer parallel to the surface or in the adjacent layers, respectively ($l + 2m = 1$); α is the classical exchange energy between Components 1 and 2 in a regular solution:

$$\alpha = Nz[E_{12} - (E_{11} + E_{22})/2] \qquad (14)$$

where N is Avogadro's number, z is the number of nearest neighbours and E_{ij} are the potential energies of the bonds between Component i and a neighbouring Component j. α is proportional to the enthalpy of mixing ΔH_{mix}. Indeed, when n_1 moles of Component 1 and n_2 moles of Component 2 are mixed, the enthalpy increases by an amount

$$\Delta H_{mix} = \alpha n_1 n_2/(n_1 + n_2) = \alpha X_1 X_2 (n_1 + n_2). \qquad (15)$$

Equations 13 make possible the calculation of the surface tension γ and the surface concentrations X_i^s/X_i when the surface tensions of pure elements and the exchange energy α are known. For example, if $\gamma_1 > \gamma_2$, the variation of γ as a function of $K = X_2/(X_1 + X_2)$ obtained by solving Equations 13 has the same non-linear outline as shown in Fig. 2a: γ decreases quickly for small K values and Component 2 segregates to the surface ($X_2^s/X_2 > 1$). Using variants of the Guggenheim model, various authors have succeeded in fitting the experimental variation of the surface tension γ_{lv} of liquid binary alloys as a function of composition [21, 27, 28]. On the basis of the same model, Eustathopoulos and co-workers have derived analytical expressions for the interfacial tension γ_{sl} in binary metallic systems [29–31].

2.4. Non-equilibrium conditions

When a liquid is brought into contact with a solid, various irreversible phenomena (reactions, diffusion, adsorption) occur until equilibrium is reached (i.e. until the chemical potentials of all components are identical in the bulk phases and at the interface). Consequently, the interface tension γ_{sl} evolves more or less quickly toward its equilibrium value. The time required for reaching equilibrium may be long (especially when diffusion in the solid phase is involved) and one is therefore concerned more often with the non-equilibrium (or dynamic) value of γ_{sl} than with its equilibrium value.

Defay *et al.* [20] have generalized the Gibbs theory to account for non-equilibrium thermodynamics. We will not deal with this approach (which provides little practical insight into the phenomena), but only discuss qualitatively how the dynamic surface tension is expected to vary with time [32, 33].

The driving force for the irreversible phenomena is the decrease of the total free energy $F = F' + F'' + F^s$. The simplest phenomenon developing after formation of the interface is adsorption by diffusion of components from the bulk phases to the interface. During this process, the interface tension γ_{lv} decreases monotonically with the time toward its equilibrium value (Curve 1 in Fig. 3).

More drastic transformations consist in the transfer of components from one phase to the other with either formation of a solution or reaction of components to form new bulk compounds. Such transformations involve a much larger decrease of the free energy of the system than simple adsorption. During the first instants after the formation of the interface, one can consider that F' and F'' remain unchanged and attribute the whole of the free energy decrease to the decrease of F^s and thus, by Equation 4, to the decrease of γ_{sl} (or, by Equation 5, to the build up of W_a). This decrease can be quite high if the enthalpy change associated with the interface interaction is large (Curve 2 in Fig. 3). According to Naidich [33], this interaction increases linearly with the difference between the chemical potentials of the components in the two phases. Aksay *et al.* [32] state that the dynamic value of γ_{sl} can even become negative.

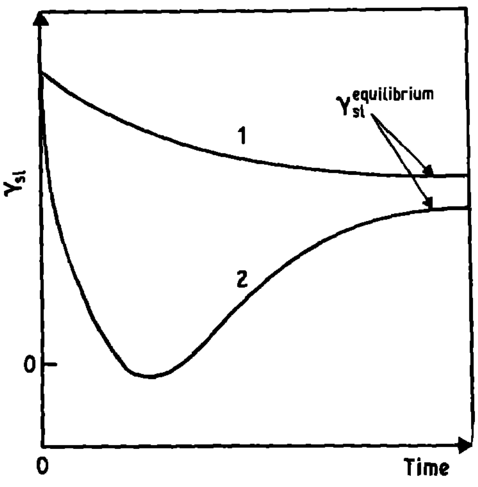

Figure 3 Variation of the interfacial tension γ_{sl} with time in non-equilibrium conditions: Curve 1, pure adsorption; Curve 2, reaction between the two phases (after Aksay *et al.* [32]).

When the transformation proceeds in the bulk phases, the difference between the chemical potentials in the two phases decreases and so does also the strength of the interaction at the interface. (F^s increases, meaning that ($F' + F''$) decreases more than F.) γ_{sl} thus gradually increases towards its equilibrium value (Fig. 3), which is always positive since the interface is always less stable than the bulk phases.

The time required to reach the minimum of γ_{sl} will depend upon the kinetics of diffusion of the components in the bulk phases. Therefore, it will thus depend very much on temperature.

In practice, quasi-equilibrium often occurs due to the presence at the interface of a thin diffusion barrier (such as an oxide layer on a (solid or liquid) metal surface) hindering the contact between the two bulk phases. The kinetics of such systems is also very dependent on temperature: sharp variation of the interface tension is usually observed when the temperature exceeds a certain minimum necessary for the breaking or disappearance of the film. Examples will be mentioned in Section 4.

2.5. Wetting and infiltration

The wettability of a solid by a liquid is indicated by the "contact angle" θ defined in Fig. 4. This angle is related to the three surface tensions γ_{sg}, γ_{sl} and γ_{lg} of the interfaces solid–gas, solid–liquid and liquid–gas, respectively, by the well-known equation

$$\gamma_{lg} \cos\theta = \gamma_{sg} - \gamma_{sl} \tag{16}$$

This equation was first introduced by Young in 1805 [34] on the basis of a mechanistic approach. It was later demonstrated on thermodynamic grounds by Gibbs [35] and more recently by Johnson [36].

A liquid is said to wet a solid surface when $\cos\theta > 0$, i.e. when $\gamma_{sg} > \gamma_{sl}$. The "driving force for

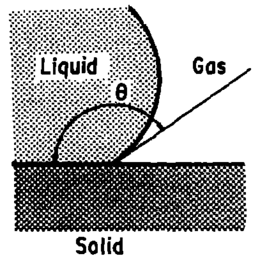

Figure 4 Definition of the contact angle.

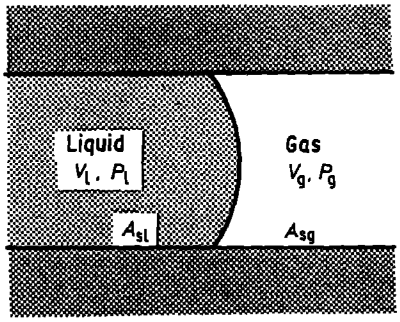

Figure 5 Infiltration of a liquid into a capillary.

wetting", D_f, may thus be defined as

$$D_f = \gamma_{sg} - \gamma_{sl} \qquad (17)$$

When $D_f \geqslant \gamma_{lg}$, $\theta = 0$ and the liquid spreads spontaneously on the solid surface.

