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Research article

In-situ reactions in hybrid aluminum alloy composites during incorporating silica sand in aluminum alloy melts

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Abstract: In order to gain a better understanding of the reactions and strengthening behavior in cast aluminum alloy/silica composites synthesized by stir mixing, experiments were conducted to incorporate low cost foundry silica sand into aluminum composites with the use of Mg as a wetting agent. SEM and XRD results show the conversion of SiO_2 to $MgAl_2O_4$ and some Al_2O_3 with an accompanying increase in matrix Si content. A three-stage reaction mechanism proposed to account for these changes indicates that properties can be controlled by controlling the base Alloy/SiO_2/Mg chemistry and reaction times. Experimental data on changes of composite density with increasing reaction time and SiO_2 content support the three-stage reaction model. The change in mechanical properties with composition and time is also described.

Keywords: silica sand; magnesium; aluminum matrix composite; microstructure; reactive wetting

1. Introduction

Lightweight metals such as aluminum and magnesium alloys find special applications when they contain hard ceramic particles like silicon carbide, alumina, zircon sand, and silica sand as reinforcement due to their superior mechanical and wear properties [1–6]. Silica sand which has high hardness, high thermal stability, and high compressive strength is a potential ceramic reinforcement particle for the development of aluminum matrix composites. However, for most application the effect of reinforcing phases, microstructural changes, and particle/ matrix interface on physical and mechanical properties need to be monitored carefully

The development of Al/SiO_2 composites has been conducted mostly on a trial and error basis since the 1960's. However, these materials have not been employed in any widespread engineering applications. A coherent description of reactions in these composites and how the reactions result in changes in density and mechanical properties is lacking. With a better understanding it may be possible to predict the reactions and control properties of these composites and thereby make them more useful.

Previously, researchers have used stir mixing to incorporate SiO_2 particles into commercially pure Aluminum [6–12]. Rohatgi et al. developed pure aluminum matrix composites by incorporating 53–125 μm size SiO_2 particles at 720–790 °C with Magnesium added as a wetting agent [11,12]. Composite castings with over 6 wt% SiO_2 could be obtained when the particles were preheated to 700 °C. However, cold or untreated sand particles were rejected by the melt. This was attributed to the presence of absorbed gases or water molecules covering the SiO_2 particles and possibly poor wettability at lower temperatures. Hot spots and hard black scum were observed at temperatures greater than 1000 °C. Analysis revealed a reaction zone rich in Mg at the surface of the dispersed SiO_2 particles. The dispersed SiO_2 particles tended to be concentrated in interdendritic regions of the matrix and did not promote nucleation of α-Al. Optimal results were obtained when a maximum of 3 wt% silica sand was mixed with 3.2 wt% Mg, where the hardness increased four-fold and the abrasion resistance increased by over three times compared to the matrix. Particle incorporation became increasingly difficult and considerable surface oxidation occurred when the silica and magnesium composition ranged as high as 4 wt%. Alumina formation was reported to begin at 800 °C [11,12].

Powdered metallurgy (PM) techniques have also been used to create ceramic particulate composites using commercially pure aluminum and its eutectic silicon alloy mixed with up to 25 wt% of 90–300 μm SiO_2 sand [13]. SEM observations showed voids around sand particles indicating poor bonding at particles-matrix interface, which was confirmed by tensile testing. The ultimate tensile strength decreased from 184 to 112 MPa with the addition of 20 wt% sand particles, while the hardness remained constant. However, the composite strength increased when magnesium was added to the matrix.

From this experimental data, it would appear that Mg may play two roles in these materials. In the case of solidification processing [14], Mg seems to assist in wetting of the SiO_2 particles with the molten alloys. Pai et al. [15] suggested that wetting agents could improve wetting of SiO_2 particles by Al alloys by increasing the surface energy of solid, decreasing surface tension of liquid, and decreasing the particle/alloy interfacial energy. Mg, a reactive element, likely fulfills all three conditions for improved wetting and, in addition, it scavenges oxygen from the surface of SiO_2 particles. The second role played by Mg is to improve bonding between the matrix and the SiO_2, which seems clear from the increase in strength of the PM-produced materials. This is likely do to reactions between the Mg and SiO_2 that take place during the elevated temperatures of processing [16,17]. However, reactions between Mg and SiO_2 in the processing of these materials have not been thoroughly investigated and the effects of Mg concentration, SiO_2 concentration and processing time on the final composition and mechanical properties of these materials remains poorly understood.

