Effect of Cu addition on the microstructure, mechanical and thermal properties of a piston Al-Si alloy

Suwaree Chankitmunkong[1, a*], Dmitry G. Eskin[2, b] and Chaowalit Limmaneevichitr[1, c]

[1]Production Engineering Department, Faculty of Engineering, King Mongkut's University of Technology Thonburi, 126 Pracha-Utid Rd., Bangmod, Tungkhru, Bangkok, 10140 Thailand

[2]Brunel University London, BCAST, Kingston Lane, Uxbridge UB8 3PH, United Kingdom

[a*]suwaree.03@mail.kmutt.ac.th, [b]dmitry.eskin@brunel.ac.uk, [c]chaowalit.lim@mail.kmutt.ac.th

Abstract

Piston Al-Si alloys are widely used for high-temperature applications especially in automotive industry. Copper is one of the most important elements for improving the strength at room and elevated temperatures. Other effects of Cu addition need to be taken into account as well, i.e. the changes in microstructure and the coefficient of thermal expansion (CTE). We studied the effects of Cu addition to an AA4032 piston alloy on its structure and properties. Thermal analysis, metallography, thermodynamic calculations, hardness, tensile and dilatometer tests were conducted. The results showed that increased Cu addition promoted the formation of primary Si particles in this Al-Si alloy and enlarged its solidification range. The increase of Cu concentration from 1 to 3.5 wt% improves hardness, tensile properties, and CTE of the near-eutectic Al-Si alloys. This work contributes to deeper understanding the role of Cu in Al-Si piston alloys.

Keywords: Copper; Primary Si particles; Thermal analysis

1. Introduction

Al-Si piston alloys are mostly used in production of car engine components by the hot forging process because of good castability, lightweight, and wear resistance. However, their mechanical properties and thermal stability at high temperature rapidly decrease due to the brittle particles (primary Si particles) and unstable second phases as they can lead to premature cracking and failure [1, 2]. Alloying elements are typically added to improve the mechanical properties. For example, Cu additions in an Al-Si alloy can improve its properties at high temperature, including dimensional stability, hardness and tensile properties through the part lifetime [3, 4]. Other alloying elements such as Ni, Zr and Nd that form thermally stable phases are added for high-temperature applications [5, 6]. Piston aluminum alloys typically have near-eutectic composition in the Al-Si system, with multi-alloying elements that can form complex phases such as Al_2Cu, Mg_2Si, γ-Al_7Cu_4Ni, δ-Al_3CuNi and Q-$Al_5Cu_2Mg_8Si_6$ phase. These phases enhance the mechanical properties at high temperature. Previous works found that the addition of alloying

elements (i.e. Cu and Ni) also affected the amount of phases [7, 8]. As Cu is one of the essential additives, it is important to understand its role.

To develop piston alloys for subsequent production and final applications at high temperature one needs to take into account the microstructure development with regard to thermally stable phases. Therefore, the objective of this research work is to study the effect of Cu addition to a piston Al-Si alloy on the primary Si formation and phase composition using thermal analysis and Thermo-Calc calculation, as well as the effects on mechanical properties at room and high temperature, and the coefficient of thermal expansion.