In a vacuum and when there is no adsorption of components of the liquid at the surface of the solid ($\gamma_{sg} = \gamma_{sv}$), one can write, using Equation 5,

$$D_f = -(\gamma_{lv} - W_a) \qquad (18)$$

When the latter conditions are fulfilled, one can furthermore combine Equations 5 and 16 to write

$$W_a = \gamma_{lv}(1 + \cos\theta) \qquad (19)$$

When the surface tension γ_{lv} of the liquid phase is known, the work of adhesion (at equilibrium) can thus be determined experimentally from the measurement of the contact angle at the edge of a sessile drop of liquid metal resting on a flat solid surface (in so far as the conditions of vacuum and absence of contamination of the solid surface are fulfilled).

The infiltration of a liquid into a solid network may be modelled by assuming that the network is made of cylindrical capillaries into which the liquid has to penetrate. Let us consider a liquid–gas interface across a capillary (Fig. 5). The minimum pressure difference $\Delta P = P_l - P_g$ necessary to move the interface isothermally ($\mathrm{d}T = 0$) along the capillary may be calculated by use of Equation 1. One can assume that this movement is too rapid to involve transfer of components between the phases and the interface ($\mathrm{d}n_i' = \mathrm{d}n_i'' = \mathrm{d}n_i^s = 0$). The change of the free energy of the system is then

$$\mathrm{d}F = -P_l\mathrm{d}V_l - P_g\mathrm{d}V_g + \gamma_{sl}\mathrm{d}A_{sl} + \gamma_{sg}\mathrm{d}A_{sg} \leqslant 0 \qquad (20)$$

($\mathrm{d}F = 0$ only for a reversible process). For a cylindrical capillary with radius r,

$$\mathrm{d}V_l = -\mathrm{d}V_g = r\mathrm{d}A_{sl}/2 = -r\mathrm{d}A_{sg}/2$$

Thus

$$\Delta P = P_l - P_g \geqslant -2D_f/r \qquad (21)$$

In other words, Equation 21 expresses that the radius of the smallest pore that will be penetrated by the liquid phase when a pressure ΔP is applied is

$$r = -2D_f/\Delta P \qquad (22)$$

This relation may be more relevant than Equation 21, as reinforcing networks probably consist of a series of bottlenecks through which the liquid has to pass.

One must also take into account the flow resistance caused by the viscosity η of the liquid. The distance x travelled by the liquid along the capillary after a time t under an applied pressure ΔP is [37]

$$x = \left[\frac{r^2 t}{4\eta}\left(\Delta P + \frac{2D_f}{r}\right)\right]^{1/2} \qquad (23)$$

As an example, let us consider the infiltration of liquid aluminium into a yarn of fibres having a diameter of $10\,\mu$m. The worst case would be the complete absence of wetting: $\cos\theta = -1$, $W_a = 0$, $D_f = -\gamma_{lg}$. The surface tension γ_{lg} of liquid aluminium is about $1000\,\mathrm{mJ\,m^{-2}}$ (see below). One calculates from Equation 21 that a pressure of 2 MPa would then be necessary for the infiltration of pores down to a radius r of $1\,\mu$m.

Liquid aluminium has a viscosity of about 10^{-3} Pa sec [38]. If a pressure of 3 MPa is applied (i.e. the excess pressure $\Delta P + 2D_f/r = 1$ MPa), use of Equation 23 shows that the liquid penetrates 1 cm of such small pores in 0.4 sec whereas 40 sec are needed for penetrating 10 cm. More detailed calculations have been proposed by Clyne and Bader [39] and by Girot *et al.* [40].

In the practice, methods described in the literature involve the use of pressures ranging from 20 to 75 MPa [11, 12, 18]. Hence, these pressures appear to greatly exceed the minimum necessary. However, as shown by Girot *et al.* [40], such pressures are needed in order to avoid solidification of the liquid during infiltration when the temperature of the reinforcing network is lower than the melting temperature of aluminium.

Equations 21 to 23 indicate that all procedures designed to facilitate impregnation should aim at increasing the driving force for wetting D_f. Both Equations 17 and 18 for D_f will be used alternately in the following discussion. The advantage of Equation 18 is that it shows that the nature of the solid affects wetting only through W_a but not through γ_{sv}. However, it should be remembered that γ_{lv} appears in Equation 17 for D_f only because of its contribution to the interface tension γ_{sl}. (The liquid–vacuum surface area remains constant in the model.) Lowering the surface tension of the liquid (e.g. by the addition of alloying elements which adsorb at the liquid–vacuum interface) would not necessarily favour infiltration. A notable exception is the complete absence of wetting: there is then no true solid–liquid interface but merely the superposition of the two interfaces, solid–gas and liquid–gas.

As infiltration is a dynamic process, equilibrium is usually not reached in the vicinity of the advancing interface. We will therefore be concerned more with the dynamic values of W_a and γ_{sl} than with their equilibrium values.

3. The surface tension of liquid metals and the wetting of solid metals by liquid metals

According to Equation 18, the driving force for wetting is affected by only two factors: the surface tension of the liquid and the strength of the solid–liquid interaction at the interface. These two factors will be discussed in succession. As the properties of metal–vacuum surfaces and metal–metal interfaces are closely related, it appeared convenient to include these two aspects in the same section.

3.1. The surface tension of liquid metals

Several methods have been developed for measuring the liquid–vacuum surface tension γ_{lv} of liquid metals (for a review, see Eustathopoulos and Joud [21]). There is a wealth of data on such measurements. Table I gives a selection of values at the melting temperature [41]. These values can be considered as quite accurate, although some disagreement remains for some metals. For example, the values of the surface tension of liquid aluminium measured in various studies during the last decade converge toward $860\,\mathrm{mJ\,m^{-2}}$. However, two recent works [42, 43] suggest that the surface tension of pure liquid aluminium is higher: $1050\,\mathrm{mJ\,m^{-2}}$. According to these works, the lower value measured previously corresponds to a surface covered by aluminium oxide: due to the large affinity of aluminium for oxygen, the formation of this oxide layer can be avoided only when working in an ultra-high vacuum or with ultra-high purity gases. As will be seen in the following, this oxide layer also drastically affects the properties of the interfaces between liquid aluminium and all types of solids.

Several empirical rules have been established relating the surface tension γ_{lv} to other properties of the metals. Skapski [44] was the first to recognize the proportionality of γ_{lv} with the heat of vaporization of the liquid metal H_{v}:

$$\gamma_{\mathrm{lv}} = K'H_{\mathrm{v}} \tag{24}$$

This relationship may be justified from the fact that both surface tension and vaporization involve the breaking of bonds between atoms in the liquid. The experimental value of the proportionality constant K' is 0.15 to 0.16 [21, 45]. Another rule was proposed by Allen [41] who showed that the surface tension of pure liquids is a function of the melting temperature:

$$\gamma_{\mathrm{lv}} = K''T_{\mathrm{m}}\left(\frac{M}{\varrho_{\mathrm{l}}}\right)^{-2/3} \tag{25}$$

where M and ϱ_{l} are the molecular weight and density of the liquid metal, respectively, and $K'' \approx 3.6 \times 10^{-7}\,\mathrm{J\,K^{-1}}$.

