EFFECT OF BERYLLIUM ADDITION ON LATTICE ARAMETER OF Al(α) and Mg₂Si DISPERSION PHASE IN THE Al -13%Mg₂Si CASTING ALLOY

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الملخص

تستخدم سبائك ألومنيوم الصب (Aluminum Casting Alloys) نوع 356 و 319 و 390 في إنتاج أجزاء محركات المركبات الآلية . وتولى شركات تصنيع السيارات اهتماما كبيراً لتطوير سبائك ألومنيوم الصب المحتواة على المركب سليسيدات المغنيسيوم (Mg₂Si Compound) لغرض استخدامه في إنتاج مكونات المحرك مثل رؤوس الاسطوانات، كتل المحركات، ومكابس المحركات. إن كمية المغنيسيوم المحتواة في سبائك الصب الألومنيوم – السليكون (Al-Si) محددة بنسبة 1 إلى 2% وذلك للتقليل من تكوين صفائح (Platelets) المركب سليسيدات المغنيسيوم الكبيرة والمتصلة بعضها ببعض والتي تسبب في هشاشة السبائك. في هذه الدراسة تمم استخدام المجهر الضوئي (Optical Microscopy (OP)) وحيود الأشعة السينية (X-ray Diffraction (XRD)) لمعرفة مدي تأثير إضافة معدن البريليوم على شبيكة (Lattice) الألومنيوم وشبيكة المركب سليسيدات المغنيسيوم المترسبة في سبيكة الصب الالـومنيوم - 13% سليسيدات المغنيسيـوم (Al -13%Mg2Si). وتحليل المعلومات المتحصل عليها من طريقة حيود الاشعة السينية دلت على زيادة في ثابت الشبيكة لوحدة خلية المحلول الجامد للألومنيوم من 0.40520 إلى 0.40585 نانومتر للسبيكة التي احتوت على معدن البريليوم، ويبين هذا أن معدن البريليوم يزيد من إمكانية ذوبانية نسب المغنيسيوم إلى السليكون (Mg/Si Ratio) في المحلول الجامد للألومنيوم ، وكذلك زيادة ثابت شبيكة وحدة خلية سليسيدات المغنيسيوم من 0.63570 إلى 0.63670 نانومتر، ويدل هذا على اندماج ذرات معدن البريليوم في وحدة خلية سليسيدات المغنيسيوم، ويرجح ذلك إلى تتقية الاطوار المترسبة. وأوضحت النتائج المجهرية بان الحبيبات الخشنة الخلوية الكبيرة للبنية اليوتكينية (بنية رقائقية) لسبيكة الصب قد تغيرت إلى حبيبات رفيعة خلوية صغيرة وذلك باحتواء السبيكة على معدن البريليوم. وبالمقارنة بين البنية الدقيقة للسبائك الملدنة أوضحت النتائج أن معدن البريليوم يزيد من كثافة المركب سليسيدات المغنيسيوم المترسبة ، ويصغر حجمها ، ويفصلها عن بعضها.

ABSTRACT

The automotive industries currently use aluminum casting alloys type 356, 319, and 390 for the production of automotive engine parts. It is the interest for automotive industries to develop aluminum casting alloys containing Mg₂Si compound for potential application in the automotive engine components, including cylinder heads, engine blocks and engine pistons. The Mg content in the Al-Si casting alloys is restricted to 1-2%, in order to minimize the formation of large interconnected platelets of Mg₂Si compound which embrittle the alloys. In this study Optical (OP) microscopy and X-ray diffraction (XRD) were used to determine the effect of beryllium (Be) addition on the

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lattice parameter of aluminum solid solution (Al (α)) and Mg₂Si dispersion phase of the Al -13%Mg₂Si alloy. The analysis of XRD data indicates an increase in the lattice parameter of aluminum unit cell (from 0.40520 to 0.40585 nm) for the Be-containing alloy, suggesting that beryllium may increase the solubility of Mg/Si ratio in the solid solution. The lattice parameter of Mg₂Si unit cell also expanded (from 0.63570 to 0.63670 nm), indicating beryllium incorporation into the Mg₂Si unit cell, is associated with the refinement of the precipitating phases. The optical results show that the large cellular coarse grains of the eutectic structure (lamellar structure) or as-cast structure of the base alloy are broken down into smaller cellular fine grains when the beryllium is contained in the base alloy. A comparison of the microstructures of the annealed alloys shows that beryllium increases the density, reduces the size of the precipitating phase, and breaks down the interconnected platelets of the dispersion phases. The above findings indicate that the beryllium enhances nucleation process and a refinement of precipitating phase has occurred.

