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Models describing the interaction of particles with a plane solid/liquid interface

D. COUPARD, F. GIROT*, J. M. QUENISSET*
*Laboratoire de Génie Mécanique (I.U.T. "A"), Université Bordeaux I, *and also Laboratoire de Chimie du Solide (CNRS) 351, Cours de la Libération, 33405 Talence Cedex, France*

Various models depicting particle engulfment or rejection in contact with a plane organic solidification front have been examined and their predictions compared with the experimental results for six particle/matrix systems. The directionally solidified composites were made of different kinds of particles such as nylon, teflon or polystyrene dispersed within biphenyl or naphthalene matrices. The thermodynamic and thermal approaches achieve a good agreement with the experimental results for low solidification rate and particle volume fraction. In order to make the particle engulfment or rejection modelling more complete, a kinetic approach has been developed considering a critical interface velocity above which particles are engulfed and below which particles are pushed. Unfortunately, the related model did not allow the behaviour of particles in front of a plane solid/liquid interface to be successfully predicted.

Nomenclature

C_P	particle specific heat
C_L	liquid specific heat
a_0	atomic spacing
V_0	atomic volume
kT	Boltzman factor
L	heat of solidification
r_P	particle radius
V_C	critical velocity
V_y	solidification rate
λ_L	liquid thermal conductivity
λ_P	particle thermal conductivity
ρ_L	liquid density
ρ_P	particle density
σ_{PL}	particle/liquid interfacial energy
σ_{PS}	particle/solid interfacial energy
ΔG_{net}	change in free energy for engulfment
k	constant
A	empirical constant
b	empirical constant
D	diffusion coefficient of the liquid
n	constant depending on the particle/ matrix system

1. Introduction

Liquid-state processing of MMCs using foundry technics would be of interest to produce high-performance materials for the automotive industry, if a perfect homogeneity in reinforcement distribution was able to be reached. To date, this phenomenon, resulting from sedimentation or rejection of the reinforcement at the solidification front, is well known to control the as-cast properties of the composites prepared by rheocasting or liquid state processing and cast into permanent or sand moulds. Investigating the influence of holding time and solidification conditions on both the significance of sedimentation and the behaviour of the reinforcement at the solid/liquid interface appears to be useful to give MMCs higher mechanical properties. Until now, the engulfment or rejection of a reinforcement by a plane metallic interface has not been investigated, despite some studies devoted to the behaviour of particles in front of a plane organic interface.

In this work, the related approaches which tend to point out the significance of only some of the parameters involved in the phenomenon, are described, and their limitations specified, in view of a presumable use for predicting the behaviour of short fibres in front of a plane metallic interface.

2. The thermodynamic model

The basic idea related to the thermodynamic analysis consists of calculating the change in free energy of the particle, liquid and solid system for the process of engulfment. If the change in free energy, ΔG_{net}, is negative, i.e. the free energy of the system decreases, then particle engulfment is expected to occur spontaneously. Otherwise, if ΔG_{net} is positive, the particle is rejected by the plane solid/liquid interface. The present model, developed by Omenyi and Neumann [1], defines the change in free energy, ΔG_{net}, as follows

$$\Delta G_{net} = \sigma_{PS} - \sigma_{PL} \tag{1}$$

where σ_{PS} and σ_{PL} are, respectively, the particle–solid and particle–liquid interfacial energies. Omenyi and

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TABLE I Comparison between the predictions related to the Omenyi–Neumann [1], Zubko *et al.* [4], Rohatgi *et al.* [5] models and experimental results

