

# Some General Considerations about an "Ideal" Ceramic Reinforcement for Structural Discontinuously Reinforced AIMC Composites Prepared by Liquid Metal Routes

## O lastnostih "idealne" keramične ojačitve za kompozite na osnovi aluminija, pridobljene z livarskimi postopki

V. M. Kevorkijan<sup>1</sup>, Maribor

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*In this paper an overview of the current understanding of mechanical properties of discontinuously reinforced metal matrix composites (DR MMCs) is presented and the 'ideal' ceramic reinforcement for light metal composites based on Al alloys is identified. Three main problems which must be solved to facilitate the expanding application of DR MMCs with light alloys matrix metals are: (i) superior cost performances - in Al based DR MMCs the quality/cost ratio should be above one, (ii) Active implementation of environmental concerns- DR MMCs should be easy recyclable, and (iii) the improved ductility - the ductility of the composite should follow the ductility of unreinforced matrix. It is almost postulated that market competitive DR MMCs should be defect free castable and re-castable. It seems that only in this way the most inexpensive processes for production of final components could be developed. Referring to this, the cost effective preparation of molten metal dispersion with at least 20 vol% of fine (less than 10  $\mu\text{m}$ ) ceramic particles produced in situ or directly introduced into a melt becomes the key technological request. In this paper, several new preparation routes for DR MMCs based on chemically improved wetting behaviour of ceramic dispersoids in molten aluminium alloys and chemically activated stabilisation of dispersoids in melt have been discussed. The intrinsic economy of these methods and some new market opportunities for DR MMCs have been also presented. Finally, a further selling of the concept of MMCs based on the improvement of the price/quality ratio and the important automotive market pull for the improved properties of DR MMCs were introduced.*

*Key words: ceramic reinforcement, reinforced Al composites, mechanical properties, interfacial reactions, quality and cost consideration*

*Delo obravnava novejši razvoj postopkov diskontinuirne ojačitve lahkih kovin s keramičnimi delci. Skušali smo odgovoriti na vprašanje, katere lastnosti diskontinuirne ojačitve odločilno vplivajo na večjo konkurenčnost teh materialov in njihovo tržno zastopanost zlasti v avtomobilski industriji. Ugotovljeno je, da nadaljnje trženje teh materialov zavirajo trije ključni problemi: (i) neugodno razmerje med ceno in kvaliteto, (ii) nerešeni problemi recikliranja in (iii) poslabšanje obdelovalnosti kompozita. Opisane so nadaljnje smeri razvoja, ki bodo, po avtorjevem mnenju, zagotovile proizvodnjo diskontinuirno ojačanih kompozitov z večjim deležem dodane vrednosti in omogočile njihovo večjo uporabo v avtomobilski industriji.*

*Ključne besede: keramična ojačitev, diskontinuirano ojačani Al kompoziti, mehanske lastnosti, razmerje med ceno in kvaliteto kompozita*

### 1 Introduction

In recent years, a considerable development has taken place in the synthesis of discontinuously reinforced cast composite materials (DR MMCs) with tailored properties. Because of potential improvements in mechanical properties such as modulus, 0,2% proof stress, hardness and tensile strength. A notable property of the new DR MMCs foundry alloys is also their extraordinary high-temperature yield strength. Such improvements are, however, usually accompanied by reduction in both tensile ductility and fracture toughness. Moreover, other technical problems arise when one intends to produce a castable DR MMCs for structural application: the matrix-reinforcement reactivity, the increased viscosity of a melt, the machinability of the cast ingot to the final shape at a reasonable price, problems of successful and cost effective recycling, etc.

In order to illustrate the complexity of an intrinsic economy of DR MMCs, cost factors for an extruded wrought automotive component are listed in **Table 1**.

**Table 1:** Cost factors for an extruded wrought automotive component

Finished component cost	100%
Extrusion billet cost	18%
Material	15%
Sawing	3%
Extrusion cost	30%
Extrusion speed	7%
Die cost	10%
Die wear	8%
Recoveries	5%
Cutting	8%
Machining	15%
Bending and forming	5%
Welding	4%
Surface finishing - anodising or painting	1%
Transportation	9%
Recycling	10%

Source: Alpha and Omega in Composites, 1996

<sup>1</sup> Dr. Vanušan M. KEVORKIJAN  
Alpha and Omega in Composites  
Borova vas 4, 2000 Maribor

The key solution for improving the quality and the economy of castable DR MMCs simultaneously is the creating of new casting techniques to reduce casting defects and to disperse fine ceramic particles in a melt, or the development of new ceramic reinforcements with superior characteristics such as: (i) spontaneous wetting and (ii) chemical stability in the melt.

The objective of this paper is to discuss both proposed routes and to recommend a general R&D strategy for further cost effective production of castable DR MMCs.

## 2 Theoretical background

### 2.1 Mechanical properties of DR MMCs

While many of the mechanical properties of DR MMCs are dependent on the type of reinforcement, matrix and processing route, they all display two main characteristics: an enhanced modulus and a decreased fracture ductility.

The modulus is essentially independent on particles size and particles distribution and is only dependent on the extent of reinforcement and the reinforcement aspect ratio<sup>1</sup>. On the contrary, the fracture ductility is a more complex property and it is potentially susceptible to many factors, some of which can be easily controlled, such as the particular combination of reinforcement and matrix i.e. the composite and volume fraction, while others such as particle distribution are very sensitive to the processing route. In melt processed composites, the distribution is controlled by the mixing conditions, the solidification rate and the final fabrication conditions.

The dominant factor controlling the elastic modulus is the volume fraction of the reinforcement, and it is relatively insensitive to particle distribution, while variations in the type and shape of the reinforcement play some but not the dominant role.

According to professor Rohatgy<sup>2</sup>, even by addition of waste by-products, such as fly ash as a filler material in light metals and alloys, like aluminium a slight increase in tensile elastic modulus has been observed. On the other hand, higher elastic modulus and greater stiffness, mean that in casting applications, where stiffness is the principal or the major design criterion, components of equivalent stiffness with smaller cross section can be economically substituted. This means diminished component weight and reduced energy consumption.

