REACTIVE WETTING BETWEEN MOLTEN AL ALLOY AND CERAMIC PARTICLES

REAKCIJSKO OMAKANJE KERAMIČNIH DELCEV Z RAZTALJENIMI ALUMINIJEVIMI ZLITINAMI

VARUŽAN M. KEVORKIJAN

Independent researcher, Lackova 139, 2341 Limbuš, Slovenia

In this paper, the linear time dependence and the exponential temperature dependence of the volume fraction of ceramic reinforcement immersed in the matrix was addressed theoretically. Applying the same theoretical approach to the dynamics of the reactive infiltration of molten aluminum into porous ceramic preform, the parabolic relation between the infiltration length and time as well as the exponential relation between the infiltration length and temperature were also derived. It was demonstrated that the rate of reactive wetting and the dynamics of reactive infiltration of molten aluminum into porous ceramic preform depend on the exergonic nature of the interfacial reaction, the kinetics of the interfacial chemistry involved and the efficiency of the system in using the energy released by the interfacial chemical reaction for the formation of new surface in the melt.

Key words: metal matrix composites, modeling of wetting, wetting

V članku je predstavljen model reakcijskega omakanja keramičnih delcev v raztaljeni aluminijevi zlitini. Pokazali smo, da je hitrost omakanja delcev s talino odvisna od termodinamskih značilnosti kemijske rekacije na fazni meji keramika-talina, od njene kinetike ter od energijskega izkoristka, oz. od zmogljivosti sistema, da uporabi energijo, sporščeno s kemijsko rekacijo, za nastanek nove površine med keramičnimi delci in talino. Teoretično smo napovedali, da je prostorninski delež keramičnih delcev v matrici linearno odvisen od časa omakanja ter da eksponentno narašča s povečevanjem temperature taline. Pokazali smo tudi, da hitrost omaknja keramičnih delcev s talino ni na splošno premo sorazmerna z hitrostjo kemijske reakcije na fazni meji keramika-talina, saj ima hitro sprošščanje energije kemijske reakcije običajno za posledico nizek energijski izkoristek. V drugem delu članka smo, na podoben način, teoretično modelirali proces reakcijske infiltracije poroznega keramičnega skeleta z raztaljeno aluminijevo zlitino. Potrdili smo, da obstaja parabolična odvisnost med dolžino infiltriranega dela vzorca in časom. Hkrati nov model napoveduje, da na hitrost infiltracije vplivajo še kinetika in termodinamske lastnosti kemijske reakcije na meji med keramiko in kovino. Iz modela je jasno, da ima energijski izkoristek kemijske reakcije na meji med keramiko in kovino tudi v tem primeru pomembno vlogo, še posebej, ko obstaja zahteva po čim hitrejši infiltraciji vzorcev.

Ključne besede: kompoziti s kovinsko osnovo, termodinamski model omakanja keramičnih delcev s talino, omakanje

1 INTRODUCTION

Because of the great technological importance of liquid processing of DR MMCs[1], especially for the next generation of vehicles, it is important to develop a predictive model of reactive immersion (i.e. immersion activated by an interfacial chemical reaction) of ceramic particles into a molten metal.

Another very popular near-net-shape production technology for manufacturing metal/ceramic composites is pressureless infiltration of the molten metal into a porous ceramic preform[2]. Notwithstanding much theoretical and practical work performed in this area, the emerging theoretical formulation of the conditions for spontaneous and rapid pressureless infiltration could substantially accelerate further industrial application of this production technique.

2 MODELING OF REACTIVE IMMERSION

The primary consideration by liquid processing of discontinuously reinforced metal matrix composites (DR MMCs) is whether the fine ceramic particles previously introduced into a melt will remain stable dispersed in the liquid metal without significant changes in their chemical composition or will be rejected. Note that in many cases, a spontaneous and almost quantitative rejection of ceramic reinforcement, from the melt occurs and its result is a catastrophic failure of liquid processing of DR MMCs.

Figure 1 represents schematically an isolated ceramic phase ideally spherical with volume V(R) and surface area S(R) which is completely immersed into a melt. Alternatively, one can suppose that the volume and the surface area of the ceramic phase presented in **Figure 1** are both in fact equal to the sum $\tilde{n}V_j$ and $\tilde{n}S_j$ of the large number of fine ceramic particles dispersed into the melt. Simultaneously, with the process of immersion, a fast interfacial chemical reaction also can occurs and, as a result, a thick layer of the new ceramic phase with volume V(P) is grown at the interface. The reaction front is localized in the reaction layer with the volume $V(P_i)$. It should be kept in mind that the chemical reaction at the interface is selected to be very rapid and proceeds faster than mass flow through the interfacial boundary layer. Accordingly, one can consider such a process of reactive wetting under chemical equilibrium conditions.

