DEVELOPMENT OF ALUMINUM ALLOYS FOR DIESEL-ENGINE APPLICATIONS

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ABSTRACT

Weight reduction in vehicles has important benefits of fuel economy and reduction in greenhouse gas emissions as well as improved vehicle performance. The current material for the diesel-engine block/head is mostly ductile iron and replacing it with aluminum alloys would result in very effective weight reduction (30-40%). Current commercial cast aluminum alloys, however, soften at engine operating temperatures exceeding 200°C and would cause early fracture in the diesel engine.

Two new alloys derived from the commercial alloy (A356) are described in terms of microstructure, creep, aging behavior and tensile properties at elevated temperatures. The alloy containing both peritectic (Cr, Zr and Mn) and age hardenable elements (Cu and Mg) shows superior aging response at 200°C (for 200 hours) and creep properties at 300°C (for 300 hours). Interestingly, the alloy has better tensile strength (161MPa) at 250°C with adequate ductility compared to the current engine alloys, A356 and A356+Cu. The improvement in mechanical properties is attributed to the newly formed thermally stable fine precipitates (ϵ -AlZrSi, α -AlCrMnFeSi...) inside the α -Al dendrites.

RÉSUMÉ

La diminution du poids des véhicules résulte dans l'apport important de bénéfices au niveau de l'économie d'essence, la réduction des gaz à effets de serre aussi bien que l'amélioration du rendement du véhicule. Le matériau principal présentement utilisé pour la fabrication de la tête et du bloc moteur est la fonte ductile. Le remplacement de la fonte par des alliages d'aluminium va conduire vèrs une diminution (30-40%) significative du poids. Les alliages d'aluminium de coulée actuels laissent voir dans le temps un ramolissement du métal lorsque les températures d'opération du moteur exèdent 200°C. Ce phénomène provoquera à plus ou moins brève échéance un bris prématuré du moteur diésel.

Deux nouveaux alliages développés à partir de l'alliage commercial A356 sont présentés dans les termes suivants : microstructure, fluage, comportement au vieillissement et propriétés de traction à des températures élevées. L'alliage contenant les deux groupes d'éléments soit péritectiques (Cr, Zr et Mn) dans un premier temps et pour le durcissement structural par le vieillissement (Cu et Mg) dans un second temps, démontre une réponse supérieure au vieillissement à la température de 200°C pour une période de 200 heures et de meilleures propriétés de fluage à la température de 300°C pour une période de 300 heures. De façon plus intéressant, l'alliage possède de meilleures propriétés de traction (161MPa) à 250°C avec une ductilité adéquate comparativement aux alliages de bloc moteur fabriqués à partir des alliages A356 et A356 + Cu. L'amélioration des propriétés mécaniques est ainsi attribuable aux nouveaux précipités fins (ϵ -AlZrSi, α -AlCrMnFeSi...) à l'intérieure des dendrites α -Al qui ont été formés et qui sont beaucoup plus stables thermiquement.

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TABLE OF CONTENTS

Abstract	i
Résumé	ii
Acknowledgements	iii
Table of Contents	iv
List of Figures	viii
List of Tables	xii
1. INTRODUCTION	1
Diesel Engines and Materials Selection	1
2. THEORETICAL BACKGROUND	5
2.1 356 Alloy (Aluminum-7Silicon-0.3Magnesium)	5
2.1.1 Cast Microstructure	5
2.1.2 Eutectic Si and Modification	6
2.1.3 Iron rich Intermetallics	9
Phase Formation	9
Effect of Fe on Porosity	10
Effect of Fe on Mechanical Properties	11
Neutralization of the effects of Fe	12
2.1.4 Precipitation Hardening	14

2.2 Recent Developments in Alloying of Al-7Si Alloys				
2.2.1 Cu Additions to Al-Si-Mg	17			
As-Cast Microstructure	18			
Effect on Precipitation	19			
Effect on Tensile Properties	20			
Effect on Creep Resistance	21			
Effect on Fatigue Properties	21			
2.2.2 Zr and Mn Additions to Al-Si-Mg-Cu Alloy	22			
2.2.3 Ni, Fe and Mn Additions to Al-Si-Mg-Cu Alloy	23			
2.2.4 Zr, V and Mn Additions to Al-Si-Cu Alloy	24			
2.3 Alloy Design Principles	25			
2.3.1 Application Requirements	25			
2.3.2 Improving Elevated Temperature Strength	27			
2.3.3 Improving Compressive Creep	29			
2.3.4 Enhancing Ductility & Fatigue Crack Resistance	30			
2.3.5 Mechanical Testing	31			
3. EXPERIMENTAL PROCEDURE	32			
3.1 Materials	32			
3.1.1 Reference Alloy	32			
3.1.2 Master Alloys	32			
3.2 Alloy Design	33			

3.3 Experimental Method	35
3.3.1 Alloy Making and Melting	36
3.3.2 Casting	37
3.3.3 Identification of the Alloys	37
3.3.4 Chemical Analysis	37
3.3.5 Heat Treatment	40
3.3.6 Differential Scanning Calorimetry (DSC)	42
3.3.7 Microstructural Investigation	43
Sample Preparation	43
Optical Microscopy (OM)	44
Scanning Electron Microscopy (SEM)	45
3.3.8 Mechanical Properties	45
Hardness Measurements	45
Tensile Tests	45
Creep Tests	47
4. RESULTS AND DISCUSSION	48
4.1 Aging Characteristics of the Alloys	48
4.2 Tensile Properties of the Alloys	52
4.2.1 Tensile Properties at Room Temperature	52
4.2.2 Tensile Properties at 150°C	55
4.2.3 Tensile Properties at 250°C	57

4.3 Compressive Creep Properties of the Alloys				
4.4 DSC Analysis of the Various Alloys				
4.5 Microstructural Analysis of the Alloys				
4.5.1 Effect of Alloying on the As-Cast Microstructures	64			
Secondary Dendrite Arm Spacing (SDAS)	65			
Eutectic Si Modification	65			
The R1 Alloy	67			
The R2 Alloy	67			
The MG1 Alloy	70			
The MG2 Alloy	73			
4.5.2 Effect of Alloying on the As-Solutionized Microstructures	75			
The R1 Alloy	75			
The R2 Alloy	76			
The MG1 Alloy	77			
The MG2 Alloy	80			
4.5.3 Effect of Alloying on the Over-Aged Microstructures	81			
4.6 Synopsis				
5. CONCLUSIONS	88			
6. RECOMMENDATIONS FOR FUTURE WORK	91			
References	93			
Appendix	99			

LIST OF FIGURES

Figure 1.1 A typical diesel engine block with the cylinder head [3] 1
Figure 2.1 A typical permanent mould as-cast microstructure of an Al-7Si-0.3Mg [8] 6
Figure 2.2 Optical micrograph of (a) an unmodified permanent mould A356, (b) amodified permanent mould A356 with 200 ppm Sr [8]7
Figure 2.3 The β -Al ₅ FeSi and π -Al ₈ Mg ₃ FeSi ₆ phases in as-cast Al-7Si-0.3Mg alloy with 0.52 % Fe [14]
Figure 2.4 The role of β -Al5FeSi in the formation of shrinkage porosity [18] 10
Figure 2.5 Effect of aging temperature and time on the yield strength and Brinell hardness of the Al-Si alloys containing different amounts of Mg [33] 16
Figure 2.6 (1) Q-Al ₅ Mg ₈ Cu ₂ Si ₆ and (2) θ -CuAl ₂ phases formed in an Al-Si-Mg alloy with 0.22% Cu [35]
Figure 2.7 TEM micrographs of the 356 alloy with (a) 0% Cu, (b) 1% Cu, (c) 3% Cu [7]
Figure 2.8 STEM micrograph of elongated Al-Si-Zr dispersoids and rounded Si clusters inside the Al dendrites [5]
Figure 3.1 Alloy synthesis and production of permanent mould tensile bars for tensile testing, aging and DSC studies 34
Figure 3.2 Alloy synthesis and production of permanent mould cast cylinders for creep testing and microstructural investigation 35
Figure 3.3 The induction furnace and casting set-up 36
Figure 3.4 (a) The schematic drawing and (b) picture of the tensile bar mould

Figure 3.5 (a) The schematic drawing and (b) picture of the hot tearing mould	39
Figure 3.6 The electrical-resistance-heated furnace	42
Figure 3.7 Sectioning of the metallurgical samples	44
Figure 3.8 Tensile testing set-up	46
Figure 3.9 Sectioning of the creep samples	47
Figure 4.1 Age-hardening curves of the alloys at 200°C	48
Figure 4.2 (a) UTS, (b) YS, (c) %E values of the alloys at room temperature	54
Figure 4.3 (a) UTS, (b) YS, (c) %E values of the alloys at 150°C	56
Figure 4.4 (a) UTS, (b) YS, (c) %E values of the alloys at 250°C	58
Figure 4.5 Compressive creep curves of the alloys at 300°C under 30MPa	61
Figure 4.6 Typical microstructures of the as-cast (a) R1, (b) R2, (c) MG1, (d) M alloys	IG2 64
Figure 4.7 As-cast microstructure of the MG1 alloy (a) without strontium, (b) v strontium	vith 66
Figure 4.8 (a) SEM micrograph of the oxide containing Sr in the MG1 alloy with (b) EDS spectra.) its 66
Figure 4.9 The different phases observed in the as-cast R1 alloy by (a) opt microscope, (b) FEGSEM	ical 68
Figure 4.10 EDS spectra of the phases in the as-cast R1 alloy (a) eutectic Si, (b) Al_5FeSi , (c) π -Al_8Mg_3FeSi ₆)β- 68
Figure 4.11 The different phases observed in the as-cast R2 alloy by (a) opt	ical
microscope (b) EECSEM	60

Figure 4.12 EDS spectra of the Cu-containing phases in the as-cast R2 alloy (a) θ -CuAl ₂ ,
(b) $Q-Al_5Mg_8Cu_2Si_6$
Figure 4.13 The different phases observed in the as-cast MG1 alloy by (a) optical
microscope, (b) FEGSEM
Figure 4.14 EDS spectro of the new phases in the as past MG1 allow (a) of (A1 Cr Mn
Figure 4.14 EDS spectra of the new phases in the as-cast MOT alloy (a) α -(AI-CI-MI-
Fe-S1), (b) AI-S1-Zr
Figure 4.15 The EDS elemental mapping of the ε -(Al-Si-Zr-Ti) phase in the as-cast MG1
allov
Figure 4.16 The typical microstructures of the as-cast MG2 alloy by (a) optical
microscope, (b) FEGSEM
Figure 4.17 The EDS elemental mapping of the phases in the as east MG2 ellow 74
Figure 4.17 The EDS elemental mapping of the phases in the as-cast WO2 andy
Figure 4.18 SEM micrograph of the as-cast MG2 alloy showing (a) θ -CuAl ₂ , Q-
Al ₅ Mg ₈ Cu ₂ Si ₆ , α-(Al-Cr-Mn-Fe-Si) and ε-(Al-Si-Zr-Ti), (b) Si, Q-Al ₅ Mg ₈ Cu ₂ Si ₆ , α-(Al-
Cr-Mn-Fe-Si), π -Al ₈ Mg ₃ FeSi ₆ and ε -(Al-Si-Zr)
Figure 4.19 SEM micrographs of the as-solutionized (a) R1 and (b) R2 alloys showing
the eutectic Si and β -Al ₅ FeSi
Figure 4.20 SEM micrographs of the as-solutionized MG1 alloy at (a) low magnification.
(b) at high magnification showing the eutectic Si α -(Al-Cr-Mn-Fe-Si) and ϵ -(Al-Si-Zr)
(c) with the first state of the
······································
Figure 4.21 SEM micrographs of the as-solutionized MG1 alloy showing α -(Al-Cr-Mn-
Fe-Si) precipitates (a) in the interdendritic region, (b) inside the dendrite
Figure 4.22 EDS spectra of the (a) Al matrix, (b) α -(Al-Cr-Mn-Fe-Si) precipitate inside
the aluminum dendrite in the as-solutionized MG1 alloy
Figure 4.23 SEM micrographs of the as-solutionized MG2 allov showing (a) the eutectic
phases in the interdendritic region. (b) the fine α -(Al-Cr-Mn-Fe-Si) precipitates inside the
dendrite
80

Figure 4.24 Typical optical microstructures of the over-aged (a) R1, (b) R2, (c) MG1, (b) R2, (c) MG1,	(d)
MG2 alloys	81
Figure 4.25 SEM micrographs of the over-aged (a) R1, (b) R2, (c) MG1, (d) MG2 allog	ys
	82
Figure 4.26 The fine precipitates in the intradendritic region of the over-aged (a) R1,	(b)
R2, (c) MG1, (d) MG2 alloys	83
Figure 4.27 EDS spectra of the (a) α -(Al-Cr-Mn-Fe-Si), (b) ϵ -(Al-Si-Zr-Ti) precipitation	tes
inside the aluminum dendrite of the over-aged MG1 alloy	85

LIST OF TABLES

Table 1.1 Gasoline versus Diesel Engines	1
Table 2.1 Room Temperature Tensile Properties of A356 Alloy Treated with Difference No. 107	ent
Modifiers [9]	8
Table 2.2 Some of the Fe Neutralization Techniques and Shortcomings	12
Table 2.3 Effect of Different Chemical Modifiers on the Tensile Properties of A356	13
Table 2.4 Effect of Aging Temperature on Room Temperature Tensile Properties	of
Permanent Mold 356 Alloy [32]	16
Table 2.5 Tensile Properties of A356 Alloys at 25°C	20
Table 2.6 Tensile Properties of A356 Alloys at 250°C.	20
Table 2.7 Tensile and Creep Properties of HIP Treated Various Alloys at 300 °C (Af	ter
100 Hours Holding)	24
Table 2.8 The Developed Alloys and the Effect of Additions on the Key Mechanic	cal
Properties	25
Table 3.1 Physical Properties of the A356 Alloy	32
Table 3.2 Liquidus Temperatures and Compositions of the Master Alloys	33
Table 3.3 Alloy Codes and Target Compositions	33
Table 3.4 The Chemical Composition of the Creep Samples	40
Table 3.5 The Chemical Composition of the Tensile Samples	41
Table 4.1 Normalized Tensile Properties of Various Developed Alloys with Respect	to
the Standard A356 (T7) at 250°C	59

Table 4.2 Creep Strain (%) of the Alloys at 300°C for 100, 200 and 300 Hours	62
Table 4.3 Effect of Alloying on the SDAS of the A356 (R1) Alloy	65
Table 4.4 Summary of the Elevated Temperature Mechanical Properties of the Alloys	
	86

CHAPTER 1 INTRODUCTION

Diesel Engines and Materials Selection

The diesel engine, introduced by Rudolph Diesel in 1892, works by self ignition via fuel injection into air which is pre-compressed in the combustion chamber. Compared to the gasoline engine, Table 1.1, the diesel achieves a higher combustion ratio and better fuel efficiency. Moreover, the Diesel has lower CO_2 emissions per gallon mile and is considered to be one of the most viable environmentally friendly technologies for transport vehicles.

	Gasoline Engine	Diesel Engine
Combustion Cycle:	Four Stroke	Four Stroke
Ignition Type:	Spark	Self
Combustion Ratio:	10:1	20:1
Fuel& Average Energy per Gallon [1]:	C_9H_{20} -132x10 ⁶ J	$C_{14}H_{30}$ -155x10 ⁶ J
CO2 emissions per Gallon mile [1]:	19.4 Ibs	13.4 Ibs

Table 1.1 Gasoline versus Diesel Engines

Although diesel engines do not have a sizeable share of the North American passenger car market, the market penetration in Europe has shown substantial growth reaching 50-70% market share especially after the introduction of the high-pressure common-rail and variable geometry turbocharger (VGT) technologies [2]. The strict environmental regulations, increasing fuel prices and availability of the lower sulphur-fuel diesels are expected to increase the market share of diesel passenger cars in North America.

The new down-sized diesel engines can compete with the gasoline engines in terms of performance. Further environmental benefits can be achieved through weight reduction of the vehicle. Since the engine itself is the heaviest component of passenger vehicles, there is ongoing research to decrease its weight in order to improve performance, to lower fuel consumption and to reduce emissions. The most potential weight reduction (30-40%) in diesel engines can be achieved by replacing the material of heavy engine components such as engine blocks, cylinder heads and pistons.

Typical diesel engine components which are significant for the possible weight reduction are shown in Figure 1.1. The cylinder head sits at the top of the cylinders and has a platform containing part of the combustion chamber and valves. The engine block is a complicated part at the heart of the engine, and it is attached to a cylinder head, a crankcase and engine mounts containing passages for lubricants and coolants. The block contains the cylindrical bored holes for pistons where the self combustion takes place. Both the block and head are cast separately and they have a complex shape. In addition, they are exposed to high ignition pressures and temperatures due to the self spark in diesels.



Figure 1.1 A typical diesel engine block with the cylinder head [3].

Historically, the most common engine material has been ductile iron because of its high temperature strength, machinability and cost. The strength of ductile iron (540MPa) remains stable at temperatures up to 300-400°C [2]. However, ductile iron with its high density ($\approx 7.1 \text{ g/cm}^3$) is not a material of choice for light weight design.

Weight reduction objectives of the engine designers has lead to efforts to replace ductile iron blocks with lightweight materials such as compacted graphite iron, magnesium alloys and aluminum alloys. Although compacted graphite iron can withstand high temperature and pressures inside the engine, it does not significantly reduce the weight. Creep resistant novel magnesium alloys give extreme weight reduction, but their mechanical properties decrease exponentially with increasing temperatures. Hence, their usage is restricted to the parts of the engine that are exposed to lower pressures. Aluminum alloys lie between these two material groups giving optimum strength with reasonable weight reduction for the engine applications.

Efforts in converting diesel engines from cast iron to aluminum alloys have started in 1996. Presently, only a small portion of the diesel engine, mainly the cylinder head that sees moderate operating condition, is cast in aluminum. However, the current diesel engine development has lead to higher ignition temperatures and pressures [4] and these increased pressures at high temperatures cause the softening of the commercial aluminum alloys which in turn results in early fracture. Therefore, aluminum alloy development activities for diesels have started.

VAW (Germany) [4] and Alcan-Pechiney (Canada, France) [5] have initiated Al diesel engine development by alloying the commercial Al-Si 3xx casting alloys (mainly 319, 356, 380 and 390) that have been already used in gasoline engines. Among the developed alloys, the Cu-added A356 seems promising in terms of high temperature mechanical

properties [6]. It is likely that the new alloy gets its high strength from the β " (Mg₂Si) and Q' (Al₅Mg₈Cu₂Si₆) precipitates which form inside the aluminum dendrites after the common T6 heat treatment [7].