The strengthening mechanisms which may operate in DR MMCs have been considered in several recent publications, and the behaviour has also been extensively modelled mathematically<sup>3</sup>.

The yield strength of DR MMCs can be predicted by the modified shear lag theory as follows<sup>4</sup>:

$$\sigma_{cy} = \sigma_{my} [V_r(S+2)/2 + V_m] \quad (4)$$

The predicted increase in yield strength of a composite is expressed in the modified shear lag theory by:

$$\Delta\sigma/\sigma_{my} = (\sigma_{cy} - \sigma_{my})/\sigma_{my} = 1/2 V_r S \quad (5)$$

Here  $\sigma_{cv}$  and  $\sigma_{my}$  are the yield strengths of the composite and matrix respectively,  $V_p$  and  $V_m$  denote the particle and matrix volume fraction respectively and  $S$  is the mean aspect ratio. For the most of the DR MMCs,  $S$  is smaller than two.

It is evident therefore that the shape, aspect ratio and the volume fraction of the reinforcement have significant effects on the strength of DR MMCs. However, Eq.(4) does not express the influence of particle distribution in matrix on the yield strength of composites. Based on experimental results<sup>3</sup>, the strength increase appears to be reduced by very high volume fraction of reinforcement. This probably reflects the difficulties in obtaining an uniform particle distribution at high volume fraction.

Some data indicate that the strength of DR MMCs can be increased more effectively by reducing the reinforcement particle size than by increasing its volume fraction<sup>5</sup>. However, it's necessary to point out that these data were obtained using vacuum hot pressed and hot extruded ingots prepared by powder metallurgy route.

The major limitation in the mechanical properties of DR MMCs is the rather limited ductility. The fracture elongation decreases rapidly with the share of reinforcing particles. According to several recent works<sup>1</sup>, the composite failure is associates with particle cracking and void formation in the matrix within clusters of particles. The particle fracture is prevalent in coarser particles, and this would be expected. First, the larger the particle the conventional fibre loading and end loading mechanisms become more operative. In addition, the coarser ceramic particles will have a higher probability of containing fracture initiation defects.

Considering all these different factors it is clear that the fracture process in DR MMCs is quite complex, and a quantitative understanding is lacking. Lloyd<sup>1</sup> proposed that in order to maximise the ductility for a particular volume fraction, the composite should have: (1) an uniform particle distribution, (2) a fine (< 10  $\mu$ m), uniform particle size distribution, (3) a high interfacial strength, (4) the control of particle shape, and (5) a ductile matrix.

The recent experiments in DURALCAN DR MMCs composites performed by Lloyd et al.<sup>5</sup>, have confirmed the importance of the reinforcement volume fraction, of the ductility of the matrix and the distribution of the reinforcement. Based on this, optimisation of composite ductility is primarily controlled by the matrix alloy, the reinforcement level and the reinforcement distribution.

The fracture toughness of DR MMCs is reviewed in several references (see <sup>1</sup>). Recently, various aspects of fracture toughness testing of DR MMC's have been also considered by Roebuck and Lord<sup>6</sup>. The extent of agreement between theoretical and experimental fracture toughness values does suggest that the control of particle volume fraction and distribution is important for an optimal fracture toughness.

For many high temperature applications the creep properties are important and several recent creep studies have been reported also on DR MMCs, (see <sup>1</sup>). Most of this theories describe the creep of metals with a constant substructure deforming by the lattice diffusion controlled creep.

Experiments confirm that a high volume fraction of fine particle reinforcement can provide a significant improvement in creep resistance up to about 350°C. At higher temperature the creep behaviour will approach that of the matrix.

## 2.2 Matrix-reinforcement reactivity

A common problem with DR MMCs is a fast reaction rate between the matrix and reinforcement. The chemical reactivity between the matrix and the reinforcement can have a significant effect on the interfacial strength and hence the deformation and fracture of the composite. However, some interfacial reaction is required to achieve the wetting of the reinforcement by the melt which, in turn, is necessary to disperse the ceramic particles uniformly in the melt.

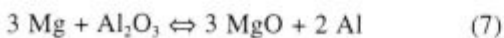
The thermodynamic stability in aluminium alloys and some other light metals of most of the reinforcement of interest has recently been reviewed.<sup>7</sup>

It is well known <sup>1</sup> that SiC is thermodynamically unstable in molten aluminium and reacts to form Al<sub>4</sub>C<sub>3</sub> and Si. The formation of Al<sub>4</sub>C<sub>3</sub> generally leads to the degradation of the mechanical properties of the reinforcement and the composite. Al<sub>4</sub>C<sub>3</sub> dissolves in water, degrading the corrosion behaviour of the composite, and since its formation involves the release of Si, modifying the matrix composition. Further, the formation of Al<sub>4</sub>C<sub>3</sub> on SiC particle surface area may be rapidly increase of the melt viscosity<sup>8</sup>.

The aluminium carbide reaction can be avoided using high silicon alloys for the matrix or a thick surface layer of SiO<sub>2</sub> on SiC particles, which is usually prepared by heating in air.<sup>9</sup> In that case, the SiO<sub>2</sub> layer is the barrier for the undesirable reaction between SiC and Al.

The SiO<sub>2</sub> layer can also improve the wetting between SiC particles and the Al-Mg melt because of the spinel formation. This chemically activated wetting is the key point in some commercially processes for DR MMCs production. However, the irreversibility of interface reactions makes the recycling life of these composites questionable.

Aluminium oxide, Al<sub>2</sub>O<sub>3</sub>, is stable in pure aluminium, but reacts with magnesium in Al-Mg alloys<sup>1</sup>. At high magnesium levels, and lower temperatures, MgO may form:



while the spinel will form at low magnesium level:



Hence, for Al<sub>2</sub>O<sub>3</sub> reinforcement, the spinel reaction can be effectively controlled by the Mg - content in the Al alloy. However, the recycling of these composites is also affected by the irreversibility of interface reactions.