TABLE I Selection of γ_{lv} values at the melting point for pure liquid metals

Metal	γ_{lv} ($\mathrm{mJ\,m^{-2}}$)*
Li	400
Mg	560
Zn	780
Al	1050
Cu	1300
Ti	1650
Ni	1780
Fe	1880
Mo	2250

*Value for aluminium from Goumiri and Joud [42]; all others from Allen [41].

In parallel with these empirical approaches, many authors have attempted theoretical calculations of the surface tension γ_{lv} on the basis of the electronic properties of the metals. Until recently, the accuracy of these calculations has remained fairly poor, owing to the large number of contributions that must be accounted for even for the simplest cases of pure liquids (i.e. without the presence of alloying elements which can adsorb at the surface) [46, 47].

3.2. Wetting in metal–metal systems

The wettability of solid metals by liquid metals has been extensively studied because of its immense importance in technological processes such as soldering, brazing, sintering, and melting in metal containers. Even though reinforcing networks in metal-matrix composites are most often non-metallic, metallic coatings have frequently been used to facilitate infiltration by metal melts. Only a brief account of the subject can be presented here.

The experimental methods for measuring γ_{sl} in metallic systems have been reviewed by Eustathopoulos [31].

For cubic metals, it appears justified to consider that a pure solid metal i is perfectly wetted by its own melt [44], i.e.

$$(\gamma_{\mathrm{sl}})_{ii} = (\gamma_{\mathrm{sv}})_i - (\gamma_{\mathrm{lv}})_i \tag{26}$$

This means that the work of adhesion is high (from Equation 5, $W_{\mathrm{a}} = 2\gamma_{\mathrm{lv}}$), indicating strong metallic bonds between the solid and the liquid at the interface. An empirical rule states that the tension of the interface of a pure metal with its melt is proportional to γ_{lv}:

$$(\gamma_{\mathrm{sl}})_{ii} = K'''(\gamma_{\mathrm{lv}})_i \tag{27}$$

with $K''' \approx 0.18$ [48, 49]. This rule may be rationalized by use of the same argument as for the relation (Equation 24) between γ_{lv} and ΔH_{v}.

After Ewing [50], the solid–melt interface tension may be approximated as the sum of two contributions:

$$(\gamma_{\mathrm{sl}})_{ii} = (\gamma_{\mathrm{sl}}^{\mathrm{s}})_i + (\gamma_{\mathrm{sl}}^{\mathrm{l}})_i \tag{28}$$

$\gamma_{\mathrm{sl}}^{\mathrm{s}}$ is the excess enthalpy possessed by the atoms in the first atomic layer of the solid. (This excess is a fraction of the enthalpy of melting.) $\gamma_{\mathrm{sl}}^{\mathrm{l}}$ is an entropic contribution accounting for the fact that atoms near the surface of the liquid have a smaller entropy than atoms in the bulk of the liquid. (This contribution may be calculated when knowing the distribution of atoms in the direction normal to the surface.)

In their early study of the wettability of solid metals by different liquid metals, Bailey and Watkins [51] concluded that mutual solubility or formation of intermetallic compounds was a necessary condition for wetting. This conclusion was interpreted by Klein Wassink [52] who recognized that, in the case of dissimilar metals, the energy of the interaction at the solid–liquid interface contains a contribution proportional to the classical exchange energy α (defined in Equation 14) between the two metals. This approach was further developed by Miedema and den Broeder [53]. As an extension of the model of Ewing [50], these authors propose that the interface tension between Solid 1 and Liquid 2 may be evaluated by merely adding a term to the expression (Equation 28) of Ewing, i.e.

$$(\gamma_{sl})_{12} = (\gamma_{sl}^{s})_1 + (\gamma_{sl}^{l})_2 + W_{12} \tag{29}$$

W_{12} is proportional to the exchange energy and thus, by Equation 15, to the enthalpy of mixing ΔH_{mix} of the two metals. The higher the affinity of the two metals for each other, the lower α and ΔH_{mix} and the lower $(\gamma_{sl})_{12}$.

Equation 29 allows a fairly simple qualitative understanding of the influence of mutual solubility (and the formation of intermetallic compounds) on wetting in metallic systems. For example, we have seen in Fig. 2 that the interfacial tension $(\gamma_{sl})_{FeCu}$ is much lower than $(\gamma_{sl})_{FeAg}$. This is due to the lower exchange energy α between iron and copper than between iron and silver. According to Miedema and den Broeder [53], the entropy term γ_{sl}^{l} in Equation 29 is practically the same for copper and silver: 183 and 184 mJ m^{-2}, respectively. The major contribution to γ_{sl} is due, in these cases, to the exchange term W_{12}, which equals 398 and 615 mJ m^{-2}, respectively.

More recent work has demonstrated that, after proper cleaning of the solid surface, the condition for wetting is not as restrictive as proposed by Bailey and Watkins [51], i.e. that wetting is observed even for couples of metals which form no intermetallic compounds and have a very low mutual solubility. (According to Naidich [33], wettability could have been impaired in the previous studies by the presence of an oxide film hindering the interaction between the two metals; the higher the mutual affinity of the two metals, the easier the penetration through the film.) Two typical examples are the wetting of iron by molten lead or molten silver. The solubilities of iron in liquid lead and liquid silver are about 3×10^{-6} and 3×10^{-4}, respectively [24, 54]; the experimental values of the contact angles θ are 69 and 35° respectively [55, 56]. This suggests that metallic bonding across the interface overcomes the repulsion resulting from the high exchange energy.

As mentioned earlier, Eustathopoulos and coworkers [29–31] have extended the monolayer model of Guggenheim to develop analytical expressions for the interfacial tension γ_{sl} in metallic systems. These expressions account more accurately than Equation 29 for the influence of the exchange energy. For systems with very low mutual solubility ($\alpha > 5RT$), Eustathopoulos and Pique [57] deduce from these expressions that the equilibrium contact angle at the melting point follows the relation

$$1 - \cos\theta = K\left(\frac{T_{m1}}{T_{m2}} - 1\right) \tag{30}$$

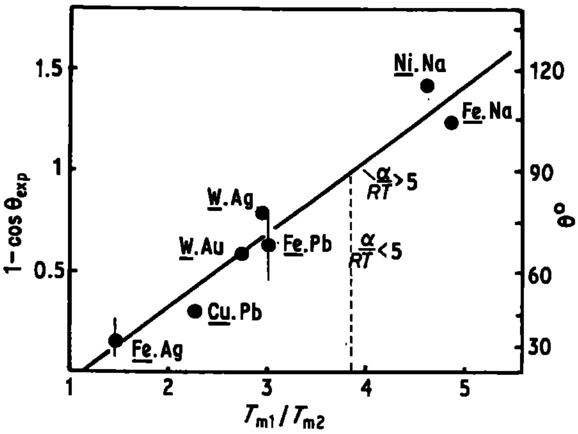

Figure 6 $(1 - \cos\theta)$ as a function of the ratio T_{m1}/T_{m2} of the melting temperatures of the solid (T_{m1}) and liquid (T_{m2}) metals (after Eustathopoulos and Pique [57], with permission).

where T_{m1} and T_{m2} are the melting temperatures of the solid and liquid metals, respectively. K is a constant the theoretical value of which is 0.28. Fig. 6 shows that experimental results are well fitted by Equation 30 using $K = 0.36$. It is worth mentioning that, in such systems with low mutual solubility, the solid–vacuum surface of Metal 1 becomes covered, at equilibrium, by an adsorption layer of Metal 2 [57].

