Transfer Processes at the Manufacture of Metal Matrix Composite Materials

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Abstract. The main elements of composite materials technological design consist of choosing the appropriate matrix/reinforcement systems and optimal thermodynamic conditions for ensuring compatibility during processing and operation. Composite material properties depend on the volumetric characteristics of components as well on the intensity of links between these components. Initially, the mass transfer takes place under unstable conditions in the liquid matrix and at the solid/liquid interface, and finally, after casting or infiltration, stationary. Modelling of reinforcement elements transfer from gas to liquid is based on total variation of transfer energy or on the variation of the amount of the forces acting on the reinforcement. Once the basis of the models investigated and of the actual model proposed are analyzed, the densities influences, particles granulations, liquid viscosity, thermal conductivities, the energies at liquid/reinforcement interface and critical speeds of reinforcement elements, transfer from liquid to solid.

1. Generalities
Composites are multiphase materials with distinct and well defined interfaces between the constituent phases which are strongly interrelated and it presents exceptional properties in well-defined directions and plans.

An important direction of research in these areas is to provide models to successfully predict if interactions of physical or chemical nature occur between matrix and reinforcement, as well as for the thermodynamic evaluation of the interfaces during processing and exploitation.

2. Physico-chemical processes at the matrix-reinforcement interface
Composites processing and its characteristic depend on the components density and the intensity of connections which are formed between them. According to Dupré’s relation, the adhesion energy, $W_a$, between two different phases can be evaluated in terms of the interfacial tension and contact angle:

$$W_a = \sigma_{SG} + \sigma_{LG} - \sigma_{SL} = \sigma_{LG} (1 + \cos \theta)$$

Where: $\sigma_{SG}$ is the solid-gas interfacial tension; $\sigma_{LG}$ is the liquid-gas interfacial tension; $\sigma_{SL}$ is the solid-liquid interfacial tension; \(\theta\) is the contact angle.

Chidanibaran et. al (1992), [1], consider that ceramics wettability by metals is achieved only if the chemical bond are formed between atoms of the two phases, totally ignoring the contribution of physical interactions. Chemical forces are much stronger and manifests themselves when the chemical
reaction between the atoms of liquid and non-metallic component, respectively, shows a negative variation of the free enthalpy. Type of chemical bond between metallic and non-metallic component structures has a particular importance because the transition layer’s structure and its mechanism of formation determine the crystallisation and hence the structure of the composite material.

The first model that tried to explain the metal-ceramic wettability was proposed by Mc Donald and Eberhart in 1965. It claims that between the chemical component of adhesion energy and the variation of metal-ceramics chemical reaction free energy a linear relation can be established in the form [2]:

\[ W_a(ch) = a - b \Delta G^o \]  \hspace{1cm} (2)

Where \( a \) is the contribution of the physical interactions, while \( b \) is a constant.

Experimentally it has been shown [3] that adhesion energy \( W_a \) does not depend on \( \Delta G^o \) when \( \Delta G^o > 300 \text{ kJ/mol} \). For \( \Delta G^o < 300 \text{ kJ/mol} \), the value of \( W_a \) increases with decreasing of \( \Delta G^o \).

Because the chemical reaction between some metals with high reactivity (such as Al) and ceramics is associated with a variation of the free energy smaller than 100 kJ/mol, we might conclude that they'll wet any solid material.

In reality, even in the most severe conditions of achievable depression an oxide layer is forming which will affect the wettability conditions. During the production of composite materials there are mechanisms of irreversible loss of energy during the processes of interface creation. These losses are sometimes very important and dictate the process parameters such as the applied pressure or preheating temperature of reinforcement elements. Under these circumstances, it is possible that a contact angle less than \( \pi/2 \) not be a sufficient condition for spontaneous wetting of ceramics during composite processing.