The purpose of the present paper is to study the wetting reaction mechanism in A206 aluminum/silica sand particles composite. Magnesium additions were used to assist in the incorporation of the silica sand into the aluminum alloy. Different levels of Mg and SiO_2 additions

were examined and a three-stage reaction model is proposed to describe the changes in density and hardness of this system.

2. Materials and Method

Silica sand with particle sizes between approximately 100 and 250 μm was wet collected from Badger Mining Corporation refinery's dust collectors and had a composition of 99.70% SiO_2, 0.12% Al_2O_3, 0.12% K_2O, 0.04% CaO, 0.02% Fe_2O_3, 0.01% Na_2O, <0.1% MgO, and <0.1% TiO_2.

In order to achieve a precise amount of reinforcement added to the melt and also to facilitate mixing in the molten aluminum, desired quantities of silica sand particles and Mg turnings were encapsulated within thin Al foil in the form of a rolled cylinder with closed ends. The crimped ends of the foil do not form an airtight seal, allowing the removal of moisture and absorbed gases when the SiO_2/Mg packets were preheated for 30 min at 120 °C.

500 gr of Aluminum Alloy A206 (Composition: 4.6% Cu, 0.25% Mg, 0.35% Mn, 0.05% Si, 0.22% Ti, and 0.10% Fe) were placed in a coated graphite crucible (ID 89 mm, Depth 127 mm) and heated using an induction furnace and held at temperatures between 850 ^oC and 900 ^oC. Various compositions and processing conditions used to prepare the composites by stir casting are listed in table 1. Once the melt reached the desired constant temperature, the measured quantities of silica particles in the Al foil packets were added to the melt. A vortex is created for various lengths of time (As listed in table 1) in the melt using a graphite stirrer coated with boron nitride revolving at 350 rpm while being held at 60° with respect to the melt surface. A steel permanent mold used to pour the melt to form castings is coated with boron nitride and preheated to 450 °C. Three measurements of density and Rockwell F Hardness were taken for each specimen and the average value is reported as the density of the composite for that specimen. For density measurements, an electronic balance with a resolution of one milligram was used while utilizing the "Archimedes Principle" and using distilled water as the auxiliary liquid to determine the density of composites and matrix alloys with respect to that of pure aluminum. SEM analysis and Energy Dispersive Spectroscopy (EDS) was carried out on selected specimens using a TopCon SM-300 Scanning Electron Microscope at 15 kV voltage with 12 mm working distance to determine morphology and EDX to determine composition.

3. Results and Discussion

Various Al-A206/Mg/SiO_2 compositions prepared by stir casting, their processing conditions, density, and hardness values are listed in table 1. It can be seen in figure 1 that in the absence of additional Mg there is no correlation between silica content and hardness or density. The microstructures of the different composites show the reason for this observation. Figure 2a shows that no bonding has taken place between the matrix and the SiO_2 particle. In fact voids can be seen at various locations immediately surrounding the particle. It appears that either no wetting reaction has occurred or that it is very slight. However when additional Mg is added it is clear from figure 2b that extensive reaction have taken place. As shown in Figure 3, it is clear that these reactions lead to increased density and increased hardness as SiO_2 concentration increases.

Table 1. Density and Mechanical Property Measurements for Various Compositions and Processing Conditions.

	SiO2/Mg	SiO_2 (wt%)	Mg (wt%)	Time (min)	Hardness (HRF)	Density (g/cc)
Mg=0	-	*0*	*0*	*0*	57.1	2.783
		9	*0*	*7*	40.7, 42.9,49.0, 59.4,60.6	2.694, 2.701, 2.767, 2.796, 2.808
				12	43.2, 51.6, 66.5	2.655, 2.679, 2.762
		13	*0*	*7*	48.7	2.685
				12	61.1	2.706
Mg>0	*1.8*	*9*	*5*	*0**	-	2.647
				7	94.9	2.638
				12	96.6	2.624
				17	84.3	2.652
				22	92.8	2.69
	2.6	*13*	*5*	*0**	-	2.645
				7	100.7	2.68
				12	99.1	2.713
				17	88.7	2.719
				22	90.2	2.736
	3	*9*	*3*	*0**	-	2.666
				7	98.1	2.684
				12	87.4	2.721
				17	82.7	2.747
				22	88.4	2.771
	4.3	*13*	*3*	*0**	-	2.664
				7	97.7	2.73
				12	95.9	2.726
				17	88.6	2.802
				22	86.3	-

