

EFFECT OF CERIUM AND BARIUM ADDITIONS AND SUPERHEATING MELT
TREATMENT ON THE MORPHOLOGY AND HARDNESS OF Al-Mg₂Si-Cu
COMPOSITE

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I dedicated this thesis to my beloved parents and family for their endless love and motivational support.

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ABSTRACT

Aluminium-based alloy, reinforced with particulate Mg_2Si phase has been widely accepted to replace Al-Si alloy due to its improved properties in producing engineering products especially for automotive and aerospace applications. However, in as-cast Al-based reinforced with Mg_2Si composite, the particles formed are coarse with large skeleton shapes and eutectic Al- Mg_2Si phase which are also present in flake-like form. These phases are known to have detrimental effect on the mechanical properties of the composite. The present research is therefore aimed to investigate the effect of elements addition and superheating melt treatment in order to modify the undesired structures and phases in Al- Mg_2Si -Cu metal matrix composite. The elements addition were Ce (0.3-1.0 wt.%) and Ba (0.1-1.0 wt.%). Meanwhile, superheating above the melting temperature of Al- Mg_2Si -Cu composite was carried out at three different temperatures (850°C, 900°C and 950°C) and three different holding times (15, 30 and 45 minutes) to further modify the microstructures. The samples were produced by melting commercial Al-Mg-Si ingot and pouring into a ceramic mould and the transformation temperatures were determined by computer aided cooling curve thermal analysis (CACCTA). The phase and microstructural changes were characterized using optical microscopy, field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Hardness test (ASTM E92) was performed in order to investigate the effect of morphology modification on the hardness of the composite. Both approaches, namely, elements addition and melt superheating with varying parameters were found to refine not only Mg_2Si_P reinforcement particles but also eutectic Al- Mg_2Si phase. Various morphologies of the phases were observed, particularly, coarse skeleton of Mg_2Si_P has been transformed to finer polygonal structure. Likewise, flake-like morphology of Mg_2Si_E has transformed to rod and fibrous-like form while the needle-like intermetallic β has transformed to α phase. The optimum concentrations to achieve the adequate refinement effect were found to be 0.8wt% Ce and 0.2wt% Ba. While, the optimum parameter for the melt superheating was 950°C and underwent 15 minutes holding melt duration. The modified composite with addition of optimum concentration of Ce and Ba were observed to increase in hardness property from 61.32Hv to 74.3Hv and 67.95Hv for Ce and Ba, respectively. Whereas, for the composite modified by melt superheating, the hardness improved from 61.32Hv to 70.22Hv.