2.1. Physico-chemical processes at metal-oxide interface

In the case of non-metallic components consisting of oxides, adherence to melt improves with increasing the metal affinity to oxygen and oxygen concentration, respectively. If it is noted with \( \text{Me} \) the matrix metal and with \( \text{M} \) the oxide-bounded metal, then at the interface the next reactions occur:

\[ \text{y Me} + \text{M}_2\text{O} \leftrightarrow \text{Me}_y\text{O} + x \text{M} \quad \Delta G^o_1 \] \hspace{1cm} (3)

\[ \text{M}_2\text{O} \leftrightarrow x\text{M} + \frac{1}{2} \text{O}_2 \quad \Delta G^o_2 \] \hspace{1cm} (4)

\[ \text{Me}_y\text{O} \leftrightarrow \text{y Me} + \frac{1}{2} \text{O}_2 \quad \Delta G^o_3 \] \hspace{1cm} (5)

\[ \text{y Me} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{Me}_y\text{O} \quad \Delta G^o_4 \] \hspace{1cm} (6)

As well as dissolutions and mass transfer between the two phases:

\[ \text{M} \rightarrow [\text{M}]_{\text{Me}} \quad \Delta G^o_5 \] \hspace{1cm} (7)

If the free enthalpy variation is negative, the reactions arise in the normal direction, and adhesion energy will increase with the increasing of the absolute value of this variation. The sign of free enthalpy variation of the chemical Equation (3) is a criterion for assessing the metal-ceramic reactivity or non-reactivity. A more rigorous criterion for assessing interface chemistry takes into account that the dissolution of \( \text{M} \) in \( \text{Me} \) will always takes place and \( \Delta G_{1,5} \) is calculated with the Equation:

\[ \Delta G_{1,5} = \Delta G^o_1 + \Delta H_{\text{M(Me)}}^o \] \hspace{1cm} (8)
Where: $\Delta H_{M(Me)}^\infty$ is the partial entropy at infinite dilution of M into Me.

In metal-oxide systems, frequently used for the production of composite materials, the maximum dissolved amount is of the order of few parts per million. Such systems with $\Delta G_{15} > 0$ are known as non-reactive systems and are characterized by a weak and limited wettability. In this case the adhesion energy, $W_a$, represents only 15-40% of the metal cohesion energy [4], which is considered to be the $W_c \approx 2 \sigma_{ls}$. On the basis of the thermodynamic considerations, in 1987 Chatain et. al show that even for nonreactive metal-oxide systems, chemical interactions occurs at the interface and they propose an expression for the adhesion work [5]:

$$
W_a = -\frac{C}{N_0 V_{Me}^{2/3}} \left[ \frac{\Delta H_{0(Me)}^\infty}{\Omega_{Me}} + \frac{1}{S} \frac{\Delta H_{M(Me)}^\infty}{\Omega_{Me}} \right]
$$

Where: $\Delta H_{0(Me)}^\infty$ and $\Delta H_{M(Me)}^\infty$ are mixture partial enthalpies at infinite dilution of oxygen and oxide metal in the metal matrix; $N_0$ – Avogadro’s number; $V_{Me}$ – molar volume of liquid metal; C and S – are constants that depend only on the nature of the oxide substrate (for alumina C = 0,2 and S = 1.5 while for silica C = 0,2 and S = 2).

The product $N_0^{1/2} V_{Me}^{2/3} = \Omega_{Me}$ represents the area occupied by a monolayer of The product $N_0^{1/2} V_{Me}^{2/3} = \Omega_{Me}$ represents the area occupied by a monolayer of a mole of matrix metal atoms.

According to Equation (9) dissolution of oxygen in the matrix metal improves its adhesion to ceramics. On consider that the dissolved oxygen combines with the metal atoms and MeO clusters are forming, clusters with partially ionic character as a result of charge transfer from the metal to oxygen. Nowadays it is widely accepted the model proposed by Naidich [6] in 1981, which assumes that dissolved oxygen forms with nearby metal dipole $Me^{2+}$ $O^2-$ which is adsorbed to the interface due to electrostatic attraction forces exerted on the $Me^{2+}$ cation by the anions existing on the ceramic surface.

