

STABILISATION IN AND REJECTION OF CERAMIC PARTICLES FROM MOLTEN Al ALLOY- MODELLING AND EXPERIMENTAL TESTING

STABILNOST SUSPENZIJE KERAMIČNIH DELCEV V RAZTALJENI ALUMINIJEVI ZLITINI – TEORETIČNE IN EKSPERIMENTALNE UGOTOVITVE

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Prejem rokopisa – received: 1999-08-31; sprejem za objavo – accepted for publication: 1999-11-02

A model has been developed to explain the stabilization of ceramic particles dispersed in a molten metal as a result of equilibrium interfacial coupling between the ceramic particles and the molten metal. Such equilibrium interfacial coupling is proposed to be an energy activated process determined by the equilibrium conversion and the overall kinetics of the applied interfacial chemical interaction. In addition, the model was experimentally verified by observing the rejection of BN-coated SiC particles from the molten aluminum alloy. The moment of rejection was experimentally determined by measuring the changes in electrical resistance of the slurry and the variations in the electrical power required for its constant stirring. Experiments also showed that the BN - coated SiC powder used in this study can be successfully immersed in an aluminum melt. Furthermore, this cost effective processing technique can be applied in order to prepare a stable and highly concentrated (> 30 vol.%) metallic suspension of ceramic particles with a range of particle size and specific surface area, which is of great practical interest in the production of discontinuously reinforced metal matrix composites.

Key words: metal-matrix composites (MMCs), coupling agents, interface, computational simulation, casting

V prispevku smo pojasnili stabilnost suspenzije keramičnih delcev, dispergiranih v raztaljeni kovini, z nastankom ravnotežnih medatomske vezi na meji keramika-talina. Predpostavili smo, da je nastajanje omenjenih vezi aktivacijski proces, pogojen s stopnjo kemijske pretvorbe reaktantov v produkte in s hitrostjo kemijske reakcije na meji keramika-talina. Predlagani model smo eksperimentalno potrdili z opazovanjem procesa izločanja SiC delcev, prevlečenih z BN iz raztaljene aluminijeve zlitine. Izločanje delcev iz taline smo časovno opredelili s pomočjo sprememb električne prevodnosti taline ter sprememb pri porabi električne energije, s katero smo zagotavljali konstantno premešavanje taline. Z eksperimenti smo potrdili, da je SiC delce, prevlečene s plastjo BN, možno uspešno dispergirati v raztaljeni aluminijevi zlitini, ter da obdelava površine SiC delcev z BN omogoča pripravo stabilnih suspenzij z več kot 30 vol% keramične faze, odvisno od velikosti delcev in specifične površine uporabljenega SiC prahu. Pridobljeni rezultati so praktičnega pomena za pripravo kompozitov na osnovi aluminija, diskontinuirano ojačanih s keramičnimi delci.

Ključne besede: kompoziti s kovinsko osnovo, vezni reagenti, fazna meja, matematično modeliranje, ulivanje

1 INTRODUCTION

Mechanical mixing methods applied to the fully molten state are among the simplest and most cost-effective methods of fabricating particulate-reinforced metal-matrix composites (MMCs), and are used routinely in large-scale manufacturing of cast composites reinforced with SiC, Al₂O₃ and other ceramic reinforcements¹. Mechanical stirring using impellers creates a vortexing flow in the fully liquid alloy, and assists in the introduction and mixing of particles in the slurry. The suspension of ceramic particles in the liquid metal is then solidified to obtain a cast composite.

The fluid physics of vortex stirring²⁻⁴ in combination with the physical and chemical aspects of wetting⁵⁻²⁵ have been extensively investigated. Experiments have shown that suspensions of non-wetting particles in metallic melts become unstable and particles are rejected from the melt when the particle volume fraction exceeds

some critical value³. Moreover, it was demonstrated that the actual percentage of particles successfully incorporated into a melt by mechanical stirring is at best approximately 10-20 vol.% even under optimum processing conditions, which depend upon the size and concentration of the particles, interparticle distance, thermal wandering (Brownian motion), and the composition of the molten metallic alloy. The size of the particles and the specific surface area of the ceramic powder are also important parameters. Particles smaller in size than some critical value cannot be stabilized in a melt, even under vigorous mechanical stirring, which results in particle segregation and their spontaneous rejection.

While many experimental studies have been concerned with the practical aspects of particle rejection, the mechanism of particle rejection is still unclear.

Ramani et al.³ assumed an analogy between a composite slurry and a colloidal suspension, and the exis-

tence of an interaction potential such that the energy required to keep the particles in the suspension varies inversely with the distance between the surfaces of any two particles. In the presence of gas films around non-wetting particles in a melt, the interparticle distance decreases as the particle concentration increases. As a result, the liquid interlayer is thinned down, and at a critical value of the interparticle distance, the intervening liquid film ruptures, resulting in the formation of gas bridges between the particles which compress the particles together, causing particle agglomeration and spontaneous rejection. In this way, rejection of the particles is suggested as being driven by the coalescence of adsorbed gases at the interface. The authors further proposed that changes in interfacial composition caused by segregation or by an interfacial chemical reaction can reduce the thickness of the gas film and thus enhance the volume fraction of the particles at rejection. Based on this, the critical value of the particle volume fraction and the particle size are correlated with the interparticle distance, and consequently with the energy required to overcome the change in potential energy of a particle on immersion from the gas phase into the liquid phase. Finally, it was derived that for a given system, the volume fraction of dispersoids is a function of particle size, interfacial energy and the stirrer speed. Fair agreement between theoretical predictions and actual measurements of particle concentrations at rejection in an Al-graphite system using particles with an average particle size of more than 60 μm was obtained. However, the authors³ did not experimentally demonstrate the existence of the proposed interaction potential in the composite suspensions considered, and also did not experimentally recognize which measurable changes at the interface really initiate the process of rejection