ABSTRAK

Aloi aluminium yang diperkuatkan dengan pengisian seramik partikel Mg_2Si telah diterima secara meluas bagi menggantikan aloi Al-Si kerana sifatnya yang memuaskan dalam penghasilan produk-produk kejuruteraan, terutamanya dalam aplikasi automotif dan aeroangkasa. Namun, dalam hasil tuangan komposit Al dengan pengisian seramik partikel Mg_2Si , partikel-partikel tersebut telah wujud dalam bentuk yang kasar dengan saiz tetulang yang besar dan fasa eutektik Al- Mg_2Si yang wujud adalah dalam bentuk kepingan-kepingan. Fasa-fasa ini telah dikenalpasti memberi kesan yang memudaratkan ke atas sifat-sifat mekanikal komposit tersebut. Maka, kajian ini adalah bertujuan untuk menyelidik kesan penambahan unsur-unsur dan rawatan lebur pemanasan lampau untuk memperbaiki struktur dan fasa-fasa dalam komposit matrik logam Al- Mg_2Si -Cu (*MMC*). Penambahan unsur-unsur tersebut adalah dengan menggunakan Ce (0.3-1.0% berat) dan Ba (0.1-1.0% berat). Sementara itu, kaedah pemanasan lampau melebihi suhu leburan komposit Al- Mg_2Si -Cu ($750^\circ C$) telah dijalankan pada tiga suhu ($850^\circ C$, $900^\circ C$ dan $950^\circ C$) dan dibiarkan dalam tempoh masa yang berbeza (15, 30 dan 45 minit), bagi penambaan selanjutnya mikrostruktur-mikrostruktur tersebut. Sampel tuangan diproses dengan meleburkan jangkong Al- Mg_2Si -Cu komersil dan dituang dalam acuan seramik dan suhu-suhu perubahan telah ditentukan dengan menggunakan perisian komputer analisa haba lengkok penyejukan (*CACCTA*). Perubahan fasa dan mikrostruktur-mikrostruktur telah dicirikan dengan menggunakan mikroskop optik, mikroskop elektron pengimbasan medan (*FESEM*), mikroskop imbasan electron (*SEM*) dan pembelauan sinar x (*XRD*). Ujian kekerasan (*ASTM E92*) telah dijalankan bagi menguji kesan pembaikan mikrostruktur ke atas sifat kekerasan komposit tersebut. Kedua-dua pendekatan iaitu penambahan unsur-unsur dan pemanasan lampau dengan pelbagai parameter telah dilihat dapat menghaluskan bukan sahaja partikel-partikel penguat Mg_2Si_P malah fasa eutektik Al- Mg_2Si . Pelbagai morfologi fasa-fasa telah diperhatikan terutamanya partikel kasar Mg_2Si telah berubah kepada struktur halus poligon. Begitu juga dengan morfologi kepingan-kepingan fasa eutektik Mg_2Si yang berubah kepada bentuk rod dan serabut halus, sementara itu, bentuk jejaram bagi sebatian antara logam fasa β juga telah berubah kepada fasa α . Komposisi optimum untuk mencapai kesan pembaikan yang mencukupi adalah 0.8% berat Ce dan 0.2% berat Ba. Bagi kaedah pemanasan lampau pula, parameter yang terbaik adalah pada suhu 950° dan dibiarkan selama 15 minit. Komposit yang berubah suai dengan penambahan unsur Ce dan Ba telah menunjukkan peningkatan dalam sifat kekerasan komposit, daripada 61.32Hv kepada 74.3Hv untuk Ce dan 67.95Hv untuk Ba. Sementara itu, nilai kekerasan komposit yang berubah suai dengan pemanasan lampau pula telah meningkat daripada 61.32Hv kepada 70.22 Hv.

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LIST OF SYMBOLS

Mg_2Si	-	Magnesium silicide
Al_3Ti	-	Titanium trialuminide
AlP	-	Alkaline phosphate
Y_2O_3	-	Yttrium oxide
SiC	-	Silicon carbide
Al_2O_3	-	Alumina
K_2TiF_6	-	Potassium fluotitanate
$Mg_3(PO_4)$	-	Magnesium phosphate
Mg_3P	-	Magnesium phosphide
Mg_3Sb_2	-	Magnesium antimonide
KBF_4	-	Potassium tetrafluoroborate
HCl	-	Hydrochloric acid
r^*	-	Critical radius
ΔG_v	-	Free energy per unit volume
ΔG_s	-	Surface free energy per unit area
G_v	-	Volume free energy
G_s	-	Surface free energy
ΔG^*	-	Activation energy
ΔG	-	Gibbs free energy
γ_{SI}	-	Solid surface free energy
γ_{SL}	-	Solid-liquid free energy
γ_{IL}	-	Liquid surface free energy
Θ	-	Wetting angle
T_m	-	Melting temperature
T_P	-	Pouring temperature

T_S	-	Superheat temperature
T_N	-	Nucleation temperature
T_{\min}	-	Minimum temperature
T_G	-	Growth temperature
T_c	-	Temperature at centre
T_w	-	Temperature at wall
CR	-	Cooling rate

LIST OF ABBREVIATIONS

MMC	-	Metal Matrix Composite
CACCTA	-	Computer Aided Cooling Curve Analysis
DTA	-	Differential Thermal Analysis
DSC	-	Differential Scanning Calorimetry
TGA	-	Thermogravimetric Analysis
FESEM	-	Field Emission Scanning Electron Microscopy
EDX	-	Energy Dispersive X-ray Analysis
XRD	-	X-ray Diffraction
BSE	-	Backscattered Secondary Electron
FCC	-	Face Centered Cubic

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CHAPTER 1

INTRODUCTION

1.1 Research Background

As a class of advanced engineering materials, aluminium metal matrix composites (MMCs) have been paid greater attention extensively owing to their excellent properties which make them useful for high performance applications. Their properties such as low density, excellent castability, excellent mechanical properties and low production cost render these materials more attractive to meet further application demands especially for light-weight components [1-3], particularly in the manufacture of automotive parts where the pressure to use light-weight material has been increasing due to environmental issues.

