



A FEASIBILITY STUDY ON THE FORMATION OF $\text{MgAl}_2\text{O}_4/\text{Al}$ IN-SITU MMC FROM SILICA SOURCES

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ABSTRACT

MgAl_2O_4 (spinel) is considered as an important reinforcement in MMC technology because of its high melting point (2135°C), low CTE ($7.6 \times 10^{-6}/^\circ\text{C}$) and high performance in electrical, electronic, nuclear and thermal applications. It is well known that the reduction of silica is thermodynamically as well as kinetically more favorable in the in-situ formation of spinel dispersoids in Al alloy compared to other oxygen sources such as ZnO and CuO. This paper aims at synthesizing $\text{MgAl}_2\text{O}_4/\text{Al}$ in-situ MMC using locally available amorphous silica sources containing $>90\%$ SiO_2 . In addition, the thermodynamics and kinetics of spinel formation have been discussed. The study has found that the locally available amorphous silica varieties are useful silica sources for the generation of MgAl_2O_4 in Al-Mg alloy.

KEY WORDS: Spinel, Particle-melt pinning, Configurational entropy

1. INTRODUCTION

MgAl_2O_4 (spinel) is one of the end-members of the spinel group minerals, which has the general chemical composition of AB_2O_4 , where A is a divalent atom such as Mg^{2+} , Fe^{2+} , Mn^{2+} , Zn^{2+} and B is a trivalent atom such as Fe^{3+} , Al^{3+} . The usual anion is oxygen. The spinel structure (MgAl_2O_4 , *fd3m*) consists of an essentially cubic close packed array of oxygen ions with metal cations occupying one-eighth of the tetrahedral interstices (Mg^{2+}) and one-half of the octahedral interstices (Al^{3+}). A unit cell has 32O^{2-} , 8Mg^{2+} and 16Al^{3+} ions.

In nature, spinel is found as gem stones with reddish color. A few properties are at par with ruby (Al_2O_3). They show similar refractive index, density (~ 3.6) and hardness ($\sim 8-9$). A single crystal MgAl_2O_4 shows exceptional transparency (75% through 1.05mm) and low scattering coefficient. Spinel phase exhibits congruent melting point at 2315°C in $\text{MgO}-\text{Al}_2\text{O}_3$ binary phase diagram². It shows a unique combination of properties like low thermal conductivity, low coefficient of thermal expansion, good thermal shock resistance, low dielectric constant and high electric resistivity. A detailed property comparison with other engineering ceramics has been given in the Table 1. Moreover, they are chemically inert or less reactive in oxidizing and reducing atmospheres³. MgAl_2O_4 (spinel) is an important advanced ceramic material possessing useful mechanical properties and wide range of applications even at high temperature. Apart from being an important refractory material, it is used in advanced areas like high temperature arc-enclosing envelopes, humidity and infrared sensors, transparent windows, domes and armor materials.

Spinel can be considered as an important reinforcement in metal matrix composites. In addition to their excellent combination of properties, the metals (usually Al) bond strongly and without reaction to this oxide. Both the materials have a cubic structure and that the lattice parameter for the close packed F.C.C. oxygen anion sublattice of the spinel unit cell is nearly equal to the lattice parameter of the F.C.C. aluminum unit cell, raising the possibility of forming low energy interfaces between spinel and aluminum for any orientation ⁴.

In practice, spinels are produced by two stage firing process: calcining the powder mixture at 1600°C to complete the spinelization reaction followed by ball milling or hot pressing ⁵, but usually product is contained in high percentage of non-stoichiometric spinel ($\text{MgO} \cdot n\text{Al}_2\text{O}_3$, where n =any number including decimals except 1). A few chemical techniques have been proposed for stoichiometric spinel fabrication⁶. In-situ stoichiometric spinel in Al can be generated at low temperature using silica sources ⁷. Silica acts as oxygen source for the fabrication of stable oxides like MgAl_2O_4 or Al_2O_3 in Al-Mg alloy. The reduction of silica is thermodynamically and kinetically more favorable compared other compounds like CuO or ZnO. Moreover, the similar densities of amorphous silica and molten Al (2.3g/cc) reduce the addition problem through vortex method. The processing cost can be reduced to a large extent by using locally available silica sources.