Improving adhesion in non-reactive conditions can be achieved by using immiscible alloying elements into the base metal, which reduce its surface tension. Thus, in the Al alloys, In, Bi, Cd, Na can be added, which are adsorbed at the surface, diffuse together with Al atoms in the ceramic surface and favour the adhesion.

2.2. Physico-chemical processes at the metal-carbon or metal-carbides interfaces
Carbon and carbides wettability by liquid metals can be analyzed by considering three chemical contributions [2]: Me metal affinity to carbon; formed $Me_xC_y$ carbide stability; mixing enthalpy of M in Me.

Liquid metal adhesion to carbon is strongly dependent on the reactivity between the two phases and it is slightly influenced by the crystallographic shape of the solid. An interdependence between metal’s position in Mendeleev’s table and their reactivity in respect to carbon was found. Metals from groups I-b, III-a, IV-a and V-a and periods 4, 5 and 6, like: Au, Ag, In, Ga, Ge, Sn, Pb, Sb, Bi are inert to carbon [7], have low adhesion energy, only 100 - 300 mJ/m² and the contact angle greater than $\pi/2$.

Elements: Al, Si, B, react and form carbides that wet the carbon, adhesion energy being 1000 ÷ 1500 mJ/m². Even in this case, wettability will practically occur only at temperatures above 900°C because the oxide films prevent direct contact between the two components.

Transition metals forming stable carbides are: Ti, V, Cr, Mn, Fe, Co, Ni from period 4, Zr, Nb, Mo, Pd from 5th period and Ta, W, Re, Pt from period 6. In their case the adhesion energy to carbon is 2000 ÷ 3000 mJ/m², increasing with the decrease of the number of electrons on the d layer. Adhesion energy between the metal matrix containing such elements and carbon is more than 90% due to the chemical interaction.

Alkaline, alkaline-earth and some rare metals, although diffuse in carbon components and form carbides, not always wet such particles or fibres [15-16].

Experimentally it was proved that Li and Na wet the graphite [17-18].
Through its influence on the nature and kinetics of metal-carbon interfacial reactions, temperature is a control parameter for wettability.

Nayeb-Hashemi and Seyyedi [8], in 1989, support the fact that the formation of rhombohedral crystalized aluminium carbide Al$_4$C$_3$ can occur in long time even at temperatures around 500°C.

Wang et. al [9] in 2015 after determining the activities and the contact angle, had been calculated the free enthalpy of reaction:

$$4[Al] + 3 C_{(s)} = Al_4C_3_{(s)}$$ \hspace{1cm} (10)

Using Equation:

$$\Delta G_2 = \Delta G_2^\theta + RT \ln \frac{a_{(Al_4C_3)}}{a_{(Al)^4}a_{(C)^3}}$$ \hspace{1cm} (11)

They have obtained a free enthalpy significant variation of aluminium carbide formation function by content of Mg from matrix Al alloy.

In Figure 1 it can be seen that up to approx. 10% Mg, the free enthalpy of reaction (10) is negative, so Al$_4$C$_3$ can form, but at higher concentrations occurs the decomposition of carbide.

To improve adhesion between the graphite’s fibres or particles and Al alloys based metal matrix, Ti or B coatings on carbon solid components were made. In this case, special measures are required to prevent titanium or boron oxidation, as well as to limit the interaction because the strong reactions increase the fragility and lead to the degradation of reinforcement.

Another measure to improve the adhesion of the aluminium metal matrix alloys and carbon or graphite reinforcement is microalloying with superficially active elements such as Mg, Li, Na or Sr.