Very recently, several US companies have announced the use of AlN powder as a filler for DR MMCs. According to the technical report from Advanced Refractory Technologies, Inc.<sup>10</sup>, aluminium nitride can be used to modify the properties of light metals and obtain a metal matrix composite with a higher elastic modulus, lower thermal expansion and/or a higher strength than the unmodified base metal. A range of mixtures can be prepared with varying properties, enabling the design engineer to tailor physical properties to match the required application requirements. AlN is completely stable in contact with Al and will not be affected during various metallurgical treatments such as mixing, casting, annealing or even recycling, it has been suggested as a desirable alternative to SiC and Al<sub>2</sub>O<sub>3</sub>. However, it's important to note that AlN doesn't wet Al alloys spontaneously. No data concerning the surface modification of AlN particles which favour the immersion of AlN particulate in an Al alloy melt were found in dispoible references.

On the contrary, the utilisation of waste by-products such as fly ash as a filler material in light metals and alloys, like aluminium has been also explored for potential applications in engineering components<sup>2</sup>. According to Rohatgi and co-workers<sup>2</sup>, cast aluminium-fly ash composites represent the lowest cost DR MMCs synthesised to date and probably are the first DR MMC which is cheaper than the unreinforced matrix.

As mentioned earlier, a carefully controlled chemical reaction between the reinforcement (or its precursor) and matrix can be used to improve the wetting behaviour of ceramic dispersoids in contact with the melt. On the other side, the same chemical procedure can be also used to produce the reinforcement in situ into a melt. Generally, there are two methods for in situ reinforcement of molten Al alloys: (i) the direct chemical reaction (e.g. oxidation or nitriding) between an Al melt and a gaseous reactant<sup>11,12</sup> and (ii) the chemical transformation of previously dispersed particulate precursor (e.g. some displacement reactions between oxides or nitrides and molten Al alloys)<sup>13</sup>.

Lanxide Corporation, Newark, Delaware, USA, has an exceptionally broad technology portfolio in metal matrix composites prepared by the DIMOX<sup>TM</sup> direct metal oxidation process in which a molten metal reacts with an oxidant to form a ceramic matrix which grows into ceramic preforms<sup>14</sup>. For example, in the reaction of molten aluminium alloy with oxygen in ambient air alumina forms and grows into the spaces between individual particles in porous ceramic preform producing the dense ceramic matrix composite - CMC with continuous interconnected ceramic and metal phases. Similar procedure named PRIMEX CAST<sup>TM</sup> could be used to produce with stirring of the melt a castable alloy composition contain-



ing up to 40 vol% particles formed in situ. In some cases, selected displacement reactions were used to obtain ceramic particles directly in a melt. For example, fine  $\text{Si}_3\text{N}_4$  particles, previously dispersed in the melt, react with Al-10Si-5Mg alloy in nitrogen atmosphere at  $1200^\circ\text{C}$  and convert to AlN. In principles, the nitrides of other metals, which are more electronegative as aluminium, could be also used if they are stable in Al melt at processing temperatures. However, to date, the economy of  $\text{Si}_3\text{N}_4$  is better. The process was fully described for AlN matrix composites fabricated via an infiltration and reaction approach (PRIMEX<sup>TM</sup> Process) of porous  $\text{Si}_3\text{N}_4$  preform converted to continuous interconnected AlN phase penetrated with Al metal<sup>13</sup>. Note that colloidal  $\text{SiO}_2$  can be also used in an Al alloy melt as an oxidant - in this process fine  $\text{SiO}_2$  particles are transformed in  $\text{Al}_2\text{O}_3$  particles according to the chemical reaction:



An other approach is the direct nitriding of molten binary aluminium alloys in a nitrogen containing atmosphere with stirring to an AlN/Al DR MMC. Simkovich et al.<sup>12</sup> observed that the addition of alkaline earth elements, such as Mg, Ca, Sr and Ba, can significantly promote the nitriding reaction of Al binary alloys. In this study, the Al-3Ca alloy exhibited the highest growth rate and the lowest activation energy at elevated temperatures.

The XD<sup>TM</sup> process, developed by the Corporation Martin Marietta around 1983, is a mean for the elaboration of materials for conventional metalworking technologies: casting, forging, extrusion, rolling, etc. In the XD<sup>TM</sup> process the elemental components of various reinforcing phases are mixed with or incorporated into the metallic or intermetallic matrix. When this mixture is heated to high temperature, typically above the melting point of the metal, or to a point where a self-propagating reaction takes place, the elemental constituents react exothermically to form a dispersion of submicroscopic reinforcing particles in the matrix<sup>15</sup>.

A new class of co-continuous ceramic-metal composites was prepared by a novel reaction-based processing<sup>16</sup>. Specimens were prepared either by reaction sintering compacts of intensively milled powder mixtures or by reaction infiltration of porous oxide precursor bodies in vacuum. Note that, upon stirring, DR MMCs can be manufactured also using this processing route. By metal or intermetallic volume fractions  $> 20$  vol%, both phases are continuous and exhibit an interpenetrating network similar to that of products of direct molten metal oxidation or reactive metal penetration processes of porous or even dense ceramic preforms<sup>16</sup>.

### 2.3 Viscosity of the composite melt

As mentioned earlier, if extensive interface reaction occurs the viscosity can increase to infinity, and the melt will not flow. For Al-7Si alloy this will happen at  $800^\circ\text{C}$ ,

when the amount of aluminium carbide will increase rapidly with time resulted in a catastrophic decrease in fluidity. As a result, after 250 min of holding time, the composite will not flow into the mould.

According to Lloyd<sup>1</sup> a few general statements can be made:

1. The viscosity increases with increasing volume fraction of particles,
2. The viscosity increases with decreasing particle size,
3. The viscosity increases with increasing interface reaction,
4. The ability to cast and fill a mould cavity is also strongly influenced by the history of the melt, in terms of temperature, time, and shear rate.

The castability defines the upper level of reinforcement into a melt which could be successfully processed into a final part and it's an extremely important technological parameter.

## 3 Discussion

Let now try to answer the main question: Which is or which will be the "perfect" ceramic reinforcement for castable DR MMCs? The following criteria should be considered: (i) the application of the composite, (ii) the matrix alloy composition, (iii) the cost of reinforcement, and (iv) the ratio between the extra cost and the achieved improvements in commercial properties of composite. Commercial properties of composite are a very complex term consisting of mechanical properties, corrosion resistance, tribological behaviour, formability of final parts, and the ability to recycle the scrap and/or the final components when their useful life is over.