The paper aims at the feasibility study of the formation of MgAl_2O_4 in commercially pure Al alloyed with 5%Mg using two varieties of locally available amorphous silica. The mechanism of spinel formation is discussed in detail. Further, the stability of spinel in different conditions are discussed.

2. EXPERIMENTAL

350g of commercially pure Al (EC Grade Al with purity 98.7%Al) with 5% Mg and two varieties of locally available silica sources with amorphous silica percentage >90% and average particle size of 20microns and 100microns for variety I and variety II respectively are taken as starting materials. A fixed amount of particles (5wt% (~17.5g)) has been taken for each variety. The composition details have been given in Table 2. The alloy was made in a clay graphite crucible in an electric resistance furnace. The addition of silica particles has been done by vortex method at temperature 730°C and the melt has been held at 800°C for 2 hours. The melt has been poured into permanent molds and the characterization has been done by optical metallography, XRD, SEM and EDS. The feasibility of different phases has been established by repeating the experiments (three times for each variety of particles).

3. RESULTS AND DISCUSSION

Observations made under optical metallography have shown that the particles have been reacted. The agglomerations of products as well as reacting particles have been observed in many regions of both composites (Fig 1 and 2). The formation of MgAl_2O_4 has been confirmed by XRD in both cases (Fig 3 and 4). In the case of variety II, the optical micrographs have shown the product crystals entrapped in partially reacted particles (Fig 2). The crystals have been identified as MgAl_2O_4 by SEM and EDS (Fig 5). In variety I, Al-Mg-O and Al-Mg-Si-O phases in the interior regions and Al-Mg-O phase on the surface of reacting particles have been identified by SEM and EDS (Fig 6(a,b and c)). The matrix phases have been identified as $\text{Al}_{18}\text{Mg}_4\text{Si}_3$ and $\text{Al}_{10}\text{Fe}_2\text{Si}$ in both varieties of composites (Fig 7 (a and b)). As the reactions of particles are not completed, the

system may not be in equilibrium state. So the phases may be in metastable state enabling the formation of the final phases like Mg_2Si , $\text{Al}_8\text{Fe}_2\text{Si}$.

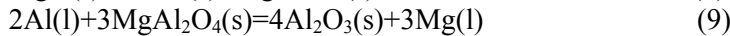
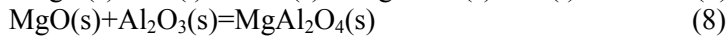
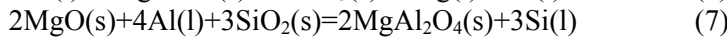
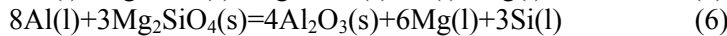
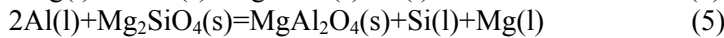
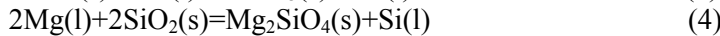
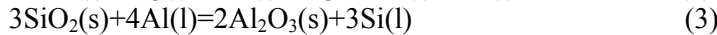
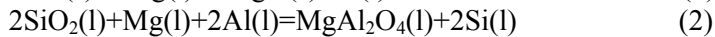
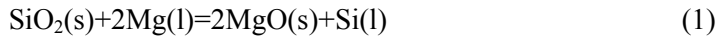
3.1 MECHANISM OF SPINEL FORMATION

Generally, the spinel formation occurs due to the phenomena of displacement reactions followed by the reactive wetting between silica particles and Al-Mg alloy.

3.1.1. REACTIVE WETTING AND DISPLACEMENT REACTIONS

The most technologically meaningful ceramics are poorly wetted by non-reactive metals. In practice, wetting may be improved by adding other reactive elements. The improvement in wetting observed through the reaction product formed by single or multiple displacement reaction at the particle-liquid interface. The beneficial effects of reactive additives on wettability have been attributed to two reasons: (i) A reduction of interfacial energy contributed by the negative free energy of the chemical reaction between the reactive element and the substrate and (ii) The formation of a reaction product at the liquid-substrate interface ⁸.

