

The Introduction of Fine SiC Particles Into a Molten Al Alloy Matrix: Application to Composite Material Casting

Vnašanje finih SiC delcev v talino iz Al zlitine: uporaba pri litju kompozitnih materialov

Kečkorkijan V.¹, zasebni raziskovalec A kategorije
B. Šuštaršič, IMT, Ljubljana

The immersion of fine SiC particulates into a Al alloys is one of the major factors hampering the commercial development of particle reinforced composites prepared by liquid metallurgy techniques. Smaller particles are generally more difficult to wet and disperse than larger particles because of their inherently greater surface area. On the other hand, smaller particles generally give MMCs with superior mechanical properties. The challenge is to control the reaction between the matrix and reinforcement particles to achieve improved wetting so that good distribution and interfacial bonding are obtained. This paper will review the actual technological challenge of fine particulate reinforced MMC fabrication, and will describe the most promising new processes.

Key words: wetting, interfacial reactions, model of wetting, activation complex theory

Uvajanje finih SiC delcev v talino iz Al zlitine je tehnološko zahtevno zaradi njihove slabe omočljivosti in izrazite kemijske reaktivnosti. Hkrati je uvajanje finih SiC delcev predpogoju za izboljšanje mehanskih lastnosti kompozitov in njihovo večjo konkurenčnost na trgu. V delu so opisani dosedANJI rezultati na tem področju in predstavljene nove smeri razvoja.

Ključne besede: omakanje, reakcije na mejah, model omakanja, teorija aktivnega kompleksa

Introduction

The interest in discontinuous reinforcement of aluminium alloy relates primarily to producing improvements in strength and stiffness combined with reduction in density. Improved wear resistance also has an important bearing on potential applications.

The ability to produce whiskers, particles and platelets at lower costs has stimulated the search for low cost routes permitting the discontinuous reinforcement of aluminium. As standard shaping methods such as forging, rolling and extrusion can be employed on discontinuous reinforced Al MMCs, their production and fabrication is more readily integrated into existing metal processing facilities than of continuously reinforced MMCs.

Reinforcement with SiC has undoubtedly received the greatest attention. Its attractions include: relatively low cost and ready availability, high modulus and strength and density only slightly higher than Al.

Developments in MMC have to date been led by the needs of the aerospace and defence industries, but there is increasing interest in their application in the automotive and other high-volume manufacturing sectors. In the leisure sector (for example, in sports goods) there is also great activity. There is a

perception that, in the near term at least, automotive applications will drive the wide-scale exploitation of MMC because of the high-volume requirements of this sector. Particular applications are envisaged in piston crowns, gudgeon pins and connecting rods where the higher-temperature strength allows improvements in engine design and greater efficiency. For example, several million MMC piston crowns are currently being manufactured each year for use in Toyota diesel engines. Other clearly identified applications for MMC are limited, but recent announcements have included forgings for helicopter parts, instrument racks for aircraft, bicycle frames and car-brake components.

However, MMCs generally have not yet achieved widespread industrial application. This situation is attributable to a number of factors including high cost, lack of commercially acceptable means of production, quality assurance of MMC products and the mechanical properties not reaching the theoretically predicted values. The latter point is particularly relevant to MMCs produced by foundry processes. This class concerns all the techniques that elaborate MMCs by stirring an alloy above the liquidus, or between the solidus and the liquidus, while proceeding to the addition of the reinforcement particulates. These techniques correspond to the most inexpensive processes for producing MMCs. It is likely that in the next decade most of the MMC volume produced in the world will be done using one of them.

¹ Dr. Varužan KEČKORKIJAN
Borova vas 4
62000 Maribor

A common problem with MMCs is excessive reaction between the matrix and reinforcement. This reaction often results in inferior properties in the composite compared with the matrix alloy. Some interfacial reaction is required, however, to achieve wetting of the particles by the melt which, in turn, is necessary to disperse the particles uniformly in the melt. Thus the challenge is to control the interfacial reactions to obtain MMCs with a uniform dispersion of reinforcement particles and acceptable interface strength, while keeping the contamination in gases and inclusions at the lowest level. These requirements, which may appear to be easily achievable, are in reality very demanding. The problems in achieving all these requirements is that surface energies of most liquid metals are very important, and their resulting high surface tension penalize the wetting of intruding ceramic particulates. This results in particulate rejection by the melt, due to non-wetting conditions. Note that smaller particles are generally more difficult to wet and disperse than larger particles because of their inherently greater surface area. Moreover, once wetted, smaller particles have a greater propensity to react with molten Al. This latter effect is attributed to the larger surface area available with the finer SiC particles and consequently a higher level of surface reaction.

Several authors^{1,2} have confirmed that there is no difference in strength between the PM and melted discontinuous MMCs if the comparison is made between composites that are comparable; in other words if the bonding between the reinforcement and the matrix is the same, and with the same size, distribution and volume fraction of the reinforcement. In order to meet these requirements, it is necessary to find a way of introducing a large amount (20-30 wt%) of fine SiC particles (less than 10 μm) into an Al alloy melt without the rejection of reinforcement and without excessive oxidation or other unwanted chemical reactions. Note that typical results achieved by vortex method are, for example, 2 wt% 53 μm silicon carbide in Al-Si alloy³. Vortex method is probably the simplest and most instinctive method that can be used for the fabrication of MMCs. The method consists of vigorously stirring an alloy maintained over its liquidus, while adding reinforcement in the vortex^{4,7}. More promising results are obtained by compocasting - a process consisting of vigorously stirring a semi-solid alloy, while adding the particulates to the surface⁸⁻¹¹. Composites containing 29 wt% 14 μm SiC in Al-Si alloy have been successfully fabricated using this technique¹². However, before commercial application can be developed, problems of excessive porosities¹³⁻¹⁷, high level of inclusions^{18,19} and tight temperature control for larger batch size, must be solved.