Other theories dealing with the stability of a suspension of ceramic particles in a metallic melt try to explain the spontaneous rejection of particles by an insufficient interaction between the particles and molten metal⁶. In all of these theories, cohesive energy in the interfacial region caused by a sufficient degree of wetting is proposed as the main contribution to the stabilization of ceramic particles in the melt. This cohesive energy between the two contacting phases results from the establishment of chemical equilibrium bonds achieved by mutual saturation (interfacial charge transfer) of the free valences of the contacting surfaces and by van der Waals interactions (dispersion forces). The chemical contribution to bonding is generally much larger than the van der Waals contribution. However, in nonreactive systems, the equilibrium chemical contribution to bonding is equal to zero and bonding in this case is determined essentially by the van der Waals interactions between atoms and ions of the solid ceramic particle and metal atoms. It is also important to note that, as discussed in⁶, the establishment of chemical equilibrium bonds is not accompanied by the rupture of the interatomic bonds in each of the contacting phases,

as takes place in chemical nonequilibrium systems. In that context, bonding is accomplished by an exchange of electrons, and the type of exchange determines the character of the bond.

The wetting properties of ceramics by liquid metals and alloys are governed by a number of variables such as heat of formation, stoichiometry, valence electron concentration in the ceramic phase, interfacial chemical reactions, temperature, time, atmosphere, porosity, roughness, and crystallography of the ceramic phase. Detailed accounts of wetting in solid-liquid metal systems have been presented by Naidich²⁴, Samsanov²⁵, Eustathopoulos⁷, Cannon²², and others^{6,8,13,19-21}. These authors have examined the fundamental physical and chemical factors that influence wetting in inert solid-liquid systems as well as in reactive systems, and have presented generalizations relative to wetting behaviour based on numerous studies. As a result of such efforts, the influence of physical and chemical characteristics such as those listed above have been experimentally documented.

In spite of this, an accurate prediction of wetting and, consequently, a quantitative understanding of bonding in ceramic-metal systems appears to be lacking. The difficulties partly arise from the fact that all instrumental techniques available for the characterization of an interface (TEM, SEM, EDS, SAD, AES, RBS, XPS, EXAFS, etc.) can inspect only solidified species and are not applicable for continuous observation of the interface between the ceramic particle and the molten metal in the fully liquid state. As such, it becomes very difficult to correlate the tendency of rejection of ceramic particles from the melt with real changes at the solid-liquid interface.

From a cost to quality standpoint, it is very important to establish user-friendly and cost-effective stir-casting technology enabling the introduction of larger amounts (>20 vol.%) of fine ceramic particles with an average particle size less than 5 μm in fully liquid suspensions of different light metal alloys based on aluminum, magnesium, lithium and titanium. For example, an aluminum-based composite produced by stir-casting and reinforced with a volume fraction of ceramic particles greater than 20 vol.% and with particles finer than currently feasible could improve strength, fatigue life, and machinability, making MMCs highly competitive in the automotive industry²⁶. In order to achieve this goal, spontaneous rejection as an important technological barrier should first be overcome.

The aim of this paper is to explain the stabilization of ceramic particles dispersed in a molten metal by the equilibrium interfacial coupling occurring between the ceramic particles and the molten metal. The equilibrium interfacial coupling is proposed to be an energy activated process determined by an equilibrium conversion and the overall kinetics of the applied interfacial chemical interaction. Based on the above assumption, experimentally observed rejection of BN ceramic

particles from molten aluminum alloy was successfully modelled.

The momentum of rejection of particles was experimentally determined by measuring changes in the electrical resistance of the slurry and the variations in electrical power required for its constant stirring.

2 MODEL

Let us consider an isolated ceramic particle completely immersed in a molten aluminum alloy, **Figure 1**. In order to explain up to which volume fraction such ceramic particles can be stably dispersed in the molten metal, an equilibrium coupling between atomic species of the ceramic particle and the metallic melt is proposed and introduced into the present model. As will be discussed later in detail, equilibrium coupling can be used instead of the wetting angle and work of adhesion for the quantitative evaluation of the process of immersion and rejection. Introduction of this new quantity is additionally justified by the fact that, even in systems with perfect wetting, under some more rigorous experimental conditions spontaneous rejection of ceramic particles regularly occurs, providing in this way an argument that wetting characteristics are not sufficient for a quantitative prediction of rejection.

In accordance with the present model, equilibrium coupling between the two contacting phases, results from the establishment of chemical equilibrium bonds achieved by the mutual saturation (interfacial charge transfer) of the free valences of the contacting surfaces and by van der Waals interactions (dispersion forces), as also suggested by Li and Hausner⁶. According to⁶ and as also mentioned earlier, the establishment of such equilibrium chemical bonds is not accompanied by the rupture of the interatomic bonds in each of the contacting phases, as takes place in chemical nonequilibrium systems. In nonequilibrium systems, which are beyond the scope of this paper, the stabilization of ceramic particles in a suspension is proposed to be the result of the formation of a new phase on the surface of the ceramic

particles with, generally speaking, some better wetting behaviour with respect to the melt.