** Theoretical values based on no-reaction composite*

It is difficult to explain the increase in density unless it is considered that reactions between Al, Mg, and SiO_2 are converting the SiO_2 into a denser oxide. There are several possible candidates. There first possibility is that SiO_2 will be reduced by liquid Al with Si being rejected into the melt according to reaction 1:

$$4Al_{(l)} + 3SiO_{2(s)} \rightarrow 2Al_2O_{3(s)} + 3[Si] \quad (1)$$

Previous research indicates that reaction 1 occurs slowly and does not result in much Al_2O_3 production [1,3]. However, the presence of Mg allows other thermodynamically stable oxides to form depending on Mg concentration according to reaction 2 and 3 [4,5].

$$2Mg_{(l)} + SiO_{2(g)} \rightarrow 2MgO_{(s)} + [Si] \quad (2)$$

$$2Al_{(l)} + Mg_{(l)} + 2SiO_{2(s)} \rightarrow MgAl_2O_{4(s)} + 2[Si] \quad (3)$$

At the melt temperatures used for these experiments MgO will only be a stable reaction product if the concentration of Mg in the melt is greater than about 1.7 wt%. The spinel, $MgAl_2O_4$, is stable in the range from 0.04-1.7 wt% Mg and Al_2O_3 is stable for Mg concentrations below 0.04 wt%. [2].

The oxide conversion reaction obviously results in changing the overall density of the composite (ρ_{Al-206}= 2.77 g/cm^3, ρ_{SiO_2} = 2.3 g/cm^3, $\rho_{MgAl_2O_4}$ = 3.579 g/cm^3, $\rho_{Al_2O_3}$ = 3.9 g/cm^3, ρ_{MgO}= 3.58 g/cm^3). Such reactions are supported by the changes in the microstructure that occur from the addition of Mg as is clearly evident in figure 2b.

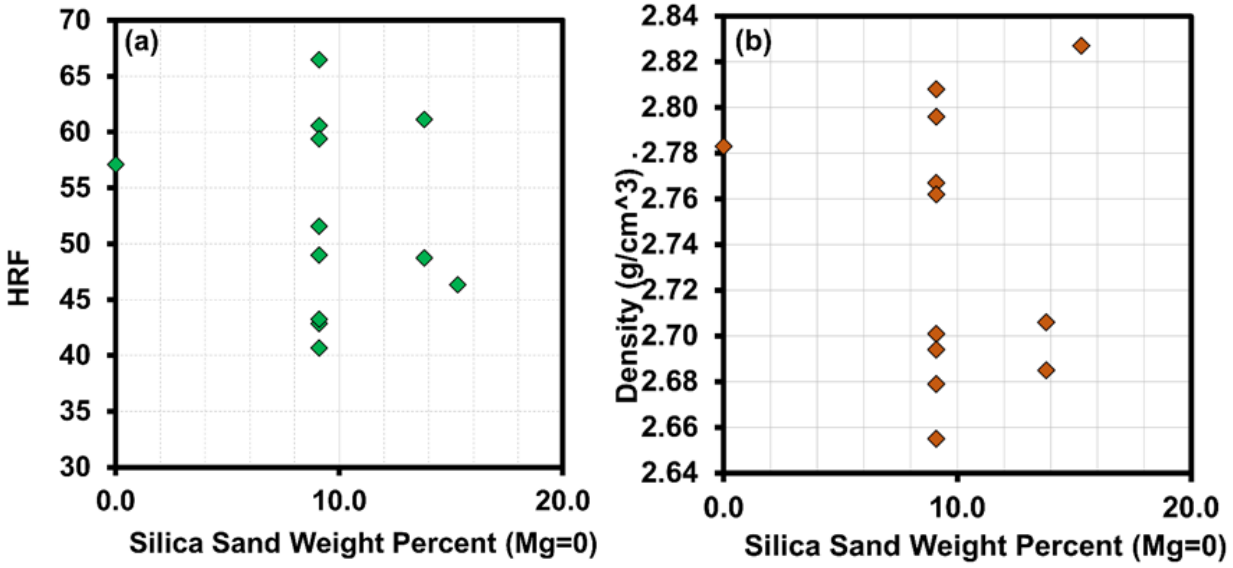

Figure 1. a) Weight Percent Sand (wt% Mg = 0) vs. HR_F b) Weight Percent Sand vs. Density (wt% Mg = 0).