2. Materials and methods

Experimental piston Al-Si alloys with different Cu concentrations were prepared using 99.99 wt% Al, high purity Si, Cu, Mg and Al-17 wt% Ni, Al-10 wt% Fe master alloys. The experimental alloys had the Cu content as Al-Si-1Cu and Al-Si-3.5Cu. The chemical compositions of the alloys were analyzed using emission spectrometry and given in Table 1. Each alloy was melted in a silicon carbide crucible using an induction furnace. The melt was covered by the flux and was degassed by argon gas purging. The impurities were then carefully removed before pouring. The melt was poured at 720 °C into a DC caster and billet 60 mm in diameter, 400 mm in length were cast at a casting speed of 190 mm/min. The microstructure was observed using optical microscopy (OM) after polishing the surface of the samples and etching by Keller's reagent (5 ml HNO_3, 3 ml HCl and 2 ml HF in 190 ml distilled water) for 20 s to observe primary Si particles. The size and area fraction of primary Si particles in the aluminum matrix were measured by I-Solutions DT image analysis software. Thermo-Calc software with the TCAL4 database was used to calculate the isopleths of the Al-Si phase diagram and to determine the mass fraction of primary Si particles and secondary phases at low and high Cu concentrations. To conduct thermal analysis and record the cooling curve, each of the specimen was heated above the liquidus temperature.The melt was then poured at 700 °C into a steel mold and the critical temperatures were recorded according to the standard [9]. The coefficient of thermal expansion (CTE) of the alloys was measured with a quench-deformation dilatometer DIL 805A/D in the temperature range 100–350 °C at a rate of 10 °C/s for heating and cooling in an argon atmosphere. Hardness tests were conducted using a Brinell hardness tester with 62.5 N load, 2.5 mm ball indenter, and 15 s dwell time. The tensile specimens were prepared according to ASTM B557B standard [10] with 6-mm gage wide, 25-mm gage length and 6-mm gage thickness, then were tested by a universal testing machine (Instron model 5969) at a strain rate of 0.01/s at different temperatures (25 °C, 250 °C, 350 °C).

Table 1 Chemical composition of Al-Si piston alloys as determined by emission spectrometry

Alloys	Elements (wt%)					
	Si	Cu	Mg	Ni	Fe	Al
Al-Si-1Cu	12.8	1.2	1.0	0.9	0.8	Balance
Al-Si-3.5Cu	12.7	3.5	1.0	0.8	0.9	Balance

3. Results and Discussion

3.1 Effect of Cu on primary Si particles and phase formation in solidification

Fig. 1 gives the microstructures of studied Al-Si alloys with different Cu concentrations. The results show that the addition of Cu in an Al-Si alloy increases the amount of the primary Si particles.

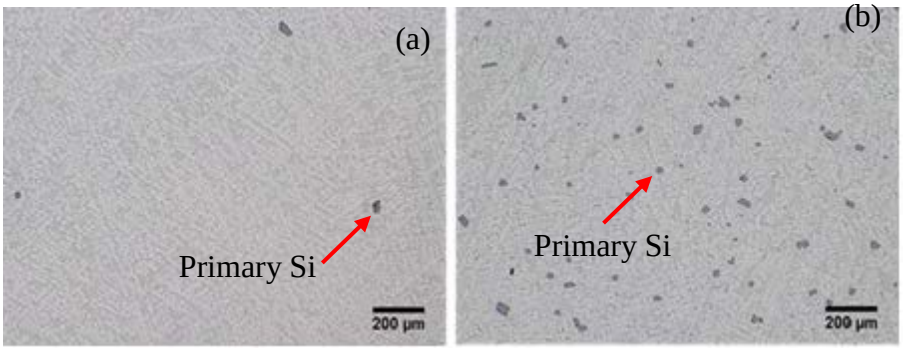

Fig. 1 Optical micrographs showing primary Si particles in piston alloys at different Cu contents; (a) Al-Si-1Cu (b) Al-Si-3.5Cu

Table 2 gives the amount of the primary Si particles measured by image analysis (the average size and area fraction) as well as the calculated results by Thermo-Calc with the mass fraction of primary Si particles. The results show that the average size of primary Si particles slightly decreases from 30±9 to 23±1 μm. The area fraction of the primary Si particles increases from 0.2% to 1.9%, which corresponded well to the calculated results that show an increase of mass fraction of the primary Si particles from 0.8% to 1.4% with the addition of Cu.