### 3.1 Application of the composite

For a structural application, the modulus, strength, and density of the composite become important. Usually, a high modulus and low density are required. Particle shape may also play an important role, since angular particles can act as local stress raisers reducing ductility. In order to improve the basic mechanical properties such as modulus of elasticity, strength and ductility, it seems the most important to find a way of introducing large amounts (20-30 vol%) of fine ceramic particles (less than  $10 \mu\text{m}$ ) directly into an Al alloy melt without rejection of the reinforcement and without excessive unwanted chemical reactions. However, as reported, finer particles increase the viscosity of the melt, making processing difficult. The introduction of fine ceramic particles into an Al alloy melt was studied by several authors<sup>17</sup>. Based on these investigations, it was postulated that a large amount of fine particulate reinforcement is generally difficult to incorporate using classical foundry processes. Several new chemically activated foundry methods have been suggested in order to overcome the major problem: the extreme difficulty of simultaneously obtaining sufficient wetting of the reinforce-

ment by the molten matrix metal without incurring excessive or disastrous reactivity between the components,<sup>18-20</sup>. However, all of these methods are based on improved wetting between ceramic dispersoids and melt caused by interface chemical reaction. Thus, the challenge is to control the interfacial reaction to the correct level to obtain MMCs with high(er) level of fine ceramic particles in matrix and to prevent, in the same time, a larger degradation of, at least, key properties of the composite material. As different research groups have reported, this is no an easy task,<sup>21</sup>. The main problem involves the natural dichotomy between the wettability of the reinforcement and the excessive reactivity with it. On this way, the choice of ceramic reinforcement for DR MMCs involves compromises between cost, wettability, excessive reactivity, and effects of interfacial reactions on the properties and heat treatment responses of the matrix itself.

The major contribution to the wetting of solids by molten metals and their alloys has been provided by the work of Naidich and co-workers,<sup>22</sup>. More recent data, concerning the same subject, have also been reviewed<sup>23</sup>. Some general conclusions are:

(i) In metal melt - substance or compound with preferably covalent character interatomic bonding (diamond, graphite, carbide, nitride phases), solid bodies are characterised by a closed stable electronic configuration of atoms, and strong saturated interatomic bonding. Interaction of most solid bodies of these types with metals is possible only with partial or complete dissociation of the interatomic bonding at the surface of solid bodies.

(ii) In metal melt - ionic compounds (high-melting metal oxides, salts), the surface is formed by anions, and their interaction with metal melts is determined mainly by the interaction with the solid body anions.

However, the surface chemistry of solid particles is usually very complex and depends on the previous particle treatment. For example, very often, the production of Al-SiC composites involves a double Al-SiO<sub>2</sub>-SiC interface, since the silicon carbide reinforcement employed is oxidised naturally or on purpose. As a result, a sharp transition from non-wetting to wetting is observed at a certain threshold temperature<sup>24</sup>. This transition temperature is determined by the kinetics of the diffusion of the metal through the oxide layer. Similar oxide layers are usually present at the surface of other non-oxide particles, such as nitrides and borides.

An other difficulty is caused by the non-equilibrium conditions. As known, under chemical non-equilibrium conditions, the effect of chemical reactions on the interfacial tensions must be considered. This resulted in time dependable properties of DR MMCs and, hence, their reproducibility become worst.

To date, there is no cost effective foundry method able to introduce 20-30 vol% of fine (less than 10  $\mu\text{m}$  ceramic particles) into Al alloy melt. Some very recent foundry improvements have been suggested in Al-SiC

system based on simultaneous changing of the composition of the Al alloy during the introduction of SiC particles incorporated in an alloy consisting of 60% Si and 35% Al and 5% Mg to the final matrix composition with 7-12% Si, 1-3% Mg and 85-92 Al. In spite of some reported improvements<sup>25</sup>, this technique seems no flexible enough for other important systems. However, further understanding of the phenomenon of the wetting and the stabilisation of ceramic dispersoids in Al alloy melt<sup>25</sup>, combined with tremendous improvements in fluidity of the dispersion, which may be caused by the introduction of selected alloying additives into a melt, could result in requested cost effective and castable DR MMCs.

The PRIMEX CAST<sup>TM</sup> of the Lanxide Corp. and the XD<sup>TM</sup> of the Martin Marietta Corp. and other *in situ* methods could be an alternative. As reported, by varying the process parameters, the reinforcement size can be varied from 0,2 to 10  $\mu\text{m}$ <sup>14</sup>. However, in open literature there are no data concerning the cost of these materials and, this could be more critical, their ability to cast and fill a mould cavity.

If the composite to be used in thermal management applications, the coefficient of thermal expansion and thermal conductivity are dominant. The coefficient of thermal expansion is generally important because it influences the composite strength. The ability to tailor properties, such as thermal conductivity and coefficient of thermal expansion, for example, provides the basis for applications demanding dimensional tolerance and stability. The thermal conductivity is reduced by the presence of ceramic elements. In the same way, the thermal expansion coefficients of aluminium alloys can be partly adjusted by addition of ceramic elements. However, the thermal properties such as thermal conductivity and coefficient of thermal expansion are not so easily predictable. In these cases, the rule of mixture predictions can usually provide an initial "ball-park" estimate. For example, the addition of 30 vol% SiC whiskers in unalloyed aluminium results in decreasing of thermal conductivity to the half of that of unreinforced aluminium<sup>26</sup>. On the contrary, the thermal expansion coefficient of an 7075 aluminium alloy is halved by incorporating 30 vol% of SiC whiskers and is 50% greater than of an 7075/25 vol% Al<sub>2</sub>O<sub>3</sub> short fibres<sup>26</sup>. The predicted changes in thermal expansion for an Al-AlN composite are obtained by using modelled data for A 500 AlN powder produced by Advanced Refractory Technologies, Inc., Buffalo, USA,<sup>10</sup>. It was found that the decreasing of thermal expansion of Al-AlN composite could be in general described by the rule of mixture. However, an extensive amount of work should be performed in the field of further much more sophisticated prediction of thermal properties of DR MMCs.