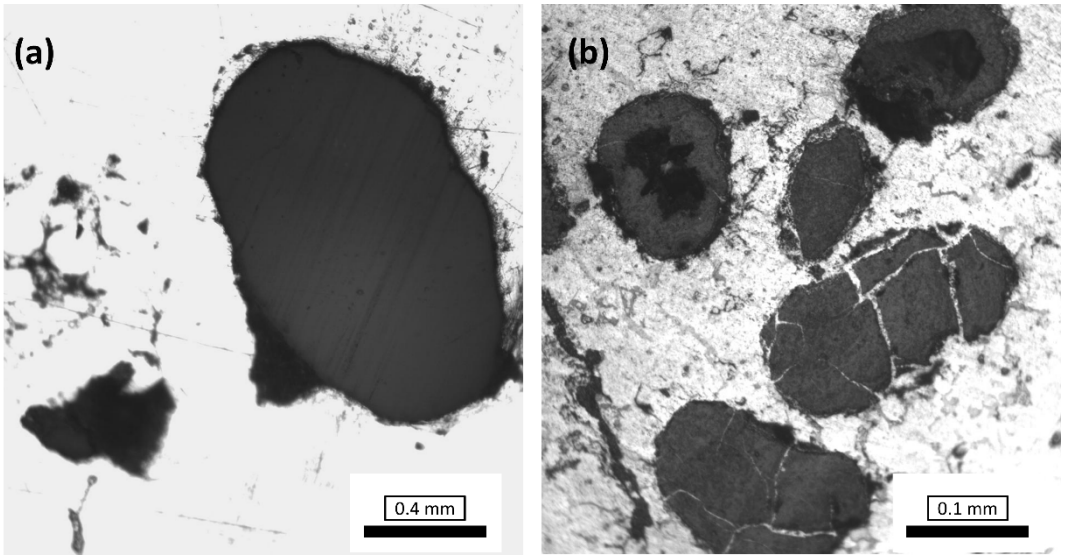

Figure 2. Optical Microstructure of a) Sand of 90.9 wt% Al-A206 + 0.0 wt% Mg + 9.1 wt% SiO2 b) Optical Microstructure of Sand of 87.7 wt% Al-A206 + 3.3 wt% Mg + 13.3 wt% SiO2 with Mixing Time of 10 Minutes.