An alternative method for estimating the tension of the solid metal–liquid metal interface at equilibrium has been proposed by Warren [58].

When an intermetallic compound is formed, the wettability at equilibrium is determined by the liquid metal–intermetallic compound interface tension. The latter usually has some ionic character which can adversely affect wetting (as will be discussed in Section 4). As a result, transition from wetting to nonwetting can be observed after formation of the compound [33].

4. The wetting of non-metallic solids by liquid metals

The wetting of non-metals by liquid metals has been extensively investigated over the past 40 years. Fundamental studies were usually based on the measurement of the work of adhesion by the sessile drop method on the basis of Equation 19. These measurements require a very precise control of experimental conditions, especially of the composition of the solid (particularly its surface), the melt, and the surrounding atmosphere. Such a control is often difficult to achieve and the literature contains many contradictions and inaccuracies attributable to "dirty" experimental conditions. This section aims at summarizing the most reliable results which have emerged up to now. A fairly extensive review of the subject has been published by Naidich [33].

4.1. The interactions determining the work of adhesion

Using Equation 18, the condition for wetting under vacuum becomes $W_a > \gamma_{lv}$. (The condition for spontaneous spreading is $W_a \geqslant 2\gamma_{lv}$.) This means that a liquid wets a solid surface only if the energy of the bonds that are created across the interface exceeds the surface tension of the liquid. This condition is much less severe for liquids, such as water or organic solvents, the surface tension of which is of the order of a few tens of mJ m^{-2} (or a few times 10^{-2} eV per surface atom), than for liquid metals which have a surface tension of the order of 1000 mJ m^{-2} (or 1 eV per surface atom) (see Table I).

When studying how gaseous molecules stick to a solid surface, one distinguishes the physical adsorption, which is governed by van der Waals type interactions, from the chemical adsorption, which involves the formation of a chemical bond. In the same way, it is convenient to divide the contributions to the metal–surface interaction energies into physical and chemical forces.

4.1.1. Physical interactions

It is widely believed that the major contribution to physical forces comes from dispersion forces. These forces arise from the attraction between an instantaneous dipole and the dipoles that it induces in its vicinity. The energy E_{12} of the dispersion interaction between two free atoms may be evaluated by use of the London formula

$$E_{12} = \frac{3}{2}\frac{\alpha_1\alpha_2}{R^6}\left(\frac{I_1 I_2}{I_1 + I_2}\right) \tag{31}$$

where I_1 and I_2 are the first ionization potentials of the two atoms, α_1 and α_2 are their polarizabilities and R is the distance between them. In the case of liquid–solid interfaces, the contribution to W_a due to dispersion may be estimated by use of Equation 31, assuming pairwise interactions between the atoms belonging to the outermost atomic monolayer of the two phases. If each monolayer contains only one atomic species,

$$W_{a\,\mathrm{disp}} = nE_{12} \tag{32}$$

where n is the number of atom pairs per unit surface area of the interface. (One neglects here the entropy contribution to the free energy change.)

It has been shown by Fowkes [59] that many properties of interfaces involving low surface tension liquids such as water or organic solvents may be fairly precisely understood when assuming that they are governed only by dispersion interactions. In the case of liquid metal–solid interfaces, the values of $W_{a\,\mathrm{disp}}$ calculated by various authors [33, 60] using Equations 31 and 32 never exceed 600 mJ m^{-2}. When comparing to the values of γ_{lv} in Table I, it may be already concluded that, in contrast to the case of common liquids, dispersion forces are too weak to allow wetting of a solid by a liquid metal: the condition for wetting $W_a > \gamma_{lv}$ can be fulfilled only when some contribution of chemical interaction complements dispersion forces.

Dispersion forces are characterized by a fairly weak dependence on temperature [33]. For different liquid metals on the same solid, $W_{a\,\mathrm{disp}}$ decreases when one proceeds from the top to the bottom of a column in the periodic table [33]. No other systematic variation across the table has been noticed.

As noted by Stoneham [61, 62], a description of the dispersion interaction on the sole basis of Equation 32 is a very crude approximation as atoms in the solid may bear little resemblance to free atoms. A completely different approach to the physical contribution to interfacial energy is provided by the dielectric continuum theory of Barrera and Duke [63]. In this model, the two phases are merely represented by continuous media characterized by different (frequency-dependent) dielectric constants. The surface energy stems from the perturbation that the presence of the discontinuity at the interface brings to the energy distribution of the two electron gases. The analytical expressions for γ_{sv}, γ_{lv} and γ_{sl} provided by Barrera and Duke can be used only for a qualitative comparison between different metal–solid systems as the unit scale contains a constant (the cut-off wave vector q_c) the value of which is unknown.

Evaluation of the bearing of this theory on the understanding of the wetting of carbon and oxides by liquid metals has been made by Stoneham [61, 62]. In view of the relatively poor agreement obtained with experiment, this study merely confirms that physical interactions are usually not the only important contribution to the liquid metal–solid interfacial energy.

4.1.2. Chemical interactions

Chemical interactions may be represented as resulting from a chemical reaction between Species A in the liquid and Species B in the outer layer of the solid surface to form a compound A_mB_n:

$$m\mathrm{A} + n\mathrm{B} \overset{\Delta F^{\ominus}}{\rightleftharpoons} \mathrm{A}_m\mathrm{B}_n \tag{33}$$

The contribution to the work of adhesion due to such a reaction may be evaluated if one can estimate the standard free energy change $\Delta F^{\ominus}$ for the reaction and the number of species A, B and A_mB_n per unit surface area of the interface [33].

Numerous examples of chemical interactions will be mentioned in the following sections. As a rule, when chemical interactions occur, their contribution to the work of adhesion largely overcomes the contribution of physical interactions. It will be shown that, for a given solid, chemical interactions depend drastically on the position of the metal in the periodic table. They are also characterized by a much larger temperature dependence than physical interactions.

4.2. The interface liquid metal–oxide

According to Weyl [64], the larger size and higher polarizability of the oxygen anions as compared to the cations cause a reconstruction of the oxide surface with displacement of the cations from the surface to the interior (Fig. 7). A double layer is created of which the extreme outer layer contains only anions. On the basis of this widely accepted model, it is generally assumed that adhesion with oxides is essentially governed by the interactions of the metal atoms with the oxygen anions only.

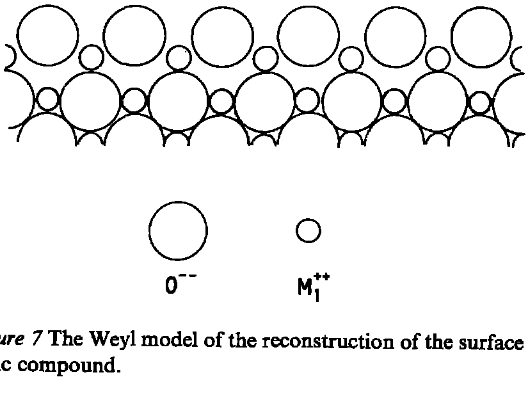

Figure 7 The Weyl model of the reconstruction of the surface of an ionic compound.