It can be noticed that a large amount of fine particulates are difficult to incorporate with these techniques, without at least partial rejection of particulates and chemical reaction (dissolution) of SiC with molten Al. Finer than 10 μm particulates also seems to be a lower limit in particulate dimension under which complete rejection and dissolution become

the rule. Hence, the possibility of using such a processes for the commercial fabrication of structural MMCs containing much finer particulates, at higher volumic fraction, remains questionable. In order to achieve this end, the new fabrication processes must be developed.

This paper will review the challenge of mass producing fine particulate reinforced metal matrix composites and will focus on the most promising new processes and composite designs.

Theoretical background

Wetting and bonding of SiC particulates to Al and Al alloys

Wetting and bonding are of practical importance in discontinuously reinforced composites technology, first in determining the effectiveness with which SiC particulates and matrix can be combined in foundry methods of composite preparation and second in determining the particulates/matrix bond strength. Improvements in wetting between the matrix and the reinforcing phase in MMCs are an important goal of surface engineering.

The wetting properties of ceramics by liquid metals are governed by a number of variables, including heat of formation, stoichiometry, valence electron concentration in the ceramic phase, interfacial chemical reactions, temperature, and contact time¹⁵. The work of adhesion between a ceramic and a melt decreases with increasing heat of formation of carbides. The high energy of formation of a stable carbide implies strong interatomic bonds and correspondingly weak with metals. This leads to a high interfacial energy and a small work of immersion, resulting in poor wetting.

High valence electron concentration generally implies lower stability of carbides and improved wettability between ceramics and metals. High temperature and long contact times promote melt-ceramic wettability due to reactions at the melt/ceramic interface, resulting in reduced contact angle.

The most common method of assessing wettability in two-phase systems is the sessile drop experiment, in which a drop of the lower melting-point constituent lies on a plane substrate of the other constituent. The angle of contact, θ , of the drop is often taken as a measure of wettability. For ideal wetting, a liquid drop must spread completely over the solid surface, that is the contact angle becomes zero, although a contact angle of less than 90° is adequate to cause effective wetting. Similarly, complete non-wettability is defined by a contact angle of 180°; however angles greater than 90° are practically sufficient to cause dewetting.

The different interfacial forces acting between solid-liquid, solid-vapour and liquid-vapour-phases are represented by vectors γ_{sl} , γ_{sv} and γ_{lv} respectively. At equilibrium conditions Thomas Young¹⁶ equated the vectors in the horizontal direction to give the following fundamental relation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos(\theta) \quad (1)$$

Since surface tension of solids in vapour (γ_{sv}) cannot be measured easily, Dupre¹⁷ suggested the work of adhesion of a solid to a liquid as given by:

$$W_{sl} = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (2)$$

where, W_{sl} is defined as the energy required to separate an solid-liquid interface into free surfaces of solid and liquid. Combining Equations (1) and (2) gives:

$$W_{sl} = \gamma_{lv}(1 + \cos\Theta) \quad (3)$$

Thus W_{sl} can be determined without direct knowledge of the interfacial energy. Note that it is a combination of Θ and γ_{lv} rather than Θ alone that gives a measure of wetting (bonding). Thus, a reduced value of Θ does not necessarily indicate improved bonding since it may occur in association with a lowering of γ_{lv} .

The relative strength of bonding can be assessed by comparing W_{sl} with $2\gamma_{lv}$ and $2\gamma_{sv}$, these being a rough reflection of the atomic bond strengths in liquid and solid respectively. A high W_{sl} value is a prerequisite but not a guarantee for good mechanical strength in the bond. In general, the mechanical strengths will depend on the weakest path in the interface, which may exist in one of the paths close to the interface or in a layer of reaction products rather than in the interface as such¹⁸.

A review of the wetting of SiC by liquid metals has been published by several authors¹⁸⁻²³. As a rule, the wettability of covalent carbides such as SiC and B₄C follows the same dependence on the nature of metal as the wettability of carbon. The magnitude of the chemical interaction is weaker than for carbon, due to the larger strength of the bonds in these carbides. Wetting was usually not observed below about 900°C and the contact angle decreased (in several steps) when the temperature increased. It was showed²⁴ that the Al/SiC system exhibits a non-wetting behaviour up to 1223 K, where a sharp transition to wetting of SiC by liquid aluminium occurs. This kind of transition is typically found in aluminium/non-metallic refractories systems (carbon, Al₂O₃, TiB₂, etc.). It has been attributed to the disappearance of the effect of Al₂O₃ layer on liquid aluminium at about 1223 K under high vacuum^{24,25} or/and SiO₂ layer on the surface of SiC particles^{18,24,25}. Note that very often, the production of Al/SiC composites involves a double Al/Al₂O₃/SiO₂&SiC interface, since the silicon carbide reinforcement employed is oxidized naturally or on purpose. Penetration of aluminium through this diffusion barrier is facilitated either by increasing the temperature, or by the addition of alloying elements²⁶. At lower temperatures, this layer prevents a true metal/substrate interface from developing^{20,24,27}. Being more electropositive than aluminium, these elements probably substitute for aluminium in the oxide layer, bringing about a weakening of the film²⁷. These elements thus enhance wetting even though they form weaker bonds with SiC than aluminium does. The same effect might al-

so explain the enhancement of wetting brought about by adding magnesium in aluminium²³.