Another version of the A356 alloy includes additional dispersoid forming elements such as V, Ti, Zr and Mn [5]. This recent alloy has superior creep resistance and high temperature tensile properties up to 300°C. At this over-aged stage, the better properties in the new alloy are attributed to the (Al-Si-Zr) dispersoids in the intradendritic region, however, a detailed microstructural investigation has not been carried out yet.

The aim of the present research work is to develop new aluminum cast alloys based on the A356 alloy for diesel engine applications requiring high temperature strength and creep resistance. The particular objectives of this study can be listed as:

- To study the effect of age-hardenable elements (Mg and Cu) as well as the additional dispersoid forming elements (Zr,Cr and Mn) on the high temperature tensile and creep properties of the A356 alloy.
- To study the effect of the additions on the aging behavior of the A356 alloy.
- To study the effect of the additions on the as-cast, as-solutionized and over-aged microstructures of the A356 alloy.

CHAPTER 2 THEORETICAL BACKGROUND

2.1 356 Alloy (Aluminum-7Silicon-0.3Magnesium)

A large portion of diesel aluminum development focuses on the alteration of the Al-7Si-0.3Mg (356) alloy. (All compositions in this thesis are given in weight percent). It is therefore important to understand its properties and microstructure. The 356 alloy is extensively used in the power tool, automobile and aerospace/military industries due to its excellent castability, corrosion resistance and mechanical properties in the heat-treated condition. The grade of this alloy is based on the amount of impurities and the primary alloy A356 has a lower amount of iron, giving better properties at the expense of cost.

2.1.1 Cast Microstructure

A typical microstructure of an Al-7Si-0.3Mg alloy is shown in Figure 2.1. It consists mainly of the primary aluminum dendrites and the eutectic mixture composed of aluminum, silicon and other eutectic phases. Mg reacts with Si to form Mg₂Si which has Chinese script morphology in the eutectic region. The amount of this phase is usually low and it is difficult to observe in the as-cast condition. Based on the composition (usually Fe/Mn) other coarse eutectic phases can also be found in the eutectic region.

The cast microstructure of Al-Si-Mg alloys strongly depends on the alloy chemistry and the casting process. The rapid cooling in permanent mold casting gives a fine dendritic structure surrounded by fine eutectic phases and small grains whereas the slower cooling rate in sand casting causes larger dendrites and coarser eutectic phases. A fine microstructure is always desired in applications requiring high strength. Refinement of the phases can also be achieved through chemical modification without changing the casting process.



Figure 2.1 A typical permanent mould as-cast microstructure of an Al-7Si-0.3Mg [8].

2.1.2 Eutectic Si and Modification

Silicon as the major alloying element significantly enhances the castability (fluidity, tearresistance, metal-feeding) and the resultant eutectic Si phase in the microstructure improves the wear resistance. The overall density and the coefficient of thermal expansion are also reduced. Due to its acicular morphology, eutectic Si decreases the ductility and impact resistance. This negative effect can be eliminated by either reaching higher cooling rates or by alloying with elements that modify the acicular morphology to give fine fibrous Si.

The chemical modification of the eutectic Si is discussed extensively in the literature and the mechanisms behind it are well understood [9]. Several elements such as Na, Sr, Ce, Ca, Ba, La, Yb, Cd, Sb, As, Se, Y are known to cause modification. Basically, these impurity atoms poison the silicon crystal growth during solidification and cause the enhanced twinning of the growing Si phase. Depending on the amount and type of element, different modified structures can be obtained, from an acicular shape to a lamellar shape, and then to a fine fibrous microstructure. Among the modifiers, only Na and Sr find any significant industrial use. Depending on the amount of silicon in the alloys more or less modifier is required. In the case of the A356 alloy a level of 0.02% of strontium is sufficient to achieve a fully modified fibrous microstructure, (Figure 2.2). When the modifier is extensively added, another phenomenon, over-modification can occur, which will cause the advantages to regress back toward the premodified state which will lessen gains.



Figure 2.2 Optical micrograph of (a) an unmodified permanent mould A356, (b) a modified permanent mould A356 with 200 ppm Sr [8].

The effect of modification on mechanical properties is sometimes non-conclusive since increased microporosity and lowered soundness is often associated with the chemical modification. However, it is well known that the acicular morphology of the eutectic Si acts as a stress raiser that causes easy fracture. With modification, a finer and rounded Si is obtained in the microstructure that contributes to somewhat higher ultimate tensile strengths (UTS) and ductility. From Table 2.1, it is evident that the effect of the modification on UTS is negligible in heat-treated alloys although a significant difference can still be found in ductility. Similar to ductility, the impact toughness is also significantly improved by the modification by about 150% in 150 ppm Sr treated A356 alloy [10]. This is due to the decreased size of the brittle phases and better dispersion of those in the more ductile aluminum matrix.

	Eutectic Si . Structure	As-Cast		Heat Treated*	
Modifier		UTS	% E	UTS	04 E
		[MPa]		[MPa]	70 E
None	acicular	180	6.8	304	11.8
Na	fibrous	195	16.4	292	15.1
Sr	fibrous	196	15.9	301	14.4

 Table 2.1 Room Temperature Tensile Properties of A356 Alloy Treated with Different

 Modifiers [9]

* Solution treated at 540°C for ten hours, quenched and then aged at 160°C for 6 hours.

The role of Si on fatigue performance is complicated. Gruzleski [9] suggests that fatigue strength drops with increased amounts of silicon in Al-Si-Mg alloys, however, the chemical modification with Sb and Sr has a little affect on fatigue fracture since the stress required to cause crack initiation along the silicon-aluminum interfaces is not affected much by the modification treatment. On the other hand, fatigue strength strongly depends on casting defects such as porosity or oxide films and any treatment that increases these, would inversely affect the fatigue strength. The increased porosity is sometimes associated with Sr modification so, a net conclusion on fatigue properties can only be drawn for alloys having a pore-free microstructure. It is known that a great portion of the porosity can be eliminated through a suitable Hot Isostatic Pressing (HIP) treatment and Wang et al. [11] state that the HIP treated Sr modified Al-7Si-0.3Mg alloy has a longer fatigue life than the unmodified one due to the small round eutectic Si particles which are less prone to microcracking. Therefore, Si modification may lead to better fatigue properties in 356 alloys.

2.1.3 Iron rich Intermetallics

Iron is considered a major impurity element in Al-Si-Mg alloys unless it is added to minimize die soldering during high-pressure-die casting and squeeze casting. Fe mainly arises from the raw materials used in the electrolytic process during the primary production of aluminum and its removal is economically difficult. Fe levels usually start from 0.1% for primary alloys and goes up to 1% for secondary alloys. The solubility of Fe in liquid aluminum is quite high and this increases the possibility of Fe intake during the melting process. On the other hand, at 660°C the solubility of Fe in solid aluminum, is very low ($\approx 0.05\%$) and at room temperature even lower [12]. Therefore, Fe combines with other alloying elements such as Si, Al and Mg to form a number of brittle phases which influence the cast microstructure. The composition, size and morphology of these phases are controlled by alloy chemistry for a given cooling rate.

Phase Formation

The β -Al₅FeSi is the most commonly observed iron phase in Al-Si-Mg alloys with Fe greater than about 1%. It is always a primary phase, having a three-dimensional form of a platelet and usually observed as needles in two dimensions, as shown in Figure 2.3. Another phase π -Al₈Mg₃FeSi₆ having a compact or Chinese script morphology can also form in the presence of Mg. It is shown that π either nucleates independently or grows from the surfaces of β platelets [13, 14]. Being less detrimental than the β phase, π usually dissolves during heat treatment and does not reprecipitate [15]. Other phases which are less frequently observed in Al-Si-Mg alloys listed in literature are α -Al₁₅Fe₃Si₂, Al₄FeSi₂, Al₉Fe₂Si₃ and Al₈Fe₂Si [16].



Figure 2.3 The β -Al₅FeSi and π -Al₈Mg₃FeSi₆ phases in as-cast Al-7Si-0.3Mg alloy with 0.52 % Fe [14].

Effect of Fe on Porosity

Several researchers [13, 17, 18] have observed that the amount of porosity and pore size distribution in the microstructure increase with increased Fe content. This behavior is mostly associated with the increased amount of β phase which serves as effective pore nucleation sites. Moreover, β phase physically blocks the metal feeding during solidification promoting shrinkage porosity, (Figure 2.4). Hence, the average length of β phase plays an important role in the formation of this type of porosity, especially in alloys solidified at slower cooling rates and/or with high Fe content.



Figure 2.4 The role of β-Al₅FeSi in the formation of shrinkage porosity [18].

Taylor [19] has found that there exists a critical Fe content in Al-10Si-1Cu and Al-5Si-1.2Cu alloys which gives the minimum porosity instead of at the lowest Fe content, as expected. This is explained by the solidification sequence of the eutectic phases in the Al rich corner of Al-Si-Fe ternary phase diagram, where at the critical Fe content, the ternary eutectic forms right after the aluminum dendrites as follows;

$$<$$
 Fe_{critical}: Al \rightarrow Al – Si \rightarrow Al – Si - Al₅FeSi

- = Fe_{critical}: Al \rightarrow Al Si Al₅FeSi
- > Fe_{critical}: Al \rightarrow Al Al₅FeSi \rightarrow Al Si Al₅FeSi

The proposed theory seems to depend on alloy chemistry and cooling rate, because a similar relationship does not hold for other alloys such as Al-9Si-3Cu [17] and Al-7Si-0.3Mg [20]. For these alloys, the overall porosity continuously increases with Fe content.

Effect of Fe on Mechanical Properties

In A356-T6 alloy, it was found that increasing the Fe content up to 0.2%, slightly increased the yield strength, lowered the ultimate tensile strength and markedly reduced the elongation [21]. Wang et al. [13] showed that the lost-foam cast engine-block/head alloys had similar results where secondary 356 (0.48%Fe) had much lower UTS and elongation values than the primary alloys (0.13%Fe). In all studies, it was noted that higher Fe contents progressively increased the amount and the size of the micropores and the Fe-rich intermetallics, particularly the β phase. Therefore, the decrease in ductility is attributed to easier void formation and cracking of Fe-rich phases. Unlike the room temperature properties, the high temperature tensile strength is increased with high Fe content. This is due to the increased amount of thermally stable iron-rich intermetallics (β and α), the morphology of which does not change much with temperature [16].

Murali et al. [15] showed that at all solidification rates, the fracture toughness of Al-7Si-0.3Mg decreases with an increase in Fe level from 0.2 to 0.8%. The power relationship between the β length/area and impact energy has been established by Ma et al. [10] where the β particles (10-50µm) in the A356 alloy extensively deteriorate the impact properties. Although needlelike Fe-rich phases are likely to facilitate crack initiation, microporosity on the other hand is more detrimental on fatigue life of the Al-Si-Mg alloys. Wang et al. [13] showed that reducing the Fe content in 356 alloys not only decreases the area fraction of porosity but also reduces the pore size which significantly improves the fatigue life of the engine alloys. Therefore, poor tensile and fatigue properties are often associated with the increased amount of shrinkage porosity rather than the size or shape of the iron phases.

Neutralization of the effects of Fe

Any treatment that inhibits the platelet morphology or promotes the compact or Chinese script morphologies of the Fe-rich intermetallics to improve the mechanical properties is considered as the neutralization of Fe. Some of the techniques are summarized in Table 2.2. The chemical modification is widely used in the industry since the additions are easy to make and inexpensive.

Method	Neutralization	Disadvantage		
Chemical Modification	Alters the morphology of β phase into other compact forms	Larger amount of Fe rich phases, no full improvement		
Superheating	Reduces the amount of nuclei on which β forms	Increased hydrogen and oxide inclusion content		
Chilling	Gives high cooling rates, fine β phase	Not applicable to different casting conditions		
Heat Treatment	Results in more fragmented and globularized β phase	Low diffusivity of Fe, incipient melting		

 Table 2.2 Some of the Fe Neutralization Techniques and Shortcomings

The alloying elements for chemical modification are Mn, Cr, Co, Be, Mo, Ni and S [16]. The most common neutralizers and their effect on morphology of β phase and tensile properties are summarized in Table 2.3. Although Be seems to be the most efficient element, due to the restriction of its use and economic reasons, only Mn found an industrial use. Mn changes the needlelike β -Al₅FeSi into α -Al(Fe,Mn)Si which has script or skeleton type of morphologies. This partially increases the tensile strength and the overall hardness but mostly improves the ductility. Interestingly, the fracture toughness of the Al-Si-Mg alloys is not affected significantly by the Mn addition, contrary to expectations [22].

The amount of Mn needed to neutralize Fe is not well established. Although most studies [22-24] show that a Mn/Fe ratio of 0.5 is sufficient to convert all of the β phase, Kumari et al. [25] have found that some β can still form. In general, increasing the Mn addition progressively reduces the number and the size of the β phase. Moreover, the combined additions with Mn are likely to give the best mechanical properties [21, 24].

% Fe		B onorted Forrich	% Improvement in		
	% Addition*	Phase	UTS [MPa]	% E	Reference
0.2	0.2 Mn	α- (Al,Mn,Fe,Si)	8	114	$[21]^{a}$
0.8 -1.3	0.4 -0.5 Mn	(Fe,Si) ₂ Mn Al ₁₄	4	40	[24] ^b
0.8 -1.3	0.3 -0.5 Cr	$(Fe,Cr)_3Si_4Al_{25}$	6	-	[24] ^b
1.0	0.2 Be	$BeSiFe_2Al_8$	21	66	[26] ^b
0.2	0.1 Mn - 0.1Cr	α- (Al,Cr, Mn,Fe,Si)	8	237	[21] ^a
0.8 -1.3	0.2 Be -0.2Mn	(Be, Mn-Fe)	34	50	[24] ^b

 Table 2.3 Effect of Different Chemical Modifiers on the Tensile Properties of A356

*Neutralizer

a: Permanent mould cast (T6), b: Sand Cast (T6)

2.1.4 Precipitation Hardening

To further improve the strength, Al-Si-Mg alloys are heat treated, most commonly to a T6 condition which consists of a solution heat treatment, quenching and artificial aging. The first step is solutionizing, which is basically soaking the alloy at a sufficiently high temperature to dissolve the phases such as Mg₂Si and Al₈Mg₃FeSi₆ into the α -Al phase, such that a nearly homogeneous solid solution forms. ASTM B-597 standards [27] recommend, for the A356 alloy, a solution heat-treatment of 540 °C for 4 to 12 hours. During solutionizing, the following might take place:

- Dissolution of Mg, Si and other elements into the α -Al,
- Homogenization of the casting (elimination of microsegregation, coring and metastable phases),
- Spheroidization, coarsening and fragmentation of the eutectic phases that are not soluble in α-Al.

Solutionizing is followed by quenching which is the rapid cooling process to get a supersaturated solid solution at room temperature. Quenching results in the supersaturation of alloying elements and quenched-in vacancies which are retained in the aluminum matrix (Al $_{s.s.s}$). Fast quenching results in higher amount of those in the matrix which gives better age-hardening response, but causes thermal stresses and distortion. Therefore, an optimum quenching rate is necessary.

Precipitation goes through a series of precipitation beginning with the formation of needlelike Guinier-Preston (G.P) zones, continuing with metastable phases (β ", β ') and ending with the formation of the β -Mg₂Si phase [23, 28-30]:

 α - Al _{s.s.s} \rightarrow Vacancy rich G.P zones \rightarrow Needlelike $\beta'' \rightarrow$ Rod-like $\beta' \rightarrow \beta$ plates.

In the precipitation sequence, coherent G.P zones (2.5-30 nm) start to elongate in the [100] matrix direction and reach a needle shape forming the metastable semi-coherent β " phase (46-70nm). These needles grow with time to rods (β ') and eventually to the equilibrium β phase. The strengthening obtained though precipitation depends on the volume fraction and the size of the precipitates. Usually the peak strength is achieved between the β " and the β ' phase.

Since the growth of precipitates is a diffusional process, it strongly depends on the aging time and temperature. The process takes a long time at room temperature. Therefore, the alloys are usually artificially aged to reach the desired phase. Artificial aging temperatures may vary, but in general to obtain the maximum strength, a temperature between 155 - 175°C for 3-5 hours is used. The increase in artificial aging temperature may enhance the room temperature tensile strength, however, the elongation is sacrificed, (Table 2.4). It should be noted this relationship is affected by the casting process for a given alloy composition.

The temperatures above the artificial aging range such as 200-240°C increase the ductility and again there is a loss of strength due to the fact that the peak-strength phases (β " and β ') start to disappear and the equilibrium phase is reached. This situation is called over-aging and the over-aging heat treatment is known as the T7 treatment. Hernandez et al. [30] stated that the average length of the precipitates in the A356 alloy changes from 22.1 nm (β ") to 203.2 nm (β) by increasing the aging temperature from 170°C to 236°C for 6 hours. The effect of aging time and temperature on the yield strength and hardness of Al-Si-Mg alloys is given in Figure 2.5. It can be seen that aging at 180°C for 16 hours is equivalent to aging at 200°C for 4 hours. Therefore, it can be concluded that the diffusion process is extremely temperature dependent but less time-dependant.

Permanent Mold 356 Alloy [32]

Other than the β phase, the excess Si can precipitate in 356 alloys [31]. These Si clusters are observed when the artificial temperature is above 200°C [5, 30].

Table 2.4 Effect of Aging Temperature on Room Temperature Tensile Properties of

Aging Temperature °C / time (h)	Y.S [MPa]	UTS [MPa]	% E
155 / 3	207	303	14.6
165 / 3	241	327	11.8
175 / 3	262	331	10.6



Figure 2.5 Effect of aging temperature and time on the yield strength and Brinell hardness of the Al-Si alloys containing different amounts of Mg [33].

2.2 Recent Developments in Alloying of Al-7Si Alloys

Despite the increased demand for engine weight reduction, not much research is conducted on the alloying of the aluminum foundry alloys for high temperature use. In the last decade, most research focused on developing new coatings of the engine parts and improving the casting processes and the heat treatments to get better microstructures of the existing alloys. However, some automakers have developed new casting alloys by alloying the commercial alloys, mostly the 356, 319 and the 390 with new elements based on statistical casting experiments [4-6, 34].

It is difficult to compare the properties of these new alloys based on what is reported in the literature due to the widely varying heat treatments and mechanical testing conditions that were used. Furthermore, there is limited data on the microstructures of the alloys since much research focuses on mechanical tests under service conditions. In this section, the new alloys will be discussed as classified according to their compositions.