Following the above considerations for an equilibrium system, the stabilization of ceramic particles in an aluminum melt caused by additional equilibrium coupling between the two contacting phases should be a thermally activated process, mainly governed by the kinetics of the relevant equilibrium interfacial coupling and by the energy of interaction between a pair of appropriate atoms.

By proposing that equilibrium coupling between a ceramic particle and the melt proceeds by establishing the following chemical equilibrium bonds:



and selecting $a = c = 1$ in order to simplify further treatment, one can now determine the energy of interaction between the introduced ceramic particle and the melt, $E_{A \leftrightarrow C}$, as:

$$E_{C \leftrightarrow A} \text{ (J/m}^2\text{)} = E_{C \leftrightarrow A} (N_{tot}/N_A) S^{-1} X \quad (2)$$

where $E_{A \leftrightarrow C}$ is the energy of interaction established between atom C and atom A in J/mol, N_{tot} is the number of possible coupling interactions at the interface (since $a = c = 1$, N_{tot} corresponds to the number of atoms A or C at the interface), S is the surface of the ceramic particle and X represents the equilibrium conversion of coupling species defined as:

$$X = S_{coupled}/S \quad (3)$$

where $S_{coupled}$ is the surface of a ceramic particle already occupied by established equilibrium pairs $C \rightleftharpoons A$.

Supposing that each individual equilibrium coupling is localized on a small interfacial area S_0 corresponding to the surface of an individual atom, one can write:

$$N_{tot} = S/S_0 \quad (4)$$

However, it is important to note that in practice, due to the different steric requirements, N_{tot} is always less than the theoretically predicted value S/S_0 . Introducing the steric factor P , one can rewrite Eq. 10 as follows:

$$N_{tot} = P(S/S_0) \quad (5)$$

P is normally found to be several orders of magnitude less than unity.

The rate, v , of coupling interaction proposed by Eq. 1 can be expressed as follows:

$$v = k \{A\}^a \{C\}^c \quad (6)$$

where k is the rate constant while $\{A\}$ and $\{C\}$ are the appropriate concentrations of the interacting species at the interface in mol/m².

Assuming that $\{A\}$ is constant and $\{C\}$ is defined as:

$$\{C\} = (N_{tot}/N_A) S^{-1} (1-X), \quad (7)$$

Eq. 6 can be rewritten as follows:

$$v = dX/dt = k_0 \exp(-E_a/(RT)) (N_{tot}/N_A) S^{-1} (1-X) = k (1-X) \exp(-E_a/(RT)) \quad (8)$$

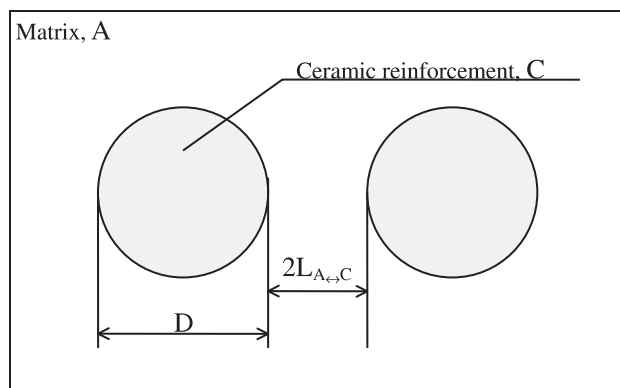


Figure 1: Diagram showing the suspension of ceramic particles in a molten metal with all the geometrical parameters used in model

Slika 1: Shematski prikaz keramičnih delcev v raztaljeni kovini z geometrijskimi velikostmi, uporabljenimi v modelu

where k_0 is the frequency factor, E_a is the activation energy for equilibrium coupling, T is the temperature, R is the universal gas constant and $k = k_0 (N_{tot}/N_A) S^{-1}$ is an additionally created constant.

After an appropriate integration of Eq. 8 and introducing:

$$X = 1 - \exp(-k \exp(-E_a/(RT))t) \quad (9)$$

into Eq. 2, one can obtain:

$$E_{C \leftrightarrow A} (J/m^2) = \frac{E_{C \leftrightarrow A} (N_{tot}/N_A) S^{-1} (1 - \exp(-k \exp(-E_a/(RT))t))}{t} \quad (10)$$

where t is the time required for equilibrium coupling between A and C .

Due to the fact that $E_{C \leftrightarrow A}$ is here considered as the overall contribution to the stabilization of ceramic particles in the suspension, the same energetic term $E_{C \leftrightarrow A}$ should also be considered, in an opposite way, as the energy of activation for the undesired process of rejection of ceramic particles from the melt. The energetic terms involved either in the process of immersion or in the process of rejection are plotted in a characteristic reaction profile shown in **Figure 2**. From this it is evident that ceramic particles dispersed in a melt become more stable with an increase of $E_{C \leftrightarrow A}$ and not necessarily with an increase of the work of adhesion, W_{adh} , as proposed by some authors in the literature²⁷.

