

# EXPERIMENTAL INVESTIGATION OF THE STABILITY OF PARTICULATE DISPERSOID SUSPENSIONS IN ALUMINUM AND MAGNESIUM MELTS

## RAZISKAVE STABILNOSTI SUSPENZIJE KERAMIČNIH DELCEV V Al IN Mg TALINAH

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The rejection of  $\text{Si}_3\text{N}_4$ ,  $\text{Mg}_3\text{N}_2$ ,  $\text{AlN}$  and  $\text{Si}$  particles from different slurries consisting of molten aluminum and magnesium alloy with 10% of silicon or pure molten metals was experimentally investigated by measuring changes in the electrical resistance of the slurries before and after rejection occurred. In stirring experiments, only individual powder fractions which passed through a 45  $\mu\text{m}$  sieve screen and remained on a 30  $\mu\text{m}$  screen were applied. The experiments showed that the rejection of  $\text{Si}_3\text{N}_4$  particles from Al-10%Si and Mg-10%Si melts occurs when more than 17-18 vol.% of the ceramic phase is dispersed into the melt, while in pure Al and Mg molten metals spontaneous rejection occurs at 7-8 vol.% of the introduced ceramic phase. A similar tendency of rejection (at 16-18 vol.% of particulate in slurry) was also observed during the introduction of silicon particles into Al-10%Si and Mg-10%Si melts.

In contrast, the incorporation of  $\text{AlN}$  and  $\text{Mg}_3\text{N}_2$  particles in Al-10%Si and Mg-10%Si melts as well as in pure molten aluminum and magnesium resulted in rejection at a low volume concentration of the ceramic phase (less than 4 vol.%).

Based on the same rejection tendency of  $\text{Si}_3\text{N}_4$  and  $\text{Si}$  particles in molten Al and Mg alloys as well as the same rejection tendency of  $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$  and  $\text{Mg}_3\text{N}_2$  particles in pure molten metals, the contribution of an in situ interfacial chemical composition (especially the presence of free silicon) and/or an in situ interfacial chemical reaction to the successful incorporation of ceramic particles into a melt is discussed.

The role of silicon was particularly investigated by the immersion of silicon particles into molten Al and Mg alloys containing 10% of silicon.

Keywords: metal-matrix composites, particle-reinforced composites, interface, surface treatments, casting, chemically activated wetting

Preučevali smo stabilnost suspenzij  $\text{Si}_3\text{N}_4$ ,  $\text{Mg}_3\text{N}_2$ ,  $\text{AlN}$  in delcev  $\text{Si}$  (sejalna frakcija med 30 in 45  $\mu\text{m}$ ), dispergiranih v raztaljenem aluminiju in magneziju ter talinah iz Al- in Mg-zlitin z 10 % silicija. Izločanje delcev iz talin smo eksperimentalno ugotavljali s spremembami električne upornosti taline.

Ugotovili smo, da prihaja do izločanja delcev  $\text{Si}_3\text{N}_4$  in  $\text{Si}$  iz raztaljenih zlitin Al-Si in Mg-Si z 10 vol.% silicija šele, ko koncentracija delcev v obeh talinah doseže 16-18 vol.%. Pri talinah iz čistega aluminija in magnezija se delci  $\text{Si}_3\text{N}_4$  večinoma izločijo, ko njihova koncentracija doseže 7-8 vol.%.

Nasprotno od tega se delci  $\text{AlN}$  in  $\text{Mg}_3\text{N}_2$  ne glede na to, ali so dispergirani v raztaljeni zlitini Al-Si in Mg-Si z 10 % silicija ali v čisti kovini, spontano izločijo pri koncentraciji keramične faze, ki praviloma ne presega 4 vol.%.

Različno stabilnost suspenzij keramičnih delcev v talini Al in Mg smo skušali pojasniti z reaktivnostjo med raztaljeno kovino in dispergiranimi delci oz. s kemijskimi reakcijami, do katerih prihaja na meji med keramično fazo in talino, v katerih igra aktivno vlogo kovinski silicij.