Therefore, keeping in view of the theories of surface energy and chemical theory of wetting²⁸ following techniques were developed to improve wetting of non-metallic solids by liquid metals: use of metal coatings^{4,29,30}, addition of elements in the liquid metal³¹⁻³⁶, heat-treatment of ceramic particles³⁷ and use of ultrasonic³⁸ and other mixing techniques³⁹⁻⁴¹.

The most widely used technique to promote wettability is to add a wetting agent, usually in the form of an alloying element in the melt. A mixture of an alloying element in a liquid metal can promote the latter's wettability with a solid surface by three mechanisms: reducing the surface tension of the liquid, decreasing the solid-liquid interfacial energy and chemical reactions at the solid-liquid interface. An early patent³² describes additions of alloying elements (wetting agents) such as lithium, magnesium, silicon and calcium to the liquid metals to promote wettability of non-metallic particles with the melts. It was observed that additions of small pieces of magnesium to the surface of the melts along with dispersoids were more effective in dispersing these particles than the case when magnesium was already present in the melt. This is probably because magnesium added to liquid aluminium initially melts and spreads on the melt surface, thereby wetting the dispersoids⁴².

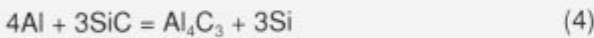
The enhanced wetting of ceramic materials resulting from the addition of magnesium to an aluminium alloy is well documented^{13,42-45}. Several mechanisms are generally discussed when the role of magnesium is considered. Authors²³ claim that the addition of an alloying element can enhance the wetting of a solid surface in three ways, namely (i) by reducing the surface tension of the alloy, (ii) by decreasing the solid-liquid interfacial energy, and (iii) by promoting a chemical reaction at the solid-liquid interface. Other investigators¹³ state that magnesium is effective in reducing the surface tension of the melt and inducing interfacial reactions. Finally, authors⁴³ who found magnesium to significantly improve wettability, believe that the promotion of interfacial reactions is the most active mechanism for enhancing the wetting of a solid ceramic surface with a molten aluminium alloy.

According to¹⁹, it was found that the wetting process of SiC by aluminium alloy initially had an incubation period that was decreased by the addition of alloying elements. Hence, authors¹⁹ proposed that the wetting process could be explained by assuming that the wetting rate is proportional to the number of wetting nuclei and to the ratio of unwetted area. They also found that the wetting rate seems to be rate determined by the dissociation of SiC because the same value of activation energy for the wetting process was obtained from the four systems: pure aluminium, Al-Ti, Al-V, and Al-Zr. Generally, the value of the reaction rate constant increased and that of an incubation period decreased with the addition of alloying elements giving high carbon solubility¹⁹.

Two other factors that are of importance in the wetting experiment are temperature and atmosphere since these can have an important influence on the various interfaces. Atmospheric impurities can markedly depress the liquid surface energy, γ_{lv} , by adsorption. However, in Al-SiC system this effect is small¹⁸. Probably more significant effects are: the influence of temperature and atmosphere on the breakdown of the passive oxide film on the free SiC surface and the effect of temperature on the breakdown of this film at SiC/Al interface. Consequently, several patented methods of fluxing and degassing composite melts has been developed which uses a rotating impeller-like device to both stir the bath and inject a blend of purge gases⁴⁶⁻⁴⁸. Purge gases can be either inert (argon or nitrogen) or reactive (chlorine, fluorine and Freon 12). The standard methods for degassing aluminium are also very effective⁴⁹ and are widely used in foundry processing of MMCs. Fluxes can also be used to minimize oxide formation (and to remove suspended nonmetallics). For this reason, melts containing magnesium are often protected by the use of salts that form liquid layers, most often of magnesium chloride, on the melt surface. These fluxes, termed covering fluxes, must be periodically removed and replaced. Carbon, graphite and boron powder also effectively retard oxidation when applied to the melt surface.

Dissolution of SiC particulates in Al alloy matrix

A common problem with metal matrix composites is excessive reaction between the matrix and reinforcement. It is well known^{50,51} that SiC is thermodynamically unstable in molten Al and reacts to form Al_4C_3 and Si according to the reaction:



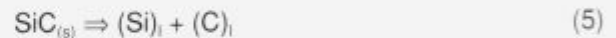
The Al_4C_3 forms at the interface while the Si dissolves in the Al matrix. The formation of Al_4C_3 generally leads to degradation of the mechanical properties of the reinforcement and the composite⁵². The SiC-Al reaction is irreversible and once Al_4C_3 formation is initiated at higher temperatures, lowering the melt temperature will only increase the viscosity and decrease the fluidity of the melt due to the bridging effect of the Al_4C_3 and silicon particle formation on the SiC particles⁵³. Hence this reaction should be avoided. Note that only the control of the kinetics of the reaction through the use of thermodynamics or protective coatings which reduce reaction rate can prevent the degradation of matrix and composite properties.