The existence of the maximum allowed interfacial surface of the system after which rejection spontaneously occurs and the maximum volume fraction of ceramic particles which can be stably dispersed in the melt without rejection are both experimentally well documented in the literature^{2,3,28}. In order to explain these experimental findings, the present model assumes that, in the case of stably dispersed particles, the energy provided by equilibrium interfacial coupling ($N_{tot} E_{C \leftrightarrow A} X$) should be higher or, at least equal to the energy required for the opening of the new surface between the solid particulate and the liquid phase involved in the system ($\sigma_{ls} \Delta S$):

$$N_{tot} S_0 E_{C \leftrightarrow A} X = \sigma_{ls} \Delta S \quad (11)$$

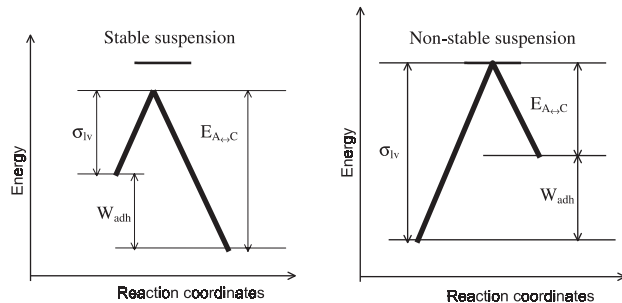


Figure 2: The reaction profile for interfacial coupling with energetic terms involved in the immersion and rejection of ceramic particles

Slika 2: Reakcijska pot za proces povezovanja na fazni meji s prikazanimi reakcijskimi energijami, značilnimi za proces potapljanja keramičnih delcev v talino in njihovo izločanje iz taline

where σ_{ls} is the surface energy between ceramic and molten metal and ΔS is the maximum increase in the surface which does not result in rejection of the dispersed particles.

Introducing Eqs. 5,9 and 10 into Eq. 11 one can finally derive:

$$\Delta S (m^2) = P S E_{C \leftrightarrow A} X \sigma_{sl}^{-1} = \frac{E_{C \leftrightarrow A} P S \sigma_{sl}^{-1} [1 - \exp(-k \exp(-E_a/(RT))t)]^2}{2} \quad (12)$$

Taking into account that the volume fraction of ceramic particles V_p is:

$$V_p (m^3) = \Delta S / (\rho S_{sp}) \quad (13)$$

where S_{sp} is the specific surface area and ρ the density of ceramic particles, one can rewrite:

$$V_p = P S (\rho S_{sp} \sigma_{sl})^{-1} E_{C \leftrightarrow A} X(t) = \frac{E_{C \leftrightarrow A} P S (\rho S_{sp} \sigma_{sl})^{-1} X^2(t)}{(N_{tot}/N_A)} \quad (14)$$

Note that maximum value for V_p is achieved for $X \rightarrow 1$:

$$V_{p, \max} = (N_{tot}/N_A) (\rho S_{sp} \sigma_{sl})^{-1} E_{C \leftrightarrow A} \quad (15)$$

Furthermore, differentiating at Eq. 14 with respect to time one can write:

$$\left(\frac{dV_p}{dt}\right)_{\max} = \frac{2 X(t) (N_{tot}/N_A) (\rho S_{sp} \sigma_{sl})^{-1} E_{C \leftrightarrow A} [dX(t)/dt]}{2} \quad (16)$$

where dX/dt is the rate of interfacial coupling. $(dV_p/dt)_{\max}$ represents the maximum allowed rate of introducing of ceramic particles into a melt from which rejection does not occur at all.

In order to avoid the rejection of particles during their immersion in the melt, the rate of introduction of particles to the melt, W , should be:

$$W \leq (dV_p/dt)_{\max} \quad (17)$$

Finally, idealizing that, in accordance with **Figure 1**, ceramic particles are homogeneously dispersed in a metallic suspension having an interparticle distance L , one can derive:

$$\Phi = V_p / (V + V_p) = \frac{[PS(\rho S_{sp} \sigma_{sl})^{-1} E_{C \leftrightarrow A} X(t)] / [(SL)/2 + PS(\rho S_{sp} \sigma_{sl})^{-1} E_{C \leftrightarrow A} X(t)]}{1} \quad (18)$$

where Φ is the volume fraction of ceramic particles in the melt.

Taking into account that Φ_{\max} is conditioned by $X \rightarrow 1$, P_{\max} and L_{\min} , one can write:

$$\Phi_{\max} = \frac{[P_{\max} (\rho S_{sp} \sigma_{sl})^{-1} (E_{C \leftrightarrow A})_{X \rightarrow 1}] / [L_{\min}/2 + P_{\max} (\rho S_{sp} \sigma_{sl})^{-1} (E_{C \leftrightarrow A})_{X \rightarrow 1}]}{1} \quad (19)$$

Furthermore, assuming than L_{\min} is defined by the length of a coupling pair $A \leftrightarrow C$,

$L_{A \leftrightarrow C}$, one can derive:

$$\Phi_{\max} = \frac{[P_{\max} (\rho S_{sp} \sigma_{sl})^{-1} (E_{C \leftrightarrow A})_{X \rightarrow 1}] / [L_{A \leftrightarrow C} + P_{\max} (\rho S_{sp} \sigma_{sl})^{-1} (E_{C \leftrightarrow A})_{X \rightarrow 1}]}{1} \quad (20)$$

3 EXPERIMENTAL PROCEDURE

3.1 Raw materials

Commercially available BN powders (supplier Advanced Ceramic Corporation), with BET specific surface listed in **Table 1** were used in this study. The main impurities in these materials include 0.3-2.7 wt% of oxygen, 0.2 wt% of borate, 0.05 wt.% of (free) carbon, 0.3 wt% of moisture and trace amounts of Cu, Al, Mg, K, Fe, Si, Ti, Cl, S, F and Na. Product information from the manufacturer indicates that the size distributions for each powder are similar ranging from 7-11 μm .

