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The role of rare earths additions to aluminium-matrix composites

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ABSTRACT

Aluminium alloy (Al-5 wt.% Mg) matrix composites with ceramic particles (SiCp) as dispersoids and additions of 1-1.5 wt.% mischmetal (55 % Ce; 20 % La; 15 % Nd; 6.5 % Pr; .36 % Fe; bal.others) have been synthesised by liquid metallurgy. During preparation of the composites a reacted layer which contains rare earths (La, Dy, Tb) has been found to form at the matrix / ceramic particles interface. The thickness of reaction layer can be controlled by vortex technique. The rare earth additions can play similar role like Mg for improving the wetting between the matrix and the surface of dispersoids.

The rare earth oxides can form spinels with other oxides. La and Ce can form intermetallic compounds with Al (LaAl₄, CeAl₄) with changes the chemical activity and viscosity of the melt thereby minimising the agglomeration of ceramic particles and improving the dispersion of SiC particles in cast composite.

INTRODUCTION

Aluminium-matrix composites with ceramic dispersed particles are being considered as an important class of advanced materials and are increasingly finding applications as critical components in the automotive and aerospace industries [1].

The poor wetting of the ceramic particles with the molten aluminium alloys and the specific gravity difference between the matrix and dispersoids, lead to segregation during mixing as well as during solidification once their volume fraction exceeds a certain critical value.

Additions of reactive elements to the melt Al(Mg, Cr, Ti, Zr) may promote wetting by decreasing of the contact angle θ , by reducing the surface tension of the melt, decreasing the solid / liquid interfacial energy of the melt, or inducing wettability by a chemical reaction.

Small additions of 1...3 wt. % of mischmetal to Al - Si alloys during synthesis of MMC by liquid metallurgy technique resulted in better incorporations of fine graphite powder up to 60 wt. % [2]. The objective of this paper is to

examine the role of rare earth additions, as mischmetal, on wettability and bonding between the dispersoid (SiCp) and AlMg5 alloy-matrix.

EXPERIMENTAL

Commercial - grade aluminium (99.97 % Al) and magnesium (99.9 %) were used to make the Al-5 % Mg matrix alloy.

The composites were prepared by adding the ceramic particles (SiC with average size 30...180 μm) in the vortex of the mechanical stirred aluminium alloy at 1020 K.

Mischmetal (55 % Ce; 20 % La; 15 % Nd; 6.5 % Pr; 0.36 % Fe; bal others) in pieces of 0.3..0.5 g was added(1...1.5%) to the melt during dispersion of particles in order to improve the wettability between ceramic particles and Al alloy.

All melts were made in an electrical resistance furnace of 1 Kg capacity using clay graphite crucibles, and were casted in preheated cast iron chill molds by the comocasting process. Temperature has been measured with a Pt - Pt - Rh 10 thermocouple and adjusted with ± 3 K error.

Aluminium bath treatment has been realised with argon , deoxidation flux and slagging flux.

The specimens collected from the lower part of the ingots (30 mm in diameter and 180 mm in length) were prepared by standard metallographic technique and etched by Keller's reagent (2 % HF + 5 % HNO₃ + 3 % HCl + 90 % H₂O) and examined under a scanning electron microscopes JEOL 200 CX and PHILIPS SEM 515 equipped with wave-length dispersive X - ray spectroscopy. More complete description of composite preparation technique are given elsewhere [3].

RESULTS AND DISCUSSIONS

The macro- and microstructure of solidified Al-5 wt.% Mg matrix alloy composite has been influenced by the presence of rare earth like (La, Ce, etc.).

Typical size distributions of SiC agglomerates in the composite ingots are plotted in Fig.1 . The results clearly indicate that by additions of mischmetal to the melt the agglomeration was minimised. Experimentally it was also observed that addition of rare earths to AlMg5 alloys increased the viscosity of the melt (Table I) and in order to keep the same shear conditions a significant increase in the power input was required to the stirrer motor.

Table I. Physical properties of some rare earths [4]

Metal	Melting point, °C	Surface tension		Viscosity	
		σ_0^* mN / m	$d\sigma / dT$ mN / mK	η^{**} at melting point mN x s / m ²	η_0 mNxs/m ²
Al	660	914	-0.35	1.30	.1492
Mg	651	559	-0.35	1.25	-

Ce	804	740	-0.33	2.88	-
La	930	720	-0.32	2.45	-
Nd	1024	689	-0.09	-	-
Pr	935	-	-	2.80	-

$$* \quad \bar{V} = \bar{V}_0 + (t - t_0) d\bar{V} / dt$$

$$** \quad \eta = \eta_0 \exp (E / RT)$$

The increase in the viscosity of the slurry (AlMg5 alloy with SiCp) was very sharp at more than 15 vol.% SiCp and the equation :

$$\eta_r = \eta (1 + 2.5 fp + 10.05 fp^2) \quad (1)$$

where fp is the volume fraction of SiC particles, don't be used. This process has very close analogy to comocasting / rheocasting process. Hence the mischmetal addition and composite making can be considered as "pseudorheocasting" technique [2].