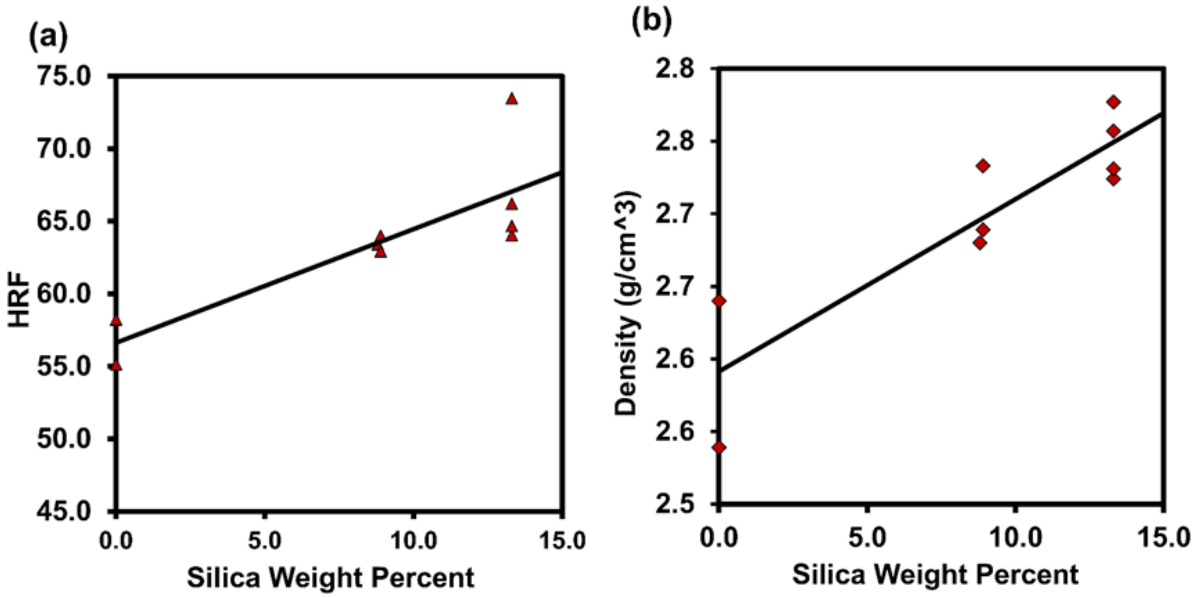

Figure 3. a) Weight Percent Silica vs. HR_F for Sand (wt% Mg > 0) and Used Sand b) Weight Percent Silica vs. Density for Sand (wt% Mg > 0) and Used Sand

The reactions thought to be involved in creating this conversion are listed in Table 2 and shown schematically in Figure 4. Initially the Mg concentration in the molten alloy is greater than 1.7 wt% and Mg reacts with the SiO_2 forming MgO. This is responsible for the initial wetting of the particle. In Stage 1 the Mg, being the most highly reactive species, is quickly used up and the Mg concentration falls to below the 1.7 wt% level. In Stage 2 the MgO is no longer stable and Al and Mg from the melt begin to react with it and the SiO_2 to form $MgAl_2O_4$. This reaction further reduces the Mg concentration in the melt until it reaches 0.04 wt% where it is then in equilibrium with the $MgAl_2O_4$. This causes the onset of stage 3 in which Al directly reacts with SiO_2 to form Al_2O_3. The mechanism is still a reduction of SiO_2 by Al, but because of the $Mg/MgAl_2O_4$ equilibrium only Al is allowed to react. While this can occur by an internal precipitation reaction at the $MgAl_2O_4/SiO_2$ interface, the large difference in densities between Al_2O_3 and SiO_2 makes it likely that cracking will occur in the scale allowing direct contact between the melt and SiO_2 which will act to increase the reaction rate. These various stages are apparent in Figure 2b in which incomplete conversion of SiO_2 to Al_2O_3 and $MgAl_2O_4$ are present in two particles, while complete conversion has occurred in the other three particles. Notice that cracking has occurred in all of the completely converted particles. Figure 5 shows an SEM micrograph where the indicated regions were examined by EDX. The reinforcement seems to consist of an Al_2O_3 center encapsulated by a magnesium-rich outer surface, which is in turn surrounded by an Al-Si matrix. The matrix is completely lacking in Mg, indicating that the greater than 2 wt% Mg originally present is now mostly present as reaction product surrounding the reinforcement particles. The XRD graph of Al-A206-3Mg-13SiO_2 after 17 minutes mixing time is shown in figure 6 which indicated the presence of Al_2O_3 and $MgAl_2O_4$ in the final composite.

Table 2. Reinforcement/Matrix Reaction Stages.

Stage	$\left(\frac{M_{Mg}}{(M_{Al}+M_{Mg})}\right)$	Stable Oxide(s)	Reaction
1	wt% Mg > 1.7	MgO	$2Mg_{(l)} + SiO_{2(s)} \rightarrow 2MgO_{(s)} + [Si]$
2	0.04< wt%Mg <1.17	$MgAl_2O_4$	$Mg_{(l)} + 6Al_{(l)} + 2MgO_{(s)} + 5SiO_{2(s)} \rightarrow 3MgAl_2O_{4(s)} + 5[Si]$
3	wt% Mg = 0.04	$MgAl_2O_4$ & Al_2O_3	$4Al_{(l)} + 3SiO2_{(s)} \rightarrow 2Al_2O_{3(s)} + 3[Si]$