Generally, the immersion of ceramic phase is thermodynamically possible only if the energy released by the interfacial chemical reaction is sufficient for the formation of the new surface between the immersed particles and the melt. Therefore, an exergonic interfacial reaction
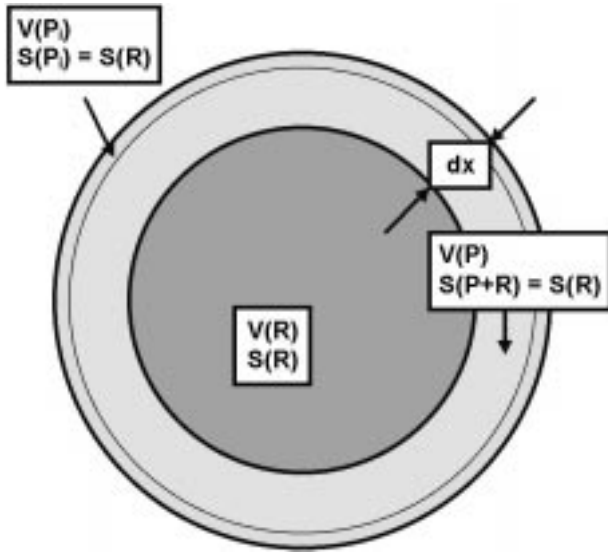
Figure 1: Ceramic reinforcement with volume V(R) and surface area S(R)
Slika 1: Shema keramičnega delca s prostornino V(R) in specifično površino S(R)

(i.e. chemical reaction with the negative Gibbs free energy) should be selected to promote wetting in the system. For the process of reactive wetting performed in real time, it is also important that the growth of surface layer to the critical thickness is fast enough to be accomplished during the time of immersion (i.e. before the melt rejects the particles). Based on this, the kinetics of the selected interfacial reaction also becomes very critical.

Let $\Delta G_r^\#$ (J/mol) represents the free energy per one mol of products of interfacial chemical reaction released during the complete chemical conversion, V(P) the volume of ceramic phase formed at the interface **(see Figure 1)**, S(P) the surface of immersed ceramic phase, T_0 the temperature of the melt before immersion, T* the temperature of the melt after immersion, and T_i the local temperature at the interface. Based on this, one can write:

$$\Delta G_r^\# V(P)\rho(P)/M(P) = \gamma_{sl}S(R) + V(P_i)\rho(P_i)c(P_i)(T_i\text{-}T_0) +$$
$$V(M)\ \rho(M)c(M)(T^*\text{-}T_0) + V(P)\rho(P)c(P)(T^*\text{-}T_0) +$$
$$V(R)\rho(R)c(R(T^*\text{-}T_0) \qquad (1)$$

where ρ is density, γ_{sl} solid-liquid interfacial energy, M molar mass, c specific heat capacity and symbols P, P_i, R and M are used to denote products, products at the interface, reactants and melt, respectively. Note that the term product refers to the new ceramic phase formed during the interfacial reaction, product at the interface means the interfacial layer of the new ceramic phase, reactant represents the raw ceramic powder introduced into the melt and the term melt denotes the molten metal without ceramic particles.

Thermodynamically, Eq. 1 represents the sum of different energy terms:

$\Delta G_r^\#$ V(P)ρ(P)/M(P) is the energy released by the interfacial chemical reaction; V(P)ρ(P)/M(P) represent the number of moles of product formed at the surface of the reactant. Note that V(P) - the volume of product layer - is time dependent and it is diffusion controlled.

γ_{sl}S(R) is the energy for the formation of the new surface in the liquid metal. One can assume that the surface of reactant covered by the product layer, S(R+S), is approximately equal to the surface of uncovered reactant, S(R). Finally, the surface of uncovered reactants can be expressed as follow: S(R) = S_0(R)ρ(R)V(R).

$V(P_i)\rho(P_i)c(P_i)(T_i\text{-}T_0)$ is the energy for local heating of the interface to the temperature T_i which is usually higher than the temperature inside the product layer or inside the melt.

The last three terms in Eq. 1 represent also energies necessary for the heating of different parts of the system (melt, product layer and reactants, respectively) to the final temperature of the melt.

Based on this, it is evident that only a part of the free energy of the system released by the interfacial chemical reaction affects the interfacial energy of the ceramic phase, γ_{sl}. This share of energy can be expressed by $\eta\Delta G_r^\#V(P)\rho(P)/M(P)$, where η represents the efficiency. In this way, one can write:

$$\eta\Delta G_r^\#V(P)\rho(P)/M(P) = \gamma_{sl}S(R) \qquad (2)$$

Note that S(R) = χV(R) where χ is a geometrical parameter (e.g. for a spherical particle, χ = R/3 where R is the radius of the particle). Hence, one can write: V(P)/V(R) = $[\gamma_{sl}M(P)]/[\eta\Delta G_r^\#\rho(P)\chi]$.