All BN powders were immersed into the melt as received.

Table 1: BET specific surface area of experimentally used BN powders

Tabela 1: BET specifična površina eksperimentalno uporabljenih BN prahov

Powder	BET specific surface area (m^2/g)
BN grade HCV	40
BN grade AC-6003	29
BN grade HCP	13
BN grade HPCL	7
BN grade AC-6004	2

3.2 Casting apparatus

The apparatus consisted of a mullite crucible placed inside a resistance heated vertical muffle furnace having a bottom pouring arrangement, **Figure 3**. The bottom

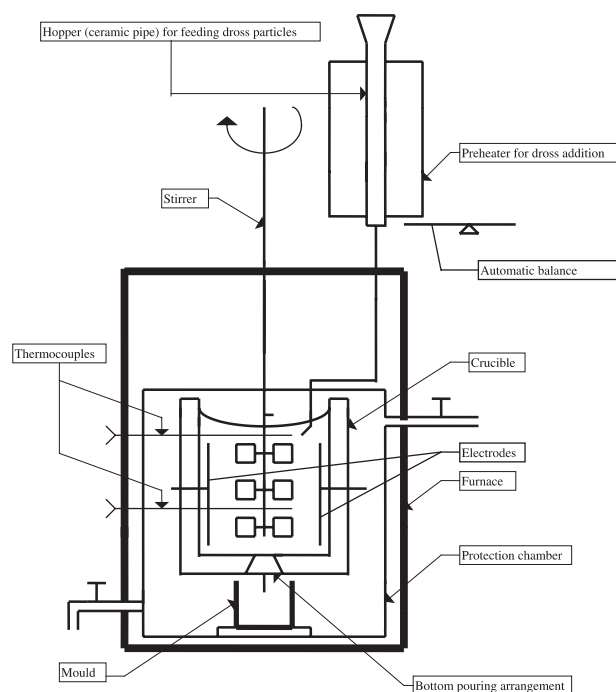


Figure 3: Diagram of the experimental set-up used
Slika 3: Shematski prikaz eksperimentalne aparature

hole of the crucible (12 mm ϕ) was plugged with a graphite stopper. The mixing assembly consisted of a DC variable speed motor, the spindle and the dispersion impeller having blades angled from about 15 to about 45 from a line perpendicular to the shaft. The use of a specially designed impeller having angled blades provided a shearing and wiping action which effectively homogenized the mixture of molten aluminum and particulate material. The impeller was machined from stainless steel and then coated with Armeco 552 ceramic adhesive.

The crucible was provided with a protective cover and an inert gas or technical vacuum protection chamber.

In order to determine the moment of rejection of ceramic particles from the melt accurately, the effective power of the stirrer (measured to within ± 1 mW on a DC motor) required for a constant stirring speed (1200 rps) was measured.

For the same reason, a pair of semi-cylindrical gold plated stainless steel electrodes was installed near the wall of the crucible (**Figure 4**) to measure the changes in electrical resistance of the metallic suspension of ceramic particles to within $\pm 1 \Omega$.

Finally, in order to correlate the moment of rejection with the experimentally measured volume fraction of ceramic particles introduced from the preheater into the melt, the preheater for ceramic reinforcement was coupled with an accurate automatic balance. In this way, the measurement of the weight of ceramic reinforcement carried away from the preheater by the constant flow of nitrogen gas was possible with an average accuracy of $\pm 10^{-4}$ kg/s.

3.3 Immersion of ceramic reinforcement into the melt

Before the particles were added, argon gas was bubbled through the melt at the rate of 100 cm^3/min for a period of about 15 minutes, in order to remove oxides, particles, dissolved gas, and other impurities that inhibit wetting.

About 8 kgs of 356-T6 alloy was placed in the 5 dm^3 mullite crucible and heated to 1200 K.

Ceramic particles were immersed into the Al alloy melt using the refractory baffle and nitrogen as a carrier gas. The baffle was immersed about 5 mm below the surface of the melt with a tilt angle of about 45 to the direction of flow.

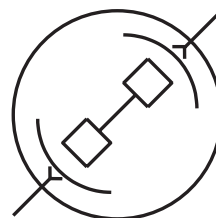


Figure 4: Diagram showing the semi-cylindrical gold plated stainless steel electrodes installed near the wall of the crucible

Slika 4: Shematski prikaz pol-valjčastih pozlačenih elektrod, ki smo jih uporabljali za merjenje električne upornosti taline

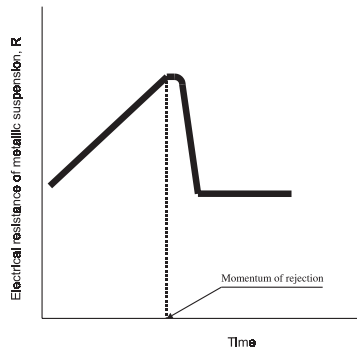


Figure 5: Variation in electrical resistance, R, of a metallic suspension of ceramic particles before and after their rejection from the melt

Slika 5: Sprememba električne upornosti taline, R, pred in po izločanju keramične faze iz taline

Ceramic particles were added to the slurry at the rate of 0.5 kg/h.

4 RESULTS

Characteristic variations in the electrical resistance, R, of a metallic suspension of ceramic particles and in the electrical power, P, of the stirrer before and after rejection occurred are illustrated in **Figures 5 and 6**, respectively. Progressive rejection appears when both functions $R = R(t)$ and $P = P(t)$ pass through the local maximum which, as evident, occurs simultaneously.