2.2.1 Cu Additions to Al-Si-Mg Alloy

As in wrought alloys, Cu and Mg together might enhance the precipitation behavior of the cast Al-Si alloys under the right heat-treated condition. Feikus et al. [6] studied two Cu versions (0.5 and 1%) of the commercial A356, where Cu addition improves the mechanical properties for the critical temperature range between 150 and 200°C. Since both versions have similar properties, the lower-Cu alloy has been investigated extensively. This alloy has started to get a big market share in Europe and is currently being used in diesel cylinder heads [5]. The microstructure, precipitation behavior and mechanical properties of this alloy are discussed in some detail here.

As-Cast Microstructure

The increased amount of copper in 356 results in the formation of two copper-enriched phases, Q-Al₅Mg₈Cu₂Si₆ and θ -CuAl₂, shown in Figure 2.6. The Q phase has a fine Chinese-script morphology in the eutectic solidification region, whereas the blocky θ phase either nucleates independently or exists with other phases such as the β -Al₅FeSi platelet. The eutectic Si, β -Mg₂Si, as well as other Fe-rich intermetallic phases (depending on the Fe/Mn ratio and cooling rate) are the other second phases in the Cu-alloyed 356.



Figure 2.6 (1) Q-Al₅Mg₈Cu₂Si₆ and (2) θ -CuAl₂ phases formed in an Al-Si-Mg alloy with 0.22% Cu [35].

Cu additions tend to increase the amount of microshrinkage and/or microporosity in the as-cast 356 microstructure, which is an effect similar to that of Fe and Sr additions. Cho et al. [36] state that the 356 alloy with 0.50% Cu, has twice the amount of shrinkage porosity of the Cu-free alloy. Further increase in the Cu content (1%) results in higher amounts (up to six times) of total porosity [35]. This is explained by a reduction in the solidification temperature which gives longer freezing time and an extended eutectic mushy-zone. The Cu-enrichment of the interdendritic liquid causes the formation of certain solid phases that solidify at lower temperatures than the Al-Si eutectic. These

solid phases physically block the liquid decreasing the feeding characteristics of the solidification. The resulting microporosity is often associated with the poor ductility of the Cu-containing alloys.

Effect on Precipitation

The effect of Cu on the precipitation behavior has been extensively studied in 6xxx (Al-Mg-Si) wrought alloys. However there is not much data on the foundry alloys. Mg- and Cu-containing phases dissolve in the aluminum matrix during the solutionizing treatment followed by quenching and it is usually assumed that the peak strength and hardness achieved with artificial aging in Cu-containing alloys are due to the precipitation of β " (Mg₂Si) and θ ' (Al₂Cu) phases. However, Li et al [7] have stated that after the artificial aging, the Q' (Al₅Mg₈Cu₂Si₆) phase having a lath-shaped morphology and the β " (Mg₂Si) phase coexist in the 356 alloy with 1% Cu. Only with higher Cu contents such as 3%, the θ ' (Al₂Cu) has been additionally observed, (Figure 2.7). This contradicts the work of Eskin [37] where no Q phase or its precursors were reported after the aging treatment of an Al-Mg-Si-Cu alloy. The λ ' (Al₅Cu₂Mg₈Si₅) or L phase has also been observed by some other authors [5, 38, 39] which can be the precursor of the Q phase and responsible for peak strengthening.



Figure 2.7 TEM micrographs of the 356 alloy with (a) 0% Cu (b) 1% Cu (c) 3% Cu [7].

Effect on Tensile Properties

Some of the tensile data are summarized in Table 2.5 and Table 2.6. It can be seen that at room temperature, Cu additions decrease the yield strength and slightly increase the ultimate tensile strength. At 250°C, a significant improvement is noted not only in the tensile but the ultimate strength of the Cu-containing alloys.

% Cu content	Aging Temperature °C / time (h)	Y.S [MPa]	UTS [MPa]	% E	References
0.0	165 / 4	214	294	9.5	[6]
0.5	165 / 4	190	280	8.0	[6]
0.0	190 / 3	233	306	12.8	[40]
0.5	165 / 3	219	319	11.8	[40]
0.0	175 / 6	310	375	12.2	[7]
1.0	175 / 6	288	380	11.0	[7]
0.0	200 / 5*	257	299	9.9	[5]
0.5	200 / 5*	275	327	9.8	[5]

Table 2.5 Tensile Properties of A356 Alloys at 25°C

* HIP treated (2 hours at 485°C, 100 MPa)

% Cu	Aging Temperature	Y.S	UTS	9/ E	References
content	°C / time (h)	[MPa]	[MPa]	70 E	
0.0	165 / 4	45	61	45.5	[6]
0.5	165 / 4	63	83	20.0	[6]
1.0	165 / 4	62	83	23.6	[6]
0.0	200 / 5*	55	61	34.5	[5]
0.5	200 / 5*	66	73	34.5	[5]

Table 2.6 Tensile Properties of A356 Alloys at 250°C

* HIP treated (2 hours at 485°C, 100 MPa)

The addition of 0.5% Cu has nearly the same effect on tensile properties as the addition of 1% Cu. The elongation values of the 356 alloy at both temperatures are lowered due to the increased microporosity when Cu is added [7, 35]. This negative effect can be overcome with a hot isostatic pressing (HIP) treatment, where a great portion of the internal porosity is healed. Hence, the HIP-treated alloys might have better tensile properties while displaying the same ductility.

Effect on Creep Resistance

The comparison in creep properties of the alloys is difficult because of the varying testing conditions. However, Cu additions usually improve the strain to failure values. Feikus et al. [6] reported that the two Cu versions (0.5 and 1%) of the Al-Si-Mg alloy give higher time-to-rupture values (up to 10 times) at 175°C and 200 °C under a load of 120 MPa. But the higher Cu level of 1% compared to the 0.5% Cu, does not bring any further improvement in creep properties as was seen in the tensile properties. On the other hand, Garat et al. [5] states that 0.5% Cu addition does not improve the stress value reached at 0.1% strain, for 100 hours ($\sigma^{0.1}_{100}$) which corresponds to the secondary creep stage at 250°C and 300°C. It is believed that this is due to the coalescence, coarsening and morphology change of the λ and β ' phases leading to a loss of the hardening effect at 300°C.

Effect on Fatigue Properties

There is not much data on the effect of Cu on high temperature fatigue properties in Al-Si-Mg alloys, but it is usually assumed that alloys with high ductility tend to have better fatigue life than the lower ductility alloys. A recent study shows [40] that Al-Si-Mg alloy with 0.5% Cu and the Cu-free version present very similar isothermal low-cycle and thermo-mechanical fatigue behavior between 100°C and 300°C. Moreover, both alloys show superior high cycle fatigue performance at room temperature and 150°C to the AlSi-Cu alloys. It can be concluded that Cu addition itself does not lead to a significant improvement in fatigue.

2.2.2 Zr and Mn Additions to Al-Si-Mg-Cu Alloy

Although the Al-Si-Mg-Cu alloy shows interesting tensile and creep properties at 150° C - 250° C, further improvement in this alloy (better ductility and fatigue life) is important since the diesel engines put severe thermo-mechanical stresses on the engine parts at temperatures up to 300 °C. In order to increase second-phase strengthening, trace amount of Zr and Mn, approximately 0.15% has been added to Al-Si-Mg-Cu alloy [5]. Even though the addition of Zr and Mn does not lead to further increase in tensile strength at 25, 250 and 300 °C in the T7 condition, the tertiary creep under a stress close to the $\sigma^{0.1}_{100}$ value (22.5 MPa at 300°C) is retarded. This interesting improvement in creep behavior is attributed to the precipitation of fine thermally stable elongated Al-Si-Zr dispersoids (300nm) inside the Al dendrites which can be seen in Figure 2.8. The new alloy has better ductility at various temperatures which can be due to the Mn addition that modifies the iron-rich intermetallics. It has been noted that the improved ductility does not lead to improved fatigue properties as it is usually assumed since the new alloy and the Al-Si-Mg-Cu have similar fatigue strengths, but different tensile elongation.



Figure 2.8 STEM micrograph of elongated Al-Si-Zr dispersoids and rounded Si clusters inside the Al dendrites [5].
2.2.3 Ni, Fe and Mn Additions to Al-Si-Mg-Cu Alloy

Further progress in alloy development has been made by Heusler et al. [4] based on a statistical design of experiments considering the elements of Ni, Fe and Mn. This alloy was designed for the engine block application requiring higher strength values than the cylinder heads where some sacrifice in ductility is usually acceptable. The alloy with 0.5% Ni, 0.4% Fe and 0.3% Mn additions (T6) has superior tensile strength from room temperature to 250°C even after the preaging treatments for 500 hours at the testing temperatures. But, a significant loss in elongation is also observed with the additions.

At 200°C under a load of 120 MPa, the alloy shows improved creep performance where the time to reach 0.2 and 0.5% strain is larger when compared to commercial engine alloys [4]. As in the case of the alloy with Zr and Mn additions, the creep rate of this new alloy during the steady-state has not been improved much whereas the tertiary creep has been delayed to a later stage resulting in better time-to-rupture values.

The fatigue limit of the existing alloy has increased by 20% with the Ni, Fe and Mn additions but when a local cooling is applied during solidification, this improvement disappears and the addition-free alloy and the developed alloy show similar but promising fatigue limits. Heusler et al. [4] concluded that the fatigue strength depends more on the microstructural features such as the dendrite arm spacing and the amount of porosity than on the alloy composition. On the contrary, further work by Feikus [34] on the same alloy disputes this statement because the chilled Al-Si-Mg-Cu-Ni-Fe-Mn alloy has the lowest cycle to failure values and shows that alloying does matter as much as the faster cooling rate.

The improvement in mechanical properties is attributed to the Ni and Cu addition which forms thermally stable precipitates inside the grains. Furthermore, Fe and Mn addition results in additional second phases in the interdendritic region. However, no microstructural investigation has been carried out to support these results.

2.2.4 Zr, V and Mn Additions to Al-Si-Cu Alloy

Since the Cu-containing phases are more stable at elevated temperatures than the Mgbearing phases such as β -Mg₂Si and λ -Al₅Cu₂Mg₈Si₅, a new Mg free 319 type alloy having Si content close to 7% has been studied by Garat et al. [5]. The alloy also has trace amounts of transition elements Zr (0.15%) and V (0.25%) as well as Mn (0.15%) and a typical Cu content of 3.8%.

The new alloy shows no significant improvement in room temperature tensile properties, but moderately higher elongation values than the regular permanent mould cast Al-Si-Cu alloys are noted. However, the reason for the improvement in ductility is not explained. Table 2.7 demonstrates that Zr, V and Mn additions to the Al-Si-Cu lead to superior YS and UTS at 300°C and a surprisingly good ductility considering its high Cu content. Moreover, a higher σ_{100} value to reach 0.1% strain is obtained with the additions making the new alloy more creep resistant at 300°C.

Allowa	Aging Temperature	Y.S	UTS	% E	$\sigma^{0.1}_{100}$
Anoys	°C / time (h)	[MPa]	[MPa]		
Al-Si-Mg	200 / 5	40	43	34.5	21.7
Al-Si-Mg-Cu	200 / 5	44	51	40	21.8
Al-Si-Cu-Zr-V-Mn	200 / 5	63	77	26	31.8

Table 2.7 Tensile and Creep Properties of HIP Treated Various Alloys at 300 $^\circ C$ (After 100 Hours Holding) [5]

The Mg-free Al-Si alloy with transition elements has better (20%) room-temperature fatigue than the Al-Si-Mg-Cu. Furthermore, this relationship is also seen in the sand cast condition with slower cooling rates and higher SDAS. Thermal and mechanical fatigue properties or the effect of the additions on the microstructure have not been studied yet. A summary of the improvements in new alloys is given in Table 2.8. It should be noted that the decrease or increase in properties are demonstrated based on the addition-free alloys in each study. It is always difficult to correlate the mechanical properties to each other but it seems that the additions increasing the high temperature tensile strength decrease the ductility.

Developed Alloys	HTTS*	Creep	Fatigue	Ductility	Reference
Al-7Si-0.3Mg-0.5Cu [T6]	↑	Ť	~	\downarrow	[4-6, 41]
Al-7Si-0.3Mg-0.5Cu-					
0.15Zr-0.15Mn [T7]	~	↑	~	Ť	[5]
Al-7Si-0.4Mg-0.3Cu-					
0.5Ni-0.4Fe-0.3Mn [T6]	Ť	Î	Ť	\downarrow	[4, 34]
Al-7Si-3.3Cu-0.25V-					
0.14Zr-0.15Mn [T7]	1	1	1	\downarrow	[5]

 Table 2.8 The Developed Alloys and the Effect of Additions on the Key Mechanical

 Properties

*High Temperature Tensile Strength

2.3 Alloy Design Principles

2.3.1 Application Requirements

In general, diesel components have similar application requirements with respect to the gasoline type. The main difference is the increased stress amplitudes and fatigue problems connected to the gas pressure resulting from the combustion, which are more severe for diesel engines. From the mechanical performance aspect, diesel engines put a

high thermo-mechanical stress on its cylinder heads and blocks which experience two distinct fatigue modes: high cycle fatigue (HCF) and low cycle fatigue (LCF).

HCF also known as mechanical fatigue originates from the variation of pressure in the combustion chamber depending on the rotation speed of the engine. In cylinder heads, the thin walls close to the water ducts, the temperature of which is in the order of 120-170°C, are the critical locations for the crack initiation and early fracture [5]. Similarly, in cylinder blocks the location around the crankshaft sees large static and cyclic loads at temperatures between 130 and 150°C [42]. The more critical area with downsized diesel engines is the intercylinder bridge section, at the top of the crank case in which temperatures here exceed 250°C for the uncooled sections and 200°C for the cooled sections. The material here sees a combination of a high static preload by the assembly (depending on the crankcase concept, monolithic, Al-GG, or other) that can exceed 150 MPa.

LCF or Thermo-mechanical fatigue arises from the engine start/stop cycles which affect both the cylinder head and the block. When the engine starts and intercylinder temperature exceeds 250°C, the combustion chamber tends to expand but cannot do so fully due to the rigidity of the cylinder head and block which creates a local compressive strength within them. Therefore material creeps to accommodate this stress and at the end a big thermal gradient is created between the combustion chamber surface and the coolant. When the engine cools down, this time the bridge tends to contract, but has to overcome the first thermal gradient due to the start operation. This creates a local tensile stress. Thermal-fatigue cracks can be nucleated at the engine cool-down temperatures if the tensile strength of the material is low and the tensile stress is above the UTS. At the same time, if the yield strength of the material is low, the accumulated plastic deformation at each cool-down cycle can cause dislocation build-up and create a local stress raiser also initiating cracks eventually. In order to prevent LCF (or crack initiation) the alloy has to have either a high yield strength where stress is accommodated elastically and no strain accumulation occurs, or a high ductility so that the crack formation is delayed. That is why the automakers favor either very ductile 356 family or high strength but less ductile 319 alloys. On the other hand, a high compressive creep resistance is also needed at the engine heat up temperatures (300°C) to minimize the initial thermal gradient.

Therefore, the challenge in alloy design for diesel applications seems to lie in obtaining a good combination of elevated temperature strength, ductility and creep resistance up to 300°C. Contrary to the cylinder head, engine block can sacrifice some ductility to reach higher strength values [4]. In addition, high heat conductivity of the material is required to minimize the thermal gradient during operation. In order to save fuel for both ecological and economic reasons, a light-weight design is essential. High wear resistance in the running surfaces and high corrosion resistance in particular for surfaces in contact with the cooling media are also desired. Good casting properties, low porosity and low hot tearing tendency are other castability requirements. Since some of these properties counteract with each other, cylinder head/ block alloys always needs to have an optimum combination of these properties.

2.3.2 Improving Elevated Temperature Strength

Pure aluminum can be strengthened up to twice the yield strength by solid solution strengthening, nine times by dispersoid strengthening and thirty times by precipitation hardening. Therefore, all strengthening mechanisms especially precipitation-hardening should be taken into account. The age hardening behavior of the alloy strongly depends on the composition of the alloy; the amount of the age-hardenable elements (Cu and Mg) and the Si ratio. The Cu containing phases (Q, λ and θ) are more stable at elevated temperature than the Mg containing phases such as β . However, since high Cu content tends to decrease the ductility, an optimum Mg, Cu and Si level should be chosen to obtain the desired ternary or quaternary phases in the Al-Si-Mg-Cu system. In wrought alloys containing low Si, the precipitation sequence is well known but in cast alloys (with high Si) containing both Mg and Cu, the age hardenable precipitates can only be determined by thermodynamic calculations with TEM and DSC validations.

One of the routes that can be followed is the use of trace elements to modify the existing age-hardenable phases or form new second phases that might change the aging behavior of the alloys. If the newly formed phases are non-coherent and well dispersed in the matrix, they might act as nuclei for the age-hardenable phases and enhance the aging behavior. Obviously, this effect is less if the new phase is coherent, since such phases could only as effective as the Al matrix.

It is known that small additions of Ag changed the θ phase into Ω phase which had a higher degree of strengthening [43]. Moreover, In, Cd and Sn were known to refine the θ ' phase. Boontein et al. [44] stated that minor Sb addition decreased the age hardening response of the A356 alloy due to possible Mg₃Sb₂ formation resulting in lower amount of β phase. Trace addition of Ca formed Al-Si-Ca phase which had a negligible effect on the age-hardening of the alloy whereas the Mn additions caused an additional peak on the age-hardening curve that was referred to the metastable phases [22].

Dipersoid (Orowan) strengthening arises due to the non-coherent second phases which are dispersed in the microstructure. The degree of the strengthening depends on the amount, size, morphology, interparticle spacing and thermal stability of the dispersoids. The maximum amount of fine closely packed dispersoids would give the most effective Orowan strengthening [43]. Moreover, lower the diffusivity and solid solubility in Al, higher is the thermal stability. The location of the dispersoids in the cast microstructure is also important and a distinction can be made based on the trace elements that "peritectic" or "eutectic". Eutectic phases tend to form in the interdendritic regions and peritectic phases can form inside the α -Al dendrites through a peritectic reaction; L + solid 1 \rightarrow (α -Al solid 2), where "solid 1" could be any peritectic element or compound that solidified before the α -Al. Depending on the size and morphology, both eutectic and peritectic phases are desired to achieve a microstructure having strong dendrites surrounded by strong grain boundaries.