The first applications for which DR MMCs have been investigated are related to wear resistance. As reported earlier, in the case of DR MMCS, the mechanical properties are not significantly altered (as in continuous-fibres composites), but the tribological properties (wear,

friction, galling) show marked improvements. It was found that soft, solid lubricant particles, such as graphite and mica, and probably fly ash, improve the seizure resistance of aluminium alloys, while hard particles such as SiC, Al<sub>2</sub>O<sub>3</sub>, WC, TiC, ZrO<sub>2</sub>, SiO<sub>2</sub>, B<sub>4</sub>C, TiB<sub>2</sub> greatly improve the resistance to abrasion of aluminium alloys,<sup>27</sup>. DR MMCs depends more on the microstructure than on the composition of the alloy and reinforcing particles,<sup>28</sup>.

It is generally recognised that larger particles are more effective against abrasive wear than smaller ones,<sup>26</sup>. However, as reported by Naslain et al.<sup>26</sup>, only 3 vol% of small alumina particles (less than 3 µm) diminish the wear rate by about 60% although the coefficient of friction slightly increases.

An extensive international work in this field is still in progress (see for example an overview prepared by Rohatgi et al.<sup>29</sup>). Because of that, it seems to early to recommend optimal microstructures and reinforcements for different wear applications of DR MMCs.

According to ref.<sup>29</sup>, the ideal solution would involve the analysis of stress distribution in a tribocomponent followed by selective reinforcement of the regions of maximum stress concentration. This reinforcement would be accomplished through the addition of high-strength and high-modulus whiskers or short fibres with a sufficiently high aspect ratio. Finally, dispersed graphite or other solid lubricant particles would be added to regions subjected to sliding contact.

In many applications the corrosion behaviour of DR MMCs is important. On the other hand, there is very little published work on the corrosion behaviour of DR MMCs. In spite of the lack of published data, all performed studies have stated that DR MMCs suffer more severe attack than the respective non-reinforced metals. Several reasons have been given for the degradation including galvanic corrosion between reinforcement and matrix, galvanic corrosion between intermetallic compounds and matrix, preferential attack because of carbon diffusion from the reinforcement into the matrix, and an increase in the number of anodic sites on the interfaces<sup>30</sup>. In general, the corrosion resistance of the metallic phase in DR MMCs is due to a passive film created on a less noble metal. Hence, the corrosion resistance of DR MMCs can be influenced by the ceramic reinforcement in several ways. The presence of a particles in the surface introduce a break in the passive film, and the break could be an initiation point for corrosion attack. As mentioned, an electrical conducting particle can act as a cathode, creating local galvanic micro elements, which increase the metal solution. Since many ceramic particles, such as Al<sub>2</sub>O<sub>3</sub>, are insulators, they would not be expected to affect corrosion behaviour directly. SiC, however, is a conductor and changes in corrosion behaviour need to be assessed<sup>31</sup>. Silicon carbide particles, if not covered by an insulating surface layer, operate as local cathodes. The locally produced hydroxy ions give rise to an increase in the pH-value of the environment near the particles. This change in pH is a destabilizing factor for the passive film

on the aluminium. However, even in the case of insulating reinforcing particles, the composite microstructure is different of that of the matrix as a result of interface reactions and other processing, and this can modify the corrosion response.

### 3.2 The matrix alloy composition

The matrix alloy should be chosen only after giving a careful consideration to its chemical compatibility with the reinforcement, to its ability to wet the reinforcement, to its own characteristic properties (the most critical is ductility), and the processing behaviour (the key requirement is sufficient fluidity).

In past, commercial DR MMCs producers have decided to use commercial wrought or casting alloy compositions as matrix material. To day, the matrix is selected following the above mentioned criteria.

On this way, it is necessary to answer on the following fundamental question: Is it a better approach to select the ceramic reinforcement and after that to look for a compatible matrix, or to select the matrix and than to define the adequate ceramic reinforcement? It seems that both approaches are reasonable. To date, the final selection of one of the variables - the matrix or the reinforcement, introduces very serious limitations in the selection of the second. Moreover, note that by selecting the matrix and the reinforcement, the technological ability for the production of a requested composite are also defined, almost in all.

To illustrate the complexity of this selection, the most important examples concerning alloy additions to aluminium matrix relative to Al-SiC DR MMCs and some additional factors which consider the interaction of metal matrix with the reinforcement are itemised in ref. 21.

### 3.3 Cost of reinforcement

It is well known that the main reason for using particles as the reinforcement in MMCs is to reduce the cost of the composite. Referring to the cost, one can recognise three categories of ceramic reinforcement:

(i) Fillers which are more expensive as the matrix. To date, in this class are all commercially available synthetic ceramic powders with well defined morphology and chemical composition. The two reinforcements receiving the most attention are SiC and Al<sub>2</sub>O<sub>3</sub>. However, very recently, AlN has also introduced as cost effective performance material for a broad array of filled light metal<sup>10</sup>. Other to costly reinforcements like zircon, alumina, silica, titanium carbide, silicon nitride, boron nitride and other, are still used in lab scale.

(ii) Fillers which cost is comparable with the matrix cost. The representatives of this class are coarser powders usually prepared by milling and some purification of natural products like graphite (carbon), shell char, clay, mica, talc etc. - for more informations see reference<sup>17</sup>.



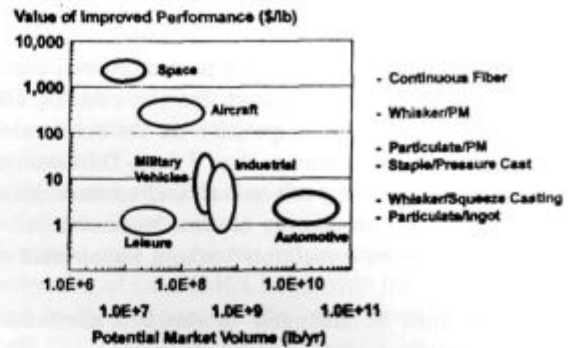
(iii) Fillers which are less expensive as the matrix. Some waste by-products like fly ash<sup>2</sup>, slag<sup>32</sup>, sludge waste from high speed steels<sup>33</sup>, etc. Note that the introduction of these fillers results in composites which are cheaper as an unreinforced matrix.