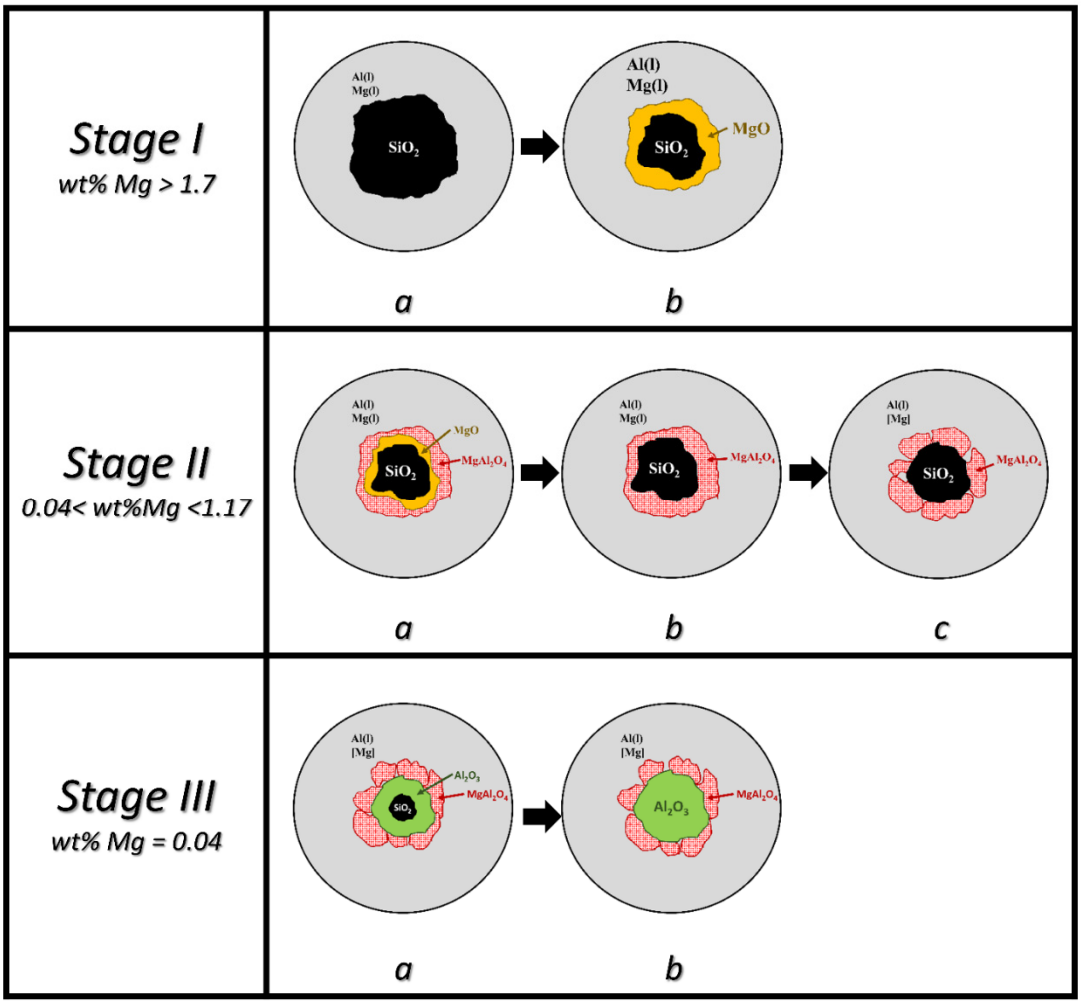

Figure 4. Schematic Representation of Reactive Wetting and Conversion of SiO_2 to $MgAl_2O_4$ and Al_2O_3.