From equation (4) it is seen that, in addition to Al_4C_3 , Si is produced, and if the Si content is sufficiently high the reaction will tend to go to the left, i.e. the SiC will be stable in the matrix and not react. The required Si levels at different temperatures can be calculated^{54,55}, and at typical casting temperatures 10 to 12 wt% Si is required for complete thermodynamic stability. However, in practice it is the kinetics of aluminium carbide formation which has to be considered. In practice melt holding times can be

many hours, depending on the foundry, and for very long times the equilibrium Si levels will be needed. However, for holding times of 2 to 4 hours, which is viable for most casting operations, much lower Si levels are sufficient to prevent extensive Al_4C_3 formation. For example, with a common hypoeutectic Al-Si-Mg casting alloy, which contains 6-7 wt% Si, 4 hours at 1023 K produces barely detectable Al_4C_3 , and even at 1073 K the rate of Al_4C_3 formation is quite slow. Note that this is not valid at higher processing temperatures. At 1400K, for example, the required Si level varied between 15 to 25 wt%⁵⁶ which is completely inconvenient for practice.

So the Si level required to limit Al_4C_3 formation will depend on the reactivity of SiC phase and the particular foundry practice. The finer SiC particles, the higher the melt temperatures and the longer the holding times involved, the higher the required Si level should be applied. A good practice is to minimize superheat and holding times as much as possible - which is normal, good foundry practice.

The reaction between SiC and Al has been studied in detail by several authors⁵⁵⁻⁶¹. They observed that the reaction proceeds in two steps. In a first stage, the silicon carbide dissolves in the liquid metal:



Secondly, the Al_4C_3 compound precipitates growing in random islands on the SiC surface. More detailed, the interfacial reactions in the Al/SiC composite with molten metal manufacturing are likely to include: (a) the chemical reaction (dissolution) of SiC with molten Al, (b) the diffusion of silicon and carbon atoms away from the SiC surface into the bulk molten Al pool, (c) the formation of Al_4C_3 , (d) upon cooling, further precipitation of Al_4C_3 and (e) the solidification of the matrix. It seems that the rate controlling step in the overall interfacial reaction is the chemical dissolution of SiC in molten aluminium⁶². The rate of the SiC dissolution may be expressed as Equation (6):

$$[Si] = 0.8 + 2.06t \text{ at } 1253 \text{ K} \quad (6)$$

where [Si] is the average silicon in wt% in aluminium matrix and t is the composite manufacturing time in hours. Applying that kinetic model developed by⁶², the rate of molten aluminium attack on SiC was determined to be:

$$\ln k \text{ (}\mu\text{m/min)} = 6.36 - 7180/T \quad (7)$$

where k is the rate of SiC dissolution in molten aluminium and T is the processing temperature for the composite.

Several modifications of the surface chemistry of SiC particulates have been also examined in order to overcome the problems of chemical reaction between the dispersoids and the matrix. The surface of the dispersoids is coated by a refractory material which is non-reactive both with dispersoid and the matrix⁶³. This prevents chemical reaction and simultaneously improves wetting with the matrix.

However, these types of coatings are very expensive. The metallic coatings to the surface of SiC particulates such as nickel⁶⁴ and copper⁶⁵ are also found to be effective. In these cases the coatings dissolve in the matrix alloy during synthesis to give precipitation of brittle intermetallics adjacent to the SiC dispersoids. In all cases the morphology of the coating structure, thickness of the coating and nature of the coating namely adhesion and bonding with the dispersoid surface, are likely to play a significant role.

An easily scaled-up method for the preparation of protective surface layer to the SiC dispersoids was suggested by several authors^{24,37,66-68}. Note that silicon carbide particles usually have a vitreous surface layer of SiO₂. Therefore, the initial interfacial reaction is between SiO₂ and Al and, hence, a thick surface layer of SiO₂ can serve as a barrier for the undesirable reaction between SiC and Al. The SiO₂ layer on SiC can easily be thickened by heating in air. It is estimated that heating in air at 973 K for 1 hour, increases the thickness of the oxide layer to between 30 and 50 nm from the native thickness of between 2 and 4 nm. As predicted, the use of SiC preheated at 973 K in air was found to reduce the reaction between Al and SiC and also to improve the wetting according to the several possible chemical reactions at the interface Al/SiO₂^{66,67}. SiO₂ can also react with Mg which is usually present in an Al alloy^{66,67}. For low oxidation levels (<4 wt%), the reaction of SiO₂ and Al leads to the formation of spinel, MgAl₂O₄. The reaction is rapid and completed during fabrication of the composites as indicated by the fact that no residual SiO₂ is observed in the reaction zone.

For high oxidation levels (≈ 16 wt% SiO₂), the transformation of SiO₂ results into a continuous layer surrounding the SiC particles and is also complete during fabrication. The interface is polycrystalline and constituted mainly of MgAl₂O₄ with some Mg₂Si and channels of Al.

The oxidation of SiC particles performed in order to improve its wettability and, in the same time, to remote Al₄C₃ formation during composite processing, seems to be the key factor in the proprietary commercial foundry process for MMCs production³⁷.

Other sol-gel coating techniques based on MgO⁷⁰, Al₂O₃⁷⁰, ZrO₂⁷⁰, K₂ZrF₆⁷¹ are also applied. None of these techniques, however, can overcome the problem of rejection at higher particulate content in Al alloy melt. These methods are, also, too costly for most commercial application.

Carbon coatings produced by pyrolysis of phenolic resin or high yield polymers⁷² which are frequently used in ceramic matrix composites are recently considered as a new promising way for the low cost large scale production of MMCs⁷³.