Of course, the above listed status is subject to rapid changes. Large efforts are invested and also planning to be applied in further improvement of economy of ceramic powders preparation routes. Nevertheless, it is unrealistic to expect that in next one or two decades the synthetic ceramic fillers will become cheaper as the light metal matrix. Hence, the further selling of the concept of MMCs will be strictly on the value added basis i.e. on the improvement of the price/quality ratio. However, there must be a market pull for the improved properties before anyone will agree to pay for them. If the final users dwell on the price first, there will be little incentive for developing innovative solutions.

### 3.3 Price for the increasing performances

The whole DR MMCs business philosophy is build up on the value added basis. In other words, the introduction of carefully selected ceramic reinforcement into a light alloy matrix should result in a profitable material. The possible target prices for the increasing performances of DR MMCs concerning different market segments are indicated in **Figure 1**. Note that automotive - the largest potential market for DR MMCs is traditionally interested in very low value of improved performance. The problem is that none of the available DR MMC's production technologies can meet these requirements. The present competition of various DR MMCs production methods is demonstrated in **Table 2**. As evident, all potential production methods are still operated in no added value region. However, it is also important to note that, according to the very low production cost, foundry methods have the largest potential shear of added value. The problem is how to meet the market specifications at the same target price or, on the other words, how to improve the quality of castable DR MMCs inside the same cost segment?

## Value of Performance vs. Cost



**Figure 1:** The target prices and the potential market for the increasing performances of DR MMCs (source: Advanced Refractory Technologies, Inc., USA)

**Slika 1:** Cene in trg za različno ojačane kompozite s kovinsko matriko (vir: Advanced Refractory Technologies, Inc., USA)

Unfortunately, there is no single, well defined type of market specification. Market requirements are sprayed up on better structural and thermal performances, cost effective machining, ability to recycle or reclaim the individual components of the composite, etc. The situation is somewhat complicated by the fact that many of these requirements are opposite and exclude each other.

It is evident that the introduction of discontinuous reinforcement into a light metal matrix can improve the mechanical properties of matrix very modestly in comparison with continuous reinforcement. However, very often in some composite applications, the mechanical properties are not critical. Addition of SiC particles to aluminium alloy can reduce the coefficient of thermal expansion of the alloy, still maintaining the thermal conductivity equivalent of the matrix alloy. As recognised many times in practice, low coefficient of thermal expansion and high thermal conductivity is an attractive combination for applications requiring dimensional stability.

In many cases, the wear resistance is the most critical composite specification. Because of their excellent wear resistance, DR MMCs are candidates for bearings, bushings, cylinder liners, and break rotors. Frequently, high

**Table 2:** Current quality and cost level for DR MMCs produced by different liquid metal routes and by powder metallurgy

	Classical foundry methods	Squeeze casting	Melt reinforcement in situ	Infiltration	Powder metallurgy
Target Quality (for structural application in automotive industry)	100	100	100	100	100
Target Price (for structural application For special in automotive industry) application	3-4	3-4	4-6	6-8	20-40
Current Quality Level	60-80	70-80	40-90	80-90	>100
Current Price Level (\$/kg) (for non-shaped ingot)	6	5-6	10	10-15	>30
Current Cost of Production (\$/kg) (for non-shaped ingot)	4-5	3,5-5	5-7	10-15	>20

Source: Alpha and Omega in Composites, 1996

wear resistance is required only at the surface of the component, and the ability to prepare a composite with some gradient of hardness and wear resistance could be the most competitive solution for a particular final user.

To date, it is well established that the castable DR MMCs will be the most competitive on the automotive market. As defined by Schuster et al.<sup>34</sup> from Duralcan, to be castable in both the economical and technological sense, DR MMCs must comply to three basic criteria:

1. The ingot must be remeltable without impairment of properties
2. The melt must be amenable to standard aluminium foundry practices, and
3. The casting must be substantially defect-free, having mechanical properties that are both consistent and superior.

The real castable systems are, unfortunately, faraway from these expectations. Very recent investigation of the influence of silicon carbide particle size, aspect ratio and volume fraction on room temperature tensile properties of DR MMC showed that, according to the strengthening mechanism, higher volume fraction and smaller particle size are beneficial<sup>35</sup>. On the other hand, because silicon carbide particles were introduced and dispersed into molten aluminium alloy by a mechanical stirring method, adding particles resulted in casting defects which deteriorate the properties of the composite. In this way, the damage accumulation processes caused by cast and extrusion defects, limit further improvement of the mechanical properties of cast MMCs based on a high reinforcement aspect ratio. Because of that, the use of costly reinforcement like SiC platelets or whiskers in cast MMCs seems unreasonable. However, the same study has shown that the introduction of fine (less than 10  $\mu\text{m}$ ) rounded-off SiC particles combined with significant reduction in cast and extrusion defects could result in much better mechanical properties of Al-SiC composites. It was also recommended that the key factor which needs to be controlled is the fluidity of the melt and not the shape and type of reinforcement.

Of course, the immersion of fine ceramic particles directly into a melt by mechanical stirring is not the only possible way for production of castable DR MMCs. Moreover, it seems that the potential of direct mechanical or even chemically activated immersion of ceramic particles in molten metal has already been explored. Most of these procedures are operated by ceramic particles in the 10-20  $\mu\text{m}$  size range. On the contrary, it was shown<sup>36</sup> that finer particles can be successfully produced in situ into a melt and this might be a new effective direction for the preparation of castable DR MMCs with superior mechanical properties.

Two types of in situ methods are currently the subject of intensive investigations:

1. In situ preparation of continuous interconnected ceramic and metal phases in ceramic-metal composites. These composites are not discontinuously reinforced

and are usually prepared by direct nitriding or oxidation of molten binary aluminium alloys, as discussed previously or in combination of the pressureless infiltration of porous ceramic preforms and the chemical conversion of the metal phase to the ceramic reinforcement. It's also important to stress that this technology allows the economical production of finished components over a wide range of size, from very small to very large in complex configurations and to net or near-net shape. However, from economical point of view, the process is down to be competitive with the conventional casting. The near-net shaping of final components by preform infiltration could be much more competitive in comparison with the rather expensive machining such as sawing, milling, drilling, reaming, and tapping of final parts.