Ključne besede: kompoziti s kovinsko osnovo, diskontinuirana ojačitev s keramičnimi delci, kemijske reakcije na fazni meji, kemično aktivirana omočljivost keramičnih delcev s talino

## 1 INTRODUCTION

Aluminum-and magnesium-based metal-matrix composites (MMCs) are an important class of high-potential engineering materials. However, material costs and processing difficulties have been identified as the two most significant barriers for their wide-spread commercial use. In order to overcome these obstacles, the incorporation of ceramic particles into a molten metal by stir-casting is still under serious engineering evaluation<sup>1</sup>.

The main limitation in stir-casting procedures is the very poor wettability of the ceramic particles with molten aluminum and magnesium alloys which leads to the spontaneous rejection of the ceramic phase from the

suspension. In many cases, rejection occurs at concentrations of the ceramic phase no higher than 2-10 vol.%, thus making processing of composites with more than 10 vol.% of particulate ceramic reinforcement via this route extremely difficult.

Consequently, an important part of the research work on the preparation of discontinuously reinforced metal matrix composites by liquid metal routes is directed towards an understanding of processes able to maintain ceramic particles in a slurry, avoiding their spontaneous rejection.

All existing theories are unique in the fact that the local chemical composition at the interface between the ceramic phase and the liquid metal plays the most

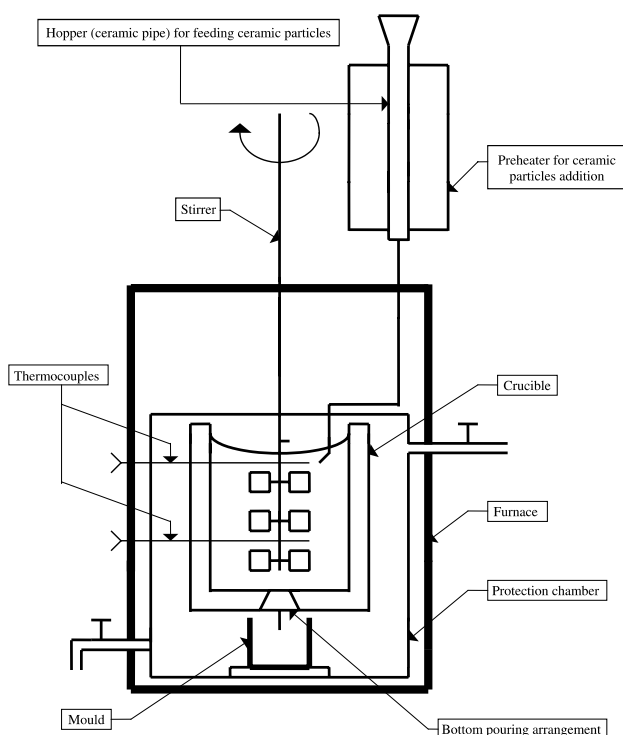
important role in retaining the immersed particles in the slurry. However, the real qualitative and quantitative contribution of this interfacial chemistry on the stabilization of ceramic particles in a slurry is still unclear and is the subject of different scientific interpretations<sup>2-4</sup>.

The purpose of this work was to demonstrate that the stable dispersion of ceramic particles in a molten aluminum- and magnesium-alloy slurry is dynamically influenced by the chemical composition of the interface. In order to point out the role of the interfacial chemical reaction in keeping the ceramic particles in a dispersion, different slurries were investigated.

In all the experiments the concentration of ceramic particles in the melt at which their rejection from the slurry occurs was experimentally determined by measuring changes in the electrical resistance of the slurry. The method of measurement of changes in electrical resistance of a slurry was described in a previous study<sup>5</sup>. Based on the results obtained for different slurries and different slurry-preparation paths, an explanation for the contribution of the interfacial reaction in keeping ceramic particles in the slurry is proposed.

## 2 RAW MATERIALS

For the preparation of different slurries, aluminum and magnesium alloys with 10% of silicon, as well as pure aluminum and pure magnesium melts, were used.