KEYWORDS: Automotive materials; Aluminium casting alloys; X-ray diffraction; Dispersion strengthening; Refinement.

INTRODUCTION

The addition of selected alloying elements to some aluminium alloys strongly affects the alloys age hardening response, which is attributed to increasing defect concentrations, combined with increasing the nucleation rate of the precipitation process. It has been reported that small additions of silicon [1] and beryllium [2] significantly enhance the grain refinement of aluminium by titanium. It was also shown that Si and Be are incorporated into the TiAl₃ compound, with the result of increasing the nucleation rate of TiAl₃, and enhancing grain refinement.

The quasi-binary Al - Mg₂Si equilibrium diagram [3-4] shown in Figure 1, is relatively simple and well established. The compound Mg₂Si is in equilibrium with Al(α), and the quasi-binary line Al - Mg₂Si in the ternary diagram (Figure 2) occurs at the Mg/Si weight ratio of 1.73. The Si, Al₃Mg₂ and Mg₂Si phases in the reactions do not differ substantially from stoichiometric compositions. The solid solubility of Mg₂Si in the Al(α) is reduced only slightly with Si above the Mg/Si ratio of 1.73, but an excess of Mg greatly reduces Mg₂Si solubility [5]. As Mg expands and Si contracts the lattice parameter of Al(α) solid solution, the lattice of the ternary Al(α) solid solution may increase or decrease depending on the ratio of Mg/Si [6]. The compound Mg₂Si (63.2%Mg, 36.8%Si) is cubic, space group Fm3m, 12 atoms in the unit cell and a lattice parameter a₀ = 0.635-0.640 nm. The melting point, Vickers hardness and density for Mg₂Si are 1085°C, 459 kg/mm², 1.88 g/cm³ respectively [5].

The effect of small additions of beryllium to the Al-7.0%Si-0.5%Mg-0.1%Fe (AA357-type) alloy has been investigated by Granger et al [7]. They found by microprobe analysis, that in addition to Si and Mg₂Si phases, the Be-free alloy contains three Fe-rich phases, while the Be-containing alloy has only one Fe-rich phase. They also report 12% of the particle area is Fe-bearing in the Be-free alloy, compared to 3% in the Be-containing alloy. Using Differential Scanning Calorimetry (D.S.C) analysis, they show that the addition of beryllium lowers the ternary eutectic melting point by 6° C, and that the second (higher) temperature peak, which is Fe- reaction, is affected by

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the Be- addition. These observations lend further support to the microprobe results, that the presence of beryllium reduces the number of Fe-bearing constituents.



Figure 1: Aluminium - Magnesium Silicide Quasi-binary Phase Diagram [3-4].



Figure 2: Partial Aluminium – Magnesium - Silicon Ternary Phase Diagram [5].

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The effect of beryllium additions on the Al-Mg-Si alloys were investigated [8-10]. The results show that the Be-containing alloy has a significantly higher age hardening rate, and reaches higher peak hardness than the Be-free alloy, when the alloy is aged at various temperatures from 22 to 300°C. A kinetic analysis showed that higher transformation rates for the Be-containing alloy, indicating a Be-enhanced nucleation stage for the transformation process, and the Be-free alloy. This study was undertaken to determine the effect of beryllium addition on the lattice parameter of aluminum solid solution (Al (α)) and Mg₂Si dispersion phase in the Al-13%Mg₂Si alloy, using X-ray diffraction and optical microscopy techniques.