Matrix/particle system	ΔG_{net} (J m^{-2})	Omenyi–Neumann prediction [1]	$\frac{\lambda_P}{\lambda_L}$	Zubko prediction	$\left(\frac{\lambda_P C_P \rho_P}{\lambda_L C_L \rho_L}\right)^{1/2}$	Rohatgi prediction	Experimental results
Biphenyl/teflon	-2.6	Engulfment	1.4	Engulfment	1.53	Engulfment	Engulfment
Biphenyl/polystyrene	-0.1	Engulfment	0.9	Rejection	1.01	Engulfment	Engulfment
Biphenyl/nylon	$+2.5$	Rejection	0.04	Rejection	0.19	Rejection	Rejection
Naphthalene/teflon	-2.7	Engulfment	1.3	Engulfment	1.53	Engulfment	Engulfment
Naphthalene/polystyrene	-0.4	Engulfment	0.9	Rejection	1.05	Engulfment	Engulfment
Naphthalene/nylon	$+2.1$	Rejection	0.04	Rejection	0.2	Rejection	Rejection

Neumann investigated the engulfment or rejection of various particles, including teflon, polystyrene and nylon, by biphenyl or naphthalene organic matrices. For each system, the predictions were in good agreement with the experimental results, as illustrated in Table I, indicating that the related approach is satisfactory for predicting the behaviour of particles in front of a plane solid/liquid interface moving slowly, i.e. a few micrometres per second [2, 3]. Unfortunately, the thermodynamic model is quite restricted, considering the problems related to the valuation of ΔG_{net} in some other systems. For instance, the experimental assessment of σ_{PL} concerning particles in contact with liquid aluminium, may give rise to doubtful results, knowing the intense oxidation of this kind of material. Thus investigations were undertaken to develop an easier approach, involving more readily available properties of materials.

3. The thermal conductivity criterion

The thermal conductivity criterion is an empirical relation based on the thermal characteristics of materials, for predicting the particle engulfment or rejection by a plane growing front. The present approach, introduced by Zubko and colleagues [4, 5], suggests absorption when the particle to liquid thermal conductivity ratio is greater than 1 in accordance with the following relation

$$\frac{\lambda_P}{\lambda_L} > 1 \tag{2}$$

This criterion, which is expected to replace the thermodynamic model, can only be used for slow growth rate, i.e.

$$V_y < \frac{\lambda_L}{k r_P} \tag{3}$$

where V_y is the solidification rate, r_P the particle radius and k a constant equalling $1\,\text{J m}^{-3}\,\text{K}^{-1}$. The physical basis for this equation arises from the investigation of the thermal field at the solid/liquid interface around a particle of various thermal conductivities. Thus, when $\lambda_P/\lambda_L > 1$, the heat flow through the particle is greater than the heat flow in the liquid, as a result of which a crater appears beneath the particle, leading to particle engulfment (Fig. 1). Otherwise, if $\lambda_P/\lambda_L < 1$, the heat flow decreases at the solid/liquid interface, modifying its curvature towards a convex form and leading to particle rejection.

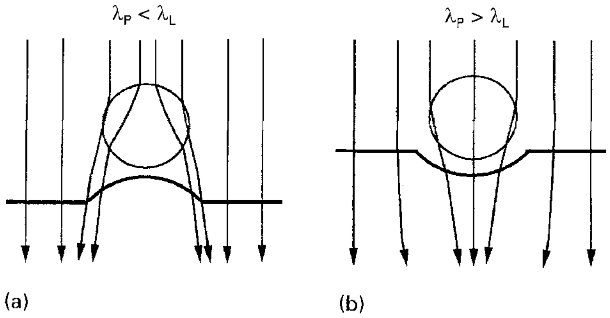

Figure 1 Heat flow at the solidification front for (a) particle rejection and (b) engulfment.

The predictions based on the thermal conductivity criterion have been compared with the experimental observations of Omenyi and Neumann [1] as illustrated in Table I. According to the related results, the present approach is able to predict successfully most types of particle behaviour, except for the naphthalene/polystyrene and biphenyl/polystyrene systems. Obviously, this deviation between the predictions and the experimental results arises when the particle and liquid thermal conductivities are similar (Table I). Thereby, a modified analysis has been suggested by Rohatgi *et al.* [5] to optimize the theoretical predictions when the particle-to-liquid thermal conductivity ratio is close to 1.