**Figure 1:** Diagram of the experimental set-up  
**Slika 1:** Shematski prikaz aparature

The following commercial powders were selected as the particulate constituents of the slurries:  $\text{Si}_3\text{N}_4$  powder (supplier: Alfa Aesar; grade: 325 mesh powder),  $\text{Mg}_3\text{N}_2$  powder (supplier: Alfa Aesar; grade: 325 mesh powder), AlN powder (supplier: ART; grade: 325 mesh powder) and Si powder (supplier: Alfa Aesar; grade: 325 mesh powder).

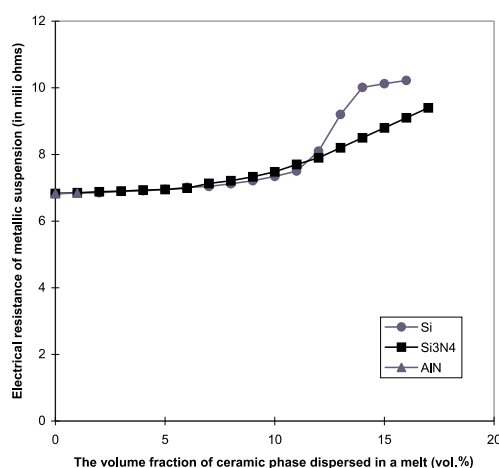
For the stirring experiments only individual powder fractions which passed through a  $45\ \mu\text{m}$  sieve screen and remained on a  $30\ \mu\text{m}$  screen were used.

## 3 APPARATUS

The apparatus consisted of a mullite (for Al slurries) or magnesia crucible (for Mg slurries) placed inside a resistance heated vertical muffle furnace, **Figure 1**. For a more detailed description of the apparatus see<sup>5</sup>.

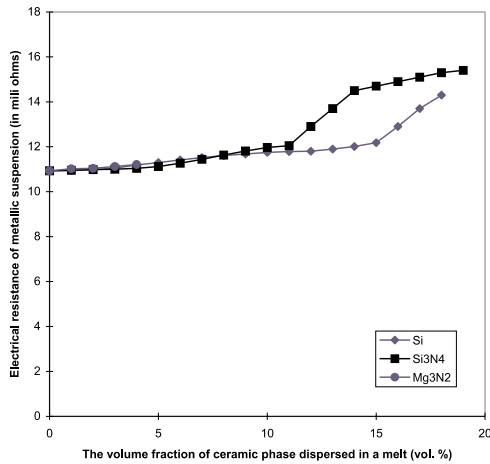
In order to accurately determine the moment of rejection of the ceramic particles from the slurry, a pair of semi-cylindrical gold plated stainless steel electrodes was installed near the wall of the crucible to measure the changes in electrical resistance of the metallic suspension of ceramic particles to within  $\pm 1\ \text{m}\Omega$ .

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



**Figure 2:** Variation of electrical resistance,  $R$ , with volume fraction of Si,  $\text{Si}_3\text{N}_4$  and AlN particles dispersed in an Al alloy with 10% of silicon

**Slika 2:** Sprememba električne upornosti,  $R$ , v odvisnosti od prostorninskega deleža Si,  $\text{Si}_3\text{N}_4$  in delcev AlN, dispergiranih v zlitini Al-Si z 10% silicija



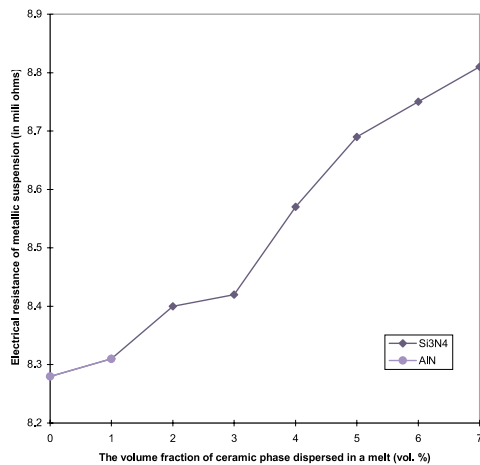
**Figure 3:** Variation of electrical resistance, R, with volume fraction of Si, Si<sub>3</sub>N<sub>4</sub> and Mg<sub>3</sub>N<sub>2</sub> particles dispersed in a Mg alloy with 10% of silicon