EXPERIMENTAL PROCEDURE

Super pure aluminium and magnesium (99.99%), Al-50%Si and Al-5.23%Be master alloys were used in the preparation of the base eutectic alloy (Al-13%Mg₂Si) and eutectic alloys containing up to 2%Be. The alloys were prepared in graphite crucibles, by induction melting in air, using a 15 kVA Ajax inductotherm unit at a frequency of 10 kHz. The melts were heated to well above the liquidus temperature ($\approx 750^{\circ}$ C), maintained for 10 minutes and stirred several times to ensure complete homogenization, and then poured into graphite molds 20 mm diameter by 70 mm length at room temperature. The melt temperature was monitored by a thermocouple embedded in the graphite crucible. Specimens for annealing treatment and analysis were cut from the central regions of the ingot (20 mm diameter by 5 mm thickness) to ensure similar initial microstructures and compositions. The annealing treatments were carried out using an electric furnace with a temperature control of $\pm 3^{\circ}$ C. Three different annealing treatments were carried out. The first set of specimens annealed at 550°C for 3 days, followed by a quench in water. The quenching was performed to avoid the formation of β' phase (Al₃Mg₂), and to determine if Si phase precipitated in the alloy. The second and third sets of specimens annealed at 550°C and 400°C (for 6 days) respectively, then furnace cooled (for 1 day). The furnace cool was to promote maximum transformation to the stable low temperature phases, and to determine in particular whether any β phase formed in the alloys.

Specimens for optical analysis were prepared by wet grinding on 240, 320, 400 and 600 grit papers, followed by polishing with 1.0 and 0.05 micron alumina media. Specimen etching was accomplished by using either a solution of 1.0 g of NaOH to 100 ml water, or 1.0 ml HF (48%) to 200 ml water. The X-ray Diffraction (XRD) scans were obtained for the solid alloys using a Phillips PW 1078 X-ray generator, with copper radiation (Cu K_{α}, λ = 1.54186 Å) filtered by Ni, and scanning rate of 2°/min. The operating voltage and current were set at 40 kV and 20mA respectively. A chart recorder was utilized to record the diffracted beams, and four runs were taken from each specimen. Also, powder alloy specimens mixed with silicon powder as an internal calibration reference were analyzed by XRD at Energy Conversion Devices, Inc., Troy, Michigan.

RESULTS AND DISCUSSIONS

X-ray Diffraction Analysis

The XRD analysis was performed on the alloys in two conditions: fully annealed at 400°C and 550°C, furnace cooled and quenched from 550°C. The XRD analysis of the alloys in the fully annealed and quenched conditions assists in identifying the Al₃Mg₂– phase and Si-phase. The equilibrated Al₃Mg₂–phase [11], with a complex FCC structure ($a_0 = 2.8239$ nm), and Si-phase [12] with a diamond cubic structure ($a_0 = 0.54301$ nm),

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have several diffraction peaks that are difficult to distinguish from several Al(α) and Mg₂Si peaks. It has been reported that Al₃Mg₂-phase has a low temperature martensitic structure [13] that develops on severe quenching. The martensitic form of Al₃Mg₂phase would be more readily distinguished from the other phases by microstructure. The results of the XRD analyses of the Al-50%Si, Al-10%Mg, and Al-5.23%Be alloys were studied and compared against the diffraction patterns obtained for the base alloy and base alloy containing 2%Be. A comparison of peaks shows that only Al(a) and Mg₂Si peaks occur in the diffraction patterns for both alloys in both conditions, fully annealed (Tables 1 and 2) and quenched (Figures 3 and 4), showing no presence of either Al₃Mg₂-phase or Si-phase, indicating that the alloy composition is essentially on the quasi-binary line. Only an excess Mg or Si over the atomic ratio of Mg/Si = 2 (or the presence of other alloying elements in sufficient quantity), will shift the composition coordinate off the quasi-binary line, up to the region of $Al + Mg_2Si + Al_3Mg_2$, or down to the region of $Al + Mg_2Si + Si$ of the ternary phase diagram(see Figure 2). Note that the diffraction patterns for Be-containing alloy are shown in Figure 4 at Bragg angle of 52.85 degree, however, it is only detectable when counts per second (cps) is set at low scale (400 cps full chart scale).

Table 1: XRD data for Al(α), specimens annealed 550°C, furnace cooled.