Effect of dispersoids size and aspect ratio on the composite mechanical properties

Strength

A very strong dependence of strength of discontinuously reinforced MMCs on particle size was ob-

served⁷⁴. This relationship is approximately linear on a semi-logarithmic plot: bend strength versus reinforcement diameter. As the particulate diameter decreases from 800 to 6 μm , bend strength increases 4 to 6 fold. More precisely, the measured bending strengths in Al/SiC MMCs with 100, 10 and 3 μm particulate diameter were 300, 500 and 600 MPa respectively. Finally, the extrapolated bending strength for SiC reinforcement with particle size only 1 μm was found to be around 700 MPa⁷⁴. The authors⁷⁴ are also found the similar strength increasing effect in MMCs with submicrometre SiC particles.

The observed increase in strength, as a function of particulate diameter may be a consequence of increased particle strength at smaller sizes due to statistical (e.g. Weibull) arguments. An alternative explanation relates to the interaction of the dislocation fields surrounding the reinforcement particles. Strengthening of discontinuous MMCs has been shown to arise from the generation of a high dislocation density around the filler during cooldown from processing^{75,76}.

Toughness

Again, as the particulate diameter decreases the composite toughness significantly increases. The increase in toughness is approximately linear on a semi-logarithmic plot (≈ 10 MPa $\text{m}^{1/2}$ in Al/SiC composites with 100 μm particulate diameter and ≈ 15 MPa $\text{m}^{1/2}$ in samples with SiC particulate diameter around 5 μm)⁷⁴.

Stiffness

Generally, there appears to be no effect of particulate diameter on the elastic modulus of either composite system⁷⁴.

Wear

All of the discontinuously reinforced composites exhibited improved wear resistance with increasing particulate diameter⁷⁴. As the particulate diameter increases from 8 to 800 μm , wear resistance increases 5 to 6 fold. However, note that further increasing of SiC particle size over 65 μm there is no significant effect on wear resistance⁷⁴.

Aspect ratio and mechanical properties

For the optimum properties in the particulate composites, high aspect ratio and uniform particle distribution is important if conventional shear-lag composite strengthening is operating. However, the high aspect ratio needs to be achieved at fine particle sizes if particle fracture during composite fabrication is to be avoided. Most of the particulate composites developed so far utilize particles with aspect ratio of less than two, and particle sizes in the 10 to 20 μm size range because higher aspect ratio are only available in much coarser powders.

While whiskers, according to its high aspect ratio, give the highest properties of all the discontinuous reinforcement, the high cost of whiskers and their potential health hazards have resulted in the major effort being concentrated on particulate reinforcement.

Whisker composites have approximately the same yield strength, a higher ultimate strength, and a lower strain to failure than do particulate reinforced composites in the extrusion direction. However, it's important to note that whisker composites have lower properties in the directions perpendicular to the extrusion.

An alternatively approach in using of particulates with high aspect ratio is based on SiC platelets produced by heating a porous alpha silicon carbide precursor composition comprising silicon and carbon in intimate contact to a temperature of from 2373 to 2773 K in a non-reactive atmosphere. By controlling the thickness, the material can be tailored to have different aspect ratio.

According to⁷⁷, silicon carbide platelets of three different sizes fabricated into 6061 aluminium powder metallurgy compacts containing 25 vol% of the silicon carbide platelets have showed improved properties with each reduction in platelet size. The SiC platelets (at 15 vol%) were also incorporated into an Al-356 aluminium alloy using a proprietary molten metal mixing method - aspect of which have been discussed previously⁷⁷. Again, the tensile properties of the platelet reinforced composites were found superior to those of the particulate reinforced. Because of the improvement in properties of MMCs with reduced platelet diameter, the development of this product was extended to include smaller thickness ($\approx 0.5 \mu\text{m}$) which resulted in aspect ratio of about 10 with particles in the 5 to 10 μm size range.

The initial results of the incorporation of SiC platelets in aluminium alloys suggest that by limiting the size of platelets and by improving their dispersion and alignment, it should be possible to improve the composite properties significantly.

Foundry processing of Al/SiC composites with fine dispersoids: the state-of-the art and future trends

This class concerns all techniques that elaborate MMCs by stirring an alloy above the liquidus (vortex method), or between the solidus and the liquidus (compcasting), while proceeding to the addition of the reinforcement dispersoids.

Mixing techniques generally used for the introducing and homogeneously dispersing a discontinuous phase in a melt are:

- Addition of particles to a vigorously agitated fully or partially molten alloy⁴⁹,
- Injection of discontinuous phase into the melt with an injection gun⁴⁹,
- Dispersion of pellets or briquettes, formed by compressing powders of base alloys and the ceramic phase, into a mildly agitated melt⁴⁹,
- Addition of powders to an ultrasonically irradiated melt. The pressure gradients caused by cavitation phenomena promote homogeneous mixing of ceramics in metallic melts,
- Addition of powders to an electromagnetically stirred melt. The turbulent flow caused by electromagnetic stirring is used to obtain a uniform suspension,

- Centrifugal dispersion of particles in a melt,
- Addition of ceramic phase to an accessory metallic melt (e.g. Si) which wets previously (or in situ) surface engineered ceramic dispersoids, and can be, after that, successfully "diluted" by the basic metallic matrix (i.e. magnesium rich Al alloy) to the required final composition⁷³.

In all the above techniques, external force is used to transfer a nonwetable ceramic phase into a melt and to create a homogeneous suspension of the ceramic in the melt.