**Slika 3:** Sprememba električne upornosti, R, v odvisnosti od prostorninskega deleža Si, Si<sub>3</sub>N<sub>4</sub> in delcev Mg<sub>3</sub>N<sub>2</sub>, dispergiranih v zlitini Mg-Si z 10% silicija

#### 4 IMMERSION OF CERAMIC REINFORCEMENT INTO THE MELT

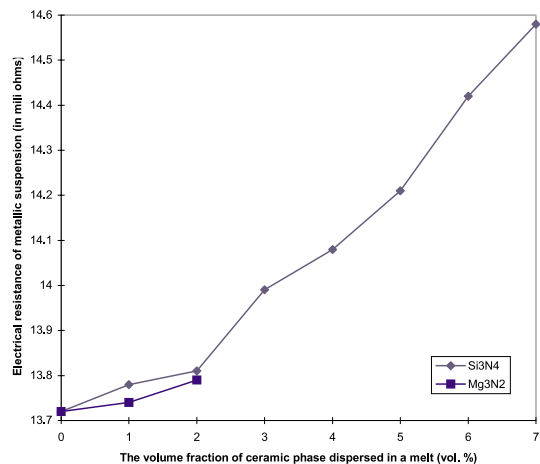
Before the particles were added, argon gas was bubbled through the melt at a rate of 100 cm<sup>3</sup>/min for a period of about 15 min in order to remove oxides, particles, dissolved gas, and other impurities that inhibit wetting. About 0.5 dm<sup>3</sup> of aluminum or magnesium alloy was melted in the 1.5 dm<sup>3</sup> crucible and heated to the appropriate temperature.

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



**Figure 4:** Variation of electrical resistance, R, with volume fraction of Si<sub>3</sub>N<sub>4</sub> and AlN particles dispersed in a pure Al melt

**Slika 4:** Sprememba električne upornosti, R, v odvisnosti od prostorninskega deleža Si<sub>3</sub>N<sub>4</sub> in delcev AlN, dispergiranih v čistem, raztaljenem aluminiju



**Figure 5:** Variation of electrical resistance, R, with volume fraction of Si<sub>3</sub>N<sub>4</sub> and Mg<sub>3</sub>N<sub>2</sub> particles dispersed in a pure Mg melt

**Slika 5:** Sprememba električne upornosti, R, v odvisnosti od prostorninskega deleža Si<sub>3</sub>N<sub>4</sub> in delcev Mg<sub>3</sub>N<sub>2</sub>, dispergiranih v čistem, raztaljenem magneziju

flow. Ceramic particles were added to the slurry at the rate of 0.6 kg/h at a constant stirring speed (1200 rpm).

#### 5 RESULTS

Characteristic variations in the electrical resistance, R, of a metallic suspension of ceramic particles before and after rejection occurred are presented in **Figures 2, 3, 4 and 5** for the different Al- and Mg-based slurries used in this work.

Using the experimental data for the volume flow of ceramic particles from the preheater to the melt, the moment of rejection can be correlated with the volume fraction of ceramic particles introduced into the melt, which is more convenient for further evaluation.

These data are summarized in **Table 1**.

**Table 1:** The volume fraction of ceramic particles introduced into the melt at which rejection occurred

**Tabela 1:** Prostorninski delež keramične faze pri katerem prihaja do izločanja delcev iz taline

System	The volume fraction of ceramic particles introduced into the melt at which rejection occurred (vol.%)*
Si <sub>3</sub> N <sub>4</sub> particles in Al alloy	17**
Si <sub>3</sub> N <sub>4</sub> particles in pure Al	7
AlN particles in Al alloy	3
AlN particles in pure Al	2
Si particles in Al alloy	16
Si <sub>3</sub> N <sub>4</sub> particles in Mg alloy	19
Si <sub>3</sub> N <sub>4</sub> particles in pure Mg	8
Mg <sub>3</sub> N <sub>2</sub> particles in Mg alloy	4
Mg <sub>3</sub> N <sub>2</sub> particles in pure Mg	3
Si particles in Mg alloy	18

\* Accuracy: ±5%

\*\* All values are an average of 25 measurements

## 6 DISCUSSION

The experiments performed in this study were aimed at clarifying the importance of the interfacial chemical reaction occurring during immersion and of the chemical composition of the interface in preventing the rejection of the ceramic phase from the slurry.