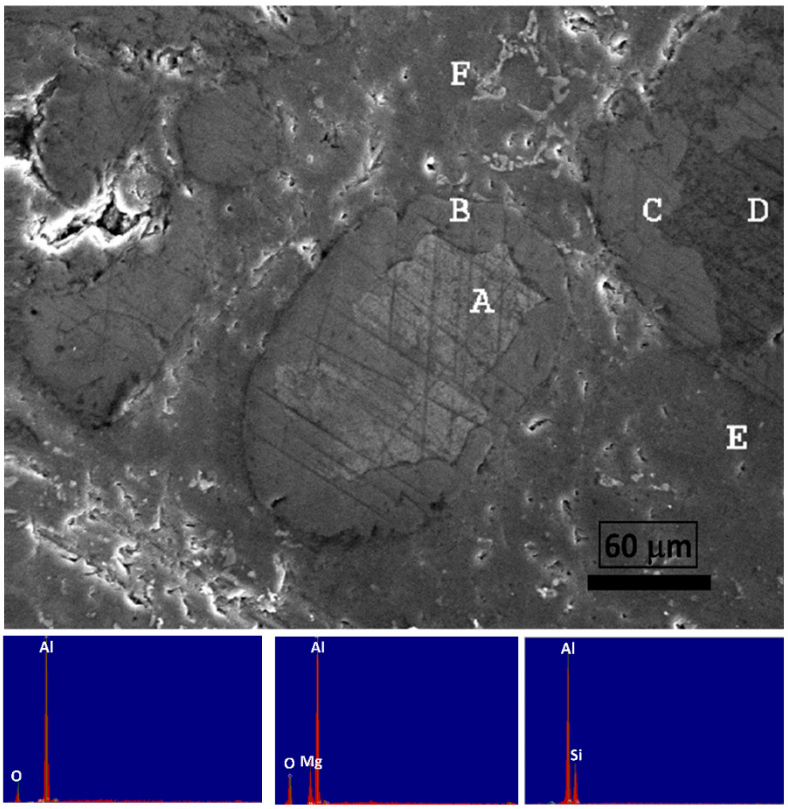

Figure 5. SEM Micrograph of Al-A206-3Mg-13SiO_2 after 17 minutes mixing time. EDX indicates Al and O at point A, Mg, Al, and O at points B, C, and D, and Al-Si at points E&F.

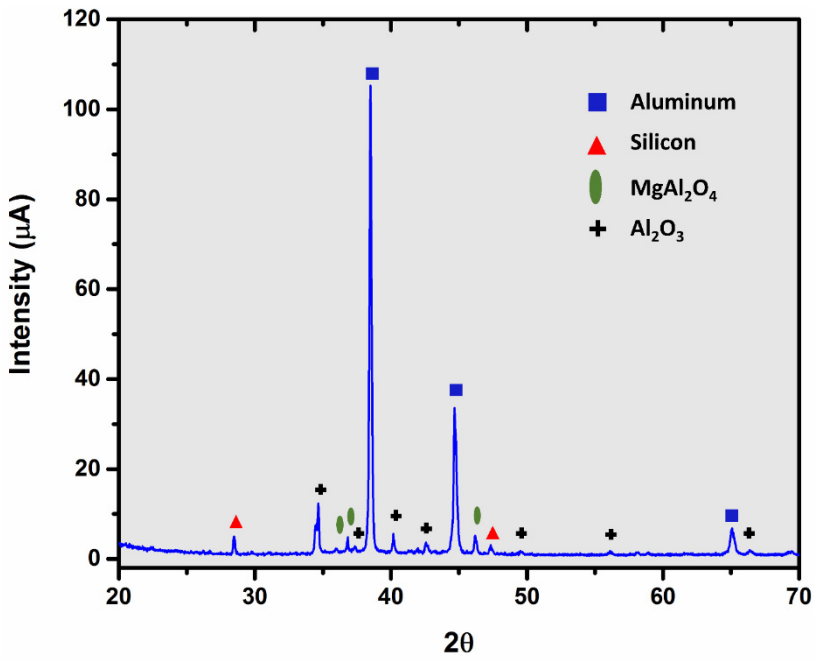

Figure 6. The X-Ray Diffraction pattern of Al-A206-3Mg-13SiO_2 after 17 minutes mixing time.

The SEM and EDX analysis for the composite with the highest SiO_2/Mg ratio shows that the reaction product consists mainly of $MgAl_2O_4$ with some Al_2O_3. Eutectic Si structures were clearly seen in the matrix away from the reinforcement particles. This is clearly an indication that the SiO_2 first is transformed into $MgAl_2O_4$ until the Mg level is too low and thereafter Al reacts with SiO_2 to form Al_2O_3, while both reaction reject Si into the melt. It also an indication that the SiO_2/Mg ratio can be an important factor to the density or hardness.

Based on this three stage reaction model it is possible to speculate on the behavior of this system. Stage 3, if limited to an internal precipitation reaction would most likely be the slowest reaction and would therefore be rate limiting. However, if cracking occurs, a more constant conversion with time would be expected. Given enough time all the SiO_2 will convert to $MgAl_2O_4$ and Al_2O_3 which are much denser oxides. Following from this it would be expected that the density of the composite will increase with increased reaction time until all SiO_2 has been converted to Al_2O_3. Figure 7 shows the change in density with reaction time for differing SiO_2 and Mg concentrations and clearly shows an approximately linear increase in density with reaction time for most cases. Furthermore, it is clear that increasing the Mg concentration results in composites with lower densities for the same reaction time. This is likely due in part to the creation of more $MgAl_2O_4$, which is the less dense phase.