Taking into account that V(P) = S(R+P)x = S(R)x with x as thickness of the product layer, the following relation can be derived:

$$x = [\gamma_{sl}M(P)]/[\eta\Delta G_r^\#\rho(P)] \qquad (3)$$

According to Eq. 3, it is evident that the interfacial energy of the newly formed ceramic layer is influenced by the thickness of the product layer, x and by the free energy of the interfacial chemical reaction, $\Delta G_r^\#$. Here x represents the critical thickness of product layer which enables the successful incorporation of ceramic particles into the melt. In this way, x and γ_{sl} are time dependent parameters, while $\Delta G_r^\#$ is constant. Of course, this assumption is valid only if the rate of the interfacial chemical reaction is faster than the rate of diffusion through the product layer. Based on this, the conversion of reactants at the reaction front is complete. However, the movement of the reaction front through the bulk of non-reacted reactants is diffusion controlled and can be described by the unreacted core model. In this way, the basic assumption that the interfacial chemical reaction is very fast does not mean that the process of reactive wetting is not time dependent. In that particular case, the rate of reactive wetting is determined by the mass flow through the reaction layer, as the rate controlling step. Theoretically, the rate of reactive wetting w_w is the per-

manent mass or volume flow of reactants which can be introduced into the melt without rejection:

$$w_w = m(R)/[(tm(M)] = V(R)\rho(R)/[(tV(M)\rho(M)] =$$
$$= n(R)M(R)/[tn(M)M(M)] \qquad (4)$$

where $m(R)$ represents the mass of reactants introduced into the melt and $m(M)$ the mass of molten metal.

Assuming that the growth of the product layer is a diffusion-controlled process[3], one can write:

$$x = k\, t^{1/2} \qquad (5)$$

where t represents the time of immersion.

The growth of the interfacial layer is a thermally activated process, and the growth rate (k) is strongly temperature dependent. This temperature dependence can be described by the following expression:

$$k = k_0 \exp(-E_a/2RT) \qquad (6)$$

with k_0 as the frequency factor and E_a the activation energy for layer growth.

Combining Eqs. 3 and 5 one can calculate the time necessary for the immersion of n mols of products:

$$t^{1/2} = [\gamma_{sl} M(P)]/[\eta \Delta G_r^{\#} k\, \rho(P)] \qquad (7)$$

Since $w_w = n(R)M(R)/[t\, m(M)]$ and taking into account that $n(R)/n(P) = \eta\, \Delta G_r^{\#} \zeta\, \rho(R)/[\gamma_{sl}M(R)]$, the rate of reactive wetting can be expressed as follows:

$$w_w = n(R)\, M(R)/[tm(M)] =$$
$$= [n(P)/t]\eta[\Delta G_r^{\#}\zeta\rho(P)/[\gamma_{sl}m(M)] \qquad (8)$$

Note that $n(P)/[tm(M)]$ corresponds to the rate of the chemical conversion at the interface, and η is the efficiency with which the free energy $\Delta G_r^{\#}$ released by the chemical reaction can be used for the formation of new surface in the melt. Assuming that the number of moles of product $n(P)$ formed at the interface corresponds to the thickness of the product layer x, and is diffusion controlled, one obtains: $n(P)/t \propto x/(k^2x^2) \propto k^2/x$ with k as defined by Eq. 6. According to Eq. 3, one can finally derive: $n(P)/[t\, m(M)] \propto k^2\eta\, \Delta G_r^{\#} \rho(P)/[\gamma_{sl}M(P)]$.

In this way, Eq. 8 can be rewritten as follows:

$$w_w = V(R)\, \rho(R)/[tm(M)] \propto e^{-Ea/RT}\, \eta^2\, [\Delta G_r^{\#}/\gamma_{sl}]^2 \qquad (9)$$

This theoretical prediction indicates that a constant processing temperature should result in a constant wetting rate. Moreover, the volume fraction of ceramic reinforcement dispersed in the matrix should increase linearly with the time of immersion and exponentially with the temperature of melt.

These theoretical predictions can be easily tested in practice, as will be demonstrated in future work.

Unfortunately, the thermodynamical formalism applied can not predict the maximal concentration of ceramic particles successfully incorporated into a melt. By applying the model, one can only predict the maximal wetting rate at which rejection will not occur.