It is well known that in reactive metal-ceramic systems the most common strategy to improve the dispersion of ceramic particles in a molten metal is by promoting chemical reactivity between the liquid and the solid<sup>6</sup>. It is widely believed that wetting is better if some interfacial reactions can occur, although the importance of whether it actually does is still unclear. According to some explanations, the main contribution to the driving force of wetting is the free energy produced by the reaction<sup>7</sup>, changes in relevant interfacial energies caused by growth of a *continuous* layer of a new phase at the interface<sup>8</sup>, or reverse interfacial coupling<sup>5</sup>.

The main difficulty in better understanding the role of the interfacial reaction is in the fact that there is no convenient method for monitoring and analyzing the interface between the solid and liquid which is the *real existing interface* in the system during immersion and mechanical stirring. Because of this, later characterization of the solid-solid interface in the solidified species can provide the correct information as to what *really* occurred at the liquid-solid interface resulting in spontaneous rejection of particles from the melt.

Recently, a simple method for determining the moment of rejection by measuring *the changes* in electrical resistance of the slurry was successfully introduced<sup>5</sup>. The method was named CER - Changes in Electrical Resistance. The simplicity of the method is due to the fact that for determining the moment of rejection it is only necessary to measure the changes in electrical resistance of the slurry and not the absolute value of the electrical resistance, which depends on the geometry of the crucible as well as the geometry and arrangement of the electrodes. Determining in this way the course of the introduction of ceramic particles into the melt before rejection occurs, one can calculate the volume fraction of ceramic particles successfully introduced before rejection, or, in other words, the critical concentration of ceramic particles at which spontaneous rejection occurred. The other great advantage of this method is its experimental repeatability which means that the value of the critical concentration of ceramic particles in the slurry at which spontaneous rejection occurs represents an average of as many as 20-30 measurements.

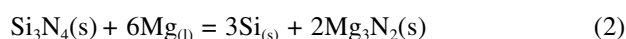
In a previous study<sup>5</sup>, it was demonstrated that during rejection, which is a very fast process completed in less than 1 s, the immersed ceramic particles are completely removed from the melt. Due to this, the electrical resistance of the melt after rejection is practically equal

to the electrical resistance of the molten alloy before immersion started.

To verify the main hypothesis of the current study that the presence of silicon at the interface between molten aluminum or magnesium alloy and the immersed ceramic phase significantly increases the volume fraction of the ceramic phase dispersed in the melt, the following different experimental paths were arranged and performed:

Si<sub>3</sub>N<sub>4</sub> particles were introduced into a molten aluminum and magnesium alloy with 10% of silicon at a temperature 40-50 °C above the melting point of the alloy and the moment of rejection of the particles from the slurry determined using the CER method.

It is well known that the following displacement reactions could proceed at the liquid-solid interface of the appropriate slurries<sup>9,10</sup>:



Since the molten alloys contain 10 % of silicon, additional silicon produced by interfacial reactions (1) and (2) could remain at the ceramic-melt interface, in this way improving the wetting behaviour of the ceramic particles during their immersion in the melt.

In the second experimental path, the same Si<sub>3</sub>N<sub>4</sub> particles were introduced into pure aluminum and magnesium molten metal at the same temperature as in the previous experimental path. Also in this case, the moment of rejection of particles from the slurry was determined using the CER method. On the previous assumption, interfacial reactions (1) and (2) can still proceed. However, the solid silicon produced by the interfacial reactions will be dissolved in the melt due to its excellent solubility in molten aluminum and magnesium. In this case, one can expect that the wetting behaviour of the ceramic particles should be governed by the wetting between the AlN layer formed on the surface of the Si<sub>3</sub>N<sub>4</sub> particles dispersed in molten aluminum and the Mg<sub>3</sub>N<sub>2</sub> layer formed on the surface of the Si<sub>3</sub>N<sub>4</sub> particles dispersed in the molten magnesium. To confirm this, as-received AlN and Mg<sub>3</sub>N<sub>2</sub> particles with the same particle size and a similar particle size distribution as the powders used in the previous experimental paths were introduced into molten Al and Mg alloys with 10% of silicon, as well as in pure molten aluminum and magnesium at the same temperature as in the previous experimental path. The moment of rejection of particles from slurry was also determined by the CER method.