The majority of the elements form eutectic phases with Al. Among the peritectic elements, Ti, Zr, V, Hf, Ta, Cr, Sc, B, Co, Mn and Mo, can be cited. These are named as "peritectic elements" because their binaries with Al-rich corner are based on peritectic reactions. However, these elements may form ternary or quaternary phases and the solidification sequence in Al-Si alloys including many alloying elements is very complex and hard to predict unless the thermodynamic calculations are performed. Therefore, there is no such rule that all peritectic elements will form binary peritectic phases inside the grains during solidification. For instance, although Mn is considered as a peritectic element, it forms the quaternary phase, α -(Al-Si-Fe-Mn), at the interdendritic regions.

2.3.3 Improving Compressive Creep

When the creep at 300°C (above $0.4T_m$) is being taken into account, dislocation (climb and intersection) and diffusional creep are the main mechanisms and they should be slowed down as much as possible. It is also possible that work-hardening and recrystallization may be occurring at 300°C, leading to softening. One way is to introduce solutes, precipitates or second phases into the matrix to hinder the dislocation motion. Only very fine, closely packed dispersoids and solutes having high melting point (e.g. Ti, Nb, Cr, Hf) inside the grains can create an obstacle for the dislocation creep [45]. The diffusion creep can be hindered by second phases at grain boundaries. Coarse grains are usually desired to minimize the grain boundary migration however, if the grain boundaries are strengthened enough by the second phases, fine grains would not be detrimental and bring more benefit in terms of elevated strength.

All second phases must be thermally stable and have large lattice resistance (such as high covalent bonding) so that they do not coarsen with increasing temperature. For effective second phase strengthening, Oswald ripening of the precipitates should be minimized. The rate constant of Oswald ripening is proportional to

 $D\gamma / (C^{\beta} - C^{\alpha})^2$

where D is the diffusivity of the rate controlling solute, γ is the precipitate-matrix interfacial energy and C^{β} and C^{α} are the equilibrium solubility of solute in the matrix and precipitate [12]. A low mismatch in lattice parameter and low diffusivity in Al would minimize the coarsening.

2.3.4 Enhancing Ductility & Fatigue Crack Resistance

Ductility and fatigue crack resistance can be improved by lowering the amount of brittle intermetallics in the microstructure. However, thermally stable intermetallics are also desired for the high temperature strength therefore, the modification of these can be a good solution for the optimization of the alloy properties. The acicular eutectic Si can be modified by Sr or Na additions and the needlelike phases such as the β -Al₅FeSi can be modified by Mn, Cr and Ni [24]. Besides alloying, a suitable heat treatment can also enhance the ductility.

Since the temperatures inside the diesel engine exceed the aritifical aging temperatures (165-180°C) of the alloys, a regular T6 treatment would turn into an over-aged condition (T7). This may cause early fractures during service; hence the microstructural design should consider an over-aged treatment where ductility is improved at the expense of

strength. This would impart more elastic deformation and considered good for the mechanical fatigue and crack initiation. Moreover, the dimensional stability is greatly improved with a T7 treatment that decreases the thermal growth during operation [40, 46].

2.3.5 Mechanical Testing

Another challenge is the testing of the alloys because it is difficult to simulate the stressstrain-temperature behavior inside the diesel engines. Many desired alloy properties do not depend on each other due to the different mechanisms and tested via different test methods (e.g. creep, tensile, compressive, fatigue). Tensile tests at various temperatures up to (300°C) are necessary to determine the yield strength and ductility, whereas compressive creep tests at peak temperatures (250-300°C) under low stresses (20-30MPa) are essential for the creep induced thermo-mechanical fatigue.

The tendency for the thermal fatigue is sometimes related to the parameter $\sigma_f k/E\alpha$, where σ_f is the mechanical fatigue strength at a mean temperature, k is the thermal conductivity, E is the elastic modulus and α is the coefficient of thermal expansion. And a high value indicates good resistance to thermal fatigue [47]. The mean temperature inside the engine can be estimated as $(T_h+T_c)/2$ where T_h is the upper limit when engine heats up and T_c is the lower limit when engine cools down. The mean temperature is roughly predicted as 150°C for diesels and mechanical fatigue tests at this temperature can be performed to obtain σ_f . The parameter then can be used to see if it correlates well with the performance of the alloys. Other than the tensile, creep and fatigue tests, the aging curves of the alloys can also be studied which would give an overall idea about the effect of time and temperature on precipitates and coarsening.

CHAPTER 3 EXPERIMENTAL PROCEDURE

3.1 Materials

3.1.1 Reference Alloy

Commercial grade A356 alloy, the physical properties of which are shown in Table 3.1, was used as both the reference alloy and the starting material for new alloys. The A356 was supplied by Rio Tinto Alcan Inc. (Beauharnois, QC, Canada) as foundry ingots (80x15x8cm) and the as-received chemical compositions of A356 ingots are given in Appendix A.

Physical Properties	A356 (T7)
Density (g/cm ³)	2.68
Poisson's ratio	0.33
Thermal expansion coefficient (10 ⁻⁶ /°C)	21.4
Melting range (°C)	560 - 615
Thermal conductivity (W/ mK)	160

 Table 3.1 Physical Properties of the A356 Alloy [48]

3.1.2 Master Alloys

Binary Al-Mn, Al-Cr, Al-Zr, Al-Cu and Al-Sr alloys were used for alloy making. All master alloys were supplied by KB Alloys Inc. (Reading, PA, USA). The chemical compositions and liquidus temperatures of those are given in Table 3.2.

Master Alloys (wt%)	Liquidus Temperature (°C) [49]
85Al - 15Zr	1320
80A1 - 20Cr	1000
75Al - 25Mn	910
90Al – 10Sr	660
66Al - 33Cu	548

Table 3.2 Liquidus Temperatures and Compositions of the Master Alloys

3.2 Alloy Design

Multicomponent alloys were prepared by adding four elements (Cr, Mn, Zr and Cu) into A356 melt. A number of different additions and combinations were investigated. Due to the time-limitations, only the promising alloys are discussed in this thesis. Among the four alloys studied, the standard Sr-modified A356 alloy was chosen as the main reference alloy (R1). The Cu alloyed (0.5%) A356, which is currently being used in certain engines, was used as the second reference alloy (R2). Two new alloys were synthesized and evaluated: the first one (MG1) included trace amounts of Zr, Cr and Mn in A356 whereas the second alloy (MG2) additionally benefitted from 0.5%Cu. The alloy codes and target compositions of the reference and developed alloys are given in Table 3.3. All compositions given in this thesis are in weight percent.

Table 3.3 Alloy Codes and Target Compositions

Alloy Codes	Target Alloy Compositions (wt%)		
R1	A356		
R2	A356 + 0.5% Cu		
MG1	A356 + 0.15% Mn +0.15% Cr +0.15% Zr		
MG2	A356 + 0.15% Mn +0.15% Cr +0.15% Zr +0.5% Cu		

During the alloy making, the peritectic elements Cr and Zr were chosen to promote the formation of favorable dispersoids in the aluminum matrix. Mn being another peritectic element, was added to create additional second phases strengthening and to transform the brittle iron rich intermetallics into less detrimental phases [24]. It also has been shown [21] that the combined addition of Mn and Cr improved the tensile strength of the A356 alloy at room temperature better than the separate additions. The level of 0.15% was chosen for peritectic elements to avoid the formation of any coarse primary phases [5] and this is the same reason why the level of Ti is usually kept at 0.12% in standard A356.



Figure 3.1 Alloy synthesis and production of permanent mould tensile bars for tensile testing, aging and DSC studies.

3.3 Experimental Method

The overall experimental method is shown in Figure 3.1 and 3.2. The main steps are

- Alloying, casting and heat treatment of the samples,
- Metallographic investigation,
- Mechanical testing,
- Aging behavior of the alloys.



Figure 3.2 Alloy synthesis and production of permanent mould cast cylinders for creep testing and microstructural investigation.

3.3.1 Alloy Making and Melting

In order to achieve target compositions, all samples and additions were cleaned with denaturated alcohol to remove excess chips and oil from sectioning prior to melting. For each casting experiment, approximately 950 g of A356 was melted in a silicon carbide crucible inside a 20kW/5kHz induction furnace as shown in Figure 3.3. The melt temperature was monitored with a chromel-alumel (type K) thermocouple. For each composition, a specific casting procedure was developed until the dissolution of the master alloys was completed. The master alloys with high liquidus temperatures were added initially and held for longer times when necessary.



Figure 3.3 The Induction furnace and casting set-up.

The additions were made by adding solid pieces into the melt A356 at temperatures between 690- 750°C and the holding time varied from 20 to 40 minutes. The melt was stirred with a graphite rod after each addition and the melt surface was skimmed to eliminate the oxide layer prior to casting. Also, all alloys were modified with 200 ppm of strontium via 90Al-10Sr rods prior to casting. The pouring temperature was kept constant as 750°C in this work.

3.3.2 Casting

The alloys were cast into two different permanent moulds; tensile bar and rod-casting. The internal surface of the moulds was coated with boron nitride slurry supplied by Pyrotech. The moulds were preheated to 425°C to avoid solidification during casting. Samples for tensile testing and aging tests were cast into a tensile bar mould shown in Figure 3.4. Each casting produced two standard ASTM-B557M-06 tensile test bars with the dimensions as given in Figure 3.4. Creep testing and metallographic samples were cast into a rod-casting mould producing a cylinder with a diameter of 28.60 mm. A schematic representation and a picture of the mould with the cast can be seen in Figure 3.5. The castings were removed from the mould five minutes after pouring.

3.3.3 Identification of the Alloys

The permanent mould alloys were identified by a sample code as follows, X-(YZ) where:

- X denotes the alloy code (either R1, R2, MG1 or MG2),
- Y identifies the casting type (either R as Rod or T as Tensile),
- Z corresponds to the casting number.

3.3.4 Chemical Analysis

Sample drillings were taken from the gate of the tensile bar moulds and the cylinder of the hot tearing moulds, shown in Figure 3.4. Prior to drilling, the oxide layer that formed on the surface was removed with a grinding paper of 600. The chemical composition of the alloys was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at Genitest Inc (Montreal, QC, Canada).



(a)



(b)

Figure 3.4 (a) The schematic drawing and (b) picture of the tensile bar mould.







(b)

Figure 3.5 (a) The schematic drawing and (b) picture of the rod casting mould.

The chemical composition of the alloys used for creep testing and microstructural investigation is shown in Table 3.4. Since many castings were performed for the tensile

tests, a composition range of the tensile alloys is given in Table 3.5. It can be clearly seen that target compositions that was mentioned in Table 3.3 has been achieved for all of the alloys tested.

(wt%)	R1-R60	R2-R82	MG1-R63	MG2-R64
Si	6.74	7.06	6.60	6.29
Fe	0.10	0.11	0.11	0.11
Mg	0.34	0.35	0.33	0.32
Cu	< 0.01	0.54	< 0.01	0.52
Mn	< 0.01	< 0.01	0.15	0.15
Ni	< 0.01	< 0.01	< 0.01	< 0.01
Cr	< 0.01	< 0.01	0.15	0.15
Ti	0.12	0.11	0.12	0.12
Zr	< 0.01	< 0.01	0.16	0.15
V	< 0.01	< 0.01	< 0.01	< 0.01
Zn	< 0.01	< 0.01	< 0.01	< 0.01
Be	< 0.01	< 0.01	< 0.01	< 0.01
Sr (ppm)	160	190	160	150
Al	Bal.	Bal.	Bal.	Bal.

Table 3.4 The Chemical Composition of the Creep Samples

3.3.5 Heat Treatment

ASTM B-597 standards [27] recommend for the A356 alloy a solution heat-treatment of 540°C for 4 to 12 hours and an over-aging temperature of 220°C for 7-9 hours. In the literature, the same solutionizing temperature is used but the aging temperatures usually vary from 185 to 240°C. In this work, all samples for tensile and creep tests were exposed to the same heat treatment [5] prior to testing which consisted of

- a two-step solutionizing treatment at 500°C for 4 hours and 540°C for 10 hours to avoid probable incipient melting ,
- quenching into a water media at room temperature (22°C),
- a natural aging of 12 hours,
- over-aging at 200°C for 5 hours.

(wt%)	R1-T	R2-T	MG1-T	MG2-T
Si	6.67 - 6.96	6.65 - 6.92	6.56 - 6.70	6.56 - 6.62
Fe	0.11 - 0.12	0.10 - 0.11	0.10 - 0.11	0.09 - 0.11
Mg	0.34 - 0.38	0.33 - 0.37	0.32 - 0.35	0.30 - 0.34
Cu	< 0.01	0.52 - 0.59	< 0.01	0.50 - 0.54
Mn	< 0.01	< 0.01	0.14 - 0.16	0.15 - 0.16
Ni	< 0.01	< 0.01	< 0.01	< 0.01
Cr	< 0.01	< 0.01	0.15 - 0.16	0.15 - 0.17
Ti	0.11 - 0.12	0.11 - 0.12	0.11 - 0.12	0.11 - 0.12
Zr	< 0.01	< 0.01	0.12 - 0.16	0.12 - 0.15
V	< 0.01	< 0.01	< 0.01	< 0.01
Zn	< 0.01	< 0.01	< 0.01	< 0.01
Be	< 0.01	< 0.01	< 0.01	< 0.01
Sr (ppm)	140 - 160	130 - 160	140 - 160	130 - 160
Al	Bal.	Bal.	Bal.	Bal.

Table 3.5 The Chemical Composition of the Tensile Samples

The aging behavior of the alloys in long-term use was studied by measuring the hardness values of the over-aged samples which were held at 200° C for various hours. For each alloy, twenty rectangular samples (4x12x20mm) were machined from the sprue of the tensile mould (Figure 3.4) and then solutionized and quenched as described above. After,

a natural aging of 12 hours, the samples were separately aged for 0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 18, 21, 24, 100 and 200 hours.

The solution heat treatment, aging and preheating of the moulds was performed in an electrical-resistance-heated, air-circulation chamber furnace as shown in Figure 3.6. A maximum variation of $\pm 1^{\circ}$ C was observed in the furnace where the heat treatment of the samples took place.



Figure 3.6 The electrical-resistance-heated furnace.

3.3.6 Differential Scanning Calorimetry (DSC)

In order to determine the phase changes during over-aging, an isothermal DSC analysis at 200° C for 10 hours was carried out at Université Laval (Quebec City, QC, Canada). The samples which were only solutionized and quenched for the hardness measurement were used for the DSC analysis. The rectangular samples (4x12x20mm) were further sectioned

with a diamond blade until three samples with a desired weight between 0.018 and 0.021 gr were obtained. The alloy codes and sample weights can be found in Appendix A.

The DSC analysis was performed in a Perkin-Elmer7 apparatus under protective argon atmosphere. Each sample was heated from room temperature to 200°C at a scanning rate of 10°C/min and held at this temperature for 600 minutes and then cooled down to room temperature with the same scanning rate. The heat flow (mW) was recorded via time and then averaged for each composition.

3.3.7 Microstructural Investigation

Three different temper conditions were studied for each alloy. These were;

- 1. as-cast,
- 2. solutionized and quenched,
- 3. solutionized, quenched and over-aged (full T7).

Sample Preparation

The samples for metallography were taken from the machined cylinders and then sectioned further with a low speed cutter with a diamond blade so as not to cause any additional heat or stress on the samples. A schematic of the sectioning and a picture of the metallographic sample with its dimensions are shown in Figure 3.7.

Optical microscopy samples were cold-mounted in an epoxy resin-hardener mixture whereas this step was skipped for any of the Scanning Electron Microscope (SEM) samples to avoid the possible charging effect during operation. Starting from a grit size of 240, respectively 320, 400, 600 and 800 SiC papers were used for grinding. The samples then were held in an ultrasonic bath for 5 minutes to remove any excess particles and dirt.



Figure 3.7 Sectioning of the metallurgical samples.

After grinding, the samples were polished with a 5 μ m and 0.3 μ m Al₂O₃ solution, respectively. The final polishing was carried out using a colloidal silica suspension. Any remaining silica particles were carefully removed using a cotton swab under running water. After each polishing step, the same ultrasonic bath treatment was applied and no etchants were used.

Optical Microscopy (OM)

The presence of some of the second phases such as Si and iron-rich intermetallic phases and their morphology were examined using a Nikon optical microscope equipped with a Clemex image analysis program. Optical images at various magnifications were obtained and then used to determine the SDAS via the mean linear intercept (MLI) method. For each measurement, twelve lines having at least seven dendrites on them were calculated and then averaged.

Scanning Electron Microscopy (SEM)

A more detailed second phase observation was carried out using a Hitachi 6700 FEG-SEM. Qualitative analysis of the second phases was performed with spot analysis by the EDS detector connected to the electron column, which was also used to create elemental maps. An accelerating voltage of 10 kV, a beam current of 10 μ A was chosen to minimize the penetration volume within the sight of the elements whereas a working distance of 12 mm was chosen to get sufficient X-Ray signals for elemental analysis.

3.3.8 Mechanical Properties

Hardness Measurements

Hardness measurements were carried out using a Mitutoyo HR-500 hardness tester with a 1/16 steel ball indenter and a load of 100 kg. The hardness tester was checked for calibration by taking several readings on the test block. At least seven readings were taken from each sample and then averaged. Hardness indentations were made across the samples and were well separated to ensure that there was no deformation overlap.

Tensile Tests

Before any testing and heat treatment was performed, the cast bars were sent to SGS-X-PER-X Inc. for radiography test in order to quantify the inclusion and shrinkage values. Under the ASTM E-155 standards, the bars having sponge shrinkage and inclusion grades better than three were selected and the rest of the samples were discarded. A typical radiographic report of the tested bars can be found in Appendix A.

The tests at room temperature were performed using an Instron 8500 automated testing system at a rate of 0.05 in./in./min at McGill University, Figure 3.8. Whereas the elevated temperature tests were carried out in Westmoreland Mechanical Testing &Research Inc.

(US) under the ASTM E8-08 standards. 150°C and 250°C were chosen as the test temperatures and the bars were held at the testing temperatures for 30 min. prior to testing. For comparison reasons, some of the room temperature tests were sent to the same lab as well and all the values obtained were well matching corresponded to the ones obtained at the University. For each composition and condition at least 4 bars were tested and then averaged. The typical strain–stress curves at each temperature and the averaged values for each alloy are given in Appendix B.



Figure 3.8 Tensile testing set-up.

Three parameters were extracted from the recorded curves: the ultimate tensile strength (UTS), the yield strength (YS) and the elongation. The UTS was recorded as the peak strength on the stress-strain curve whereas the YS was determined as the stress corresponding to the intersection of the curve with a line parallel to the elastic part of the curve offset by a strain of 0.2%. The elongation was determined by taking measurements of before and after gage length as follows:

$$ef = \frac{Lf-L0}{L0}$$

where e_f is the % elongation, L_f is the final gage length and L_0 is the initial gage length.