Using the experimental data for the volume flow of ceramic particles from the preheater to the melt, the moment of rejection can be correlated with the volume fraction of ceramic particles introduced into the melt, which is more convenient for further discussion. Note that before progressive rejection occurs, one can assume that the flow of ceramic particles from the preheater to the melt corresponds to the rate of immersion.

In this way, the volume fraction of ceramic phase at which spontaneous and complete rejection occurs can be correlated with the specific surface area of ceramic

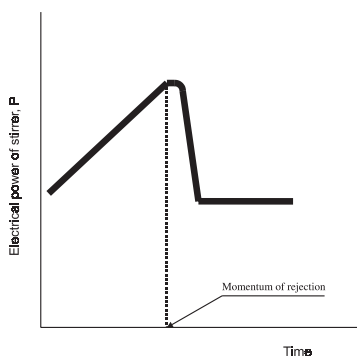


Figure 6: Variation in electrical power, P, of the stirrer required for constant stirring of the melt before and after rejection of ceramic particles

Slika 6: Sprememba električne moči mešala, ki zagotavlja konstantno premešavanje taline, pred in po izločanju keramične faze

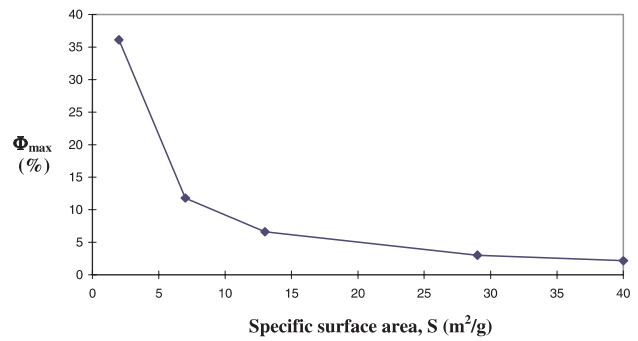


Figure 7: The volume fraction of ceramic phase dispersed in a melt at which spontaneous and complete rejection occurs, correlated with the specific surface area of the ceramic reinforcement

Slika 7: Odvisnost prostorninskega deleža keramične faze, ki privede do spontanega izločanja vseh keramičnih delcev, dispergiranih v talini, od specifične površine keramične ojačitve

reinforcement and the temperature of the melt. The results referring to the experimentally used BN powders are presented in **Figures 7 and 8**.

5 DISCUSSION

5.1 Validity of the model

Let us modify Eq. 19 by writing:

$$\Phi_{\max}^{-1} = [(L_{\min} \rho S_{sp} \sigma_{sl}) / (2 P_{\max} (E_{C \leftrightarrow A})_{X \rightarrow 1})] + 1 \quad (21)$$

If the proposed model is valid, then a plot of Φ_{\max}^{-1} vs. S_{sp} should be linear. This was experimentally confirmed, as demonstrated in **Figure 9**. Moreover, **Figure 9** also provides evidence that when $S \rightarrow 0$, the extrapolated value of Φ_{\max}^{-1} approached unity, as predicted by Eq. 21.

Another confirmation of the model is based on the temperature dependence of Φ_{\max}^{-1} . Proposing that:

$$P_{\max} = P_0 \exp (-E_1/(RT)) \quad (22)$$

$$\sigma_{sl} = \sigma_{sl}^0 \exp (E_2/(RT)) \quad (23)$$

and $X = 1$, Eq. 21 can be rewritten as:

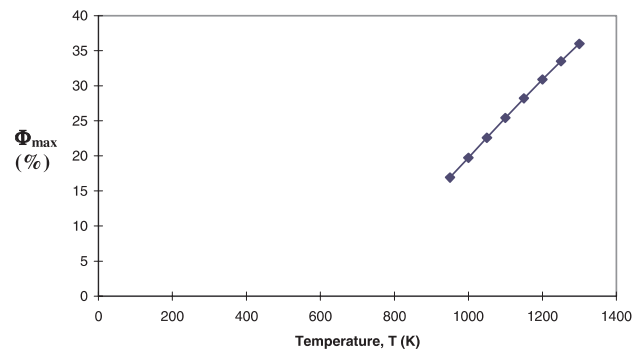


Figure 8: The volume fraction of ceramic phase dispersed in a melt at which spontaneous and complete rejection occurs, correlated with the temperature of the melt

Slika 8: Odvisnost prostorninskega deleža keramične faze, ki privede do spontanega izločanja vseh keramičnih delcev, dispergiranih v talini, od temperature taline

$$\Phi_{\max}^{-1} = [(L_{\min} \rho S_{sp} \sigma_{sl}^0) / (2P_0 (E_{C\leftrightarrow A})_{X\rightarrow 1})] \exp [(E_1 + E_2)/(RT)] + 1 \quad (24)$$

Finally, in accordance with Eq. 24, the logarithms of $(\Phi_{\max}^{-1} - 1)$ plotted vs. $1/T$ should result in a linear dependence:

$$\ln (\Phi_{\max}^{-1} - 1) = \ln [(L_{\min} S_{sp} \rho \sigma_{sl}^0) / (2P_0 (E_{C\leftrightarrow A})_{X\rightarrow 1})] + [(E_1 + E_2) / R] 1/T \quad (25)$$

The agreement between the theoretical projection expressed by Eq. 25 and the actual measurements of the temperature dependence of Φ_{\max}^{-1} plotted in **Figure 10** appears to be enough to confirm the validity of the model. Moreover, from the slope of the line $\ln (\Phi_{\max}^{-1} - 1) - 1/T$ one can also calculate the value of the term $E_1 + E_2$ which corresponds to the activation energy of the process of the equilibrium interfacial coupling. The calculated value, 28.3 kJ/mol further substantiates the assumption that the equilibrium interfacial coupling caused by the establishment of chemical equilibrium bonds is the main contribution to the stabilization of ceramic particles in the melt.