Al-13%Mg ₂ Si			Al-13%Mg ₂ Si-2%Be		$\Delta(I/I_1)$	$\Delta(2\theta)$	ASTM data, Al (FCC)		CC)	
20	d, nm	I/I ₁	20	d, nm	I/I ₁			Hkl	d, nm	I/I ₁
38.42	0.23411	100	38.25	0.23514	100		-0.17	111	0.23380	100
44.65	0.20279	43	44.47	0.20356	44	+1.0	-0.18	200	0.20240	47
65.05	0.14326	23	64.86	0.14365	23	0.0	-0.19	220	0.14310	22
78.20	0.12214	23	78.00	0.12240	18	-5.0	-0.20	311	0.12210	24
82.39	0.11696	5	82.21	0.11716	4	-1.0	-0.18	222	0.11690	7
99.01	0.10130	1.4	98.85	0.10141	2.2	+0.8	-0.16	400	0.10124	2

Table 2: XRD data for Mg ₂ S	i, specimens annealed 550°C	, furnace cooled.
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Al-13%Mg ₂ Si			Al-13%Mg ₂ Si-2%Be		$\Delta(I/I_1)$	$\Delta(2\theta)$	ASTM data, Mg ₂ Si			
						(FCC)	(FCC)			
20	d, nm	I/I ₁	20	d, nm	I/I ₁			Hkl	d, nm	I/I ₁
24.18	0.36778	51	24.01	0.37034	31	-20.0	-0.17	111	0.36680	41
40.05	0.22495	100	39.89	0.22582	100		-0.16	220	0.22456	100
57.95	0.15901	12	57.81	0.15936	12	0.0	-0.14	400	0.15881	13
72.85	0.12973	28	72.64	0.13005	24	-4.0	-0.21	422	0.12965	21

The results of the XRD analysis for the powder alloys in Table 1 for $Al(\alpha)$ show that the lattice planes have shifted to higher values for the Be-containing alloy, giving an increase from 0.40520 to 0.40585 nm in the lattice parameter "a_o", as shown in Table 3.

Table 3: Unit cell da	ta for Al(α). Specim	iens annealed 550°C, furnace	cooled

Alloys	a _o , nm	ρ, g/cm ³
Al-13%Mg ₂ Si	0.40520 ± 0.0005	2.6947
Al-13%Mg ₂ Si-2%Be	0.40585 ± 0.0012	2.6852

The increase in "a_o" suggests the possibility of Be-atoms is associated with GP zones, causing lattice strain (Be-atoms are smaller than Al, Mg, and Si atoms) and so increases scattering; the solute is also said to be a more effective scattered inside a zone than when occupying a normal lattice position [14].

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Figure 3: X-ray diffraction Pattern for Al-13%Mg₂Si, specimens annealed 550⁶C, water quench.

The presence of Be-atoms in solid solution may cause the efficient trapping of vacancies [15]. The size and the magnitude of the solute-vacancy binding energy depend basically on two factors: electronic effects arising from differences in valence, and differences in the volume of the solute and solvent atoms. Vacancies may be considered to possess negative charge. The doubly charged positive Be-ion cores; and the negative charged vacancy interact by the electrostatic screened coulomb attraction. The reported binding energy values for Mg-vacancy, Si-vacancy, and Be-vacancy in Al(α) are 0.17-0.19 eV, 0.20 and 0.23 eV [16-19], and 0.26 and 0.28 eV [5,20] respectively. The high Be-vacancy binding energy will result in a higher retained vacancy concentration in the matrix to increase the critical scattering size of the GP zones, which may influence the rate of precipitation [21]. The significant increase in "a_o" calculated from the XRD results for Al(α), indicates that beryllium increases the solubility of the atomic ratio of Mg/Si as approaches the ratio of 2 in the Al(α).

Table 2 shows that the lattice planes of Mg₂Si phases have shifted to the higher 2Θ values for the Be-containing alloy, giving an increase in lattice parameter "a_o" from 0.63570 to 0.63670 nm (Table 4), suggesting that beryllium may be incorporated into Mg₂Si unit cell interstitially not substitutionally. A calculation of the interstitial dimensions for Mg₂Si lattice, using atomic diameters based on the closest distance of approach in the crystals of elements gives a value of "D" shown in Table 5 and Figure 5, indicates that beryllium can be accommodated as an interstitial atom into Mg₂Si unit cell. Thus a ternary compound having the approximate formula of Mg₂SiBe_x is possible compared to the calculated of Mg₂SiBe_{0.25}.