A broad range of SiC particulates size (10 to 120 μm) and amount of dispersoids (3 to 20 vol%) which have been successfully incorporated into Al alloy matrix by foundry procedures is well documented^{49,78}. However, these reports mainly discuss the introduction of relatively large SiC dispersoids (with particle size range between 15 and 60 μm). It can be noticed that there is only a few existing reports about the immersion of fine (less than 10 μm in size) SiC particulates into Al melt using above described foundry routes^{11,73,79}. As mentioned earlier, finer than 10 μm particulates also seems to be a lower reasonable limit in particulate dimension under which almost complete rejection becomes the rule. Hence, these routes can be used mainly for the fabrication of wear resistant composites, for which larger particulates results in better performance. However, the possibility of using such a processes for the commercial fabrication of structural MMCs containing much finer particulates, at higher volumic fraction, remains questionable.

The exception is the last of the above listed techniques, based on the combination of two compatible metallic melts. In the first of them, ceramic particulates can be successfully dispersed according to the chemical reaction between the melt and SiC particulates with previously (or in situ) surface engineered layer. Once dispersed, ceramic particulates will not be rejected during the introduction of the second melt, if the process performs by carefully wetting control⁷³.

By following this procedure, Al/SiC composites with 10 - 20 vol% of SiC particulates in the size range less than 10 μm are successfully prepared. This process is also advantageous in the fabrication of composites with particularly difficult to deal with reinforcements, such as whiskers or platelets⁷³. According to author's proposal, chemically treated fine SiC particles (or other morphologies with high aspect ratio) were first dispersed into a Si melt (at approx. 1773 K in vacuum). The wettability of SiC by Si₀ was enhanced by chemical reaction between a carbon layer previously deposited on the surface of the SiC particles and the matrix. Carbon layer was produced by pyrolysis of phenolic resin or high carbon yield polymer source. When a sufficient portion of SiC particles was incorporated into Si matrix, an Al alloy was carefully added at a controlled rate under vigorous stirring conditions and in a protective atmosphere in order to fit the final matrix composition.

The main advantages of this MMC preparation technique are:

- The concentration of both matrix constituents - Al and Si can be time programmable, and,
- The temperature of the intermediately melt can be effectively regulated, especially during the addition of Al-alloy into previously formed suspension of SiC particulates in Si melt.

In this way, it is possible to regulate:

- The wetting kinetics of SiC particulate reinforcements in the metallic matrix, and,
- The kinetics of unwanted interfacial reaction which leads to the formation of Al_4C_4 (Reaction 4). Note that the rate of Reaction 4 is expressed as:

$$v = k_1[Al]^4 \cdot [SiC]^3$$

At the beginning of the alloying process, the concentration of Al is practically zero which results in a low Al_4C_3 formation rate. Consequently, the processing temperature can be kept sufficiently high in order to maintain the wettability of ceramic particulates with Al in the wetting region⁷³.

However, this method has also some limitations. In practice, it's difficult to select a pair of compatible metallic matrixes with all requested performances. Another important inconvenience is the high processing temperature caused by high melting point of silicon.

The commercial importance of this method should be carefully evaluated in future, based on the improvement of the mechanical properties of MMCs caused by the introduction of finer SiC particulates.

Conclusions

Foundry processes, generally used for the preparation of MMCs, concerns all the techniques that elaborate MMCs by stirring an alloy above the liquidus (Vortex method, Duralcan technology) or between the solidus and the liquidus (Compocasting).

In spite of many existing problems, it is likely that in the next decade most of the MMC volume produced in the world will be done using one of them.

Discontinuously reinforced Al/SiC composites can be generally classified in wear resistant grade, for which larger particulates ($20 \mu m < d < 60 \mu m$) at medium volumic fraction (10-15 vol%) results in better performance, and structural MMCs containing much finer particulates ($< 10 \mu m$), at higher volumic ratio (20-25 vol%).

It can be noticed that a current foundry processes are used mainly for the fabrication of wear resistant composites. However, the possibility of using such a processes for the commercial fabrication of structural MMCs still remains questionable. Regarding poor wettability of fine ceramic particulates with molten metals, finer than $10 \mu m$ particulates seems to be a lower limit in particulate dimension which could be successfully introduced by existing foundry techniques. Also, the incorporation of large amount of SiC particulates ($> 20-25 \text{ vol}\%$) becomes difficult or even impossible.

In order to overcome these problems, the new foundry processes which enable the routinely intro-

duction of larger amount of finer SiC particles into metallic melt, must be developed.

One possible solution, based on the combination two compatible metallic melts, is presented in this review and theoretically evaluated.