4. The thermal diffusivity criterion

The thermal diffusivity criterion proposed by Rohatgi and Surappa [6, 7] is expected to improve the predictions given by the previous approach when the particle and liquid thermal conductivities are similar. The present analysis gives rise to an empirical relation allowing particle engulfment to be predicted as follows

$$\left(\frac{\lambda_P C_P \rho_P}{\lambda_L C_L \rho_L}\right)^{1/2} > 1 \tag{4}$$

where C and ρ are, respectively, the specific heat and the density. It is noteworthy that this relation can only

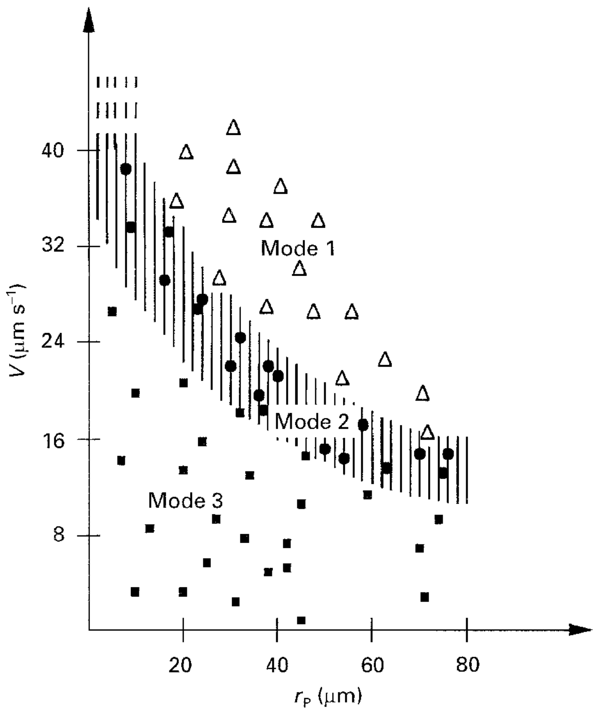

Figure 2 Engulfment or rejection velocity versus the particle radius related to the naphthalene/nylon system. (△) Engulfment, (●) engulfment followed by rejection, (■) rejection.

be used for low solidification rates, as expected from Equation 3. According to Table I, the predictions based on the thermal diffusivity criterion are in complete agreement with the experimental results of Omenyi and Neumann [1], particularly on both the naphthalene/polystyrene and biphenyl/polystyrene systems. Consequently, the empirical analysis developed by Rohatgi and Surappa [6, 7] is a simple indicator for predicting particle engulfment or rejection by a plane organic interface at low solidification rate. However, the present approach, as well as that developed by Zubko *et al.* [4], is only based on thermal aspects occurring at the solid/liquid interface and does not take into account various other parameters which may influence the behaviour of particles in front of a solidifying front. For instance, the particle volume fraction, V_F, is expected to act as an influencing parameter, because the drag force resulting from pushing may increase with V_F, leading to engulfment while rejection was predicted. The related phenomenon has been pointed out by Omenyi and Neumann [1] concerning the behaviour of the nylon particles. Considering a low volume fraction, the particles were first rejected as expected from the predictions, until a critical value was reached above which particles were engulfed. Thereby, a more complete modelling of the engulfment/rejection phenomenon should include the related parameter to obtain better predictions. The solidification rate, V_y, may also influence the particle engulfment or rejection because increasing V_y is known to induce a greater drag force, able to modify the behaviour of a particle. According to the experimental results on naphthalene/nylon and biphenyl/nylon systems, Omenyi and Neumann [1] predict three kinds of behaviour of the nylon particles with regard to the solidification rate. For high values of the related parameter, the nylon particles are immediately engulfed, while particles are rejected for slow growth rate, as expected from the predictions and results reported in Table I. For intermediate interface velocities, the nylon particles are first pushed and suddenly captured. Moreover, the transition between engulfment and rejection depends on the particle radius, r_P, as a result of which the related parameter may also act as an influencing characteristic (Fig. 2). According to these observations, Omenyi and Neumann [1] suggested that a critical interface velocity, V_C, corresponding to the intermediate zone of Fig. 2, and depending on various parameters such as the particle radius, was a rather good indicator, which can be defined as

$$V_C = \frac{A}{r_P^b} \tag{5}$$

where A and b are empirical constants depending on the particle/matrix system. This preliminary kinetic approach of the engulfment/rejection phenomenon has been improved by Uhlmann *et al.* [8], whose analysis is presented in the following section.