The common aluminium metal matrix composites (Al-MMC) are mostly based on the Aluminium-Silicon (Al-Si) casting alloys reinforced with hard ceramic particles, such as silicon carbide (SiC) and alumina (Al_2O_3) [4, 5]. However, these metal matrix composites suffer from thermodynamic instability of interfaces between the ceramic reinforcement and matrix, in addition to poor wettability of the reinforcements [6]. Moreover, small particle size of the reinforcement and the density differences between reinforcement and matrix make the fabrication of these composites more difficult due to settling and agglomeration issues [7].

Al-based composite, reinforced with particulate Mg_2Si phase have recently been shown to possess advantages [5, 8]. However, mechanical properties in normal cast Al- Mg_2Si in-situ composite is unsatisfactory due to the nature form of dendrite and coarse morphology of primary Mg_2Si phase which lead to stress concentration at sharp edges and corners of Mg_2Si structure [9, 10]. This would cause more brittle phase of structure [11] and low ductility of the in situ composite [2]. Thus, mechanical properties of the composite are rather limited especially at high temperature [10, 12]. Therefore, melt treatment by refinement and modification of the coarse primary Mg_2Si structure as well as corresponding matrix phase of Al- Mg_2Si in-situ composite is crucial in order to improve the morphology of Mg_2Si reinforcement and achieve better mechanical properties.

Various methods have been employed and developed to enhance the composite properties by refining the structure of the primary Mg_2Si as well as that of the matrix. Among the techniques [13, 14], melt treatment method with modifier or refiner elements is chosen due to result effectiveness in addition to low cost because of the use of Al, Mg and Si as starting materials [6, 7]. Furthermore, the technique results in an even distribution of reinforcing phase, good particle wetting and less steps of processing for industrial utilization. Besides, reinforcement particles are thermodynamically stable in the matrix, leading to less degradation in high temperature services [5, 11, 12].

It has been reported that potassium fluotitanate, K_2TiF_6 [15], potassium fluotitanate + potassium tetrafluoroborate ($K_2TiF_6+KBF_4$) [16], strontium (Sr) [17-19], sodium (Na) [19] and phosphorus (P) [9, 18, 20] are important additives to be introduced to the melt alloy in order to refine or modify the morphology of the primary Mg_2Si and enhance the properties. However, some of the findings from this research have reported drawbacks as described by and Zhao *et al.* [19] and Wang *et al.* [16] in their research respectively. In particular, Na has limited solid solubility in Al melt and has a very high vapour pressure. Thus, Na is readily volatilized during the modification process, resulting in negative effects [19]. Another case, addition of K_2TiF_6 and KBF_4 individually in Mg-Si composite have refined and modified the shape of primary Mg_2Si respectively. However, combination of $K_2TiF_6+KBF_4$ in the

composite has reduced the role of KBF_4 as modifier and as a result, primary Mg_2Si become coarser again [16].

Previous research also showed that the refinement effect have been achieved by addition of extra silicon (Si) [9, 21] since the morphology of coarse primary Mg_2Si particles resulted in finer polyhedral shape with a reduced size. The addition also caused modification in the eutectic Mg_2Si phase by altering the flake-like structure to a finer fiber shape. Similar results of refined primary and eutectic Mg_2Si structures have also been obtained with the addition of lithium (Li) to Al- Mg_2Si melt composite [11, 22], addition of antimony (Sb) [23, 24], Sr [25, 26] and bismuth (Bi) [10, 27].