Figure 2 gives the amount of phases formed in Al-Si piston alloy at different Cu concentration during equilibrium solidification as calculated by Thermo-Cal software. It shows that the main possible phases in the piston Al-Si alloy include primary Si, θ-Al_2Cu, Mg_2Si, ε-Al_3Ni, γ-Al_7Cu_4Ni, δ-Al_3CuNi,

$Al_9Fe_2Si_2$, and Q-$Al_5Cu_2Mg_8Si_6$. We also observed, with the 3.5 wt% Cu addition, that there are more Cu rich phases such as θ-Al_2Cu and γ-Al_7Cu_4Ni. Therefore, increase in the amount of Cu not only affects to the amount of the primary Si particles but also contributes to an increase in the amount of the thermally stably phases, i.e. θ-Al_2Cu and γ-Al_7Cu_4Ni. Moreover, the calculated results also provide the information about the temperature range at which the different phases precipitate during solidification. We observe that the γ-Al_7Cu_4Ni phase starts to form at above 500 °C (Fig. 2b), followed by ε-Al_3Ni, θ-Al_2Cu and other phase precipitates. This reaction corresponds to the experimental cooling curve that have peaks at about 520 °C and 500 °C as indicated in Fig. 3b. Thus, the amount of Cu rich phases increases with increasing Cu due to the θ-Al_2Cu and γ-Al_7Cu_4Ni phases formation at the expense of the ε-Al_3Ni and δ-Al_3CuNi phases. This agrees with the sequence of peritectic–eutectic reactions of L → (α-Al+Si+ε), L+ ε → (α-Al+Si+ δ) and L+ δ → (α-Al+Si+ γ) [11, 12].

Table 2 The quantitative results of size, area fraction and mass fraction of Primary Si particles

Alloys	Size (μm)	Amount of Primary Si particles	
		Area fraction (%) (Image analysis by i-solution DT)	Mass fraction (%) (Calculation by Thermo-Calc)
Al-Si-1Cu	30 ± 9	0.3	0.8
Al-Si-3.5Cu	23 ± 1	1.9	1.4

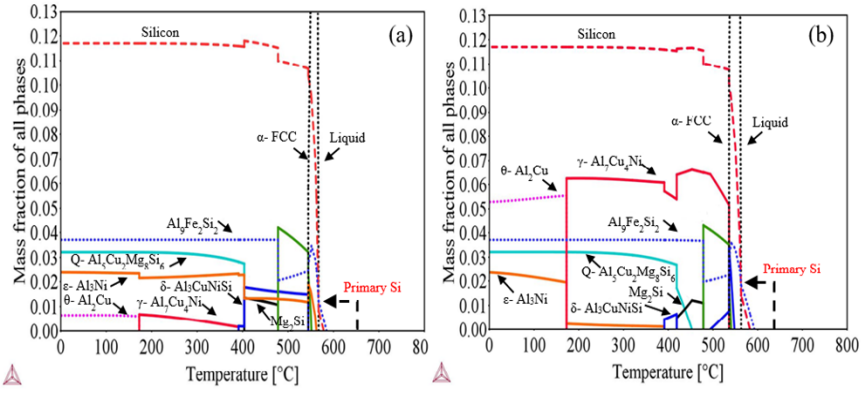

Fig. 2 Thermo-Calc results for the mass fraction development of constituent phases at different Cu contents; (a) Al-Si-1Cu (b) Al-Si-3.5Cu