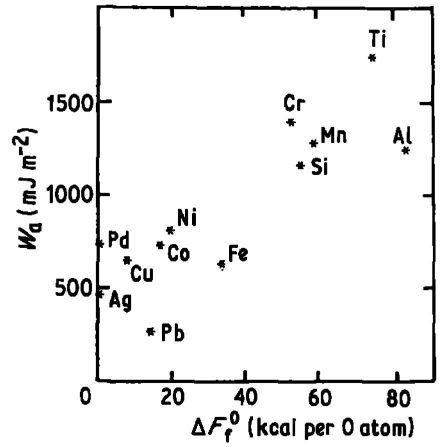

Figure 8 Work of adhesion of various liquid metals on polycrystalline Al_2O_3 as a function of the free energy of formation of the corresponding oxide (after Eustathopoulos and Passerone [69], with permission).

As a rule, the wettability of oxides by liquid metals is poor. Referring to Weyl's model, Livey and Murray [65] state that this low wettability is due to the repulsion of the negative electron gas of the metal by the negative anion monolayer. This qualitative argument, which has often been mentioned in the literature, has never been evaluated in quantitative terms. Other authors have suggested that, on the contrary, the electrostatic attraction between cations in the liquid metal and the negative anions should favour wetting [66].

It was early recognized by Humenik and Kingery [67] that the work of adhesion of liquid metals on oxide surfaces increases with increasing affinity of the metal for oxygen, i.e. with increasing standard free energy of oxide formation $-\Delta F_f^{\ominus}$. In the case of binary melts, this manifests itself by a strong interface adsorption of the most electropositive metal (e.g. titanium in Ni–Ti alloys) [68]. Fig. 8 is a compilation by Eustathopoulos and Passerone [69] (based on the work of Ukov *et al.* [70] of values of W_a at equilibrium for the wetting of Al_2O_3 by various metals. It is clear that wetting is related to the tendency of the metal to react with the surface oxygen anions.

McDonald and Eberhart [60] and Naidich [33] made use of Equations 31 and 32 to calculate the contribution to W_a due to the dispersion interaction between the outer oxygen monolayer of the oxide and one monolayer of metal atoms. In the case of metals such as gold and silver which have practically no affinity for oxygen, the calculated values agree roughly with the measured works of adhesion on Al_2O_3 (500 mJ m^{-2}). The higher values measured for the other metals must be explained by a contribution of chemical interactions.

McDonald and Eberhart [60] showed that, for measurements carried out on the same type of alumina under the same atmosphere, the work of adhesion varied linearly as a function of $-\Delta F_f^{\ominus}$, i.e.

$$W_a = -a\Delta F_f^{\ominus} + b \qquad (34)$$

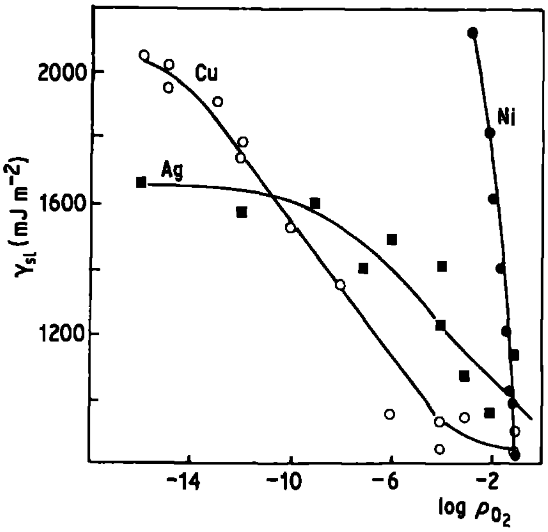

Figure 9 Variation of γ_{sl} for liquid (○) copper, (■) silver and (●) nickel on sapphire as a function of the oxygen partial pressure (after Mehrotra and Chaklader [73], with permission).

In order to account for the value of the slope a, these authors proposed the existence of specific sites on the alumina surface where the metal could undergo strong chemical binding with the surface. The number of these sites would be equal to one-third of the number of oxygen anions exposed on the surface and the energy (per atom) of the interation ΔF would be equal to half the standard free energy of formation of the corresponding oxide. The constant b arises from the dispersion interactions between metal atoms and oxygen on the other sites of the surface. Although this dispersion contribution is not precisely the same for different metals, it does not vary greatly for the transition metals. Although accounting for the variation of wetting with F_f, the model of McDonald and Eberhard [60] gives no clue to two other experimental results that emerge from the literature. The first result concerns the variation of wetting with the nature of the solid. According to the survey of Naidich [33], experiment shows that, in the same way as W_a increases with increasing affinity of the metal for oxygen, W_a also increases with decreasing bond strength between metal and oxygen in the solid. This increased interaction is often correlated with some dissolution of the oxide in the metal melt [71].

The second result concerns the drastic increase of W_a with increasing concentration of oxygen (or sulphur) in solution in the melt [65, 72]. Fig. 9 illustrates this phenomenon for the wetting of sapphire by different metals (after Mehrotra and Chaklader [73]). In a wide range of oxygen partial pressures, γ_{sl} decreases roughly linearly with the logarithm of the partial pressure, the slope depending upon the nature of the metal. Empirically, Mehrotra and Chaklader [73] find that this slope increases with increasing free energy of formation of the corresponding aluminate ($CuAlO_2$, $AgAlO_2$ and $NiAl_2O_4$) normalized with respect to temperature. In this context, it is worth mentioning also the growth of $NiAl_2O_4$ at the sapphire–nickel interface after heat treatment in air [74] and the formation of $MgAl_2O_4$ at the Al_2O_3–Al–Mg alloy interface ([75] and references therein).

A more comprehensive model accounting for these results is proposed by Naidich [33]. Naidich attributes a major role to oxygen in solution in the metal melt.

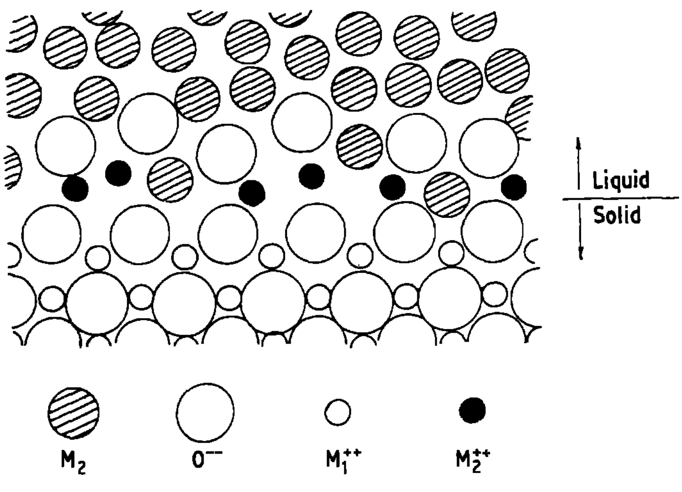

Figure 10 The interface liquid metal–oxide according to the model of Naidich [33].