Thermodynamically feasible reactions in this case are



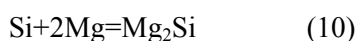
The phenomenon of reactive wetting can be explained by using the principle of interfacial tension instead of interfacial energy which is not equal to the former always. The wettability is enhanced by the formation of MgO , MgAl_2O_4 or Al_2O_3 crystals, but not by the Gibbs free energy contribution involved in the chemical reaction itself. Aksay et al ⁹ have proposed a model combining the process of reaction and equilibrium state of wetting. According to their model, the contact angle would decrease first due to a chemical reaction, but then increases by de-wetting process due to the formation of a more stable ceramic at interface which is rarely observed in the experiments.

In this case, the equilibrium contact angle θ_{eq} can be approximately written as

$$\cos\theta_{\text{eq}} = \frac{\sigma_{\text{sv}}^{\text{r}} - \sigma_{\text{ls}}^{\text{r}}}{\sigma_{\text{lv}}}$$

where σ_{lv} , $\sigma_{\text{sv}}^{\text{r}}$, $\sigma_{\text{ls}}^{\text{r}}$ are the interface tensions of liquid metal-vapor, reacted ceramic-vapor and liquid metal-reacted ceramic substrate respectively. σ_{lv} may vary during as the reaction product like Si in this case may diffuse into the liquid melt. According to the reactions (1,2 and 3), the equilibrium contact angle between reacted ceramic and liquid metal is generally large ⁸.

In the dynamic conditions of composite processing through vortex route, the mechanism of reactive wetting can be explained by a modified version combining the phenomenon of particle-melt pinning. The complete reaction mechanism has been explained in different stages as shown in Fig 8. During particle addition, the loosely bonded gases on the surface of the particle increase the interface tension between the melt and particles, which reduce the wetting characteristics. The gas film can be partially eroded either by the turbulence created in the melt or by the reaction with the melt. The wetting starts with the pinning of melt on the surface of particles. But, the reactive wetting starts only in the active centers where the pinning occurred as shown in stage I. Active centers are reactive regions on the particle, where partially bonded atoms are situated. Here, the partially bonded Si and O atoms in the broken network of SiO_4 tetrahedra are the active centers. The wetting of particle proceeds further with simultaneous reaction on the surface (stage II and III). At first, the reaction between Mg and SiO_2 layer takes place forming MgO or MgAl_2O_4 by (1) and (2), where MgO being formed more easily due to the higher diffusion coefficient of Mg compared to Al in the matrix. The bulk reaction of the particle also happens along with the surface reaction. After the first layer of MgO or spinel formed on the pinned region, Mg, Al and the released Si must diffuse through the reaction layer for the reaction to be continued to the interior of the particles. As the bulk diffusion coefficients of these elements in oxides at temperatures between 700-800°C are very small and the reaction products are extremely fine crystals, crystal boundary diffusion plays an important role. Formation of MgAl_2O_4 and MgO from SiO_2 will result in a 27 pct and 13.6 pct volume contraction respectively¹⁰. Due to this contraction, there will be gaps between the newly formed crystals or between the newly formed crystals and the rest of SiO_2 . Liquid Al and Mg infiltrate into these gaps and form so-called “diffusion channels”, as Legoux et al suggested¹¹. When the Mg content in the melt changes to very low level, the reaction (3) starts dominating over others. Since the volumetric shrinkage from 3SiO_2 to $2\text{Al}_2\text{O}_3$ nearly 38%, the diffusion channels get widened and diffusion of reactive elements enhanced⁸. The surface reaction and wetting are continued at a faster rate in front of the triple line till the particle surface is completely reacted (stage IV). The bulk reaction of the particles may be decreased with the time as the product crystals get accumulated on the path of diffusion channels. Released Si diffuses through these channels into the liquid and forms Mg_2Si using the Mg available in matrix during solidification by the reaction



The similar mechanism of spinel formation has been proposed in SiC/Al-Mg alloy MMCs¹⁰. The wettability problem of SiC has been reduced largely by introducing an oxide layer (SiO_2) on the surface. The chemical reaction between SiO_2 and Al-Mg alloy results in MgAl_2O_4 -MgO crystals on the reinforcement surface. MgAl_2O_4 crystals are largely found in the materials with 0.3 and 1wt% Mg, whereas a mixture of MgAl_2O_4 and MgO fine crystals are the reaction products in the materials made with 5 wt% Mg.