3.2 Thermal analysis

Figure 3 shows the cooling curves and first derivative curves taken from the experimental alloys and compared with the calculated results of Al-Si phase diagram at low and high Cu concentrations, which supplements the experimental work. The characteristic temperatures of solidification were evaluated from the cooling curves to examine the nucleation and growth behavior of each phase, and summarized in Table 3. The nucleation temperature of primary silicon ($T_{N, Si}$), the nucleation temperature of eutectic Si ($T_{N, Eu}$), and the nucleation temperature of Cu rich phases ($T_{N, Cu}$) are marked in Fig. 3a-b. We observed that there are three characteristic points on the cooling curve of the low Cu alloy in Fig. 3a., the first point at 572 °C and the second point at 566 °C are due to the nucleation of primary Si and eutectic Si phases, respectively. The third point at about 526 °C, we speculate that this point results from the formation of Cu rich phases such as Q-$Al_5Cu_2Mg_8Si_6$ and γ-Al_7Cu_4Ni, which is consistent with previous works [3, 10]. On the other hand, the high Cu alloy shows four characteristic point (Fig. 3b), with the nucleation temperature of primary Si increasing to 581 °C and eutectic temperature decreasing to 562 °C. This shows that Cu addition to the Al-Si piston alloy enhances the nucleation of the primary Si and decreases the onset of eutectic solidification with the primary Si solidification range enlarging to 581-562 °C at 3.5 wt% Cu as compared to 572-566 °C at the 1 wt% Cu. Also the undercooling of eutectic reaction increases from about 6 °C to 19 °C (Table 3). The larger primary solidification range of the high Cu alloy results in the increase of the amount of primary Si particles and eutectic phases. In addition, it can be clearly seen that there are two peaks of Cu-rich phase formation at temperatures about 520 and 500 °C. This is because Cu addition results in the formation of more Cu-rich phases (mostly γ-Al_7Cu_4Ni and θ-Al_2Cu), which correlates to the increased amount of Cu-rich phases as can be seen in Fig. 2. Moreover, the calculations with Thermo-Calc show that the 3.5 wt% Cu addition to the Al-Si piston alloy moves the eutectic point to a lower Si content as compared to the 1 wt% Cu alloy as shown in Fig. 3c. The results agree with the cooling curves that show that the eutectic temperature of the high Cu alloy (562 °C) shifts to a lower temperature than that of the low Cu alloy (566 °C).

Table 3 Solidification characteristics of the experimental alloys

Alloys	Al-Si eutectic reaction				
	$T_{N, primary Si}$	$T_{N, Eutectic}$	$T_{undercooling}$	$T_{N, Cu rich phases}$ (i.e. γ, Q phases)	$T_{N, Cu rich phases}$ (i.e. θ phase)
Al-Si-1Cu	572	566	6	526	-
Al-Si-3.5Cu	581	562	19	520	500