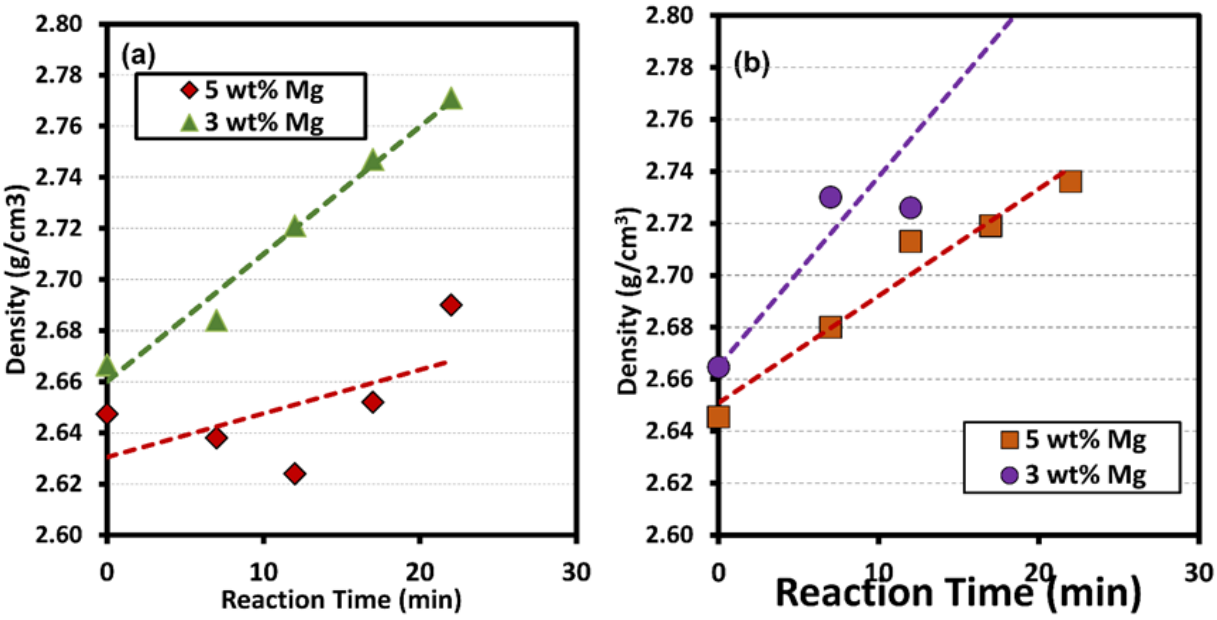

Figure 7. Variation in Density with Reaction Time and Mg concentration for a) SiO_2 = 9 wt% and b) SiO_2 = 13 wt%.

4. Conclusion

Silica sand particles were dispersed in the matrix of cast A206 alloy, modified with Mg as a wetting agent using stir casting, and the effects of the reaction time and SiO_2 content were investigated. Measurements for various aluminum/ silica sand compositions show that in the absence of additional Mg there is no correlation between silica content and hardness or density. This behavior

is attributed to weak or lack of bonding between the matrix and the SiO_2 particle. Also, voids are present in the particle matrix interface.

Addition of magnesium leads to increased density and increased hardness of the Al-A206 based composite as SiO_2 concentration increases. Reactions between Al, Mg, and SiO_2 which converts the SiO_2 into a denser oxide is proposed as an explanation for the overall change in density of the composites. A three-stage reaction mechanism is proposed. At the first stage Mg reacts quickly with the SiO_2 forming MgO until the Mg concentration falls to below the 1.7 wt% level. In Stage 2, the melt react with MgO and SiO_2 to form $MgAl_2O_4$ until the Mg concentration in the melt reaches its equilibrium concentration with the $MgAl_2O_4$. At stage three, where Mg and $MgAl_2O_4$ are in equilibrium Al_2O_3 forms as a result of direct reaction between Al and SiO_2. This likely occurs through direct contact of Al and SiO_2 due to cracking of the particles as a result of differences in oxides densities. Based on the proposed reaction model, changes in both physical and mechanical properties of A206-Mg-SiO_2 metal matrix composites may be explained in terms of the base Alloy / SiO_2 / Mg chemistry and reaction times.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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