However, it is necessary to note that all the above considerations are valid as long as the real rate of introduction of ceramic particles into the melt does not exceed the maximum value defined by Eq. 16.

Combining Eq. 16 and Eq. 8, the maximum allowed rate of immersion can be expressed as:

$$W = dV_p/dt = 2k (N_{tot}/N_A) [(E_{C\leftrightarrow A})_{X\rightarrow 1}]/(\rho S_{sp} \sigma_{sl}) X (1-X) \quad (26)$$

From Eq. 26 it becomes evident that, if the immersion of ceramic particles into an aluminum melt is favoured by equilibrium interfacial coupling, the maximum allowed rate of introduction of ceramic particles into the melt should be influenced by equilibrium conversion of the interfacial coupling species, X . The situation is illustrated in **Figure 11**, where the maximum allowed rate of immersion, calculated by Eq. 8, is plotted as a function of the equilibrium conversion of the interfacial coupling species, X . In order to use this theoretical prediction and to select an optimum rate of introduction of ceramic particles into the melt, the kinetics of interfacial coupling and, hence, the quantitative relation between the equilibrium interfacial conversion, X , and the time of immersion, t , should be well known, this data however, is typically not available. Hence, the prediction expressed in **Figure 11** should be applied in practice in another way.

Let us assume an equilibrium value for the conversion of the coupling species, X_{equil} . Then, with respect to Eq. 26, the "safe" processing area for the introduction of ceramic particles into the melt can be defined as:

$$W \leq 2k (N_{tot}/N_A) [(E_{C\leftrightarrow A})_{X\rightarrow \text{equil}}]/(\rho S_{sp} \sigma_{sl}) X_{\text{equil}} (1-X_{\text{equil}}) = W_{\text{equil}} \quad (27)$$

However, from **Figure 11** it is evident that W_{equil} can be practiced only after an initial period of interfacial coupling defined by $X \leq X_{\text{initial}}$. Moreover, if Eq. 26 is correct, then the tendency for rejection of the ceramic phase from the melt should be especially strong during the initial period of coupling characterized by $X \rightarrow 0$. Hence, in order to avoid rejection at that critical stage, the applied rate of introduction of ceramic particles to the melt should be kept at a very low level or a vigorous mixing regime should be applied.

In this way, the maximum volume fraction of ceramic particles which can be processed into the melt without rejection can be written as:

$$V_{\max} = \int_0^{X_{\text{initial}}} W(X) dX + W_{\text{equil}} (X_{\text{equil}} - X_{\text{initial}}) \quad (28)$$

Of course, the theoretical value for V_{\max} is higher and expressed as:

$$V_{\max} = \int_0^{X_{\text{equil}}} W(X) dX \quad (29)$$

Justification of the above predictions is difficult due to the fact that the value of the constant $2k (N_{tot}/N_A) [(E_{C\leftrightarrow A})_{X\rightarrow 1}]/(\rho S_{sp} \sigma_{sl})$ in Eq. 26 is unknown. Also, as mentioned earlier, in many cases, the kinetics of interfacial coupling and, hence, the quantitative relation between the equilibrium interfacial conversion, X , and the time of immersion, t , are not clear.

However, if Eq. 26 is correct, then, in the initial stage of coupling characterized by $X \rightarrow 0$, the rejection of ceramic phase from the melt should occur simultaneously with the stopping of the vigorous mixing of the melt, which was actually well observed in all the experiments performed.

In contrast, if interfacial coupling is really involved in the stabilization of ceramic particles in the melt, then at an equilibrium stage, stopping the vigorous mixing will not result in rejection. This prediction was also experimentally confirmed.

In other words, in all experiments performed, clear evidence was found that once successfully immersed, particles remain stably dispersed in the melt.

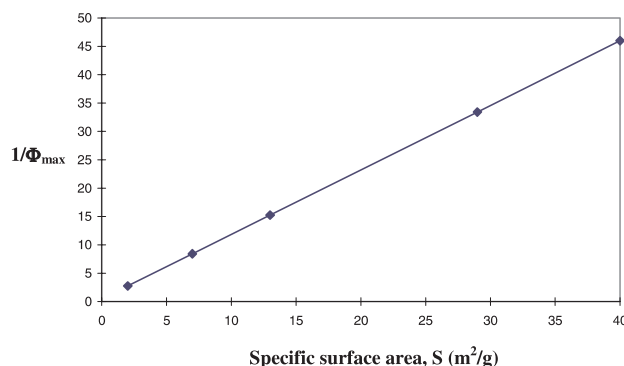


Figure 9: Plot showing the relation between Φ_{\max}^{-1} and S_{sp}
Slika 9: Diagram prikazuje odvisnost Φ_{\max}^{-1} od S_{sp}