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Figure 4: X-ray diffraction Pattern for Al-13%Mg₂Si-2%Be, specimens annealed 550⁰C, water quench.



Figure 5: Mg_2Si structure (CaF₂ – type), unit cell and (110) plane.

Table 4: Unit cell data for Mg ₂ Si, specimens annealed 550°C, furnace cooled.						
Alloys	a _o , nm	ρ, g/cm ³				
Al-13%Mg ₂ Si	0.63570 ± 0.0016	1.9790				
Al-13%Mg ₂ Si-2%Be	0.63670 ± 0.0019	1.9729				

	Table 5: Comparison of interstice D values					
	$A*_{Mg2Si}$, nm	Calculated D, nm	a** _{Mg2Si} , nm	Calculated D, nm		
	0.6390	0.2318	0.6357	0.2261		
	0.6351	0.2251	0.6367	0.2278		
*	values obtained from	m ref.[12,22]	** values obtained	from Table 4.		

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As-cast and Annealed Microstructures

Figure 6 shows optical micrographs of the as-cast microstructures for the base and Be-containing alloys respectively. A cellular grain structure of typical eutectic composition alloys, with the Al solid solution (light) and Mg₂Si (dark) phases combine in a fine lamellar structure as shown in Figure 6a. The addition of other alloying components to eutectic composition alloy tends to break down the lamellar structure if the alloying components are in one or both of the eutectic constituents as shown in Figure 6b. Karov and Youdelis [23] have shown that as little as 0.5%Be, which is soluble in the metalloid constituent (CuAl₂) up to 0.8% severely disrupts lamellar growth during solidification, tending to form two irregular two phase microstructures.



Figure 6: Optical photomicrographs showing as-cast structure for (a) Al-13%Mg₂Si alloy;(b)Al-13%Mg₂Si-2%Be alloy.

It is evident that the addition of Beryllium has a similar effect in the quasi-binary Al- Mg_2Si eutectic, and suggests incorporation of Beryllium into Mg_2Si may be occurred. The excess beryllium has separated as essentially pure beryllium. Figure 7 and Figure 8 show the microstructures after annealing for 6 days and then furnace cooled of the base and Be-containing alloys respectively. It is clear that the beryllium has higher density of fine precipitating particles (Figure 7b) than the base alloy (Figure 7a), and the higher magnification microstructures (Figure 8a and Figure 8b) show that beryllium addition reduces the size of precipitating particles and breaks down the interconnected particles, suggesting that beryllium enhances nucleation rate. It has been shown that the addition of small amount of beryllium to Al-Mg-Si wrought alloys, significantly increases the density of the precipitate particles, indicating that the Be-enhanced the age hardening response of the alloy is associated with a refinement of the Mg_2Si precipitate [1,2,8,9].

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Figure 7: Optical photomicrographs of alloys annealed at 550°C and furnace cooled. (a) Al-13%Mg₂Si alloy; (b) Al-13%Mg₂Si-2%Be alloy.



Figure 8: Optical photomicrographs of alloys annealed at 550°C and furnace cooled. (a) Al-13%Mg₂Si alloy; (b) Al-13%Mg₂Si-2%Be alloy.

CONCLUSIONS

The X-ray diffraction analysis indicates that some of beryllium is dissolved by $Al(\alpha)$ and Mg_2Si as reflected by the expansion of lattice parameters for both $Al(\alpha)$ and Mg_2Si , when beryllium is contained in the alloy. The optical photomicrographs show that beryllium decreases the interlamellar spacing of as-cast structure. Also, it shows that beryllium increases the density and reduces the size of the precipitating phases, and breaks down the

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interconnected platelets of Mg₂Si compound. The XRD results suggest that beryllium enhances nucleation rate, which is in agreement with the observed refinement of microstructures, as indicated by optical results.

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