The role of rare earth elements as modifiers or refiners have also been investigated but most research have focused on Al-Si alloys [28-30]. It was reported that addition of rare earth elements (RE) such as lanthanum (La), cerium (Ce), neodymium (Nd), yttrium (Y) and mischmetal could be capable to modify the eutectic structure but not the primary Si phase [31]. However, in a recent research by Qin Lin *et al.* [28] it has been shown that addition of Ce has a significant refining effect on the primary Si crystals besides modifying the eutectic Si structure as well. Knuutinen *et al.* [29] in their research on barium (Ba), calcium (Ca), Y and ytterbium (Yb) also concluded that both Ca and Ba can act as modifiers while Y and Yb act as refiners to modify and refine the morphology of Al-Si alloy respectively.

Similar refinement result was obtained with the use of Ce into Al-Si-Cu composite on the primary Mg_2Si structure as reported by Zhang *et al.* [32]. In other research, Zheng *et al.* [33] have proved that addition of Y_2O_3 compound has caused modification of the morphology of primary Mg_2Si in Mg-Si base composite while other findings have claimed that Y itself just affect the size and not the morphology of Mg_2Si particles. However, Emamy *et al.* [34] claimed that Y individually could modify both the morphology of Mg_2Si phase as well as its size and produce a refined structure. In addition, Wang *et al.* [35] who investigated the effect of La in Mg-Si composite have revealed that La could refine the morphology of Mg_2Si from coarse to refined polygonal structure.

Instead of melt treatment by the elements addition approach, the morphology of cast alloys can also be affected by superheating melt treatment. It is a process that involves preheating the cast alloy at higher temperature, basically above the melting temperature and holding it for a certain period of time and then immediately cooled to pouring temperature before casting or solidifying [36-38]. The process of preheating at elevated temperature would cause a change in heredity of the alloy by remelting the particles and clusters completely and homogeneously in the melt, then resolidify as finer particles. This would result in finer grain nucleation [37, 39].

It was reported that melt superheating temperature on $Mg_2Si/Al-Si-Cu$ composite resulted in a change of coarse dendritic primary Mg_2Si particles to equiaxed shape and a decrease in their size while the eutectic Mg_2Si phase has been improved from Chinese script type to irregular type [39]. Similar result was observed by Zhamin *et al.* [33] who claimed that superheating melt treatment on $Mg-3.5Si-1Al$ composite caused reduction in heredity phenomenon of the composite such that both primary and eutectic Mg_2Si phase have been refined.

Besides that, Chen *et al.* [38] in their study on Al-Si melt alloy have claimed that eutectic Si phase could be modified and refined by reducing heredity phenomenon in the melt and changing its growth phase to get better final structure. Meanwhile, Haque *et al.* [40] have clarified that superheating technique with addition of Sr results in better modification effect compared to modified alloy with Sr without superheating. Indeed, the morphology of eutectic Si phase has been refined. Although most of the research concerning superheating melt treatment focused on the eutectic Si phase in Al-Si alloy, it is believed that superheating could also result in similar modification effect on the primary Mg_2Si phase in Al- Mg_2Si in-situ composite.

In summary, modification and refinement of coarse morphology of any material by addition of inoculation agents and superheating melt treatment are important and may be considered as useful routes to enhance the mechanical properties of the material. Inoculation agents, similar to neutralizer or modifier elements would be induced to the Al melt alloy/composite in order to treat the undesirable structure and produced modified and refined morphology. Although,

most of research studies on refinement and modification treatment are related to the Al-Si alloy, there is great similarities between the solidification behaviour of Al-Si and Al-Mg₂Si systems [31]. Therefore, it is believed that element additions of Ce and Ba as well as superheating melt treatment at certain temperature ranges and holding time can be effective routes to alter the morphology of primary Mg₂Si structure in the Al-Mg₂Si in-situ composite. Control of their microstructure is more practical and cost effective method because of low production cost commercially and is the same as that practiced in casting of metallic alloys.

1.2 Problem Statement

High performance of Al-Mg-Si composites containing Mg₂Si reinforced phase are attractive candidates to manufacture industrial products especially for automotive and aerospace components. However, the presence of Mg₂Si reinforced particles in the form of dendrite and coarse shape have adverse effect on the mechanical properties of the composites due to ease of crack formation at sharp edges and corners of the Mg₂Si particles. Therefore, modification and refinement of the coarse morphology is required in order to improve the structure and thus enhance the mechanical properties such as reduce the brittleness of the Al-Mg₂Si in-situ composite.