References

- 1 R. J. Arsenault, S. B. Wu, in *Proceedings of the International Symposium on Advances in Cast Reinforced Metal Composites*, Chicago, September 1988, edited by S. G. Fishman and A. K. Dhingra (ASM International, Ohio, 1988), 231
- 2 R. J. Arsenault, S. B. Wu, *Scripta Metallurgica*, 22, 1988, 767
- 3 P. K. Rohatgi, B. C. Pai, S. C. Panda, *J. Mater. Sci.*, 14, 1979, 2277
- 4 F. A. Badia, P. K. Rohatgi, *Trans. AFS*, 77, 1969, 402
- 5 F. A. Badia, *Trans. AFS*, 77, 1971, 347
- 6 M. K. Surappa, P. K. Rohatgi, *J. Mater. Sci.*, 16, 1981, 983
- 7 M. K. Surappa, P. K. Rohatgi, *Met. Tech.*, 5, 1978, 358
- 8 R. Mehrabian, R. G. Riek, M. C. Flemings, *Metal. Trans.*, 5A, 1974, 1899
- 9 B. F. Quigley, G. J. Abbaschian, R. Wunderliand, R. Mehrabian, *Metal. Trans.*, 13A, 1982, 93
- 10 C. G. Levi, G. J. Abbaschian, R. Mehrabian, *Metal. Trans.*, 9A, 1978, 697
- 11 F. M. Hosking, F. FolgarPottillo, R. Wunderlinand, R. Mehrabian, *J. Mater. Sci.*, 17, 1982, 477
- 12 C. Miliere, M. Suery, *J. Mater. Sci. Technol.*, 4, 1988, 41
- 13 J. M. McCoy, C. Jones, F. E. Wawner, *SAMPE Quarterly*, 19, 1988, 2, 37
- 14 S. Ray, in *Proceedings of the International Symposium on Advances in Cast Reinforced Metal Composites*, Chicago, September 1988, edited by S. G. Fishman and A. K. Dhingra (ASM International, Ohio, 1988), 77
- 15 J. V. Naidich, *Prog. Surf. Membr. Sci.*, 14, 1981, 353
- 16 T. Young, *Trans. Roy. Soc.*, 95, 1805, 65
- 17 A. Dupre, *Theorie Mechanique de la chaleur*, (Gauthier Villars, Paris, 1869)
- 18 R. Warren, C. H. Andersson, *Composites*, 15, 1984, 101
- 19 T. Choh, T. Oki, *Mater. Sci. Technol.*, 3, 1987, 1
- 20 V. Laurent, D. Chatain, N. Eustathopoulos, *J. Mater. Sci.*, 22, 1987, 244
- 21 J. P. Rocher, J. M. Quenisset, R. Naslain, *J. Mater. Sci. Lett.*, 4, 1985, 1527
- 22 F. Delannay, L. Froyen, A. Deruytere, *J. Mater. Sci.*, 22, 1987, 1
- 23 A. Banerji, P. K. Rohatgi, W. Reif, *Metallwiss. Technik*, 38, 1984, 656
- 24 V. Laurent, D. Chatain, N. Eustathopoulos, X. Dumant, in *Proceedings of the International symposium on Advances in Cast Reinforced Metal Composites*, Chicago, September 1988, edited by S. G. Fishman and A. K. Dhingra (ASM International, Ohio, 1988), 27
- 25 J. G. Legoux, L. Salvo, G. L'Esperance, M. Suery, in *Proceedings of the International Conference on Fabrication of Particulates Reinforced Metal Composites*, Montreal, September, 1990, edited by J. Masounave and F. G. Hamel) ASM International, Ohio, 1990), 31
- 26 W. Kohler, *Aluminium*, 51, 1975, 443
- 27 C. R. Manning, T. B. Gurganus, *J. Amer. Ceram. Soc.*, 52, 1969, 115
- 28 V. Naidich, N. Chuvashov, *J. Mater. Sci.*, 18, 1983, 2071
- 29 B. C. Pai, P. K. Rohatgi, *Mater. Sci. Eng.*, 21, 1975, 161
- 30 H. Tokisue, G. J. Abbaschian, *Mater. Sci. Eng.*, 34, 1978, 75