2. In situ preparation of discontinuous reinforcement into a melt via the use selected chemical reactions and the following stirring of the dispersion. There are only few very recent articles in open literature concerning these methods<sup>12,14</sup> as an alternative for the production of castable DR MMCs and it is difficult to assess the final cost of these materials, hence, also the real level of added value. However, there is no doubt that these research programs are all focused on the production of castable DR MMCs with finer ceramic dispersoids and with improved mechanical properties.

#### 4 Some general comments

Following different criteria and accumulated data one can conclude that DR MMCs will become an engineering material of general use. At the end of 1970s, the automobile and transport industries all around the world had a very strong interest in and high hopes for DR MMCs, due to their superior specific strength and rigidity over conventional aluminium alloys. After two decades of development, the first DR MMCs application, an engine connecting-rod is ready to market. Also, major applications in the automobile industry, such as brake rotors and drive shafts, are now in the late stages of development, and other engineering applications are already well advanced. DR MMCs technology is now recognised in the world-wide industry and research groups in this field are also able to introduce remarkable applications of these materials to the market.

Three main problems must be solved in order to facilitate the expanding application of DR MMCs with light alloys matrix metals. These are:

1. Superior cost performances - in Al based DR MMCs the quality/cost ratio should be more than one (the values between 1,3 - 1,5 are strongly requested). That means DR MMCs should be a class of high profitable materials with, at least, 30-50% of added value.
2. Active implementation of environmental concerns - DR MMCs should be the easy recyclable or, at least, reclaimable materials.



3. The improved ductility - the ductility of the composite should be near to the ductility of the unreinforced matrix.

In this moment, the solving of these problems is impossible. However, many researchers and managers firmly believe that solutions will be found if the same amount of energy is devoted to solving these problems as that which was expended during the last two decades of DR MMCs research and development.

It is also necessary to point out that the long history of steel could learn us how difficult is to optimise the microstructure of advanced materials especially if their consist from several phases. There are some estimations that the final optimisation of the DR MMCs will take next 20-30 years<sup>37</sup> and, it will be a very dramatic episode of material of science - i.e. much more as the story of advanced monolithic materials.

To date, it's too early to predict what the "perfect" solution will be. It seems that DR MMCs should be defect free castable and re-castable - on this way the most inexpensive processes for production of final components could be established. Referring to this, the cost effective preparation of dispersion with at least 20 vol% of fine (less than 10  $\mu\text{m}$ ) ceramic particles produced in situ or introduced directly into a melt becomes as, probably, the key technological request. Three main questions - big 3Q's - are:

1. How to improve the wetting behaviour between ceramic particles and molten alloy in order to make their immersion much more easier and cost effective?
2. How to stabilise fine ceramic dispersoids into dispersion and to prevent their agglomeration, settling and rejection after a successful immersion?
3. How to improve the fluidity of dispersion of small ceramic particles? As reported, a sufficient fluidity is required to enable ingot casting directly from the composite processing reactor and, also, the casting fluidity after remelting of composite billets, is necessary for the secondary shape casting of composite parts.

The "Big 3Q's" are fundamental questions and the answers will be found through the opening of the new frontiers in the knowledge of wetting, surface engineering and the interfacial chemistry. It is speculated in ref. 38 that the wetting of ceramic particles by the molten metal could be improved by introducing very exothermic interface reactions which provide sufficient energy for the wetting activation. The same authors suggested that, in principle, the stabilisation of ceramic particles previously dispersed in molten metal could be promoted by some endothermic interfacial reactions which binds a part of intrinsic energy of ceramic dispersoids. The authors demonstrated some progress made on this way in the Al-SiC system<sup>39</sup>. However, the effectiveness of the offered solution is still very close to the existing commercial foundry procedures which operate with particles in size 10 to 20  $\mu\text{m}$ .

The improvements in fluidity could be, probably, achieved using new alloying elements or additives or, even, increasing the melt temperature (the rising of working temperature could also enhance the wetting tendency between particles and melt, but, unfortunately, in the same time, also the reactivity between particles and molten alloy).

However, it seems that the type and the shape (aspect ratio) of discontinuous reinforcement don't play the dominant role in further improvements of mechanical properties of DR MMCs but mostly the size and the volume fraction of successfully incorporated particles into a melt.

## 5 Conclusions

The further commercialisation of DR MMCs will be strictly on the value added basis. To be successful on market, DR MMCs should become a class of high profitable materials. With only modest improvements in most mechanical properties and even by a worse ductility as in unreinforced matrix, the producers of DR MMCs now offer to final users preferably superior wear resistance and some flexibility in tailoring of thermal properties of DR MMCs and still not profitable concept for their future structural applications.

In order to achieve this end, castable, defect free DR MMCs with at least 20 vol% of fine (less than 10  $\mu\text{m}$ ) ceramic particles in matrix should be prepared in cost effective way.

In the present paper, some general recommendations concerning this aim have been suggested. It was estimated that the type and the shape (aspect ratio) of ceramic reinforcement will not play the dominant role in further improvement of mechanical properties of castable DR MMCs but their size, homogeneous distribution and volume fraction.

On the contrary, the immersion of fine particles into a melt or their in situ formation as well as their stability into dispersion will be mostly governed by the surface chemistry of ceramic dispersoids and interfacial chemical reactions between particles and melt.

However, prior to take all advantages of discontinuous reinforcement of light metals on high profitable way, further, very fundamental knowledge, concerning the wetting of ceramic particles by the molten metal and the fluidity of dispersions, should be developed.