Creep Tests

Since the engine often experiences low compressive pressures (20-30 MPa) during operation, a compressive creep test was designed to compare the alloys. Creep samples having a diameter of 20 mm and length of 30 mm were sectioned from the cast cylinders as shown in Figure 3.9. After the T7 heat treatment, the samples were creep-tested at Westmoreland Mechanical Testing &Research Inc. (US) under the ASTM E139-06 standards. Creep curves were recorded up to 300 hours at 300°C under a pressure of 30 MPa. From these curves, % creep strain values were extracted. For each composition, two samples were tested and then averaged.





Figure 3.9 Sectioning of the creep samples.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Aging Characteristics of the Alloys

Figure 4.1 shows the variation in Rockwell B hardness (HRB) values as a function of the logarithm of aging time at a constant temperature of 200°C for different alloys. The data points on the figure represent the average of at least seven repetitions with the error bars showing the standard deviation. The curves show a typical precipitation-hardening behavior in which the hardness increases at first with increasing time, reaches a maximum, and finally slopes down. Although all alloys show this typical trend, there are differences in aging behavior of each composition.



Figure 4.1 Age-hardening curves of the alloys at 200°C.

Without any artificial aging treatment at the as-solutionized condition, the standard A356 alloy (R1) has the lowest hardness value of 19.1 HRB. The Cu-added reference alloy R2 has hardness of 21.7 HRB whereas the MG1 alloy with trace amounts of Zr, Cr and Mn has a hardness of 25.6 HRB. The Cu-added new alloy (MG2) has the highest as-quenched Rockwell hardness value at 32.8.

With an increase in the duration of aging time, hardness increases until it reaches the first peak, also known as the maximum peak strength, for all of the alloys. The maximum peak strength is associated with the precursors (β ', Q', θ ') of the equilibrium age-hardenable phases (β , Q, θ) [7, 29], though the aging sequence of MG2 and MG2 are not known precisely. However, since the peak strength times are identical it can be postulated that the aging sequence may be similar. At the peak point, the alloys keep their assolutionized hardness ranking. The R1 alloy again has the lowest peak hardness of 48.9. The R2 alloy, with a peak hardness of 53.6, gets closer to the MG1 alloy having a peak hardness of 54.9. Among the four alloys, the MG2 alloy has the highest peak strength of 61.2 HRB.

The alloys containing Cu, in addition to Mg, as the age-hardening elements (R2 and MG2) have broader aging curves than the alloys containing only Mg (R1 and MG1). An explanation for this can be that the growth of Mg-bearing phases is much more affected by the aging time at 200°C so that their growth into the equilibrium phase is accelerated and the amount of these phases is reduced resulting in lower hardness. Therefore, the precursors of the Cu-containing phases having lower growth kinetics have slower overaging behavior.

For the four alloys studied, the maximum peak strength occurs in the early stages of aging, approximately within an hour, which is expected. This is mainly due to the

temperature (200°C) at which the aging is carried out. It is known that the lower aging temperatures (160 -180 °C) results in higher peak hardness values which are obtained at longer aging times. For instance, an artificial aging at 165 °C for 8 hours gives a maximum peak hardness of 110 BHN (equivalent to 70 HRB) for an Al-7Si-0.3Mg-0.6Fe alloy [22]. Hence, the aging responses of the alloys are accelerated with increasing temperature.

After the first peak in the aging curve, at the early intermediate stage of aging, the hardness decreases until it reaches a plateau. Interestingly, this plateau is observed for all the alloys at the same aging time between 2 and 4 hours. The R2 alloy reaches the MG1 alloy at the end of its plateau whereas the hardness of MG1 tends to decrease after this point. The MG2 alloy has the highest hardness value of 59.9 at 4 hours of aging and 42.3 is the lowest hardness value recorded for the R1 alloy. This again indicates that the precipitation sequences in all four alloys are very similar.

After the commonly observed plateau, the general trend is a sharp decrease in hardness. The R1 and MG1 alloys lose all their strength after 21 hours of aging and reach their assolutionized hardness values. However, 24 hours of aging brings a further decrease for MG1 which approaches the R1 alloy. At this point, both alloys have a hardness of 16.1 HRB, which is even lower than their as-solutionized values. The R2 alloy shows good aging behavior in which it retains its hardness higher than its as-quenched condition after 24 hours of aging with an HRB value of 40. At this point, the MG2 alloy has an even better aging response with a hardness value of 45.6.

Aging times longer than the 24 hours give a better idea on the overall over-aging behavior of the alloys. After 100 hours of aging, the R1 and MG1 alloys have very low hardness values (which are out off the HRB scale and shown as 0 in Figure 4.1). On the

other hand, the Cu-containing alloys, the R1 and MG2, maintain hardness values of, 32.5 and 37.5, respectively. At the end of 200 hours of aging, the hardness decreases further however, the MG2 alloy still has superior aging behavior since the difference in hardness between the R2 and MG2 alloys is still maintained. At this end point, the R2 alloy has a hardness of 23.6 whereas the MG2 alloy has 28.7 HRB. Moreover, the small error bars at the very last aging times show that there is no overlap and the relationship held between the two alloys is significant.

The significant improvement in hardness of MG1 and MG2 over R1 and R2 in the assolutionized state indicates that certain second phase hardening is occurring in these alloys due to the Zr, Cr and Mn additions since the solubility limits of these elements in Al are low. However, this improvement disappears in MG1 (gets closer to R1) when the alloy is exposed to aging for longer times. Therefore, it can be concluded that the second phases including Zr, Cr and Mn in the MG1 alloy get coarsened with the increased duration of aging at 200°C resulting in lower strength values.

The Cu additions significantly improve the aging behavior of the standard A356 alloy at any stage of aging. The increase in the peak strength might be due to the increased density of β " and β ' phases and the newly formed phases containing Cu such as λ ' and θ ' [7]. At longer aging times, since the Mg-bearing phases lose their strength as in the A356 alloy, the growth of Cu-containing phases could provide strength through Orowan strengthening even in the over-aged state. The Zr, Mn and Cr additions to the R2 alloy gives the best aging behavior as shown in the MG2 alloy and this might be due to the combined effect of the alloying elements on the Cu-containing second phases. The common observation from aging of Cu containing alloys is that the rate of decrease in hardness is lower than the alloys containing only Mg. This is mainly due to the Cu containing phases which retain their strength for longer times at 200°C. Other than the maximum hardness peak, some smaller peaks are also observed in the aging curves of the alloys. These double peaks occur at different aging times for each composition. The R1 alloy has a second peak at 12 hours of aging whereas the R2 alloy experiences its second peak after 8 hours of aging. A second peak is observed for both the MG1 and MG2 alloys at around after 15 hours. These peaks are often associated with the metastable phases which form during the aging treatment and they are responsible for the increase in hardness. However, a detailed TEM work supported with a thermal analysis confirming the phase transitions can only determine the nature of these additional peaks and shed light onto the precipitation sequence of the age-hardenable phases. Moreover, in this work, the error bars before and after these points seem large enough that the observed second peaks might actually be in the decrease trend instead of being considered as individual peaks that are responsible for the increase in hardness due to the metastable phases. The large error bars may be due to the non-homogeneous casting microstructure of the alloys. The indentations on the large and soft aluminum dendrites give lower hardness values whereas the stronger eutectic phases are harder and the difference in between these two is thought to be responsible for the large error bars.

4.2 Tensile Properties of the Alloys

4.2.1 Tensile Properties at Room Temperature

The results of the tensile tests at room temperature are given in Figure 4.2. The tensile properties, UTS, Y.S and % elongation are extracted from the strain–stress curves for each alloy over-aged at 200°C for 5 hours. The bars show the average values of the four repeats and the standard deviation.

As noted (Figure 4.2 a,b), the standard A356 alloy has a UTS of 265 MPa and a YS of 239 MPa. The Cr, Mn and Zr additions have a negligible effect on the room temperature strength of the A356 alloy as the UTS and YS of the MG1 alloy are 262 MPa and 240









Figure 4.2 (a) UTS, (b) YS, (c) %E values of the alloys at room temperature.

MPa, respectively. The Cu-containing R2 alloy has better strength (UTS: 275 MPa, YS: 249 MPa) than both the R1 and the MG1 alloy. Of the four alloys, MG2 has the highest yield strength at 256 MPa. Its UTS (271 MPa) is slightly lower than of the R2 alloy, mainly due to the lower elongation.

The % elongation values at room temperature are 2.8 (R1), 2.9 (R2), 1.8 (MG1) and 1.6 (MG2), (Figure 4.2 c). The addition of Cu seems to have a positive effect on the ductility of the A356 alloy although the error bars on the alloys R1 and R2 complicates the comparison. The trace additions of Cr, Zr and Mn have markedly reduced the elongation at room temperature for both MG1 and MG2 alloys. One reason for this could be the increased amount of microporosity with additions, although microporosity studies have not been performed yet. Secondly, the additions may have formed brittle second phases that influence the crack initiation and cause early fracture.

The ranking of the R1 and R2 alloys with respect to tensile properties agrees well with the literature. However, the actual strength values obtained in this work seem to be lower. For instance, the difference in the UTS between A356 and Cu version of it in Garat's work [5] was noted as 9 % whereas in this study, the % improvement is 4. This could be due to the HIP and degassing treatments which reduced the microporosity and homogenized the bars prior to testing that improved the mechanical properties.

Even though attention was paid during melting and casting experiments and test bars were radiographied prior to testing, oxide films were found on the fracture surface of the bars. Due to these undesired oxides and porosity, lower strain to failure values are obtained than the literature values which can also explain the lower UTS values reached.

4.2.2 Tensile Properties at 150°C

The results of the tensile tests at 150°C are given in Figure 4.3. The bars show the average values of the four repeats and the standard deviation. It can be seen that the strength values are lower than the room temperature values and the elongation is higher due to the increased testing temperature.

It is noted in Figure 4.3 (a,b) that at 150°C, the R1 alloy has the lowest UTS (217 MPa) and YS (201 MPa). The Cu-containing R2 alloy and MG1 alloy have the same UTS of 225 MPa and YS of 208 MPa. The Cr, Mn, Zr and Cu additions to A356 give the highest strength at 150°C, with a UTS of 234 MPa and YS of 222 MPa.

The elongation values follow the trend in UTS. The R1 and R2 alloys have similar elongation at 3.3 and 3.2, respectively (Figure 4.3 c). On the other hand, the Cr, Zr and Mn additions seem to lower the % elongation values of the A356 and the Cu added A356, since 2.0 and 1.9 are the elongations of the MG1 and MG2 alloys. Therefore, at 150°C the Cu addition does not seem to affect the elongation very much but it improves both YS and UTS regardless of the other additions. When a high ductility is desired, the R2 alloy seems the best candidate whereas the MG2 alloy offers the highest strength with lower elongation at 150°C.

The tensile results of the R1 and R2 are in agreement with the literature values except for the lower elongation values. Feiskus et al [6] stated that the elongation values at 150°C are lower than the room temperature values for both alloys. On the contrary, Heusler et al. [4] found a lower elongation value at 150°C only for the A356 alloy, whereas the 0.5% Cu addition slightly increased the strain to failure value. In this work, for both alloys the elongation increases with the test temperature. One reason for the difference in results could be due to initial heat treatment that was applied (T6 in the literature, T7 in







(b)



Figure 4.3 (a) UTS, (b) YS, (c) %E values of the alloys at 150°C.

this work) and/or the varying presoaking times (500h in literature, 0.5h in this work) at the testing temperature. Although, an initial T6 was used in the literature, 500 hours of presoaking at 150°C prior to testing should have resulted in a T7 condition. Therefore, it is likely that the difference can be due to the varying casting conditions (different PMs and SDAS) and/or defect formation (oxides and porosity) that influenced the tensile properties. Moreover, the large standard deviation present complicates the comparison of the alloys.

4.2.3 Tensile Properties at 250°C

The results of the tensile tests at 250°C are shown in Figure 4.4. Since 250°C is considered to be close to the peak temperatures at the diesel engine, more tests have been performed at this temperature. The bars show the average values of at least seven repeats and the standard deviation. It can be seen that the strength values are even lower and the elongation is higher than the tensile properties at 150°C due to the increased test temperature.

At 250°C, the standard A356 alloy has a UTS of 126 MPa and a YS of 124 MPa, (Figure 4.4 a,b). The Cr, Mn and Zr additions have a negligible effect on the strength of the A356 alloy and the UTS and YS of the MG1 alloy are 128 MPa and 125 MPa, respectively. The Cu-containing R2 alloy has better strength (UTS: 152 MPa, YS: 145 MPa) than both R1 and MG1 alloy. Among all the alloys, the MG2 seems the best one with the highest ultimate tensile strength of 161 MPa and yield strength of 152 MPa at 250°C.

The % elongation values at 250°C are 5.1 (R1), 3.2 (R2), 4.9 (MG1) and 4.1 (MG2). The Cu addition alone seems to have a negative effect on the ductility of the A356 alloy. The MG1 alloy is close to the R1 alloy, whereas the MG2 alloy has lower elongation but still











(c)

Figure 4.4 (a) UTS, (b) YS, (c) %E values of the alloys at 250°C.
better than the R2. From these results, it can be said that at 250°C the Zr, Cr and Mn additions to the A356 alloy are less detrimental on the elongation than the Cu additions. This could be due to the increased porosity with the Cu addition and/or the newly formed Cu-containing phases, which are harder but more brittle than the other phases at 250°C. However, the standard deviation in elongation values are high and it can be considered that the ductility of the alloys is close. Furthermore, the testing temperature and the soaking time at this point play an important role in the elongation.

Table 4.1 summarizes the % improvement in tensile properties of the developed alloys at 250°C. The normalized values were calculated with respect to the standard A356 alloy under a common T7 treatment based on the literature. It can be seen that the 0.5% Cu addition have a similar improvement in tensile strength which supports the results of this work with respect to the literature. The 0.15% Cr addition to the A356-0.5Cu-0.15Mn-0.15Zr brings the maximum improvement in UTS and YS, as in the MG2 alloy.

Additions to A356	Alloy Code	%UTS	% YS	% E
0.5%Cu,[5]*	-	19.7	20.00	0
0.5%Cu +0.15%Mn +0.15%Zr , [5]*	-	24.6	18.2	+7.3
0.5%Cu	R2	20.6	16.9	-37.5
0.15%Cr +0.15%Mn +0.15%Zr	MG1	1.6	0.8	-4.0
0.5%Cu +0.15%Mn +0.15% Zr +0.15% Cr	MG2	27.8	22.6	-19.6

Table 4.1 Normalized Tensile Properties of Various Developed Alloys with Respect to the Standard A356 (T7) at 250 $^\circ C$

*HIP treated (2 hours at 485°C, 100 MPa)

The elongation values that are obtained in this work are always lower than the literature values and the differences are shown as negative in the Table. As mentioned before, one reason could be the presoaking time at 250°C which was 100 hours for the Garat's work

[5] and 0.5 hour in this study. This obviously increases the over-aging behavior of the alloys prior to testing and homogenizes the bars further that results in higher elongation values. Moreover, the applied HIP and degassing treatments and/or the variation in casting conditions could be the other reasons for the higher elongation values that are reached in literature.

Based on the tensile properties at various temperatures, it can be concluded that the MG2 alloy would perform better in the thermal-fatigue condition of the engine cool-down cycle due to its high yield and ultimate tensile strength. The higher yield strength would allow elastic accommodation of higher stresses. The improved ultimate tensile strength would delay the crack initiation stage to higher stresses.

Mechanical-fatigue behavior was not investigated in this project. However, high mechanical fatigue resistance is usually proportional to UTS. Since, the thermal-fatigue behavior is sometimes estimated by mechanical-fatigue at the cycle mean temperature as mentioned in the theoretical background (2.3.5), it can also be concluded that MG2 which would exhibit high UTS at 150°C would potentially show improved thermal-fatigue performance in engine cylinder head applications.

Ductility is also an important parameter for thermal-fatigue since ductile alloys would exhibit a more extended fatigue stage before cracks are initiated. Firm conclusions cannot be drawn from this study since the elongation values of the alloys were affected most probably by casting defects (porosity and inclusions). Based on the ductility values at 150°C, it can be stated that the R2 alloy would provide higher ductility at engine cooldown.

4.3 Compressive Creep Properties of the Alloys

Figure 4.5 shows the compressive creep curves of the alloys at 300°C under a stress of 30MPa. Each curve represents the average of two samples from the same composition and the initial curves for each experiment can be found in Appendix B. And Table 4.2 summarizes the % creep values reached at the different stages of the testing for each alloy.

It can be seen that the total creep in four alloys increases with the increased time at 300°C, which is expected. The Zr, Cr and Mn additions as in the MG1 alloy, improves the compressive creep resistance of the A356 alloy in a consisted manner. Whereas, the Cu-added A356 alloy shows better creep resistance only up to the medium stages of testing (175 hours). After this point, the R2 alloy reaches higher creep values than both the R1 and the MG1 alloy.



Figure 4.5 Compressive creep curves of the alloys at 300°C under 30MPa.

Of all the four alloys, the MG2 alloy shows the superior compressive creep resistance by reaching only a creep strain of 4.9% after 300 hours at 300°C. The improvement in the MG2 alloy can be noted up to three times better than the R1, R2 and the MG1 alloys. Therefore, it can be concluded that the alloying additions of Cr, Zr and Mn only bring a certain improvement in A356 alloy but the creep resistance is much more obvious when the combined addition of Cu with these elements is considered.

100 hours	200 hours	300 hours
4.3	9.5	15.5
2.7	9.1	16.8
3.6	8.7	14.3
1.1	2.6	4.9
	100 hours 4.3 2.7 3.6 1.1	100 hours 200 hours 4.3 9.5 2.7 9.1 3.6 8.7 1.1 2.6

Table 4.2 Creep Strain (%) of the Alloys at 300°C for 100, 200 and 300 Hours

The effect of alloying on the creep mechanisms (dislocation and diffusional creep) and certain creep properties (the steady-state creep rate and $\sigma^{0.1}_{100}$) can only be studied with more experiments. However, under these testing conditions, it seems that the slopes of the creep curves of the R1, the R2 and the MG1 alloys are steeper than of the MG2 alloy. Therefore, it can be concluded that the combined addition would result in most likely a lower minimum creep rate (steady-state).