3.2. THE STABILITY OF SPINEL

The formation of spinel by the reaction of silica and Al-Mg alloy is an oxidation-reduction process which involves interdiffusion of reactive elements. The common crystal structure of silica is the SiO_4 tetrahedral building unit where central silicon is surrounded by four oxygen atoms. The tetrahedra share one or more oxygen with surroundings tetrahedra and their relative orientations define the types of structure. The diversity of silica structures and their relative ease of interchange is related to the glass forming behavior of silica. Amorphous silica is built from

tetrahedral building blocks that are not given enough time to find the energetically most favorable orientation. Amorphous structures typically show preservation of short range order (upto a few angstrom) and loss of the long range order that we see in crystalline phases. They show broken networks of SiO_4 having O and Si atoms in their lattice¹². Thus they have more melt like distribution and are highly reactive in nature compared to quartz silica. Usually in reactions, between liquid metals (Mg or Al) and oxides (Al_2O_3 or SiO_2), the diffusion of O^{2-} is neglected because of its large ionic size and low diffusivity (the ion radial ratios of Mg^{2+} , Al^{3+} , Si^{4+} to O^{2-} are 0.47, 0.34 and 0.38 respectively). Only the interdiffusion of Al^{3+} and Mg^{2+} cations and Si^{4+} ion between O^{2-} 'frame' is considered in the reaction¹⁰. During any structural change, the condition of the neutralization of the charge around an anion in an ionic structure should be satisfied.

All the aforementioned reactions involve interdiffusion of Al^{3+} , Mg^{2+} and Si^{4+} ions and oxidation-reduction processes. The Al^{3+} and Mg^{2+} ions diffuse into the interstitial sites of SiO_4 tetrahedra and replace the Si atom. Simultaneously, the O^{2-} ions are rearranged accordingly to maintain the charge neutrality. The partially bonded oxygen atoms in the broken network of SiO_4 tetrahedra can easily get reacted. The process continues till the formation of a stable crystal structure, MgAl_2O_4 , with minimum configurational entropy and free energy of formation. The stability of spinel at the experimental temperature and Mg concentration can be underlined with several theoretical evidences like spinel crystallography¹³, MgO- Al_2O_3 phase diagram, Stability diagram of MgO/ MgAl_2O_4 / Al_2O_3 system¹⁴ and Ternary phase diagram of Al-Mg-O¹⁵. The inversion nature of spinel increases the configurational entropy of atoms for rearranging themselves to form stable crystals. This increases the solubility of Al and Mg atoms along with oxygen in spinel. But, the configurational entropy is very negligible below 800°C and zooms up after 1000°C . Because of this reason, the solubility of MgO and Al_2O_3 in spinel increases in MgO- Al_2O_3 phase diagram after 1000°C and below that is restricted to 1:1 proportion of MgO and Al_2O_3 to form spinel which is called stoichiometric spinel (MgAl_2O_4). The stability of spinel at various Mg concentrations has been studied widely. The Stability diagram of MgO/ MgAl_2O_4 / Al_2O_3 system and Ternary phase diagram of Al-Mg-O give a range of Mg concentration in the matrix to stabilize the spinel at given temperature. The Mg range in Al-Mg-O system for the thermodynamic stability of spinel is 0.11-10wt% at 1075°C and 0.7-1.2wt% at 723°C as per ternary phase diagram and stability diagram respectively. The above mentioned spinel forming reactions are thermodynamically stable but vary in the kinetics. The selection of the reactions depends on the Mg concentration on the reaction sites of silica particle.

The variety I particles are porous with interconnected network of porosities of submicron sizes starting from the surface. The reactive wetting cum infiltration can explain the total reaction mechanism here. The phases identified in a reacting particle (Fig 6 (a,b and c)) have shown the increase in Mg content and decrease in Al content in the interior and reverse on the surface. The oxygen content in both cases remains the same. The MgAl_2O_4 found on the surface of particle is due to the combination of reaction (1) and reaction (7). Al may take part in the process due to the longer exposure time, large surface area and available Al on the reaction sites. Thus, the spinel formation may takes place by the reactions (2,3and 8) along with the reaction (7). The particles get reacted and infiltrated with melt. There may be an enrichment of Mg in the channels and deficiency of Al due to the higher diffusion coefficient of Mg. Hence, the reaction (1) will be the prominent followed by the reactions (2,7and 8) taking part in the final phase formation i.e, spinel. The channeling nature of infiltration rules out the gradual infiltration into the pores and reactions. This may be the reason for observing Si containing phases near to the surface.