According to him, this oxygen creates, with a metal in its vicinity, an Me^{2+}–O^{2-} complex. Such a complex strongly adsorbs at the interface as a result of the electrostatic attraction between the Me^{2+} cation so formed and the anionic layer at the solid surface. The higher the affinity of the metal for oxygen, the lower the solubility of the Me^{2+}–O^{2-} complex and the higher its interface activity. Naidich suggests that, when enough oxygen is present in the melt, a layer of (liquid) metal oxide is formed in contact with the surface of the solid oxide. (We have tried a sketch of this model in Fig. 10.) The work of adhesion becomes then approximately equal to the energy required to break the (ionic) bonds between the two oxides. As neutral atoms cannot bind with the oxygen anions of the solid surface, the presence of oxygen in the bulk is essential.

In the absence of oxygen in the melt, the formation of the Me^{2+}–O^{2-} complexes involves the reduction of the oxide. In such a case, Naidich evaluates the chemical contribution to the work of adhesion from the reaction

$$\mathrm{Me_2} + \mathrm{Me_1O} \overset{\Delta F^{\ominus}_{2,1}}{\rightleftharpoons} \mathrm{Me_2O} + \mathrm{Me_1} \qquad (35)$$

where Me_1 and Me_2 are the metal of the solid oxide and the metal of the melt, respectively. Obviously, the chemical contribution to W_a increases with decreasing standard free energy of this reaction:

$$\Delta F^{\ominus}_{2,1} = \Delta F^{\ominus}_{f2} - \Delta F^{\ominus}_{f1} \qquad (36)$$

However, as pointed out by Klomp [76], one should also take into account the free-energy change associated with the solution of Metal 1 in the melt.

As an illustration, Fig. 11 (from the paper of Aratani and Tamai [71]) shows the variation of the work of adhesion of liquid copper at 1373 K (Fig. 11a) and liquid iron at 1823 K (Fig. 11b) on the surface of different Al_2O_3–Cr_2O_3 solid solutions. No dependence of W_a on the Cr_2O_3 content is observed for copper, whereas a twofold increase between Al_2O_3 and Cr_2O_3 is observed for iron. The reduction of Cr_2O_3 by iron was demonstrated by the presence of up to 1.5 wt % Cr in solution in iron. Considering the reactions

$$\mathrm{Fe} + \tfrac{1}{3}\,\mathrm{Cr_2O_3} \underset{1823\,\mathrm{K}}{\overset{\Delta F^{\ominus}_{\mathrm{Fe,Cr}}}{\rightleftharpoons}} \mathrm{FeO} + \tfrac{2}{3}\mathrm{Cr}$$

and

$$2\mathrm{Cu} + \tfrac{1}{3}\mathrm{Cr_2O_3} \underset{1373\,\mathrm{K}}{\overset{\Delta F^{\ominus}_{\mathrm{Cu,Cr}}}{\rightleftharpoons}} \mathrm{Cu_2O} + \tfrac{2}{3}\mathrm{Cr}$$

one calculates [77]

$$\Delta F^{\ominus}_{\mathrm{Fe,Cr}} = +5.8\ \mathrm{kJ\ (g\text{-}atom\ O)^{-1}}$$

and

$$\Delta F^{\ominus}_{\mathrm{Cu,Cr}} = +12.3\ \mathrm{kJ\ (g\text{-}atom\ O)^{-1}}$$

The difference between the two systems becomes much larger when one takes into account the different solubilities of chromium in liquid iron and copper: according to Niessen *et al.* [78], the enthalpy of mixing at infinite dilution is -6 kJ (g-atom)$^{-1}$ for chromium in iron and $+51$ kJ (g-atom)$^{-1}$ for chromium in copper. Obviously, the solubility difference contributes significantly to the difference between the work of adhesion with Cr_2O_3. In summary, although the major factors governing the wetting of oxides by liquid metals today appear fairly qualitatively apprehended a satisfactory quantitative thermodynamical theory of the phenomenon is still lacking.

This section would not be complete without mentioning the problems associated with presence of the

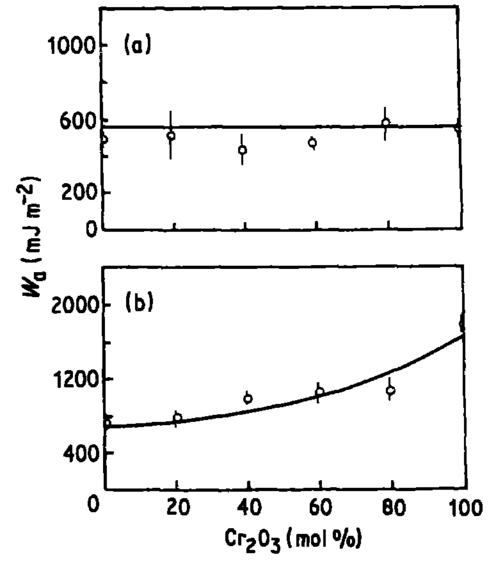

Figure 11 Work of adhesion for (a) molten copper at 1373 K and (b) molten iron at 1823 K on Al_2O_3–Cr_2O_3 solid solutions (after Aratani and Tamai [71], with permission).

aluminium oxide layer at the surface of liquid aluminium. The influence of this layer has been elucidated in a recent study by Coudurier *et al.* [79] of the wettability of alumina by liquid aluminium. The work of adhesion W_a equals about 100 mJ m^{-2} at the melting point of aluminium; it increases drastically with temperature and reaches its "normal" value ($\approx$ 1000 mJ m^{-2}) only above 950° C, which is the threshold temperature for the penetration of liquid aluminium through the oxide barrier.

4.3. The interface liquid metal–carbon or carbide

The major contribution to this subject has been provided by the work of Naidich and co-workers. Unless otherwise specified, details on the information summarized in this section may be found in the review of Naidich [33].

The wettability of carbon by liquid metals is little dependent on the crystallographic form of the carbon: graphite or diamond. These two forms are indeed very similar energetically. The reactivity of metals with carbon varies greatly across the periodic table. We shall proceed from the less reactive metals to the more reactive ones.

Metals belonging to Groups Ib to VIb and to Periods 4 to 6 are practically inert to carbon. The measured work of adhesion of these metals with carbon is small (70 to 300 mJ m^{-2}) and fairly independent of temperature: these metals do not wet carbon. Such values of W_a agree with the values of $W_{a\,disp}$ that can be calculated using Equations 31 and 32.

Alkali metals react with graphite to form intercalation compounds where positive ions of the metal are inserted between the basal layers. Although the enthalpy of this reaction is not high, it is sufficient to induce wetting because of the low value of the surface tension γ_{lv} of alkali metals (100 to 400 mJ m^{-2}). Lithium and sodium were indeed found to wet graphite. The same argument should hold for alkaline-earth metals but the literature provides no data in this respect.

Boron, aluminium and silicon form carbides with covalent metal–carbon bonds. These metals wet carbon: the work of adhesion reaches 1000 to 1200 mJ m^{-2}, which indicates some contribution of chemical interaction.

The wetting of carbon by aluminium has been much studied, owing to its importance in relation to the preparation of metal-matrix composites [80–82]. Wetting was usually not observed below about 900° C and the contact angle decreased (in several steps) when the temperature increased. Eustathopoulos *et al.* [82] showed that this phenomenon is due to the presence of the aluminium oxide layer preventing the direct contact of aluminium with carbon. Penetration of aluminium through this diffusion barrier is facilitated either by increasing the temperature, or by the addition of alloying elements [82]. Being more electropositive than aluminium, these elements probably substitute for aluminium in the oxide layer, bringing about a weakening of the film. These elements thus enhance wetting even though they form weaker bonds with carbon than aluminium does. The same effect might also explain the enhancement of wetting brought about by alloying magnesium in aluminium [81].