Elements addition and superheating melt treatment have been proposed to alter the coarse morphologies of the phases in the melt alloys. The first approach is by element addition. Examples of elements addition are cerium (Ce) and barium (Ba). However, scarcity of Ce and Ba elements has limited their use as modifier or refiner elements and restricted their use in general industrial applications. Research findings, albeit very little have proved that addition of such elements causes modification and refinement effects of phases in many melt alloys. Moreover, the interaction between these rare earth elements and the exact mechanism of

modification is still unclear. In fact, focus of Ce and Ba elements are rather limited that inspired to further emphasis its role as modifier and refiner agents.

Superheating melt treatment as a second approach has been suggested to achieve refinement in the in-situ composite melt. Preheating the melt composite at elevated temperature, normally above the melting temperature of Al-20%Mg₂Si-2%Cu in-situ composite, causes complete dissolution of particles and yet lead to nucleation of finer particles. However, the exact reasons and role of modifying effect is not clearly understood, in addition to very little research work done regarding the superheating treatment on primary phase and in Al-Mg-Si composite.

Therefore, this current research is carried out in order to investigate the effect of elements addition namely Ce and Ba as well as superheating melt treatment on the primary Mg₂Si phase. Both methods will be carried out with computer aided cooling curve thermal analysis (CACCTA) technique in order to monitor the solidification behavior of the composite and to determine the characteristic temperatures for each phase. Understanding the characteristic temperatures can be beneficial in controlling the solidification process of the cast alloy, yet producing improved microstructure of composite with the corresponding desired mechanical properties. As both methods are expected to improve the morphology and properties of the in situ composite, they will be compared and the best method will be proposed at the end of this research study.

1.3 Objectives of the Research

The primary aim of this research is to investigate the effect of elements addition (Ce and Ba) and superheating melt treatment on the morphology of primary Mg₂Si phase and mechanical property namely hardness of commercial Al-20%Mg₂Si-2%Cu in-situ composite.

The specific objectives of the research are:

1. To evaluate the characteristic temperatures of the in-situ composite during solidification process by elements addition and superheating melt treatment using computer aided cooling curve thermal analysis (CACCTA) technique.
2. To determine the effects of elements addition (Ce and Ba) on the morphology of in-situ Mg_2Si reinforced particles in Al- Mg_2Si -Cu composites and the hardness of respective in-situ composites using gravitational casting process.
3. To determine the effect of superheating temperature (850-950°C) and holding time (15-45 minutes) on primary Mg_2Si structure phase and the hardness of the corresponding Al- Mg_2Si -Cu in-situ composite.
4. To determine the optimum concentration of Ce and Ba addition and the optimum parameter of superheating melt treatment that resulted in adequate modification and refinement effect on the morphology of Al- Mg_2Si -Cu in-situ composite.
5. To propose the mechanisms related to phase transformation of Al-20% Mg_2Si -2%Cu in situ composite, in addition to modification effect of primary Mg_2Si as a result of Ce and Ba additions as well as superheating melt treatment.

1.4 Scopes of the Research

The scopes of the research are as follows:

1. Preparation of ceramic moulds for the casting process.
2. Preparation of samples by casting as-cast commercial Al-Mg₂Si-Cu composite with and without elements addition (Ce and Ba) and superheating melt treatment.
3. Analysis of the as-cast molten Al-Mg-Si-Cu in-situ composite with and without elements addition using computer aided cooling curve thermal analysis (CACCTA) in order to determine the characteristic temperatures of the primary Mg₂Si phase.
4. Analysis of Al-Mg₂Si-Cu composite melt during superheating melt treatment using CACCTA to characterize the characteristic temperatures of the primary Mg₂Si.
5. Microstructural and phase analysis of as-cast prepared samples using optical microscopes, field emission scanning electron microscopy (FESEM) with energy dispersive x-ray analysis (EDX) and x-ray diffraction (XRD).
6. Perform hardness test on as-cast samples that have treated with elements addition and superheating melt treatment.

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