- ³¹ S. K. Rhee, *J. Amer. Cer. Soc.*, 54, 1971, 332
- ³² G. Imich, *US Patent No.2*, 793 949, 1957
- ³³ J. V. Naidich, V. S. Zhuravlev, G. V. Chuprina, L. V. Strashinskaya, *Soviet Powder Metallurgy and Metal Ceramics*, 12, 1973, 895
- ³⁴ Hitachi Ltd., *Jpn. Kokai Tokyo koho 8073*, 839, 1980
- ³⁵ B. N. Keshavaram, A. Banerji, M. K. Surappa, P. K. Rohatgi, *J. Mater. Sci. Letters*, 1, 1982, 29
- ³⁶ T. P. Murali, M. K. Surappa, P. K. Rohatgi, *Met. Trans.*, 13B, 1982, 485
- ³⁷ M. D. Skibo, D. M. Schuster, *US Patent No.4*, 865, 806
- ³⁸ Y. Babaskin, *Russian Castings Production*, 1972, 328
- ³⁹ R. Mehrabian, A. Sato, M. C. Flemings, *Light Metals*, 2, 1975, 177
- ⁴⁰ R. Mehrabian, M. C. Flemings, *New Trends in Materials Processing*, (ASM Publication, Metals Park, Ohio, 1976), 98
- ⁴¹ H. V. Walter, G. Ziegler, *Eur. Space Agency*, Special Publication ESA SP/35, 1978
- ⁴² S. Das, T. K. Dan, S. V. Prasad, P. K. Rohatgi, *J. Mater. Sci. Lett.*, 5, 1986, 562
- ⁴³ S. Y. Oh, J. A. Cornie, K. C. Russell, *Ceram. Engng. Sci. Proc.*, 8, 1987, 912
- ⁴⁴ J. A. Cornie, A. Mortensen, M. C. Flemings, in *Proceedings of the Sixth International Conference on Composite Materials and the Second European Conference on Composite Materials (ICCM and ECCM)*, London, UK, Vol.2, edited by F. L. Matthews, N. C. R. Buskell, J. M. Hodgkinson and J. Morton (Elsevier Applied Science, London, 1987), p.2.297
- ⁴⁵ T. Choh, R. Kammel, T. Oki, *Z. Metallkde*, 78, 1987, 286
- ⁴⁶ D. O. Kennedy, *Advances Materials&Processes*, 6, 1991, 42
- ⁴⁷ M. D. Skibo, D. M. Schuster, *US Patent No.4*, 786,467, 1988
- ⁴⁸ M. D. Skibo, D. M. Schuster, *US Patent No.4*, 759,995, 1988
- ⁴⁹ *Metal Handbook*, Ninth Edition, Vol.15 (Metals Park, Ohio, 1988)
- ⁵⁰ M. Skibo, P. L. Moris, D. J. Lloyd, in *Proceedings of the International Symposium on Advances in Cast Reinforced Metal Composites*, Chicago, September 1988, edited by S. G. Fishman and A. K. Dhingra (ASM International, Ohio, 1988), 257
- ⁵¹ D. J. Lloyd, I. Jin, *Met. Trans.*, 19A, 1988, 3107
- ⁵² A. Mortensen, in *Proceedings of the 9th Riso International Symposium on Metallurgy and Materials Science*, Roskilde, September 1988, edited by S. Anderson, H. Lilholt and O. Pedersen, (Riso National Laboratory, Roskilde, 1988), 144
- ⁵³ A. M. Samuel, H. Liu, F. H. Samuel, *Compos. Sci. and Techn.*, 49, 1993, 1
- ⁵⁴ D. J. Lloyd, *Compos. Sci. and Techn.*, 35, 1989, 159
- ⁵⁵ J. C. Viala, P. Fortier, J. Bouix, *J. Mater. Sci.*, 25, 1990, 1842
- ⁵⁶ J. C. Viala, P. Fortier, C. Bernard, J. Bouix, *Developments in the Science and Technology of Composite Materials* (A. E. C. M., Bordeaux, 1985)
- ⁵⁷ T. Yano, S. Kato, T. Iseki, *J. Am. Ceram. Soc.*, 75, 1992, 580
- ⁵⁸ S. D. Peteves, P. Tambuyser, P. Helbach, M. Audier, V. Laurent, D. Chatain, *J. Mater. Sci.*, 25, 1990, 3765
- ⁵⁹ T. Iseki, T. Kameda, T. Maruyama, *J. Mater. Sci.*, 1984, 1692
- ⁶⁰ R. J. Arsenault, C. S. Pande, *Scripta Metall.*, 18, 1984, 1131
- ⁶¹ D. J. Lee, M. D. Vaudin, C. A. Handwerker, U. R. Kattner, *Mat. Res. Soc. Symp. Proc.*, 120, 1988, 357
- ⁶² R. Y. Lin, K. Kanniceedings, *on the International Conference on Interfaces in Metal-Ceramics Composites*, Anaheim (CA), February, 1990, edited by R. Y. Lin, R. J. Arsenault, G. P. Martins and S. G. Fishman (TMS, Warrendale, 1990), p.153
- ⁶³ R. K. Everett, R. J. Arsenault, *Metal Matrix Composites: Processing and Interfaces*, (Academic Press, Boston, 1991)
- ⁶⁴ C. Y. Liue, J. W. Wang, Y. M. Peng, H. J. Chen, J. H. Shen, C. A. Hung, *MRL Bull. Res. Dev.*, 4, 1990, 31
- ⁶⁵ *ibid.*, 4, 1990, 35
- ⁶⁶ J. G. Legoux, G. L'Esperance, L. Salvo, M. Suery, in *Proceedings of the International Conference on Fabrication of Particulates Reinforced Metal Composites*, Montreal, September 1990, edited by J. Masounave, F. G. Hamel, (ASM, Ohio), p.31
- ⁶⁷ T. Sritharan, K. Xia, J. Haethcock, J. Mihelich, in *Proceedings of the International Conference on Metal and Ceramic Matrix Composites: Processing, Modeling and Mechanical Behavior*, Anaheim (CA), February 1990, edited by R. B. Bhagat, A. H. Clauer, P. Kumar and A. M. Ritter, (TMS, Warrendale, 1990), p.13
- ⁶⁸ H. Ribes, M. Suery, *Scripta Metall.*, 23, 1989, 705
- ⁶⁹ N. I. A. Lattef, A. R. I. Khedar, S. K. Goel, *J. Mater. Sci. Lett.*, 4, 1985, 385
- ⁷⁰ B. Kindl, Y. H. Teng, Y. L. Liu, *Composites*, 25, 1994, 671
- ⁷¹ J. P. Rocher, J. M. Quenisset, R. Naslain, *J. Mater. Sci.*, 24, 1989, 2697
- ⁷² K. Sugihara, M. Yamamoto, T. Kida, M. Fukazawa, *US Patent No. 4*, 929,472, 1990
- ⁷³ V. M. Kevorkijan, B. Šuštaršič, *Paper no. SIV-25-95 on the 97th Annual Meeting of the American Cer. Soc.*, Cincinnati, May 1995
- ⁷⁴ J. T. Burke, M. K. Aghajanian, M. A. Rocazella, *Proc. Int. SAMPE Symp.*, 34, 1989, 2440
- ⁷⁵ D. McDanel, *Met. Trans.*, 16A, 1985, 1105
- ⁷⁶ M. Vogelsang, R. J. Arsenault, R. M. Fisher, *Met. Trans.*, 17A, 1986, 379
- ⁷⁷ M. K. Jain, D. J. Lloyd, S. P. Tremblay, in *Proceedings of the International Conference on Metal and Ceramic Matrix Composites: Processing, Modeling and Mechanical Behavior*, Anaheim (CA), February 1990, edited by R. B. Bhagat, A. H. Clauer, P. Kumar and A. M. Ritter (TMS, Warrendale, 1990), p.549
- ⁷⁸ P. Rohatgi, *Adv. Mater. Proc.*, 137, 1991, 39
- ⁷⁹ R. Chen, G. Zhang, *Composite Science and Technology*, 47, 1993, 51