For a practical use of the model, the efficiency η, the specific surface energy γ_{sl} of the product layer, and the

activation energy, E_a for the selected interfacial reaction should be all known. The efficiency η can be estimated for those systems for which experimental values of γ_{sl} and $\Delta G_r^{\#}$ are available. By TEM and SEM inspection of the product layer formed on the surface of the ceramic particles during immersion, one can also determine the average value for x. Based on this, one can now calculate the efficiency using Eq. 3. It was found that the value of η lies between 10^{-4} and 10^{-3}. It seems that only a small amount (0.01-0.1%) of the energy released by the interfacial reaction can be transformed into the energy of the new surface created during immersion.

The measurement of γ_{sl} is difficult and it is more convenient to estimate its value on the basis of thermodynamic considerations[4,5]. For example, in the simple thermodynamic model suggested by Warren[4], the value of γ_{sl} for pseudo-binary systems in contact with liquid metal is correlated with the melting point temperature of the ceramic species, T_m, the molar volume of the compound, V_M (cm^3) and the number of atoms in the molecule, by the following relation: $\gamma_{sl}^{\#} = kT_m/b(V_M/b)^{2/3}$; where k is an empirical constant between 5×10^{-4} and 8×10^{-4}.

3 WETTING ASSISTED PRESSURELESS INFILTRATION - THEORETICAL CONSIDERATION

Spontaneous infiltration of a liquid into a porous medium is probably caused by the negative capillary pressure generated at the infiltration front as a result of the enhanced wetting between the molten alloy and the solid preform. Otherwise, external pressure should be applied which results in the pressure-assisted infiltration process.

The only appreciable difference between the initial state (metal and ceramic particles surrounded by the atmosphere) and the final state (the composite) from an energy point of view is the replacement of the ceramic/atmosphere interface by the ceramic/liquid metal interface, including possible chemical changes at the interface. The energy W released by the process is:

$$W = -P\, \Delta V \qquad (10)$$

where ΔV is the volume over which the metal was displaced and P is the pressure drop at the infiltration front.

In order to achieve spontaneous infiltration, the energy necessary for the movement of the infiltration front should be equal to the energy released by the chemical reaction:

$$W = P\, \Delta V = \eta \Delta G_r^{\#}\, V(P)\, \rho(P)/M(P) \qquad (11)$$

Taking into account that $V(P) = S(R+P)\, x = S(R)\, x$, with x as the thickness of the product layer defined by Eq. 5, one can write:

$$P\, \Delta V = \eta \Delta G_r^{\#}\, S(R)\, k\, t^{1/2}\, \rho(P)/M(P)$$

with t as the infiltration time.

The volume fraction of metallic phase penetrating into a ceramic network is equal to the relative volume fraction of the voids, w:

$$\Delta V = (1-w)^{-1} \, wV \qquad (12)$$

where V is the volume of the preform.

For the pressure drop at the infiltration front one can derive:

$$P = [\gamma_{sv} - \gamma_{sl}] \, (1-w) \, w^{-1} \, \rho \, S^o \qquad (13)$$

where ρ is the density of the ceramic network and S^o the specific surface area.

Finally, by combining Eqs. 11, 12 and 13, the infiltration dynamics can be described as follows:

$$L \propto \eta \Delta G_r^{\#} k t^{1/2} \qquad (14)$$

As expected, the expression derived indicates a parabolic relationship between the infiltration length and time. However, Eq. 14 also predicts the influence of the kinetics, the exogonic nature and the efficiency of the interfacial reaction on the infiltration dynamics. As will be demonstrated in future work, the influence of these parameters on infiltration dynamics can be also experimentally monitored and compared with the above theoretical prediction.

4 CONCLUSION

According to the suggested model, the rate of reactive wetting and the infiltration length are both affected by the exergonic nature and the kinetics of the interfacial reaction. However, the importance of the additional parameter named the efficiency of the system in transforming the energy released by the interfacial chemical reaction to the energy of the new ceramic-molten metal interface was also emphasized.

As a rule, the efficiency of an interfacial reaction decreases with increase of reaction rate and its exergonic nature. Based on this, it was predicted that a very rapid and exergonic interfacial reaction will result in only a modest improvement in the rate of reactive wetting and infiltration.

Experiments and theoretical analysis, such as described here, are in progress for purposes of achieving higher rates of immersion and more rapid spontaneous infiltration.

5 REFERENCES

[1] D. J. Lloyd, *Int. Mat. Rev.*, 39 (1994) 1

[2] M. K. Aghajanian, M. A. Rocazella, J. T. Burke, and S. D. Keck, *J. Mater. Sci.*, 26 (1991) 447

[3] Z. Fan, Z. X. Guo and B. Cantor, *Composites Part A*, 28A (1997) 131

[4] R. Warren, *J. Mater. Sci.*, 15 (1980) 2489

[5] N. Eustathopoulos, *Inter. Met. Rev.*, 28/4 (1983) 189