5. The Uhlmann, Chalmers and Jackson model (UCJ) [8]

The present model assumes that a particle is (i) pushed in front of the solid/liquid interface when the sum of the particle–liquid and liquid–solid interfacial free energies is less than the particle–solid interfacial free energy, and (ii) incorporated in the solid if a liquid matrix cannot diffuse sufficiently quickly to the growing solid beneath the particle. According to the preliminary kinetic approach, the UCJ model introduced a critical interface velocity, V_C, above which particles are engulfed and below which particles are rejected by the front. The related critical velocity is defined as

$$V_C = \frac{(n+1)La_0V_0D}{kTr_P^2} \tag{6}$$

where L is the latent heat of solidification of the matrix per unit of volume, a_0 the atomic spacing, V_0 the atomic volume, D the diffusion coefficient of the liquid matrix, kT the Boltzman factor and n a constant approximately equal to 5, depending on the particle/matrix system.

The validation of the present model has been achieved on two systems, i.e. xylene or graphite particles in a water matrix. The experimental critical velocities reported in Table II point out a complete disagreement with theoretical values, indicating that the model is unsuited for predicting particle engulfment or rejection by plane interfaces. It is not surprising that this deviation resulted from an assumption suggesting similar particle, liquid and solid thermal conductivities. Indeed, it has been shown by Zubko *et al.* [4] and Rohatgi and Surappa [5, 6], that those

TABLE II Theoretical and experimental critical interface velocity related to the water/xylene and water/graphite systems

Matrix/particle system	Theoretical critical interfacial velocity ($\mu m\,s^{-1}$)		Experimental critical interfacial velocity ($\mu m\,s^{-1}$)
	$r_P = 1\ \mu m$	$r_P = 2\ \mu m$	
Water/xylene	2.5	0.6	13
Water/graphite		0.6	20

characteristics were able to strongly influence the behaviour of particles in front of a plane organic interface. Moreover, it seems quite relevant to assess the phenomenon related to the supply of liquid in the region of contact by means of the fluid mechanics, instead of introducing the unknown diffusion coefficient for the liquid matrix between the particle and the solid.

6. Conclusion

Although the thermodynamic analysis is in good agreement with the experimental results of Omenyi and Neumann [1], two empirical criteria have been proposed to predict the particle engulfment or rejection by means of more readily available parameters. The thermal conductivity criterion defined by Zubko *et al.* [4] enables the particle behaviour in front of a plane solid/liquid interface to be assessed at a low solidification rate, except when the liquid and particle thermal conductivities are similar. Thereby, the thermal diffusivity criterion was suggested by Rohatgi and co-workers [5] and allowed the inaccuracy of the previous approach to be corrected. Although this criterion is satisfactory for predicting the behaviour of particles within the investigated systems at low solidification rate and particle volume fraction, Omenyi and Neumann pointed out the significance of these two influencing parameters regarding the related phenomenon with the result that a more complete approach was needed. Thus, a kinetic analysis, defining a critical interface velocity above which particles are engulfed and below which particles are pushed, has been developed taking into account some of the physical characteristics of particles and matrix. However, experimental results showed that this model has failed to predict the particle behaviour at a plane solid/liquid interface. Finally, according to these observations, there is a need to develop a new analytical model which includes most effects involved in the related phenomenon such as the different thermal characteristics of particle, liquid and solid, particle volume fraction, thermal gradient or reinforcement geometry.

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