Metallographic (SEI) examination of the composites exhibited the formation of surface layer containing new reaction products that provide a strong bond between the ceramic particles and matrix (Fig.2).

Energy dispersive X-ray microanalysis (EDX) of the SiCp -matrix interface revealed an important feature of the microstructure here is that Al, Mg and rare earths are surrounding the SiC particles (Fig.3 and Fig.4).

The rare earth can play similar role like Mg for improving the wetting between the matrix and the surface of the SiC dispersoid.

According to Omenyi and Neumann [5] the net change in free energy during engulfment:

$$\Delta F_{net} = \sigma_{PS} - \sigma_{PL} \quad (2)$$

(where σ_{PS} and σ_{PL} is surface energy between ceramic particle and solid alloy respectively between particle and liquid alloy) is positive; this suggests that SiC particles should be pushed in an AlMg5 / SiCp composite by a moving solidification front and finally will be entrapped in the solid at the end of the local solidification [6].

The rare earth oxides as well as MgO can form spinels with other oxides which are thermodynamically stabler than individual oxides ($\Delta G \text{ Al}_2\text{O}_3 = -1360 \text{ KJ/mol}$, $\Delta G \text{ La}_2\text{O}_3 = -1582 \text{ KJ/mol}$) [4]. The thickness of reacting layer decreased at increasing in stirring speed, due to mechanical erosion caused by particle collisions in the turbulent melt. This way the thickness of reacted layer can be controlled by vortex technique.

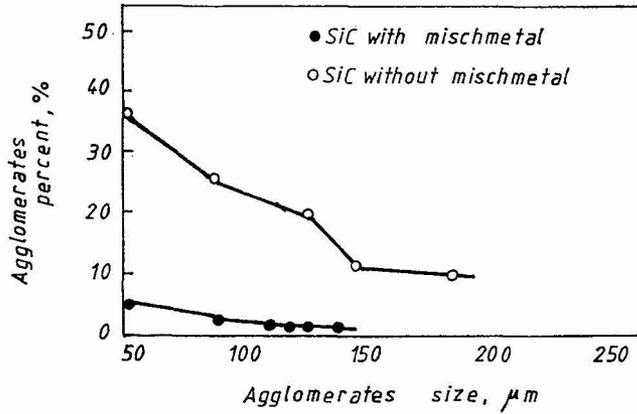


Fig.1. Typical size distribution of the SiC particles in AlMg5-matrix composites.



Fig.2. Electron probe microanalysis (SEI) of AlMg5/SiCp composite with addition of 1.5 % mischmetal

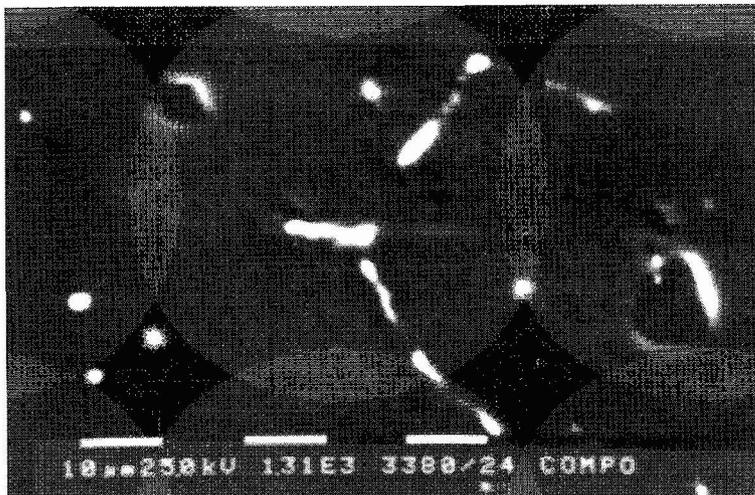


Fig.3.SEM of AlMg5 / SiCp composite.