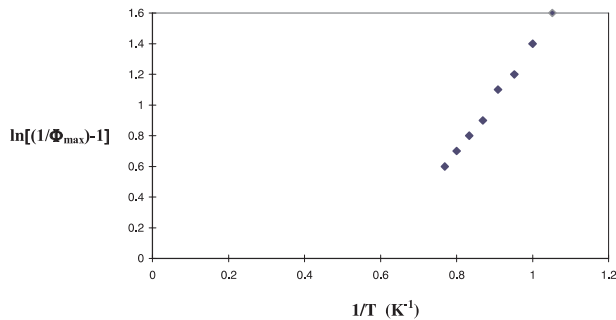


Figure 10: Plot showing the relation between $(\Phi_{max}^{-1} - 1)$ and $1/T$
Slika 10: Diagram prikazuje odvisnost $(\Phi_{max}^{-1} - 1)$ od $1/T$

5.2 The role of stirring

In accordance with the present model, the importance of the stirring action in the stabilization of ceramic particles in a metallic melt is directed toward on improvement in the coupling kinetics, especially in the initial period of immersion, increasing X and P and, probably, decreasing L . For optimal agitation of the melt, $\Phi \rightarrow \Phi_{max}$.

Introducing dimensionless groups of fluid dynamics such as the impeller Reynold's number, Re , and the power number, N_p , which govern the nature of the flow and power consumption during the stirring operation, one can write:

$$Re = [\rho N D_i^2] / \mu \quad (30)$$

$$N_p = P_w / [\rho N^3 D_i^5] \quad (31)$$

where ρ is the suspension density (weighted average density of constituents), N is the impeller speed (rps), D_i is the impeller diameter, P_w is the power input in watts and μ is the dynamic viscosity of the suspension in (kg/(ms)).

Assuming that X , P and L are all influenced by Re and N_p , as follows:

$$X = X(Re, N_p) \quad (32)$$

$$P = P(Re, N_p) \quad (33)$$

$$L = L(Re, N_p) \quad (34)$$

one can finally speculate that optimal agitation will result in $X \rightarrow 1$, $L \rightarrow L_{A \leftrightarrow C}$ and P_{max} .

5.3 Influence of particle volume fraction and specific surface area on stabilization of the suspension

With respect to the model, ceramic particles will be rejected from the melt when their volume fraction exceeds some critical value predicted by Eqs. 19-20.

According to the model, this critical value mainly depends on the specific surface area of the ceramic particles, S_{sp} , the interfacial surface energy, σ_{sl} and the strength of the interfacial interaction, $E_{C \leftrightarrow A}$.

Due to the fact that the overall interfacial surface energy and the overall interfacial interaction are both influenced by the specific surface area of the ceramic

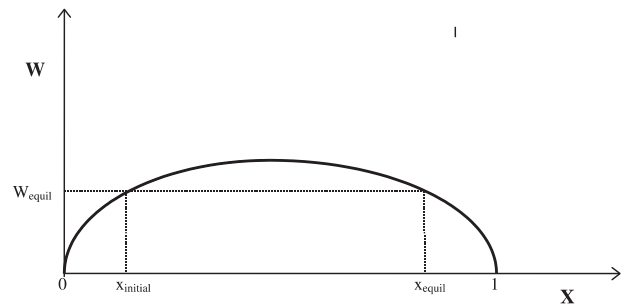


Figure 11: Plot showing the relation between the maximal allowed rate of introduction of ceramic particles into a melt, $(dV_p/dt)_{max}$, and the equilibrium conversion of the interfacial coupling species, X

Slika 11: Diagram prikazuje odvisnost med največjo dopustno hitrostjo uvajanja keramičnih delcev v talino $(dV_p/dt)_{max}$ in stopnjo ravnotežne kemijske pretvorbe X veznega reagenta na fazni meji

powder, it seems that this parameter is the dominant one in determining the critical volume fraction of ceramic particles which may be successfully introduced into a melt, also influencing the value of the steric factor, P .

5.4 Wetting behaviour and stability of the suspension

As reported in the literature²⁹, the equilibrium wetting angle in the boron nitride-aluminum system approaches zero at 1273 K in an oxygen-free atmosphere.

In spite of BN's excellent wetting, the present study confirmed that a maximum 36.1 vol.% of BN-surface coated SiC powder with a specific surface area of 2 m²/g and a maximum of 2.2 vol.% of BN-surface coated SiC powder with a specific surface area of 40 m²/g can be successfully introduced to an Al melt without rejection. These experimental findings support the conclusion expressed earlier in model, that the main criterion for the stabilization of ceramic particles in a melt and the conditions for their rejection are predominantly conditioned by interfacial coupling and only in some indirect way by the general wetting characteristics of the ceramic phase.

6 CONCLUSION

In the present model, the stabilization of ceramic particles dispersed in a molten metal is explained by equilibrium interfacial coupling between the ceramic particles and the molten metal.

The experiments performed confirm the validity of the suggested model for the systems used in this study.

In all experiments, clear evidence was found that once successfully immersed, particles remain stably dispersed in the melt.

Furthermore, it was also demonstrated that the importance of the stirring action is directed toward an improvement in coupling kinetics, especially in the initial period of immersion.

All experiments also confirm that ceramic particles will be rejected from the melt when their volume fraction exceeds some critical value predicted by the model.

However, this critical value is also influenced by the specific surface area of the ceramic particles, the interfacial surface energy, the strength of the interfacial interaction and the overall kinetics of interfacial coupling.

Finally, the experimental findings indicate that the stabilization of ceramic particles in a melt and the conditions for their rejection are predominantly conditioned by the interfacial coupling and only indirectly by the general wetting characteristics of the ceramic phase.

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