Variety II particles have closed porosities separated from other by thin walls with smooth surface. The reactive wetting starts from the surface. The surface gets thinned and pores get opened with the time of reaction. The metal starts impinging into the pores and reaction occurs on the pore walls. The grown crystals get separated and accumulated inside the pores. The thinning of walls and impinging of metal into other pores are continued until the total particles get reacted. The product crystal accumulations inside the partially reacted particles are clearly visible in optical micrograph (Fig 2) and they have been found as MgAl_2O_4 (Fig 5) by SEM and EDS.

The presence of Al-Si-Fe phase found (Fig 7(b)) in the matrix along with Al-Mg-Si phase may be due to the iron pickup from the steel stirrer as well as the Fe_2O_3 impurities present in the particle. A detailed analysis is needed to detect other phases.

4. CONCLUSIONS

- (1) The locally available amorphous silica varieties are found to be useful silica sources for the generation of MgAl_2O_4 in Al-Mg alloy.
- (2) The particle-melt pinning, reactive wetting and displacement reactions are the fundamental mechanisms for the MgAl_2O_4 formation in Al-Mg alloy using silica particle processed by vortex method.
- (3) The solubility of Mg, Al and O in spinel is limited to the phase formation, MgAl_2O_4 i.e., stoichiometric spinel at given experimental condition. The metastable phases found in the partially reacted particle lead to the final phase formation, MgAl_2O_4 .
- (4) The metastable phase identified in the matrix may constitute the final phases like Mg_2Si and $\text{Al}_8\text{Fe}_2\text{Si}$.

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TABLES

Table 1: Property comparison of MgAl_2O_4 with other ceramic reinforcements

Material	AlN	Al_2O_3	BeO	SiC	Si_3N_4	MgAl_2O_4	PureAl
Density g/cm^3	3.26	3.9	2.9	3.2	3.3	3.6	<u>2.7</u>
Melting point $^\circ\text{C}$	2400	2030	2530	2700	1900	2135	660
Thermal conductivity(RT)($\text{W/m}^\circ\text{K}$)	110-170	10-35	150-250	90	10-40	48	<u>230</u>
Mean coefficient of thermal expansion (RT-100 $^\circ\text{C}$)($10^{-6} \text{ }^\circ\text{K}^{-1}$)	2.65	5.5	5.4	3.31	3.1	7.6	<u>23.6</u>
Electrical resistivity (RT) (Ωcm)	4.0×10^{11}	$>10^{14}$	$10^{13}-10^{15}$	$>10^5$	10^9	10^{10}	<u>2.96</u>
Modulus of elasticity(GPa)	300-310	300-380	300-355	380	280-320	300	<u>70</u>
Bending strength (MPa)	280-350	240-250	170-230	500	600-700	101	
Hardness Mohs (Knoop 500g)	8 (1200)	9 (2000)	8-9 (1000)	9 (2000)	8-9 (1250)	7.5-8 (1200)	

Table2: Composition details of amorphous silica varieties

Composition	varietyI (in wt%)	varietyII (in wt%)
SiO_2	97.5	99.82
Fe_2O_3	0.3	<0.01
Al_2O_3	0.7	0.01
Na_2O	0.3	0.03
CaO	0.3	0.02
K_2O	0.6	-
Carbon	0.8	-
L.O.I	1.0	<1.0
moisture	0.8	-