## 6 References

- <sup>1</sup> D. J. Lloyd, *Intern. Materials Reviews*, 39, 1994, 1-23
- <sup>2</sup> P. K. Rohatgi, *Foundry: Management & Technology*, 10, 1995, 32-37
- <sup>3</sup> H. Sekine and R. Chen, *Composites*, 26, 1995, 183-188
- <sup>4</sup> A. L. Geiger and J. A. Walker, *JOM*, 1991, august, 8-15
- <sup>5</sup> D. J. Lloyd, *Intrinsic and Extrinsic Fracture Mechanisms in Inorganic Composite Systems, Proceedings of a Symposium held during the TMS Annual Meeting in Las Vegas, Nevada, February, 12-16, 1995*, Eds. J. J. Lewandowski and W. H. Hunt, Jr.
- <sup>6</sup> B. Roebuck and J. D. Lord, *Mater. Sci. Technol.*, 1990, 6, 1199-1209

- <sup>7</sup> D. J. Lloyd, H. P. Lagace and A. D. McLeod: in "Controlled Interphases in Composite Materials-ICCM-III", (ed. H. Ishida), 1990, 359-376, London, Elsevier Applied Science
- <sup>8</sup> M. K. Surappa and P. K. Rohatgi, *Metall. Trans.*, 12B, 1981, 372-332
- <sup>9</sup> T. Sritharan, K. Xia, J. Heatcock and J. Mihelich, *Metal & Ceramic Matrix Composites: Processing, Modeling & Mechanical Behaviour*, Eds. R. B. Bhagat, A. H. Clauer, P. Kumar and A. M. Ritter, The Minerals, Metals & Materials Society, 1990, 13-22
- <sup>10</sup> Advanced Refractory Technologies, Inc. Company Paper-AIN-9606
- <sup>11</sup> M. K. Aghajanian, N. H. Macmillan, C. R. Kennedy, S. J. Luszcz and R. Roy, *J. Mat. Sci.*, 24, 1989, 658-670
- <sup>12</sup> D. W. Yuan, V. S. Chengn, R. F. Yan and G. Simkovich, *Cer. Eng. Sci. Proc.*, 15, 1994, 4, 85-89
- <sup>13</sup> M. K. Aghajanian, J. P. Biel and R. G. Smith, *J. Am. Ceram. Soc.*, 77, 1994, 7, 1917-20
- <sup>14</sup> G. H. Schiroky, D. V. Miller, M. K. Aghajanian and A. S. Fareed, will be published in *Proc. of CMMC 96*, September 9-12, 1996, San Sebastian, Spain
- <sup>15</sup> U.S. Pat. 4 710 348, 1987
- <sup>16</sup> R. E. Loehman, K. G. Ewsuk, W. F. Fahrenholtz, B. B. Lakshman and A. P. Tomsia, will be published in *Proc. of CMMC 96*, September 9-12, 1996, San Sebastian, Spain
- <sup>17</sup> P. K. Rohatgi, R. Asthana and S. Das, *Intern. Metals Reviews*, 31, 1986, 3, 115-139
- <sup>18</sup> U.S. Pat. 4 759 995, 1988
- <sup>19</sup> U.S. Pat. 4 786 467, 1988
- <sup>20</sup> U.S. Pat. 4 865 806, 1989
- <sup>21</sup> M. G. McKimpson and T. E. Scott, *Mater. Sci. Eng.*, A107, 1989, 93-106
- <sup>22</sup> J. V. Naidich, *Prog. Surf. Membr. Sci.*, 14, 1981, 353-483
- <sup>23</sup> F. Delannay, L. Froyen and A. Deruytere, *J. Mater. Sci.*, 22, 1987, 1-16
- <sup>24</sup> R. Warren and C. H. Andersson, *Composites*, 15, 1984, 101-111
- <sup>25</sup> V. M. Kevorkijan and B. Šuštaršič, *Composite Materials, Mechanics and Processing, Proc. of the 10th Technical Conference on Composite Materials*, Santa Monica, October 18-20, Lancaster, Technomic Publishing Company, ISBN 1-56676-376-2, 1995, 569-581
- <sup>26</sup> F. A. Giro, J. M. Quenisset and R. Naslain, *Composites Science and Technology*, 30, 1987, 155-184
- <sup>27</sup> S. V. Prasad and P. K. Rohatgi, *Journal of Metals*, 1987, 22-26
- <sup>28</sup> S. Turenne, S. Caron, O. Weiss and J. Masounave, *Fabrication of Particulates Reinforced Composites, Proc. of International Conference on Fabrication of Particulate Reinforced Metal Composites*, Montreal, 17-19 September, 1990, ASM International, Materials Park, Ohio 44073, 1990, 271-276
- <sup>29</sup> P. K. Rohatgi, in *Metals Handbook*, 9th Edition, Vol.15, Casting, ASM International, Metals Park, Ohio 44073, 1988, 840-854
- <sup>30</sup> T. Otani, B. McEnaney and V. D. Scott, *Cast Reinforced Metal Composites, Proc. of the International Symposium on Advances in Cast Reinforced Metal Composites*, Chicago, 24-30 September 1988, ASM International, 1988, 383-389
- <sup>31</sup> E. Maahn and S. Roepstorff, *Metal Matrix Composites-Processing, Microstructure and Properties, Proc. of the 12th Riso International Symposium on Material Science*, Roskilde, Denmark, 2-6 September 1991, 497-502
- <sup>32</sup> V. Kevorkijan, investigation report on the project J2-6184-0795, Slovene Ministry of Science and Technology
- <sup>33</sup> K. U. Kainer and M. Opoku-Adusei, will be published in *Proc. of CMMC 96*, September 9-12, 1996, San Sebastian, Spain
- <sup>34</sup> D. M. Schuster, M. D. Skibo and W. R. Hoover, *Light Metal Age*, 1989, 15-19
- <sup>35</sup> V. M. Kevorkijan and B. Šuštaršič, will be published in *Proc. of CMMC 96*, September 9-12, 1996, San Sebastian, Spain
- <sup>36</sup> R. M. Aikin, Contract Report 4276, NASA, 1990
- <sup>37</sup> J. LLorca and C. Gonzalez, will be published in *Proc. of CMMC 96*, September 9-12, 1996, San Sebastian, Spain
- <sup>38</sup> V. Kevorkijan, will be published in *Ceramic Transactions*, 1996
- <sup>39</sup> V. Kevorkijan, will be published in *Proc. of the 11th Technical Conference on Composite Materials in Atlanta*, October 7-9, 1996