There is not much data on the compressive creep resistance of the alloys in the literature. An alloy similar to MG2 studied by Garat et al. [5], which contains Cu, Zr and Mn shows good creep resistance over the Cu-added A356 alloy under 22MPa for 300 hours at 300°C. However, the improvement in total strain becomes significant after 300 hours. Whereas in this work, the MG2 alloy shows almost three times better creep resistance than any of the alloys at all stages of testing which would provide improved performance at engine heat-up.

4.4 DSC Analysis of the Various Alloys

In the literature, the DSC analyses are usually performed with a non-isothermal method (by heating the samples from room temperature up to 600°C), to determine the transition temperatures of the age-hardenable phases (GP, β ", β ' and β) and the precipitation temperatures of the other phases [23, 29, 50]. However, in this work, in order to elucidate the precipitation sequence at 200°C, isothermal DSC analyses for 10 hours were conducted on the as-solutionized samples.

In total, twelve tests were performed (three for each composition), however, the results obtained from each experiment were found to be inconclusive. The typical graphs obtained for each alloy are given in Appendix B. The heat flow (mW) versus time (min) graphs were acquired and the derivative of the graphs were calculated to examine if there was any endothermic or exothermic reactions during the 10 hours of holding. It was initially expected that the formation of the phases should give an exothermic peak whereas the dissolution of the phases should cause an endothermic peak. However, no common peaks were observed within the alloys studied and the range of the heat change was not comparable.

One of the reasons for the inconclusive results could be the small mass of the samples. In order to achieve an arrangement that can detect heat flows as small as 0.1 mW, small samples (\approx 20 mg) are desired. The amount of the phases that forms and dissolves in such a small volume could be insufficient for the heat detection or the phases could have been distributed non-homogeneously within the samples. Moreover, the amount of heat generated or absorbed during the isothermal test could be small and out of the sensitivity range of the calorimeter. Further study of the alloys to determine the reasons for the differences in mechanical properties was therefore focused on microstructural investigation. Optical and electron microscopy (SEM) were carried out as discussed in the next section.

4.5 Microstructural Analysis of the Alloys

4.5.1 Effect of Alloying on the As-Cast Microstructures

The results of the microstructural investigation are based on the three stages of the heat treatment cycle (as-cast, as-solutionized and over-aged). The "as-solutionized" stage in this work, refers to solutionized and then water-quenched (as described in 3.3.5). The typical optical microstructures of the various alloys at low magnification are shown in Figure 4.6. The microstructure of all alloys exhibits primary aluminum dendrites which are surrounded by a mixture of eutectic aluminum phase, eutectic silicon particles and other eutectic phases. It can be seen that as-cast microstructures also have casting defects such as porosity and inclusions which appear as dark spots in the optical microstructures. However, these features were not quantified in this study.



Figure 4.6 Typical microstructures of the as-cast (a) R1, (b) R2, (c) MG1, (d) MG2 alloys.

Secondary Dendrite Arm Spacing (SDAS)

Table 4.3 presents the SDAS of the different alloys studied. No significant variation among the four alloys was noted in the measurements made at the equivalent positions of the castings. SDAS is usually related to average cooling rate in cast alloys and the alloying elements do not seem to have influenced the local solidification time of the permanent mould cast A356. Furthermore, SDAS refinement can occur as a result of the poisoning of the dendrite arms growth by trace elements. Only Sr is known to provide this effect and since the Sr level is similar in all alloys, no difference is observed.

Additions to A356	Alloy Code	SDAS (µm)
-	R1	29.43 ± 3.06
0.5%Cu	R2	29.55 ± 2.74
$0.15\% Cr \ +0.15\% Mn \ +0.15\% Zr$	MG1	30.61 ± 2.11
$0.15\% Cr \ +0.15\% Mn \ +0.15\% Zr \ +0.5\% Cu$	MG2	30.23 ± 2.23

Table 4.3 Effect of Alloying on the SDAS of the A356 (R1) Alloy

Eutectic Si Modification

For all four alloys, the eutectic Si was usually modified by the addition of 200 ppm strontium. The typical modification effect is shown in Figure 4.7 for the MG1 alloy. It can be seen that in the Sr-free alloy, the eutectic Si is lamellar and has an acicular morphology whereas the alloy containing Sr has a more fibrous eutectic Si. Additionally, some of the eutectic silicon in all compositions was found to be partially modified and unmodified although the same amount of addition was made. The levels of modification may be due to the amount of strontium and/or the cooling rate. For full modification, generally 200 ppm strontium level is sufficient. However, from the chemical analysis, the strontium concentration obtained was approximately 160 ppm for the alloys studied for the microstructural investigation (Table 3.4). Hence, one of the reasons may be the

insufficient amount of the modifier whereas the other reason can be the different levels of freezing rate. Moreover, it is known that strontium produces less uniform modification when compared to other modifiers such as sodium [9]. Some Sr-containing oxides (Figure 4.8) were also found in some alloys supporting that not all Sr added may have taken part in eutectic Si modification.



Figure 4.7 As-cast microstructure of the MG1 alloy (a) without strontium, (b) with strontium.



(a)

(b)

Figure 4.8 (a) SEM micrograph of the oxide containing Sr in the MG1 alloy with (b) its EDS spectra.

The R1 Alloy

Figure 4.9 shows the typical microstructure of the standard as-cast A356 (R1) alloy. Besides the eutectic Si, the other main phases are β -Al₅FeSi, π -Al₈Mg₃FeSi₆ and β -Mg₂Si. The equilibrium β -Mg₂Si phase has Chinese script morphology (appears in dark color, as in Figure 4.9a) and the amount of this phase is very low and not uniformly dispersed when compared to the other coarse intermetallics. It was only observed with an optical microscope. The reason for this is the very low amount of β -Mg₂Si phase together with the fact that the atomic numbers of Mg and Si are very close to Al giving a low Z contrast for a compositional SEM imaging.

The β -Al₅FeSi usually forms as thin plates which appear as needles on the polished sections. The β phase is closely associated with the eutectic Si along the primary aluminum dendrites and the average length of the particles varies between 5µm and 30µm. The π -Al₈Mg₃FeSi₆ forms independently in the interdendritic region or else grows from the surfaces of β -Al₅FeSi phase as in Figure 4.8b. The π phase has either Chinese script or blocky type morphology. It is usually coarser (35µm) than any of the other eutectic phases and its amount is higher. This could be another reason for the low amount of β -Mg₂Si phase observed in the as-cast condition since Mg favors the formation of π . The differentiation of the β -Al₅FeSi and π -Al₈Mg₃FeSi₆ phases is difficult with an optical microscope (only possible via their morphologies), especially when no etchant is used. However, due to the difference in Fe ratios within the phases, the β -Al₅FeSi phase is brighter in the SEM micrographs. The EDS spectra of the each phase observed by SEM are given in Figure 4.10.

The R2 Alloy

Figure 4.11 shows the typical microstructures of the as-cast R2 alloy. It can be seen that 0.5% Cu addition forms two new phases: θ -CuAl₂ and a quaternary Al-Si-Cu-Mg phase.



Figure 4.9 The different phases observed in the as-cast R1 alloy by (a) optical microscope (b) FEGSEM.









Figure 4.10 EDS spectra of the phases in the as-cast R1 alloy (a) eutectic Si, (b) β -Al₅FeSi, (c) π -Al₈Mg₃FeSi₆.

The EDS spectra of the Cu-containing phases are presented in Figure 4.12. The θ phase usually coexists with other eutectic phases but it forms independently in the interdendritic region as well. It has more rounded blocky-type morphology and sometimes appears as many pockets connected to each other. The average size of this phase starts from 10µm and goes down to 1µm.



Figure 4.11 The different phases observed in the as-cast R2 alloy by (a) optical microscope (b) FEGSEM.



Figure 4.12 EDS spectra of the Cu-containing phases in the as-cast R2 alloy (a) θ -CuAl₂, (b) Q-Al₅Mg₈Cu₂Si₆.

Although no quantitative identification was performed, due to its morphology the quaternary Al-Si-Cu-Mg phase is believed to be the equilibrium Q-Al₅Mg₈Cu₂Si₆ having blocky-script morphology. Caceras et al. [35] also reported the same phase in the as-cast A356 alloy containing 0.22%Cu (as in Figure 2.6). The average size of the Q phase is found to be between 3µm to 15µm.

The other Fe-containing phases such as β -Al₅FeSi and π -Al₈Mg₃FeSi₆ complicate the observation of the Q phase in the optical microscope and in this work the Q phase was mainly observed with the FEGSEM. The β -Mg₂Si was not seen in any of the optical micrographs suggesting that Mg favors the formation of Q phase instead of the β in the presence of Cu. Additionally in this study, it was experimentally observed that the amount of the Cu-containing Mg phase (Q) is less than the amount of Fe-containing Mg phase (π).

The MG1 Alloy

Figure 4.13 shows the typical microstructures of the as-cast MG1 alloy. Mg forms two phases, β -Mg₂Si and π -Al₈Mg₃FeSi₆ which were already observed in the standard A356 alloy. Again the amount of β phase is less than the π phase which is observed only in the SEM micrographs. The Cr and Mn additions have converted the needlelike β -Al₅FeSi phase into a complex Al-Cr-Mn-Fe-Si phase, (Figure 4.14 a). Usually the separate addition of Cr and Mn in A356 alloy forms different phases such as (Fe,Si)₂MnAl₁₄ [24] and (Fe,Cr)₃Si₄Al₂₅ [14] but when a combined addition of Cr and Mn is made, none of these phases exists. The complex phase was observed by many authors [16, 21] and named as α -(Al-Cr-Mn-Fe-Si), (hereafter called the α phase, not to be confused with α -Al). However, a specific chemical formula was not derived for this phase and it is likely that it has a varying composition range based on the ratios of the elements present in the alloy.



Figure 4.13 The different phases observed in the as-cast MG1 alloy by (a) optical microscope (b) FEGSEM.



Figure 4.14 EDS spectra of the new phases in the as-cast MG1 alloy (a) α -(Al-Cr-Mn-Fe-Si), (b) Al-Si-Zr.

The α phase has mostly an irregular blocky shape and sometimes its morphology is referred as Chinese script. The average size of this phase starts from 5µm and goes up to 30µm and α is always found in the interdendritic region. With the 0.15%Cr and %15Mn addition, no β -Al₅FeSi phase is observed in the as-cast microstructure. It is believed that a Fe/(Mn or Cr) ratio of 1 is sufficient for a complete transformation of β into α . Since the detrimental β phase is eliminated from the microstructure, lower microporosity levels are expected that might enhance the mechanical properties. On the other hand, the Cr and Mn additions obviously increased the volume fraction of brittle Fe-rich intermetallics in the standard A356 alloy. This could inversely affect the tensile properties at room temperature.

The 0.15%Zr addition forms a new phase, Al-Si-Zr, (Figure 4.13b and Figure 4.14b), named as ε in this work. The ε phase is a eutectic phase which is observed between the dendrites similar to the other eutectic phases. It appears as rods and the average size of it varies between 3µm and 20 µm. During the EDX spot analyses of the ε phase, some Ti is also found. The FEGSEM image and the elemental map of the ε -(Al-Si-Zr-Ti) phase are shown in Figure 4.15. It is experimentally noted that not all of the ε phases include Ti. This is similar to the Fe-rich intermetallics in Al-Si casting alloys [16] where Mn can replace some of the Fe in the α -Al₁₅Fe₃Si₂ phase forming α -Al₁₅(Fe,Mn)₃Si₂ when the Mn free α still exists in the microstructure based on the Fe/Mn ratio.



Figure 4.15 The EDS elemental mapping of the ε -(Al-Si-Zr-Ti) phase in the as-cast MG1 alloy.

The MG2 Alloy

Figure 4.16 shows the typical microstructures of the as-cast MG2 alloy. Among the four alloys, the MG2 has the most complex as-cast microstructure due to the four different additions. It can be noted that (Figure 4.16b) the amount of the second phases in the intedendritic region is markedly increased. The elemental mapping of the second phases in the as-cast MG2 alloy is presented in Figure 4.17. The 0.5% Cu addition has caused the formation of two phases; θ -CuAl₂ and Q-Al₅Mg₈Cu₂Si₆ which were also observed in the R2 alloy. Besides the Q phase, Mg is found in the π -Al₈Mg₃FeSi₆ phase as well. It is seen that the amount of the π phase is relatively lower than the Q phase. On the other hand, the β -Mg₂Si is not observed in the as-cast MG2 alloy. This agrees with the microstructure of the R2 alloy suggesting that the 0.5% Cu addition to A356 alloy causes the formation of Q-Al₅Mg₈Cu₂Si₆ instead of β -Mg₂Si. The 015% Cr and 0.15% Mn additions forms the α -(Al-Cr-Mn-Fe-Si) phase and no β -Al₅FeSi phase is found in the as-cast microstructure. The 0.15% Zr addition forms the ϵ -(Al-Si-Zr-Ti) as well as the Ti free ϵ , as shown in Figure 4.18 which is similar to the MG1 alloy.



Figure 4.16 The typical microstructures of the as-cast MG2 alloy by (a) optical microscope (b) FEGSEM.







20µm

20µm

20µm



Figure 4.17 The EDS elemental mapping of the phases in the as-cast MG2 alloy.

The differentiation of the Q, α , π phases in the optical microscope is not possible without any etching. Also, the ε phase is not observed in any of the optical images obtained. In order to differentiate these phases, SEM investigation is essential, however, certain second phases e.g. the eutectic Si and the β -Mg₂Si are better observed with an optical microscope. A combined study, therefore, seems to be the most efficient method for the phase identification in cast Al-Si alloys having new additions.

4.5.2 Effect of Alloying on the As-Solutionized Microstructures

The R1 alloy

The solutionizing step (at 500°C for 4 hours and 540° for 10 hours) followed by quenching causes significant changes in the as-cast microstructure of the alloys. Figure 4.18a, shows the typical microstructures of the as-solutionized R1 alloy. It can be seen that the only second phases that remained after the solutionizing step are the β -Al₅FeSi and Si. The maximum length of the β was found to be 20µm which is smaller than in the as-cast alloy; suggesting that some refinement of β occurred during the heat treatment although the needlelike morphology remains the same. The heat treatment also altered the



(a)

(b)

Figure 4.18 SEM micrograph of the as-cast MG2 alloy showing (a) θ -CuAl₂, Q-Al₅Mg₈Cu₂Si₆, α -(Al-Cr-Mn-Fe-Si) and ε -(Al-Si-Zr-Ti) (b) Si, Q-Al₅Mg₈Cu₂Si₆, α -(Al-Cr-Mn-Fe-Si), π -Al₈Mg₃FeSi₆ and ε -(Al-Si-Zr).

morphology of the eutectic Si where the Si particles became more globular, (compared to Figure 4.9). Furthermore, the π -Al₈Mg₃FeSi₆ and β -Mg₂Si phases which were seen in the as-cast R1 alloy, dissolved during the solutionizing step. Therefore, the as-quenched microstructure consists of the eutectic Si and β phases with a matrix of super saturated solid solution of aluminum.

The R2 alloy

The as-solutionized microstructure of the R2 alloy is very similar to the R1 alloy, as shown in Figure 4.19b. This is basically due to the dissolution of the Cu- and Mgcontaining phases (θ , Q and π) during the solutionizing treatment. The needlelike β -Al₅FeSi and globular eutectic Si are the second phases observed in the microstructure. During some of the spot analyses of the β phase, Cu is also found in the EDS spectra, however, when an elemental mapping is performed; Cu is only seen in the matrix and not inside the β intermetallic. It is likely that the β phase does not have Cu and the Cu signals are coming from the Al matrix. After solutionizing, all of the Cu is expected to enter into the solid solution of Al. Therefore, it can be concluded that Cu does not form a new Fe-



Figure 4.19 SEM micrographs of the as-solutionized (a) R1 and (b) R2 alloys showing the eutectic Si and β -Al₅FeSi.

rich intermetallic after the solutionizing treatment. Garat et al. [5] also observed that 0.5% Cu addition complicated the phase identification of the new phases.

The MG1 alloy

Figure 4.20 shows the typical microstructures of the as-solutionized MG1 alloy. The major second phases are the eutectic Si, α -(Al-Cr-Mn-Fe-Si) and ε -(Al-Si-Zr). Similarly to the R1 alloy, the Mg-containing phases (β and π) dissolved during the solutionizing treatment in the MG1 alloy. The only Fe-containing phase, α -(Al-Cr-Mn-Fe-Si), was found to be more rounded possibly due to the solutionizing (compared to Figure 4.13b). The Zr-containing ε phase still exists and retains its rod type morphology. However, Ti was not found in any of the ε -(Al-Si-Zr) phase. This suggests that the ε with Ti, could be a metastable phase and Ti dissolves into the matrix during the solutionizing treatment.



Figure 4.20 SEM micrographs of the as-solutionized MG1 alloy at (a) low magnification (b) at high magnification showing the eutectic Si, α -(Al-Cr-Mn-Fe-Si) and ϵ -(Al-Si-Zr).

Interestingly, other than the coarse eutectic phases, fine second phases are also observed both in the interdendritic region and inside the dendrites, as shown in Figure 4.21. The particles near the eutectic Si were found to be coarser (0.4-1 μ m) whereas the ones in the intradendritic region were fine in size, less than 300nm and homogenously distributed in the matrix. The EDS analyses revealed that the fine precipitates are the α -(Al-Cr-Mn-Fe-Si) phase. The EDS spectra of the Al matrix and the α precipitate inside the dendrite are shown in Figure 4.22. The signals from the precipitate were not very strong due to the small size of the precipitate and the large interaction volume created in the sample. It is believed that more signals from the Al matrix were acquired. However, the EDS analysis still gives useful information about the qualitative identification of these precipitates. Since these precipitates were not observed in the R1 or R2 alloy, it can be concluded that these are due to the peritectic element additions (Cr, Mn and Zr).

Kim et al. [23] also observed similar fine precipitates, α -(Al-Mn-Fe-Si), in the A356 alloy (with 0.2%Fe and 0.2%Mn) apart from the crystallized α -(Al-Mn-Fe-Si), after the solutionizing treatment. The size of the granular α particles varied from 50nm to 200nm and the precipitation temperature was noted as 487°C. The additional Cr in this work caused the formation of α -(Al-Mn-Cr-Fe-Si) instead of the α -(Al-Mn-Fe-Si) and it is believed that the Cr substitutions in α , is beneficial for the high temperature stability.



Figure 4.21 SEM micrographs of the as-solutionized MG1 alloy showing α -(Al-Cr-Mn-Fe-Si) precipitates (a) in the interdendritic region (b) inside the dendrite.



Figure 4.22 EDS spectra of the (a) Al matrix (b) α -(Al-Cr-Mn-Fe-Si) precipitate inside the aluminum dendrite in the as-solutionized MG1 alloy.