FIGURES

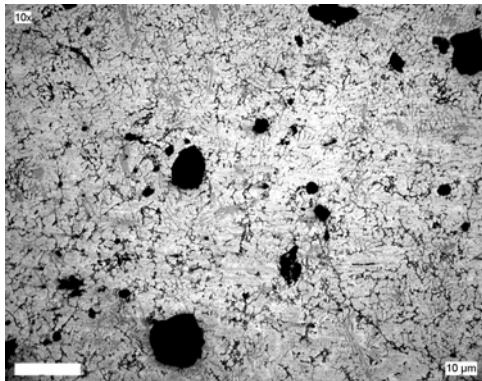


Fig1: Optical micrograph of variety I added composite after 2 hrs of reaction

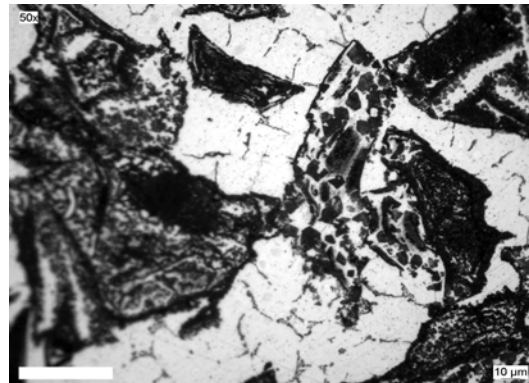


Fig2: Optical micrograph of variety II added composite after 2 hrs of reaction

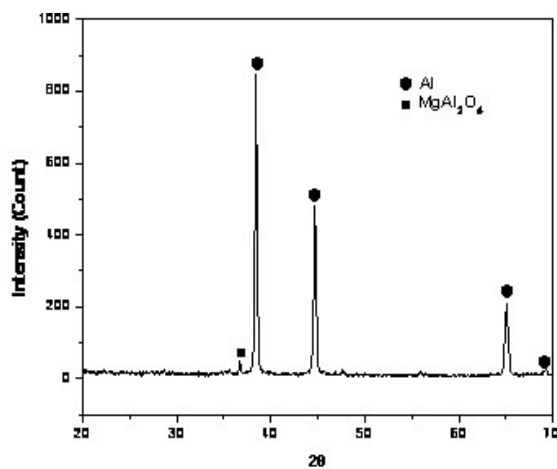


Fig3: XRD of variety II added composites after 2 hrs of reaction

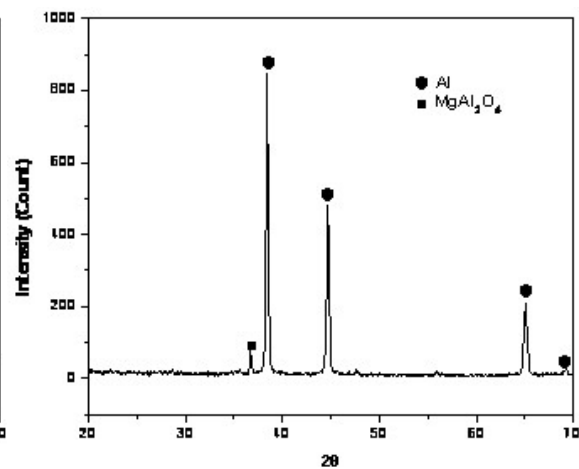


Fig4: XRD of variety I added composites after 2 hrs of reaction