Transition metals (metals with an unfilled d-electron shell) react strongly with carbon to form carbides where binding involves some electron transfer from carbon to the d-shell of the metal [33]. The work of adhesion with graphite is large (up to 2000 to 3000 mJ m^{-2}). It increases with increasing temperature and with decreasing number of d-shell electrons (Ti > V > . . . > Ni). Chemical interactions amount for 90 to 95% of the work of adhesion. In such reactive systems, W_a is a very dynamic quantity. When a pure metal is brought into contact with graphite, a significant part of the chemical interaction arises from the dissolution of carbon in the melt. As soon as the reaction front proceeds in the solid, one deals with an interface of the type liquid metal–carbide rather than liquid metal–carbon.

As a rule, the wettability of covalent carbides such as SiC and B_4C follows the same dependence on the nature of the metal as the wettability of carbon. The reason is probably that metals that do not react with carbon do not react either with silicon or boron. (A notable exception is copper: silicon enters into solution in liquid copper and a layer of free solid graphite is formed near the interface [83].) The magnitude of the chemical interaction is weaker than for carbon, due to the larger strength of the bonds in these carbides. The larger wettability of SiC as compared to B_4C may be attributed to the higher heat of formation of the latter. (A review of the wetting of SiC by liquid metals has been published by Warren and Andersson [84].)

The wetting of SiC by metals is often hindered by the presence of a layer of silicon oxide on the solid surface. As a result, a sharp transition from non-wetting to wetting is observed at a certain threshold temperature [84]. This transition temperature is determined by the kinetics of the diffusion of the metal through the oxide layer. It can be varied by the addition of alloying elements [85].

The metal-like carbides of the transition metals are wetted better than the covalent carbides. The dependence on the nature of the metal is again similar as for carbon: the highest wetting is exhibited by transition metals. The interface tension γ_{sl} for a series of transition metal carbide–liquid metal interfaces has been evaluated by Warren [58] on the basis of a simple thermodynamic model. In all cases, γ_{sl} is several times lower than the estimated surface tension γ_{sv} of the carbides. The excellent properties can be explained, as in metallic systems, by the formation of metallic bonding across the interface.

5. Evaluation of wetting enhancement techniques for the preparation of metal-matrix composites

We can now attempt the exercise of interpreting the literature concerning liquid metal infiltration in the framework of the science of wetting presented in the preceding sections. Most of this literature concerns aluminium composites. We do not aim at being exhaustive. We will restrict ourselves to the major methods proposed for application to reinforcements making use of multifilament fibres for which liquid metal infiltration is the most convenient preparation route. (These methods are also widely applicable for composites reinforced by SiC or Al_2O_3 whiskers.) We will concentrate on wetting and give little mention of the advantages and drawbacks of the methods for the mechanical properties of the composite.

5.1. General considerations

The multifilament fibres presently on the market are made of carbon, alumina or silicon carbide. Whiskers of alumina and silicon carbide are also available. Only these three solids will therefore be considered. Owing to the fabrication procedure, the nature of the surface of the fibres (which determines wettability) is much less well characterized than the surface of the solids used in fundamental wetting studies. The surface of as-received multifilament carbon fibres is heavily contaminated by adsorbed species which lower its reactivity and may prevent wetting by metals that, in principle, wet carbon. For example, Rossi *et al.* [86] report that multifilament graphite fibres can be properly infiltrated by molten aluminium only after thorough removal of the contaminants by multiple chemical washings. Thermodynamically, SiC is very prone to oxidation and the surface of SiC fibres is always covered by a stable film of SiO_2. Wetting SiC fibres thus amounts to wetting an SiO_2 surface. Some SiC filaments are also heavily contaminated by carbonaceous species. It has therefore been proposed that, in order to provide good wettability, such filaments should be oxidized at high temperature so as to burn away contaminants and to form a stable, clean SiO_2 surface film [87].

Wetting is favoured by the formation of strong chemical bonds at the interface. Good wetting thus often also involves a good bond strength at the interface in the final composite. The formation of these bonds may be accompanied by mutual dissolution and/or reaction of the two bulk phases. The latter phenomena are very detrimental to the composite as they bring about a decrease of the mechanical properties. A compromise must therefore be found between the contradictory requirements of good wetting and absence of reaction. Carbon fibres tend to react too strongly with the metal by forming carbides (as soon as the contaminant layer that prevents wetting has disappeared). Alumina fibres are very stable but their wettability is poor. The best compromise between wetting and stability appears to be offered by SiC. The cause may be the presence of the SiO_2 film: this film seems to provide a barrier against reaction [84] and its wettability is reportedly high enough to make possible pressure infiltration of the bundle by aluminium without requiring wetting improvement recipes [12]. With reference to Section 4, the rather good wettability of SiO_2 by aluminium may be understood from the fact that SiO_2 is reduced by liquid aluminium [88]).

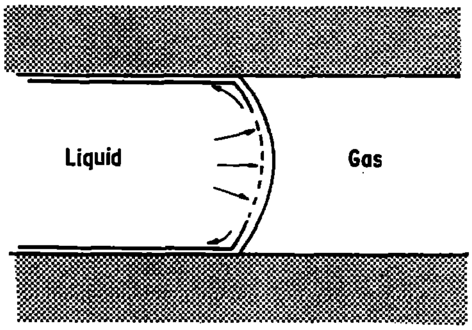

Figure 12 Possible diffusion path of components toward the interfaces during the infiltration of a capillary.

In order to avoid the inclusion of gas bubbles (a phenomenon that can be eliminated completely only when $\cos \theta = 1$), infiltration is often carried out under vacuum. However, the vacuum is never very high so that solid and liquid surfaces are covered by a layer of adsorbed gaseous molecules. In particular, electropositive metals such as aluminium, lithium and magnesium are always covered with an oxide layer which lowers wetting by preventing metal–solid contact. The presence of this oxide barrier probably contributes to the fact that uncoated multifilament carbon fibres cannot be satisfactorily infiltrated by aluminium, lithium or magnesium melts [9, 89, 90] even though these metals should, in principle, wet graphite (Section 4). In order to explain this phenomenon, one must assume that, when such a liquid metal penetrates through a capillary (Fig. 12), the oxide layer "slides" from the liquid–gas to the liquid–solid interface. The oxygen concentration in the surrounding atmosphere is probably usually high enough to cause the continuous restoration of the oxide layer at the liquid–gas surface. Indeed, a quantitative estimate performed by Cappleman *et al.* [91] suggests that the formation of a monolayer of oxide on the liquid aluminium surface can keep pace with the rapid infiltration of a network of fine, densely packed fibres.