The fine precipitates were not observed in the as-cast microstructure, (Figure 4.13b). Therefore, these particles must have precipitated from the supersaturated α -Al matrix during solutionizing. The larger α -(Al-Cr-Mn-Fe-Si) particles in the interdendritic region are the eutectic phases that have precipitated eutectically during solidification. Moreover, the refinement of these also occurred during the solutionizing resulting in a smaller size of the eutectic α phase in the as-solutionized condition.

It was challenging to perform the EDS spot analyses on the small precipitates in the matrix. Therefore, it cannot be concluded that all the fine precipitates are α -(Al-Cr-Mn-Fe-Si). For instance, Garat et al. [5] observed the rod like Al-Si-Zr precipitates in the Al dendrites after the solutionizing treatment in A356 alloying with 0.15%Zr and the precipitation temperature was claimed to be above 500°C. However, no Zr containing precipitates were observed during the microstructural analyses in this work. It cannot be ruled that the Al-Si-Zr did not precipitate during the solutionizing treatment. Instead, they might have precipitated but maybe due to their fine size, a proper phase identification could not be performed with FEGSEM.

The MG2 alloy

Figure 4.23a, shows the typical microstructure of the as-solutionized MG2 alloy. It is very similar to the as-solutionized MG1 alloy. The coarse Cu- and Mg-containing phases (θ , π and Q) dissolved during the solutionizing treatment and the only second phases observed are the eutectic Si, α -(Al-Cr-Mn-Fe-Si) and ϵ -(Al-Si-Zr). No Ti was found inside the ϵ phase and some Cu is observed inside the α -(Al-Cr-Mn-Fe-Si) phase similar to the R2 alloy. Very fine α -(Al-Cr-Mn-Fe-Si) precipitates (less than 300nm) can be seen inside the aluminum dendrites (Figure 4.23b), as well as in the intradendritic regions. It is believed that Cu does not have an effect on α precipitates since the amount and morphology of α seem to remain the same as in the MG1 alloy. However, it is very difficult to draw firm conclusions due to the small size of the precipitates. Moreover, similar to the MG1 alloy, only α precipitates are observed in the as-solutionized stage.



Figure 4.23 SEM micrographs of the as-solutionized MG2 alloy showing (a) the eutectic phases in the interdendritic region (b) the fine α -(Al-Cr-Mn-Fe-Si) precipitates inside the dendrite.

As a general observation, it can be stated that the precipitates due to the peritectic additions are responsible for the improved hardness of the MG1 and MG2 alloys over the R1 and R2 alloys, in the as-solutionized condition, (when time=0 in the Figure 4.1). These would also provide increased tensile properties to the alloys in the as-solutionized condition.

4.5.3 Effect of Alloying on the Over-Aged Microstructures

After solutionizing and quenching, an over-aging for five hours at 200°C causes further microstructural evolution. Figure 4.24 shows the typical optical microstructures of the over-aged alloys. It can be seen that the β -Al₃FeSi phase is common in the R1 and R2 alloys whereas the α -(Al-Cr-Mn-Fe-Si) is observed both in MG1 and MG2 alloys. The refinement of the both Fe-rich phases is obvious, (Figure 4.24a, d), due to over-aging treatment. Moreover, in all alloys the eutectic Si is very globular when compared the ascast condition, (e.g. Figure 4.16a).



(a)





(c)

(**d**)

Figure 4.24 Typical optical microstructures of the over-aged (a) R1, (b) R2, (c) MG1, (d) MG2 alloys.

Figure 4.25 shows the over-aged SEM microstructures of the alloys. The needlelike β -Al₅FeSi and eutectic Si phases are observed in the R1 and R2 alloys. No other coarse eutectic phases that were previously dissolved during solutionizing can be seen. On the other hand, the Ti-free eutectic ϵ -(Al-Si-Zr) phase which has platelike morphology and the blocky type α -(Al-Cr-Mn-Fe-Si) are observed in the interdendritic regions of the MG1 and MG2 alloys similarly to the as-solutionized condition (Figure 4.20a and Figure 4.23a). The coarser α -(Al-Cr-Mn-Fe-Si) precipitates (0.4µm-1µm) are also seen near the eutectic Si in both new alloys. Again, no Cu- or Mg-containing coarse phases are observed in the interdendritic region.









Figure 4.25 SEM micrographs of the over-aged (a) R1, (b) R2, (c) MG1, (d) MG2 alloys.

Figure 4.26 shows the fine precipitates inside the dendrites of each alloy. It can be seen that there are some fine precipitates in the R1 alloy, however, the amount is low and due to the contrast the observation is difficult. It is likely that these precipitates could be the equilibrium β -Mg₂Si phase. Moreover, due to the high over-aging temperature, Si clusters might have also precipitated.



Figure 4.26 The fine precipitates in the intradendritic region of the over-aged (a) R1, (b) R2, (c) MG1, (d) MG2 alloys.

The amount of precipitates inside the dendrites is higher in the R2 alloy possibly due to the Cu addition, (Figure 4.26b). From literature it is known that the Q'-(Al₅Mg₈Cu₂Si₆) and the β "-(Mg₂Si) phases coexist together inside the primary aluminum dendrites in Cuadded (below 1%) A356 alloys at T6 condition [7]. However, the alloys were analyzed in the over-aged condition in this work and the precipitation sequence has not been investigated. It is likely that the β " phase was converted to the equilibrium β phase due to the T7 condition (5 hours at 200°C) in this study. A firm conclusion for the Q' phase is more difficult to make since the Cu-containing alloys show slower aging response at 200°C, (Figure 4.1). Therefore, the high hardness of the Cu-containing phases in the aging curves could be due to the Q' phase which still exist at 200°C (and results in higher hardness than the Q phase) and/or due to nature of the Cu-containing phases in general which are harder than the only Mg-containing phases.

Contrary to the R1 and R2 alloys, coarser precipitates in the interdendritic region are seen in the MG1 alloy, (Figure 4.26c). The EDS analyses on these reveal that these are the fine α -(Al-Cr-Mn-Fe-Si) precipitates whose size is lower than 300 nm, as shown in Figure 4.27a). Further spot analyses on the precipitates, (Figure 4.27b), showed that very fine ε -(Al-Si-Zr-Ti) (less than 300 nm) have also precipitated. It is interesting that the coarser eutectic ε phases (3-20µm), do not include any Ti whereas the fine precipitates do. During the EDS analyses, only the ε precipitates containing Ti was observed inside the dendrites but this does not mean that the Ti-free ε have not precipitated. As mentioned before, the ε -(Al-Si-Zr-Ti) precipitates were not observed in the as-solutionized alloys (Figure 4.21b). Therefore, the fine precipitates could have either precipitated during solutionizing and could not have been observed due to the challenges of the EDS spot analyses at high magnifications or they have precipitated during the aging treatment at 200°C.

84



Figure 4.27 EDS spectra of the (a) α -(Al-Cr-Mn-Fe-Si) (b) ϵ -(Al-Si-Zr-Ti) precipitates inside the aluminum dendrite of the over-aged MG1 alloy.

Furthermore, the equilibrium β -Mg₂Si precipitates as well as the Si clusters are also likely to present in the over-aged state of the MG1 alloy, however, there is no sufficient evidence to support this statement. It can be concluded that the phase identification of the fine precipitates (less than 500nm) is very challenging due to the resolution of the FEGSEM.

Figure 4.26d shows the precipitates in the intradendritic region of the over-aged MG2 alloy. It can be seen that the amount of precipitates in MG2 is the highest among four alloys. This is mainly due to combined addition of Cu, Zr, Cr and Mn. The peritectic additions cause the formation of fine ε -(Al-Si-Zr-Ti) and α -(Al-Cr-Mn-Fe-Si) phases. The Cu-and Mg-containing age-hardening phases are also believed to be present in the microstructure. The peritectic elements could have a positive effect on the density, the morphology and/or even the composition of the age-hardening phases (Q and β). Similarly the Cu addition also might have influenced the ε -(Al-Si-Zr-Ti) and α -(Al-Cr-Mn-Fe-Si) precipitates. A firm conclusion on the precipitate sequence and identification can only be made with a detailed TEM work on four alloys. The increased amounts of precipitates not only in the interdendritic but also inside the dendrites in the MG2 alloy are responsible for the improved creep, hardness and tensile strength at high temperatures.

4.6 Synopsis

Two new alloys, MG1 (A356+0.15%Cr+0.15%Zr+0.15%Mn) and MG2 (A356+0.15%Cr+0.15%Zr+0.15%Mn+0.5%Cu) were developed and tested. The commercial A356 (R1) and 0.5%Cu added A356 (R2) were studied as reference alloys as well. A summary of the elevated temperature mechanical properties of the alloys are presented in Table 4.4.

Table 4.4 Summary of the Elevated Temperature Mechanical Properties of the Alloys

	At 250°C		At 200°C, 200 hours	At 300°C, 300hours, 30 MPa	
Alloy Code	UTS	% F	Hardness (HRB)	% Creen	
	[MPa]	70 L		% creep	
R1	126	5.06	-	15.52	
R2	152	3.17	23.6	16.82	
MG1	128	4.86	-	14.27	
MG2	161	4.07	28.7	4.95	

It can be seen that the R2 alloy, which is currently used in diesel cylinder heads, shows good high temperature strength and hardness over the commercial A356 alloy (R1), although it displays lower ductility. The improvement is possibly due to the Cu-containing age-hardening phases which form after the solutionizing treatment and grows during aging. However, the Cu addition does not improve the creep resistance of A356. Therefore, it is believed that this alloy would experience crack initiation and fracture especially near the places close to the water ducts inside the engine due to the creep deformation.

The Cr, Zr and Mn additions alone to A356 do not bring a significant improvement in strength and hardness, as in the MG1 alloy. However, the creep resistance of the A356 is improved by 8%. The fine ε -(Al-Si-Zr-Ti) and α -(Al-Cr-Mn-Fe-Si) precipitates inside the dendrites are believed to retard the dislocation creep whereas the precipitates around the dendrites are good for diffusional and grain boundary creep occurring at 300°C. In MG2, the combined additions of Cu and peritectic elements led to the highest UTS and hardness among all the alloys. MG2 also exhibits better elongation than R2. It can be presumed that inside the engine, the potential stress caused during the engine cool-down could be accommodated elastically due to the higher strength, at the same time the possible the crack initiation could be delayed to further stages because of the improved ductility in the MG2 alloy. Moreover, it has three times better creep resistance at 300°C than any of the alloys making it even more promising for delaying the formation of the creep induced thermal-fatigue. Therefore, the MG2 alloy is superior to R2, the current diesel engine alloy, because it has higher strength, ductility and creep resistance. It should be emphasized here that MG2 has high potential for development into a promising cylinder head alloy for diesel engines.

The superior mechanical properties of the MG2 alloy are attributed to the increased amount of fine precipitates both inside and around the dendrites after the over-aging treatment. This significant improvement is only noted with the combined addition suggesting that either the peritectic elements or Cu have a positive effect on the precipitation behavior of the possible precipitates e.g. α , ε , β and Q.

CHAPTER 5 CONCLUSIONS

Based on the results presented in the previous chapter, the following conclusions were derived.

- The trace additions of Cu, Zr, Mn and/or Cr do not seem to play an important role in the SDAS of the permanent mould cast alloys.
- 160 ppm Sr in all alloys changes the acicular morphology of the eutectic Si into a more fibrous form.
- 0.3% Mg in the A356 alloys forms the β-Mg₂Si and π-Al₈Mg₃FeSi₆ phases. When
 0.5% Cu is added into A356, the β phase disappears and the eutectic θ-CuAl₂ and
 Q-Al₅Mg₈Cu₂Si₆ phases form in the interdendritic region. All Mg- and Cu containing phases dissolve during the solutionizing treatment.
- The 0.15% Cr and 0.15% Mn additions in A356, cause the formation of blocky type α -(Al-Cr-Mn-Fe-Si) phase instead of the needlelike β -Al₅FeSi phase. The 0.15% Zr forms the eutectic platelike ϵ -(Al-Si-Zr) phase instead of the peritectic binary Al₃Zr in A356 alloys. Sometimes, Ti is also observed in this new ternary phase. Both the eutectic α and ϵ remain in the interdendritic region after solutionizing.
- The solutionizing treatment at 500°C for 4 hours and at 540°C for 10 hours (T7) causes the precipitation of fine (less than 400nm) α -(Al-Cr-Mn-Fe-Si) and ϵ -(Al-Si-Zr) precipitates inside the dendrites of the alloys which have peritectic additions.

- The total amount of precipitates inside the α -Al dendrites of the MG2 alloy is higher due to the combined addition of Cr, Zr, Mn and Cu at the over-aged condition.
- The solutionizing and over-aging have a refinement effect on the eutectic phases in the microstructure.
- The MG2 alloy has the highest peak hardness of 61.2 HRB, followed by MG1 (54.9 HRB), R2 (53.6 HRB) and R1 (48.9 HRB). The maximum peak strength in all alloys occurs within an hour of aging due to the high over-aging temperature, 200°C, at which the aging is carried out.
- At the end of 200 hours of aging at 200°C, the hardness decreases significantly in all alloys, however, the MG2 alloy still has superior aging behavior having a hardness value of 28.7 HRB.
- The precursors of the Cu-containing phases have slower growth kinetics resulting in slower over-aging behaviour than the only Mg-containing phases. Therefore, Cu-containing phases are more thermally stable than the only Mgcontaining phases.
- The Cr, Zr and Mn additions alone have a negligible effect on the room temperature tensile strength of the A356 alloy in T7 condition, whereas the 0.5% Cu addition significantly increases the YS and UTS. The combined addition of Cr, Zr ,Mn and Cu gives the highest YS of all the alloys.
- At 150°C and 250°C, highest YS and UTS are obtained with the MG2 alloy having combined additions.

- At room temperature and 150°C, the Cr, Zr and Mn additions result in lower elongation values as in the MG1 and MG2 alloys. However, at 250°C this effect seems to decrease since all the alloys except for R2 exhibit similar elongation values.
- The 0.5% Cu addition only improves the compressive creep resistance of the A356 alloy at the early stages of the creep testing at 300°C. On the other hand, the peritectic additions alone as in the MG1 alloy cause a slight but consistent decrease (approximately 8-14%) in the % total creep of the A356 alloy.
- The MG2 alloy shows superior creep resistance almost three times better than all of the alloys at all stages of the creep testing (up to 300 hours).

CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

Based on the results and conclusions presented previously, the following recommendations for future work are made.

- A detailed transmission electron microscopy (TEM) study should be utilized to better understand the effect of alloying elements on the precipitation sequence and on the nature of the precipitates in the alloys studied.
- Future research may also perform similar tests using different combinations of peritectic elements such as V, Nb, Co, Ta...as well as different amounts of those. An optimum Mg and Cu level should be determined in Al-Si alloys, which gives a good combination of strength and ductility in T7 condition.
- In order to improve the ductility, degassing can be made prior to casting. Hot isostatic pressing can be performed prior to uniaxial mechanical tests to eliminate the microporosity. However, this treatment is not believed to be feasible due to the complex diesel block/head shape in the service use. Therefore, the effect of alloying on the porosity can also be studied via using different microscopy methods.
- If possible, the soaking time should be extended (up to 500-1000 hours) during the tensile tests at elevated temperatures. This parameter can be also studied since it plays an important role in the applications where alloys are exposed to stresses for longer times.
- Mechanical-fatigue tests at the mean diesel cycle temperature as well as the thermal conductivity and expansion tests should be performed, to estimate the

" $\sigma_f k/E\alpha$ " parameter and to see actually that alloys with a high number exhibit better performance.

- Similar compressive creep tests at different conditions (varying T°C and stresses) should be performed to see if the significant improvement in the MG2 alloy is consistent.
- Non-isothermal DSC tests can evaluate the precipitation temperatures of the new precipitates in new alloys. This could also be supported with the thermo calculations, TEM and aging studies.
- Similar aging experiments can also be performed at different temperatures. Higher aging temperatures than 200°C would give an idea about the further over-aged condition whereas the artificial aging temperatures such as 165°C can be used to determine the maximum strength that can be achieved with the MG2 alloy. This could be very useful for other applications where A356 (T6) is currently used due to its high strength.

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APPENDIX A

Pare 1 de	LIMITES	GROUPE	∞ J O U A U N H		1111	თთთთ	ហហហហ	<u>م</u> مم	ພ ພ ພ ພ	0000	ECHANT. 1 1 1 1	Id du'Grou Analyste
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	0.005	0.002 6.17%	0.003 0.003 0.002 0.002 0.002 0.002 0.002 0.002	0.00216 0.00216 0.002 0.06%	0.00220 0.00222 0.002 0.37%	0.00224 0.00223 0.002 0.20%	0.00226 0.00221 0.002 1.42%	0.00229 0.00232 0.002 0.79%	0.00246 0.00243 0.002 0.68%	0.00250 0.00252 0.003 0.71%	N1 0.00248 0.00258 0.003 2.90%	t Final d'An
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	0.14 0.1	0.11 0.95%	0.11 0.11 0.11 0.11 0.11 0.11 0.11 0.11	0.10910 0.10691 0.11 1.44%	0.11008 0.10840 0.11 1.09%	0.10810 0.10752 0.11 0.38%	0.11083 0.10637 0.11 2.91%	0.10900 0.10792 0.11 0.71%	0.11067 0.10858 0.11 1.35%	0.10921 0.10954 0.11 0.21%	Ti 0.11228 0.10973 0.11 1.63%	44502
	0.005	0.000 17.51%	0.000	-0.00012 -0.00022 0.000 40.85%	-0.00020 -0.00025 0.000 17.53%	-0.00019 -0.00016 0.000 12.06%	-0.00013 -0.00020 0.000 29.12%	-0.00022 -0.00019 0.000 10.87%	-0.00009 -0.00034 0.000 80.56%	-0.00029 -0.00024 0.000 12.23%	Pb -0.00017 -0.00018 0.000 0.18%	Alliage
	0.01	0.00 7.21%	0.0000000000000000000000000000000000000	-0.00005 -0.00005 0.00 4.27%	-0.00006 -0.00005 0.00 8.07%	-0.00005 -0.00005 0.00 2.74%	-0.00006 -0.00005 0.00 9.72%	-0.00005 -0.00006 0.00 15.91%	-0.00005 -0.00005 9.90%	-0.00004 -0.00005 0.00 11.83%	Cd -0.00006 -0.00005 0.00 14.78%	Concer : 356AC
	0.005	0.000	0.001 0.000 0.000 0.001 0.001 0.001 0.001	0.00044 0.00033 0.000 21.16%	0.00057 0.00055 0.001 2.74%	0.00035 0.00032 0.000 6.77%	0.00058 0.00052 0.001 7.23%	0.00041 0.00061 0.001 27.97%	0.00040 0.00051 0.000 16.92%	0.00034 0.00049 0.000 26.77%	B 0.00085 0.00056 0.001 28.49%	ntration

As-received Composition of A356 Ingots.