Finally, in the fourth experimental path, solid silicon particles with the same particle size and similar particle size distribution as the Si<sub>3</sub>N<sub>4</sub> particles used in the previous two experimental paths were dispersed in molten Al and Mg alloys with 10% of silicon, and additionally, in a separate experiment, into molten pure aluminum and magnesium. As before, the moment of

rejection of particles from the slurry was determined by the CER method.

From the collected results it is evident that there is no significant difference in the volume concentration of silicon and  $\text{Si}_3\text{N}_4$  particles rejected from molten Al and Mg alloys with 10% of silicon. This similarity is probably caused by the same chemical composition at the interface. Unfortunately, there is no experimental technique capable of confirming this assumption by measuring the real chemical composition at the interface in situ during immersion and rejection.

The only way of checking the validity of the above assumption is by immersion of particles with no silicon on the interface (as-received AlN and  $\text{Mg}_3\text{N}_2$ ). As evident from the experimental data, rejection occurred at very low volume fractions of ceramic particles introduced into the melt, which indirectly confirms the importance of silicon on the interface for the stabilization of ceramic particles in a melt. Moreover, the results obtained indicate that rather than an interfacial reaction, an appropriate chemical composition of the interface plays the dominant role in stabilization of ceramic particles in a melt. Of course, the validity of this conclusion is limited to the systems used in this study.

## 7 CONCLUSION

In accordance with the collected data it is evident that the mixing of  $\text{Si}_3\text{N}_4$  particles in Al and Mg alloys with 10% of silicon is possible without rejection up to 17-18 vol.%.

In contrast, the incorporation of  $\text{Si}_3\text{N}_4$  into pure Al and Mg molten metals leads to the spontaneous rejection of all particles at 7-8 vol.% of introduced ceramic phase.

The incorporation of AlN and  $\text{Mg}_3\text{N}_2$  particles into Al and Mg alloys with 10% of silicon, as well as into pure aluminum or magnesium molten metals, resulted in rejection of the ceramic phase at an early stage of mixing (typically at less than 4 vol.%).

Immersion of silicon particles into Al and Mg alloys with 10% of silicon was successful up to 16-18 vol.% of the ceramic phase.

Based on these results one can conclude that the mixing capabilities of  $\text{Si}_3\text{N}_4$  and Si particles in molten Al and Mg alloys with 10% of silicon are almost the same, while the introduction of AlN and  $\text{Mg}_3\text{N}_2$  particles into the same melts soon result in rejection.

However, the mixing behaviour of  $\text{Si}_3\text{N}_4$  particles in pure molten metals (Al and Mg) is completely different and resembles the behaviour of AlN and  $\text{Mg}_3\text{N}_2$  particles.

A possible explanation for this could be in the chemical reactivity of  $\text{Si}_3\text{N}_4$  with Al and Mg alloys

containing 10% of silicon, as well as with pure Al and Mg. However, in molten Al and Mg alloys with 10% of silicon, additional silicon produced by a chemical reaction remains at the interface while in pure Al and Mg melts this is probably not due to the excellent solubility of free silicon in pure molten metals. This speculation, which cannot be confirmed by the direct chemical analysis of the interface during the immersion, was indirectly proved by the immersion of silicon particles into molten Al and Mg alloys containing 10% of silicon. Very similar experimental data obtained for Si and  $\text{Si}_3\text{N}_4$  particles indicate that in the systems analyzed the most important contribution to the successful incorporation of ceramic particles in a melt is the chemical composition of the interface, which provides optimal in-situ wettability, and not so much the interfacial chemical reaction responsible for thermodynamic changes at the interface.

## ACKNOWLEDGMENTS

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