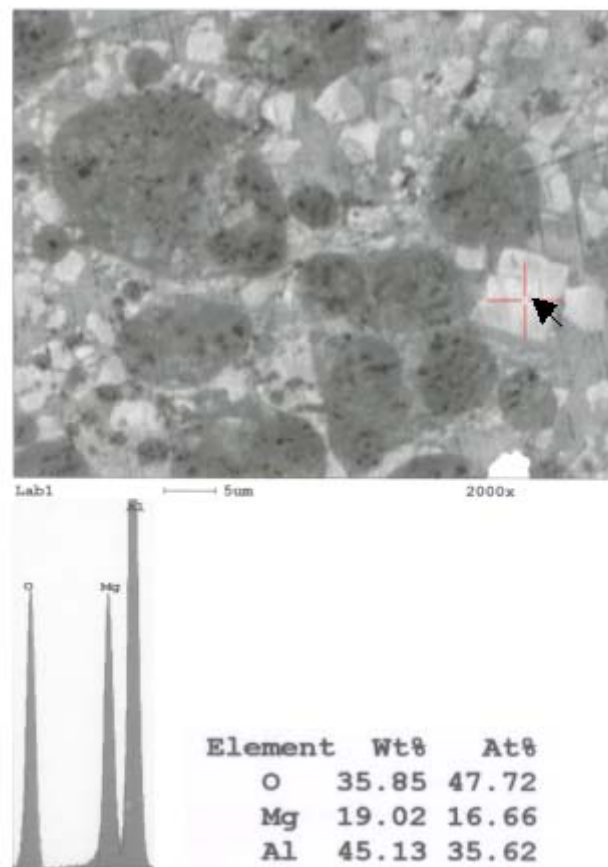
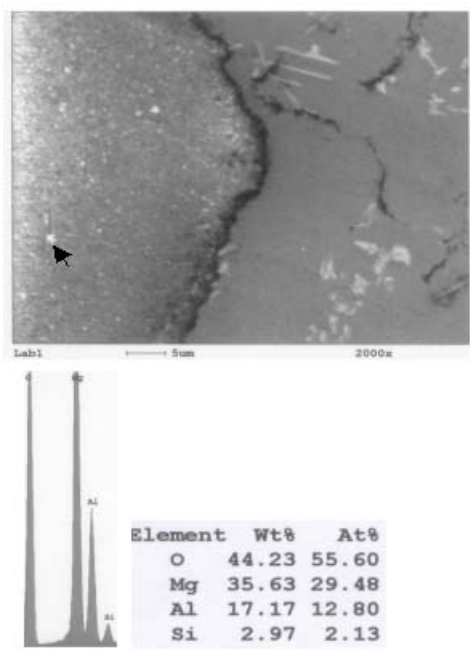
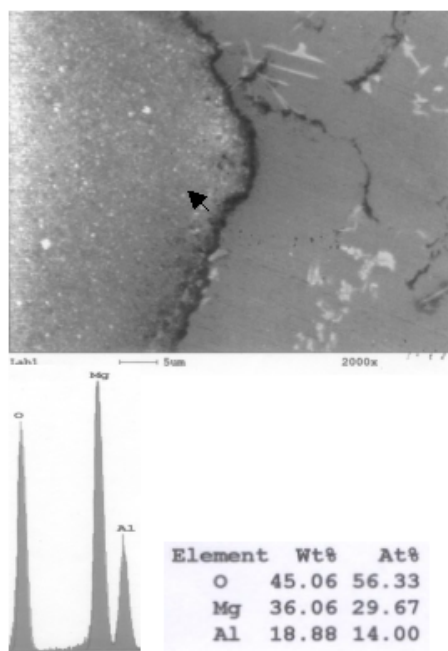


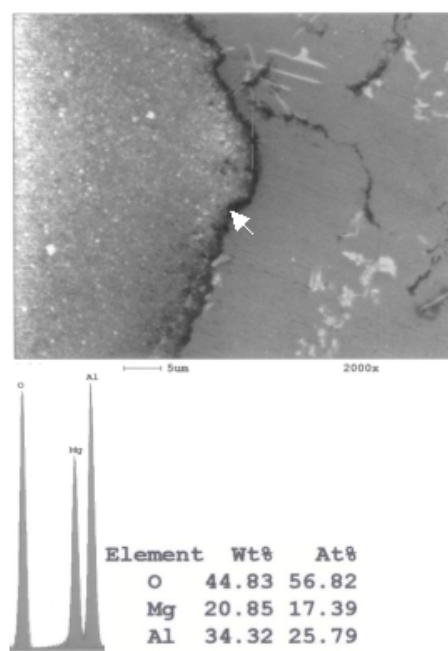
Fig 5: SEM and EDS of product crystals (variety II added composite after 2 hrs of reaction)



6(a)



6(b)



6(c)

Fig 6 (a),(b)&(c):SEM and EDS at different locations of reacting particle (variety I added composite after 2 hrs of reaction)