Page 2 de 3	LIMITES	GROUPE	9 4 9 5 7 9 4 9 4 9 4 9 4 9 4 9 4 9 4 9 4 9 4 9	00 00 00	777	თთთთ	თ თ თ თ	444	ເບ ເບ ເບ ເບ	0000	ECHANT. 1 1 1 1 1	Id du Grou Analyste :
	MAX MIN	MOY ETR	MOY MOY MOY MOY MOY	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	ETIN. ET 1 2 MOY ETR	pe: 0817700 NP
	0.0001	0.0000 0.70%	0.0000	0.00001 0.00001 0.0000 0.86%	0.00001 0.00001 0.0000 1.62%	0.00001 0.00001 0.0000 1.02%	0.00001 0.00001 0.0000 1.80%	0.00001 0.00001 0.00000 1.44%	0.00001 0.00001 0.0000 1.64%	0.00001 0.00001 0.0000 2.45%	Be 0.00001 0.00001 0.0000 0.96%) Lo
	0.001	0.000 38.08%	0.000	-0.00006 -0.00006 0.000 1.21%	-0.00004 -0.00003 0.000 20.41%	-0.00005 -0.00001 0.000 83.18%	-0.00006 -0.00005 0.000 14.29%	-0.00006 0.000 8.69%	-0.00002 -0.00004 0.000 52.21%	-0.00003 -0.00006 0.000 32.29%	Bi -0.00004 0.00000 0.000 0.000 166.48%	ocation: Ling
	0.001	0.000 14.21%		0.00006 0.00005 0.000 11.85%	0.00005 0.00010 0.000 45.29%	0.00005 0.00005 0.000 0.44%	0.00007 0.00005 0.000 23.84%	0.00005 0.00005 0.99%	0.00006 0.00005 9.18%	0.00006 0.00005 0.000 14.58%	Ca 0.00008 0.00005 0.000 36.11%	otiere
	0.02	0.00 2.56%	00000000000000000000000000000000000000	0.00063 0.00063 0.00 0.31%	0.00063 0.00062 0.99%	0.00063 0.00064 0.00 1.70%	0.00064 0.00064 0.00 0.48%	0.00064 0.00065 0.00 1.35%	0.00066 0.00065 0.00 1.61%	0.00067 0.00067 0.00 0.16%	Cr 0.00067 0.00067 0.00 0.00 0.21\$	Usage: A
	0.02	0.01 0.78%	0.01 0.01 0.01 0.01 0.01 0.01	0.01178 0.01172 0.01 0.40%	0.01168 0.01163 0.01 0.29%	0.01187 0.01196 0.01 0.51%	0.01165 0.01186 0.01 1.23%	0.01160 0.01181 0.01 1.26%	0.01176 0.01175 0.01 0.08%	0.01184 0.01197 0.01 0.77%	Ga 0.01158 0.01193 0.01 2.07%	, Li 1
	0.00035	0.00014 2.96%	0.00014 0.00014 0.00014 0.00014 0.00014 0.00014 0.00014 0.00015 0.00015	0.00015 0.00015 0.00015 2.09%	0.00015 0.00015 0.00015 0.66%	0.00014 0.00014 0.00014 0.91%	0.00015 0.00014 0.00014 1.43%	0.00014 0.00014 0.00014 0.14%	0.00014 0.00015 0.00014 1.62%	0.00014 0.00014 0.00014 0.46%	Li 0.00014 0.00014 0.00014 0.00014 1.04%	Sp
	0.001	0.000	0.0000000000000000000000000000000000000	-0.00001 -0.00002 0.000 42.71%	-0.00002 -0.00002 0.000	-0.00003 -0.00003 0.000 4.60%	-0.00001 -0.00003 0.000 47.12%	-0.00002 -0.00002 0.000 1.31%	-0.00002 -0.00002 0.000	-0.00001 -0.00002 0.000 36.15%	Na 0.00000 -0.00001 0.000	ec: Alcan -
	0.001	0.000 7.21%	0.001 0.000 0.000 0.001 0.001 0.001 0.001 0.001	0.00055 0.00045 0.001 14.60%	0.00053 0.00039 0.000 21.55%	0.00052 0.00051 0.001 1.13%	0.00053 0.00051 0.001 3.88%	0.00050 0.00051 0.001 0.66%	0.00062 0.00037 0.000 35.01%	0.00037 0.00046 0.000 16.18%	P 0.00047 0.00054 0.001 9.87%	44502
	0.01	0.00 1.41%	0.0000000000000000000000000000000000000	-0.00119 -0.00114 0.00 2.89%	-0.00116 -0.00112 0.00 2.46%	-0.00112 -0.00121 0.00 5.16%	-0.00114 -0.00116 0.00 1.24%	-0.00115 -0.00116 0.00 0.29%	-0.00113 -0.00120 0.00 4.40%	-0.00114 -0.00111 0.00 1.72%	Sb -0.00111 -0.00114 0.00 1.61%	Alliage:
	0.002	0.000 2.86%	0.0000	0.00027 0.00027 0.000 1.11%	0.00026 0.00027 0.000 3.05%	0.00030 0.00025 0.000 13.29%	0.00024 0.00028 0.000 10.37%	0.00028 0.00025 0.000 7.80%	0.00029 0.00024 0.000 14.66%	0.00028 0.00028 0.000 0.20%	Sn 0.00028 0.00024 0.000 9.46%	356AC
	0.005	0.000 39.11%	0.001	0.00022 0.00023 0.000 4.80%	0.00026 0.00022 0.000 11.74%	0.00023 0.00021 0.000 6.09%	0.00045 0.00025 0.000 40.34%	0.00025 0.00034 0.000 20.84%	0.00026 0.00028 0.000 7.12%	0.00038 0.00026 0.000 24.73%	Sr 0.00065 0.00054 0.001 12.76%	racion

As-received Composition of A356 Ingots.

Carry entry entry Control in any entry Description Control in any entry Control in any entry<														
Instruction Instruction <thinstruction< th=""> <thinstruction< th=""></thinstruction<></thinstruction<>	Page 3 de	LIMITES LIMITES	GROUPE GROUPE	ч си си ч си си ч ч си си ч си си си си си	∞ ∞ ∞ ∞	7 7 7	୶୶୶୶	ហហហហ	<u>م</u> م م م	ພ ພ ພ ພ	N N N N	ECHANT. 1 1 1 1	Id du Gro Analyste	1007.187.18
Instruction Instruction <thinstruction< th=""> <thinstruction< th=""></thinstruction<></thinstruction<>	ω	MAX MIN	MOY ETR	MOY MOY MOY MOY	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	1 2 MOY ETR	ETIN. ET 1 2 MOY ETR	upe: 081770 : NP	LU:U/:51 A
Decension of a Penper Final d'Analyse Concentration vature: interriter territer per: final d'Analyse Attaure: state a a per: final d'Analyse per: final d'Analyse Attaure: state a a per: final d'Analyse per: final d'Analyse Attaure: state a a a per: final d'Analyse Attaure: state a a a a a a a a a a a a a a a a a a a a a a a a a a a a a a <td< td=""><td></td><td>0.02</td><td>0.01 0.75%</td><td>0.01 0.01 0.01 0.01</td><td>0.01376 0.01351 0.01 1.33%</td><td>0.01359 0.01352 0.01 0.36%</td><td>0.01365 0.01375 0.01 0.52%</td><td>0.01379 0.01357 0.01 1.16%</td><td>0.01358 0.01363 0.01 0.24%</td><td>0.01371 0.01367 0.01 0.01 0.17%</td><td>0.01370 0.01385 0.01 0.76%</td><td>V 0.01383 0.01393 0.01 0.51%</td><td>0 Lo</td><td>M</td></td<>		0.02	0.01 0.75%	0.01 0.01 0.01 0.01	0.01376 0.01351 0.01 1.33%	0.01359 0.01352 0.01 0.36%	0.01365 0.01375 0.01 0.52%	0.01379 0.01357 0.01 1.16%	0.01358 0.01363 0.01 0.24%	0.01371 0.01367 0.01 0.01 0.17%	0.01370 0.01385 0.01 0.76%	V 0.01383 0.01393 0.01 0.51%	0 Lo	M
BEDA400-035 - Rapport Fund ('Analyse Concentration Usag: A' Spc: Alen * 4502 Allage: 3562		0.01	0.00 1.04%	00000000000000000000000000000000000000	0.00156 0.00154 0.00 0.00 0.75%	0.00157 0.00155 0.00 0.00 0.99%	0.00158 0.00155 0.00 1.16%	0.00158 0.00153 0.00 2.16%	0.00155 0.00156 0.00 0.53%	0.00161 0.00155 0.00 2.65%	0.00159 0.00159 0.00 0.00 0.23%	Zr 0.00158 0.00159 0.00 0.26%	ocation: Lingotiere	
nal d'Anaiye Concentration Spec: Alcan - 4502 Alliage: 356A													Usage: AF	BEA4460-0365 - Rapport Fi
Concentration Alliage: 356AC													Spec: Alcan - 44502	nal d'Analyse
													Alliage: 356AC	Concentration

As-received Composition of A356 Ingots.

Alloy Code	A (mg)	B (mg)	C (mg)
R1-T31	0.019	0.018	0.021
R2-T32	0.018	0.020	0.019
MG1-T34	0.021	0.018	0.021
MG2-T35	0.020	0.018	0.023

Alloy Codes and Actual Weight of the Samples for the DSC Tests.

S	GS	Adresse : Address: À l'attention	346 Moi n de:	5 Durocher ntreal, Qc			NOM DE LA I NAME OF PA Commande N°: P.O. N°.:	PIÈCE : Alumi RT : PO154551	Date:	2008-07-01
		N° Dossier:	Pier	D-08172-1			Marque pièce:		Coulée Nº:	
		File N°: Notre N° Équ	ipement.:	07		-	Piece Mark :	N/A	Heat N°:	N/A
		Our Equipmen	nt Nº.: RX	-07			Control Nº.:	N/A	Joint Nº:	N/A
		Order:	N//	4			Matériau : Material :	Aluminum Alloy	Epaisseur : Thickness :	0.260"
	RAP	PORT RAD	OIOGRA	PHIQUE	: /	RAI	DIOGRAI	PHIC REP	PORT	
Source: S.F.D.:	32"		Proc. de so Weld proce	ud.: ess:		No.	Fil N	1et :		
Dimensions : Size :	1.5mm		Proc. de so Weld proce	ud.: edure :				e.	10 10 10 10 10 10 10 10 10 10 10 10 10 1	
Kv Ci: Ci Kv:	70kV, 4.0mA									
Temps : Time :	35 sec		État de la si Casting finis	urface coulée: sh:	AS	CAST	r			
Pen :	10									
Film : Écran:	AGFA D7	v. / Fr.	Norme d'ac Acceptance	ceptation: Std:		clic	its -	Ref A	som k	155
Screens:	NIL A	ur. / Bk.	R.S.S. N°.:							
Film N°.	Cote Rating		Remarques Remarks	a constant	F N	ilm N°.	Cote Rating		Remarque Remarks	s
41 A	1	INCLUSI	in gRADe	3	41	B		SHRIN	K SPase	is ghave.
51 A				2	51	B		5.1	. 1 .	2
65 A	-	SPANCE	suin lie	1	65	B	-	Incuis	on grad	e 2
66 A	-	11	h	1	66	В		SHAWK	spange	2 F
67 A					67	В		SHICHNI	operior	0
68 A					68	В	-	14.11.14	00 00	110 2
69 A	-	SPONGE :	SHRIJK	2	69	В		- nocus	you you	2
70 A	-	INCLUSION	GOMP.	3	70	В	-	SUL ILE	P. L. H	11
71 A	-		paneo	-	71	В		SULA	SPONGE SA SIC	2
72 A		SPORGE SH	HINKA	1	72	В	-	SHO JK C	Pa (26	2
73 A		4	h	1	73	В	-	INCLUCIO	i Ga	loe I
74 A	-	11	h	1	74	В	-	Lifely Cin	A GOAR	0 1
75 A	-				75	В	-	INCLUSIO	1 CRAA	1
76 A	~				76	В	-	INCLUSIO	S GRADE	2
Cote « A » :	Acceptable	Superviseur de la ra Radiography Sup	diographie: ervisor:	N.I	NEDIR/	J.HAN	NA		2008- Di	07-01
Cote « R » Rating marked "A Rating marked "	: Rejeté A'': Acceptable "R": Rejected	Réviseur du Film Review Inspecteur du	film: rer: client:		-				Da	te
		Customer Insp	ector:		-			-	Da	te
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Typical Radiographic Report of the Tensile Bars.





Typical Stress-Strain Curves of the R1 alloy at 25°C, 150°C and 250°C.

Alloy Code	Testing Temperature	Y.S	UTS	% E
	(° C)	[MPa]	[MPa]	
R1-T5	25	277.85641	246.83026	3.0
R1-T5	25	281.99323	250.96708	3.0
R1-T78	25	242.69344	230.97245	2.5
R1-T78	25	257.17231	228.21457	2.5
R1-T3	150	219.94093	201.32524	3.5
R1-T3	150	222.69881	207.53047	3.0
R1-T67	150	215.80411	202.70418	4.0
R1-T67	150	210.28835	193.74107	2.5
R1-T5	250	126.86248	123.41513	5.5
R1-T5	250	129.62036	128.93089	7.0
R1-T66	250	137.20453	135.82559	3.5
R1-T51	250	134.44665	130.9993	6.0
R1-T40	250	126.86248	125.48354	3.0
R1-T40	250	126.17301	124.1046	4.0
R1-T31	250	111.69414	111.00467	6.5
R1-T31	250	115.14149	111.69414	5.0

Tensile Properties of the R1 Alloy at Various Temperatures.



Typical Stress-Strain Curves of the R2 alloy at 25°C, 150°C and 250°C.

Allow Codo	Testing Temperature	Y.S	UTS	0/. F
Alloy Code	(° C)	[MPa]	[MPa]	70 E
R2-T75	25	275.09853	249.58814	3.0
R2-T76	25	282.6827	249.58814	3.5
R2-T29	25	265.44595	248.2092	2.5
R2-T29	25	279.23535	247.51973	2.8
R2-T71	150	225.45669	209.59888	4.0
R2-T68	150	229.59351	211.66729	3.0
R2-T24	150	220.6304	205.46206	2.8
R2-T24	150	224.07775	206.841	3.0
R2-T68	250	148.92552	145.47817	3.0
R2-T46	250	144.7887	139.27294	3.5
R2-T45	250	156.50969	149.61499	3.0
R2-T45	250	153.06234	148.92552	2.0
R2-T32	250	146.16764	136.51506	3.5
R2-T32	250	160.64651	152.37287	4.0

Tensile Properties of the R2 Alloy at Various Temperatures.



Typical Stress-Strain Curves of the MG1 alloy at 25°C, 150°C and 250°C.

	Testing Temperature	Y.S	UTS	0/ F
Anoy Code	(° C)	[MPa]	[MPa]	70 E
MG1-T11	25	277.85641	250.27761	1.5
MG1-T11	25	273.71959	247.51973	2.0
MG1-T74	25	277.85641	250.27761	1.5
MG1-T74	25	273.71959	247.51973	2.0
MG1-T38	150	205.46206	198.56736	1.0
MG1-T38	150	235.79874	212.35676	2.5
MG1-T9	150	220.6304	209.59888	1.5
MG1-T9	150	240.62503	215.11464	3.0
MG1-T7	250	124.79407	119.96778	4.5
MG1-T7	250	128.24142	126.17301	5.5
MG1-T27	250	127.55195	126.86248	5.5
MG1-T79	250	133.06771	131.68877	3.0
MG1-T79	250	132.37824	131.68877	4.5
MG1-T34	250	122.72566	121.34672	5.0
MG1-T34	250	124.1046	121.34672	6.0
MG1-T38 MG1-T38 MG1-T9 MG1-T9 MG1-T7 MG1-T7 MG1-T27 MG1-T79 MG1-T79 MG1-T34 MG1-T34	150 150 150 250 250 250 250 250 250 250 250 250 2	205.46206 235.79874 220.6304 240.62503 124.79407 128.24142 127.55195 133.06771 132.37824 122.72566 124.1046	198.56736 212.35676 209.59888 215.11464 119.96778 126.17301 126.86248 131.68877 131.68877 121.34672 121.34672	1 2 1 3 4 5 5 3 4 5 6

Tensile Properties of the MG1 Alloy at Various Temperatures.



Typical Stress-Strain Curves of the MG2 alloy at 25°C, 150°C and 250°C.

	Testing Temperature	Y.S	UTS	0/ E
Alloy Code	(° C)	[MPa]	[MPa]	%0 E
MG2-T4	25	279.92482	255.79337	1.5
MG2-T4	25	288.88793	265.44595	1.5
MG2-T73	25	253.03549	252.34602	1.5
MG2-T73	25	259.93019	251.65655	2.0
MG2-T8	150	237.86715	228.21457	1.5
MG2-T8	150	219.25146	214.42517	1.5
MG2-T44	150	239.93556	223.38828	2.0
MG2-T44	150	260.61966	234.4198	2.0
MG2-T72	150	218.56199	216.49358	1.5
MG2-T65	150	233.04086	218.56199	3.0
MG2-T10	250	159.26757	154.44128	2.5
MG2-T10	250	161.33598	148.23605	3.0
MG2-T22	250	155.82022	151.6834	4.0
MG2-T22	250	171.67803	162.71492	4.5
MG2-T65	250	149.61499	145.47817	3.0
MG2-T35	250	159.95704	149.61499	6.5
MG2-T35	250	164.78333	153.75181	5.0

Tensile Properties of the MG2 Alloy at Various Temperatures.



The isothermal DSC trace of the R1 alloy at 200°C.



The isothermal DSC trace of the R2 alloy at 200°C.



The isothermal DSC trace of the MG1 alloy at 200°C.



The isothermal DSC trace of the MG2 alloy at 200°C.





Compressive Creep Curves of the R1 alloy at 300°C under 30MPa.





Compressive Creep Curves of the R2 alloy at 300°C under 30MPa.





Compressive Creep Curves of the MG1 alloy at 300°C under 30MPa.





Compressive Creep Curves of the MG2 alloy at 300°C under 30MPa.