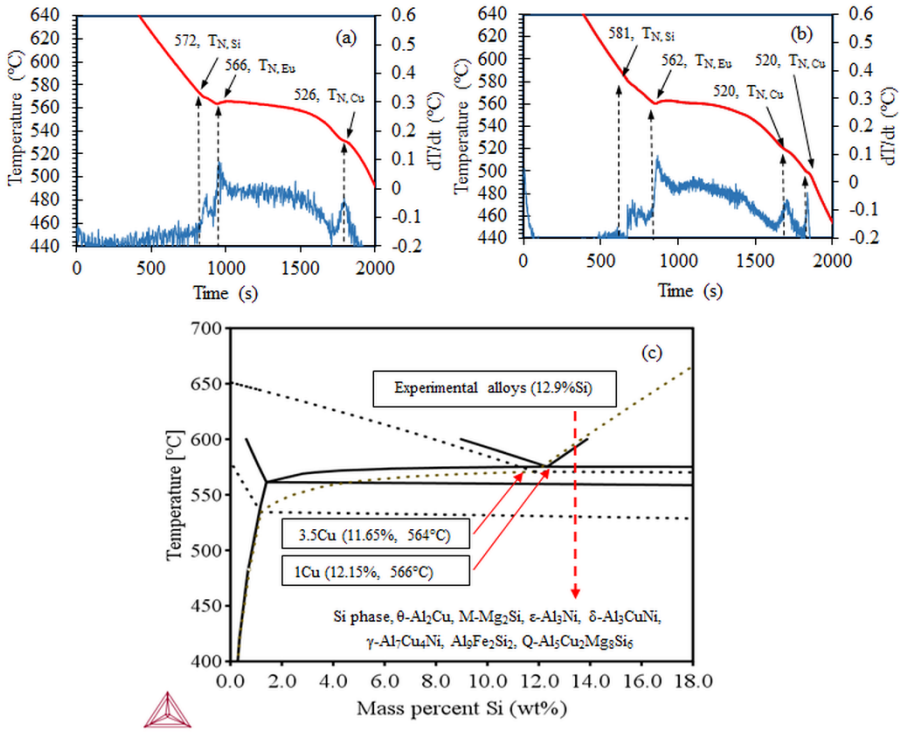

Fig. 3 The cooling curves and first derivative curves during solidification of piston Al-Si alloys; (a) Al-Si-1Cu and (b) Al-Si-3.5Cu with measured the characteristic points ($T_{N,Si}$, $T_{N,Eu}$ and $T_{N,Cu}$) at eutectic reactions, and (c) the isopleth of the equilibrium phases diagram with different Cu concentrations

3.3 Mechanical properties at room and high temperature

In general, the hardness of as-cast alloys depends on the presence of hard particles and on the solute-saturated solid solution. From the data given in Table 4, hardness of the Al-Si-3.5Cu alloy is about 138 HB, which is 16% higher compared to the Al-Si-1Cu alloy. Obviously, the Cu addition to Al-Si alloy leads to an increase in the amount of hard primary Si particles. In addition, the other phases in the high Cu alloy such as θ-Al_2Cu and γ-Al_7Cu_4Ni contribute to the hardness increase. The average values of tensile properties including ultimate tensile strength (UTS), yield strength (YS) and percentage elongation (%El) of the experimental alloys at different temperatures are shown in Table 4 (standard deviations of the averages shown in bracket below each values). At room temperature, the increased amount of Cu somewhat improves UTS, which may reflect supersaturation of the aluminum solid solution with Cu upon solidification. At the same time, the ductility decreases indicating the increased amount of excess phases

such as Si, θ-Al_2Cu and γ-Al_7Cu_4Ni (Fig. 2). At 250 °C, this advantage in the tensile strength disappears (Table 4), apparently due to the decomposition of the aluminum solid solution and partial dissolution of Al_2Cu and Mg_2Si phases. These phases usually start coarsen and dissolve at temperatures above 200 °C as has been reported elsewhere [13-15]. The low-Cu alloy gains better tensile properties due to the lesser amount of secondary brittle phases. When the testing temperature increases to 350 °C, the high-Cu alloy equals the low-Cu alloy in strength but demonstrates significantly higher ductility (15.5.% as compared to 8.5%, Table 4). Although not completely understood, this effect may be due to a combination of dissolving phases such as Al_2Cu and Mg_2Si [16] with the overall better stress distribution upon tensile deformation due to a more heterogeneous structure with relatively fine particles of thermally stable phases such as γ-Al_7Cu_4Ni and Q-$Al_5Cu_2Mg_8Si_6$ [17]. Therefore, the improvement in tensile properties at low and high temperatures in the alloy with 3.5% Cu can be achieved due to the effects of solution hardening (at low temperature) and more uniform deformation (at higher temperatures).

Table 4 Hardness and tensile properties of Al-Si piston alloys with low and high Cu concentration at room elevated temperature with standard deviations in brackets

Alloys	Hardness (HB) (25°C)	Temperatures								
		25 °C			250 °C			350 °C		
		UTS (MPa)	YS (MPa)	El (%)	UTS (MPa)	YS (MPa)	El (%)	UTS (MPa)	YS (MPa)	El (%)
Al-Si-1Cu	115	274 [3.6]	140 [2.6]	0.91 [0.3]	241 [3.1]	128 [4.1]	2.5 [0.2]	113 [4.6]	70 [5.3]	8.5 [0.7]
Al-Si-3.5Cu	138	297 [6.5]	144 [6.1]	0.84 [0.2]	233 [4.5]	105 [10.1]	1.5 [0.1]	110 [6.8]	67 [5.2]	15.5 [1.5]