During a non-equilibrium process, the interface tension γ_{sl} varies with time until equilibrium is reached (Fig. 3). One may wonder which value of γ_{sl} governs the process of infiltration. One may assume nearly instantaneous physical and chemical interactions between the components present at the surfaces which are brought into contact. Most of the arguments developed in the preceding sections thus apply. At the other extreme, the equilibration of bulk chemical potentials by reaction between the phases involves undoubtedly a much longer time than the time needed for completion of infiltration. Such a reaction will only affect the stability of the interface. As concerns adsorption, it might also be argued that infiltration occurs faster than the diffusion of components toward the interface. In such a case, infiltration would be little affected by additions to the melt. However, it may be speculated that, in a similar way as in Fig. 12, enough time is allowed for adsorption to occur at the liquid–gas surface; the enriched layer could then slide into contact with the solid. This hypothesis implies that the components that adsorb at the solid–liquid interface adsorb also at the liquid–vacuum surface. This suggests that the surface tension γ_{lg} of the liquid may have a larger influence than expected from the capillary model used in Section 2.

5.2. The use of coatings

As discussed in Section 3, liquid metals almost always wet solid metals and the wettability is the highest in the case of mutual solubility or formation of intermetallic compounds. Infiltration is thus made easier by the deposition of a metallic coating on the surface of the reinforcing solid.

The most frequently mentioned metal for such coatings is nickel [9, 17, 92–95]. Nickel coatings are especially used for aluminium composites. However, they have also been applied on reinforcements for titanium and nickel [95]. Nickel reacts strongly with aluminium to form stable intermetallic compounds ($NiAl_3$, Ni_2Al_3 etc). Wetting is thus excellent. The drawback is the brittleness of these compounds, which is detrimental to the mechanical properties of the composite.

Silver, copper and chromium coatings have also been proposed [9, 90, 94, 96–99]. Silver coatings can be conveniently formed by impregnation of the reinforcing network with a colloidal silver solution [96, 97]. The high solubility of silver in aluminium provides good wetting without involving the formation of brittle compounds [9].

For aluminium composites, an alternate method is the so-called sodium process developed by the Aerospace Corporation [17, 100]. This process (which has only been applied to carbon and alumina fibres) consists in immersing the fibres successively in liquid sodium at 550° C, in a tin–2% Mg bath at 600° C and then in the aluminium melt. The method may be rationalized on the basis of the previous sections. Sodium wets carbon and diffuses in the bulk by intercalating between the graphite planes. Being very electropositive, sodium should also wet alumina. As sodium is very soluble in liquid tin and forms intermetallic compounds with tin, the sodium coating makes possible the wetting of the fibre by tin (which would not directly wet carbon or alumina). In turn, the tin–sodium coating promotes wetting by aluminium. According to Goddard [100], the role of magnesium is to form high melting-point intermetallic compounds which help by stabilizing the coating during infiltration by aluminium. This may prevent dewetting of the surface (as the coating melts at a lower temperature than aluminium).

A completely different approach was proposed recently by Rocher *et al.* [101]. These authors report that the infiltration of liquid aluminium into an SiC network is highly facilitated by deposition of a fluoride compound (K_2ZrF_6). It is suggested that fluoride species cause the dissolution of the Al_2O_3 barrier as the liquid front propagates through the network.

The primary role of coatings is not always the enhancement of wetting. When reaction between fibre and metal is a major concern (which is especially the case with carbon), coatings were designed to provide a diffusion barrier. Such coatings usually lower wettability. The best solution is then the deposition of a second coating which promotes wetting. For carbon-fibre reinforced aluminium, titanium boride was proposed as a suitable protective coating; the wettability of this is high enough to make possible direct infiltration by the metal [17] (although other authors disagree on this latter point [99]). Coatings of tantalum, TiC, TiN and SiC have also been studied; an additional nickel coating was then necessary to provide satisfactory wetting [91]. B_4C coatings have been used for preventing degradation and promoting wetting of SiC filaments by aluminium [88]. The wettability of B_4C is, in principle lower than that of SiC (Section 4), but it may be higher than the wettability of the SiO_2 film.

5.3. The addition of alloying elements to the metal melt

Elements that have a high affinity for oxygen lower the interface tension of liquid metals with oxides. In the presence of oxidizing molecules, these elements also segregate toward the free liquid surface. Even in a perfect vacuum, the lower surface tension of molten alkali metals and alkaline-earth metals causes their surface adsorption.

The most efficient alloying element reported to promote the wettability of reinforcing networks is lithium. Lithium additions were mainly developed for composites reinforced by alumina fibres [10]. However, it appears that lithium is beneficial also for the impregnation of SiC and carbon fibres [102, 103]. On SiC fibres, the role of lithium may be understood from the existence of the SiO_2 film. On carbon, the primary role of lithium may be the weakening of the diffusion barrier created by the Al_2O_3 film covering liquid aluminium [82].

Apart from lithium, the only addition whose beneficial influence has been repeatedly reported is magnesium [75, 104–106]. The role of magnesium may be justified in a similar way as the role of lithium. Quite surprisingly, little other reliable information emerges from the open literature. Kimura *et al.* [107] have recently studied the dewetting of various aluminium alloy coatings deposited on carbon fibres by vacuum evaporation. These authors conclude that alloys containing indium, lead and thallium show excellent wetting behaviour. In fact, the experiment merely shows that dewetting is prevented because these elements lower the surface tension γ_{lv} of liquid aluminium.

6. Concluding remarks

The purpose of this review was to provide a reliable scientific basis for the engineer concerned with the design of liquid-metal infiltration methods. Although continuous progress is being made, one cannot refrain from the impression that, in many aspects, the present body of knowledge remains unsatisfactory. This is, for example, the case of the wetting of oxides by liquid metals: the phenomena appear qualitatively understood but the development of a comprehensive quantitative theory is still needed. Obviously, the difficulties arise from experimental constraints: perfect control of the composition and cleanliness of solid and liquid surfaces at high temperature is a formidable challenge.

Fundamental studies of the energetics of liquid metal–solid interfaces are usually based on contact angle measurements by the sessile drop method. This static method provides mainly data on the equilibrium properties. As discussed, infiltration is a dynamic process where non-equilibrium phenomena are likely to play a dominant role. For example, the extent of surface adsorption or the stability of diffusion barriers ought to be better understood. More fundamental studies should therefore be oriented toward wetting under dynamic conditions.

The chemical nature of the interface determines not only wetting but also the strength and stability of the interface. (As discussed, these properties are intricately related.) In order that this interface does not remain a "black box", it is mandatory to be able to characterize its nature, namely to detect the presence of oxide barriers or the segregation of bulk components. A more precise understanding of the thermodynamics of the interfaces therefore requires a more systematic use of modern microanalytical techniques such as the scanning transmission electron microscrope (STEM).

The major part of literature data on metal-matrix composites for structural applications deals with aluminium and aluminium alloys. The dissemination of information regarding metal-matrix composite manufacturing technology is specifically restricted in the USA since 1979 by the provisions of the United States Munitions Control List. It is thus possible that the publication of some important new developments is being delayed. There is little doubt that metal-matrix composites remain one of the fastest growing classes of advanced materials. This growth is reflected in the conspicuously large number of papers devoted to metal-matrix composites in the proceedings of the most recent conferences on composite materials [108, 109]. Work is likely to develop toward the use of magnesium, titanium and silicon matrices for which new manufacturing techniques will have to be designed. These techniques will probably be based on the same science of wetting presented in this review.

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