In Figure 2, SEM and EDS investigations conducted by Anna J. Dolata et. al [10] in 2016 in AlSi7Mg2Sr0.03/SiC$_p$+C$_{gp}$ composites highlighted a good bond between matrix and reinforcement, as well as an increase in the concentration of the strontium and magnesium concentrations at the interface between matrix and glassy carbon.
Figure 2. The AlSi7Mg2Sr0.03/SiCp+Cgp composite: linear distribution of elements at the interface between Al matrix alloy and Cgp, EDS [10].

While Nayeb-Hashemi and Seyyedi [8] noted the formation of chemical compounds at interface: Al₄O₃C, Al₄C₃, other, Siemens [11], in 1989, highlights the dependence existing between carbide concentration and temperature, as it can be observed in Figure 3. Research has revealed that the interaction between metal matrix with reinforcement elements containing carbides is much weaker because of the high energy of carbides formation.

Wettability of solid carbides like: SiC, B₃C, etc. is similar as in the case of carbon because the metals generally have similar behaviour against these elements which forms the carbides.

Estimations made on the processes at the SiC-metal interface or on the link between the two phases are not yet theoretically and experimentally grounded. First, the nature and composition of the interface are not precisely known.

Figure 3. Variation of carbides concentration at the interface with metallic melt temperature [7].
Thus, in the case of Al-SiC interfaces, three hypotheses exist:
- a SiO$_2$ film forms at the interface [12];
- no interactions exist at interface, distinct areas being one of SiC and another of Al [13];
- an Al$_4$C$_3$ film forms at the interface [4];

**Figure 4.** The AlSi7Mg2Sr0.03/SiC$_p$+C$_{gp}$ composite: linear distribution of elements at the interface between Al matrix alloy and SiC$_p$, EDS [10].

In the case of Al-Mg alloys an MgO film may form at the interface, as it is deduced from Figure 4.

3. **Conclusion**

The theoretical study at atomic level of the interface is too complex due to reduced symmetry, high number of atoms in the elementary cell and complications that occur when trying to use interatomic potentials along the interface.

Li and Arsenault [14] in 1988, claim that for a good understanding of the bond at interface it is necessary to take into consideration the following:
- a. interface may consist of areas with different aluminium and silicon carbide crystallographic orientations;
- b. SiC has two different structures: $\alpha$ and $\beta$; whiskers have $\beta$ structure, and particles have $\alpha$ structure which may be in six polymorphic forms;
- c. interface can be form between carbon and aluminium films or between Si and Al;
- d. at the interfaces formed with different orientations between SiC and Al, the atoms cannot form a commensurable structure, i.e. it is a network mismatch at the interface;
- e. it is expected that at the interface atoms move in positions of minimum energy, but there is no experimental or theoretical studies confirming this.

Eustathopoulos and Mortensen [4] in 1993 supports the idea of slow decomposition of SiC, the enrichment of aluminium in Si and C at the interface and formation of fine and flat particles of Al$_4$C$_3$. To verify this hypothesis, large additions of Si and Al have been made, finding an increase of SiC thermodynamic stability and a reduction of Al$_4$C$_3$ formation. Wettability kinetics is limited by the
dissociation velocity of SiC and the stationary value of contact angle is reached when Al surface layers are saturated in Si and C. The initial angle of 160° is due to Al₂O₃ film on the Al surface.

![Figure 5](image_url)

**Figure 5.** Variation of contact angle θ with time t, for Al-18%Si alloy with SiC, at 800°C under vacuum of 10⁻⁵Pa [7].

The real value of θ for Al-SiC is 120°, and after a three-hour contact angle θ decreases to 60°. Improvement of silicon carbide wettability by the Al is obtained by Li addition, which is a superficially active element, and Cu addition, which easily dissolves Si. Much stronger the interatomic links of carbides are, much higher the interphase energy is and a lower degree of wetting is obtained. Since the formation heat of B₄C is higher than that for SiC forming, the contact angle formed with an Al melt is 120° and 106.3°, respectively, at a temperature of 700°C.

4. References

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