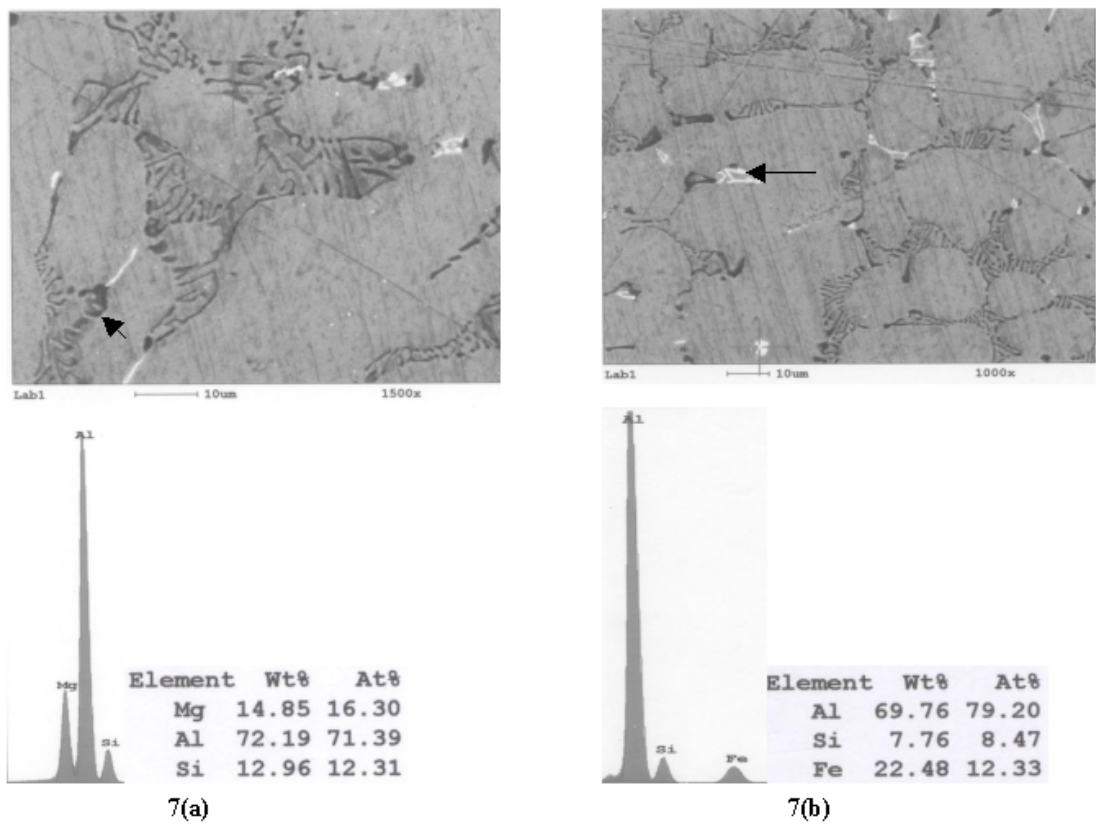


Fig7 (a)&(b):SEM and EDS of matrix phases (variety II added composite after 2 hrs of reaction)

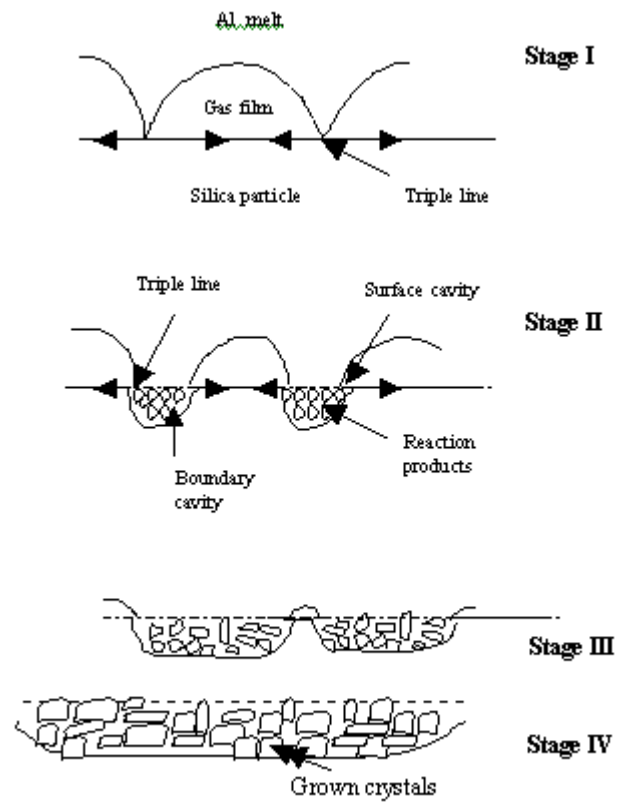


Fig 8: Particle-melt pinning and reactive wetting on silica particle