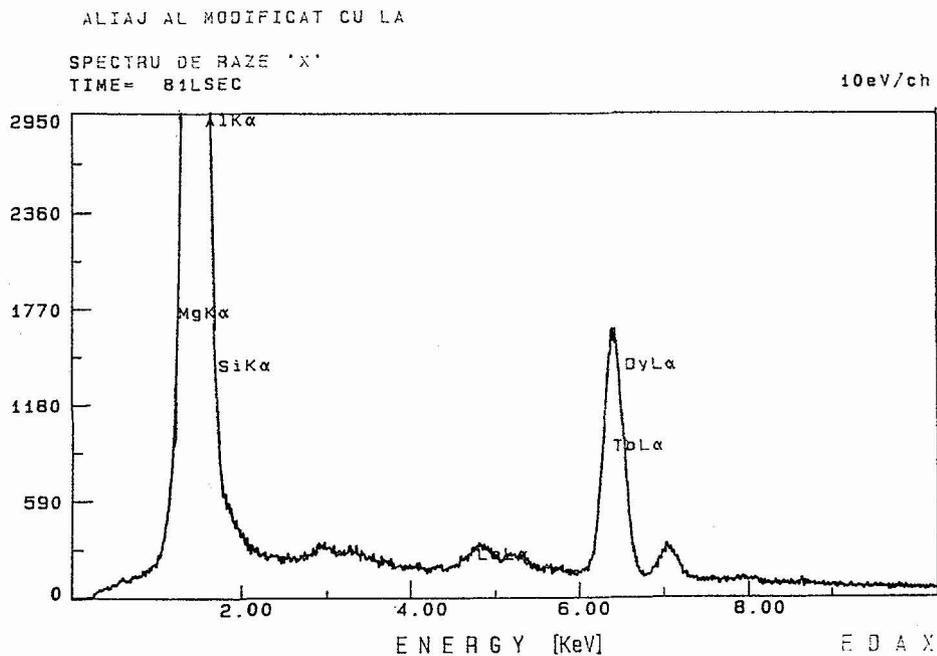


Fig.4.Energy dispersive X-ray (EDX) for matrix/ceramic particles interface.



Fig.5.(a) SEI image AlMg5 / SiCp composite.

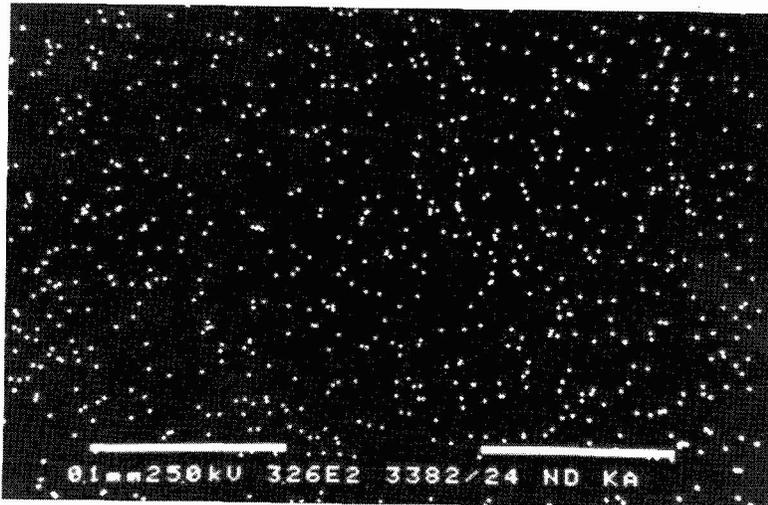


Fig.5.(b) Elemental map of area shown in (a) using Nd-K characteristic X-ray line.

The rare earths like La and Ce can form intermetallic compounds with Al ($LaAl_4$, $CeAl_4$) which change the chemical activity and viscosity of the melt thereby improving the dispersion of ceramic SiC particles in cast composite.

Addition of Nd - another component of mischmetal don't have any role in the bonding between matrix and ceramic particles (SiCp); in Fig.5 a and 5 b a relative uniform distribution of Neodim is observed in microstructure of the composite.

CONCLUSIONS

1.Additions of rare earth (as MM) AlMg5 / SiCp composite increased the viscosity of melt requiring a significant increase in the power input to the stirrer motor, minimizing the agglomeration of ceramic particles;

2.SEI and EDX examination of the composite exhibited the formation of surface layer, with rare earth, providing a strong bond between the matrix and dispersed particles;

3.The rare earth oxides as well as MgO can form spinels with other oxides which promote wetting between matrix and SiC particles; the thickness of reacted layer can be controlled by vortex technique;

4.The rare earths like La and Ce can form intermetallic compounds with Al ($LaAl_4$, $CeAl_4$) which change the chemical activity and viscosity of the melt thereby improving the dispersion conditions of ceramic SiC particles;

5.Addition of Neodim don't have any role in the bonding between AlMg5 matrix and SiC particles.

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