To clarify the failure behavior and fracture mode of piston Al-Si alloys with Cu additions, longitudinal sections normal to the fracture surface of the tensile tested specimens at room and elevated temperature were examined and shown in Fig. 4. The high-Cu alloy, at room temperature, mainly cracks along the primary Si particles as compared to the Al-Si-1Cu alloy. When the temperature reaches 250 °C, the fracture path of the low-Cu alloy is more transgranular. On the other hand, the high-Cu alloy shows the fracture path going through the trans-dendritic regions as well as through the eutectic regions and primary Si. This correlates with decreasing ductility. In addition, this alloy changes the fracture behavior from brittle to ductile because of high-temperature effects, i.e. at 350 °C, such as secondary phases (Al_2Cu, Mg_2Si) dissolution and the easier deformation of the ductile Al matrix, while other thermally

stable phases still retained in the structure. The fracture path is transgranular, which agrees well with the improved ductility.

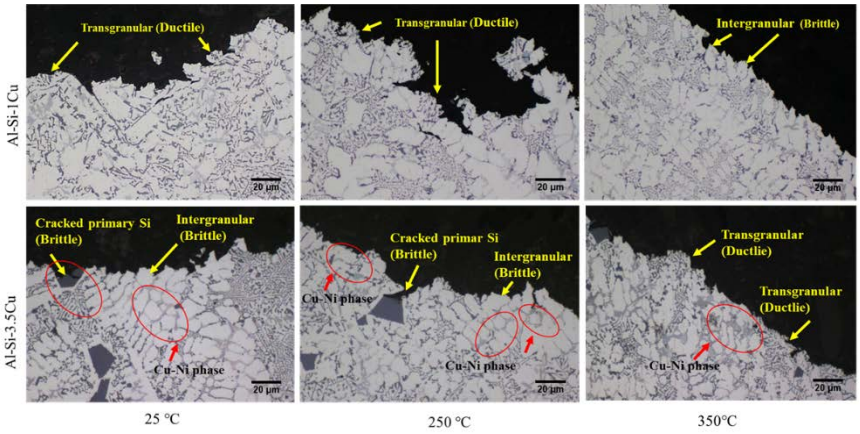

Fig. 4 Fracture surface of tensile tested of experimental alloys; (a) Al-Si-1Cu (b) Al-Si-3.5Cu, and each alloys were conducted at different temperatures; (a, d) 25 °C, (b, e) 250 °C, (c, f) 350 °C

3.4 Coefficient of thermal expansion (CTE)

Thermal stability of piston Al-Si alloys with Cu additions was assessed by the coefficient of thermal expansion (CTE). The results show that the CTE of the Al-Si-1Cu alloy tends to increase with temperature, especially at above 300 °C. On the other hand, the CTE is constantly lower with the addition of 3.5 % Cu. This advantage becomes even more pronounced at temperatures above 300 °C as demonstrated in Table 5. This phenomenon can be attributed to the stability of secondary phases. At temperatures above 200 °C, low melting secondary phases in the alloy, particularly Al_2Cu and Mg_2Si phases, start to dissolve. However, the stability of other Cu rich phases such as γ-Al_7Cu_4Ni and Q-$Al_5Cu_2Mg_8Si_6$ can be retained over 300 °C, which results in better stability of this alloy at high temperature (300-350 °C).

Table 5 The variation of coefficient thermal expansion (CTE) with temperature for Al-Si piston alloys with low and high Cu concentration

Alloys	Coefficient Thermal Expansion, CTE (x10 $^{-6}$ K)
	Temperature range

	100 °C - 200 °C	200 °C - 300 °C	300 °C - 350 °C
Al-Si-1Cu	17.6	19.5	21.2
Al-Si-3.5Cu	16.5	18.5	19.5

4. Conclusions

- Addition of Cu to near-eutectic piston Al-Si alloys significantly increases the amount of primary Si particles and thermally stable phases due to the eutectic composition shift to lower Si and the increased solidification range.
- An addition of 3.5 wt% Cu to the Al-Si piston alloy results in the change from ε-Al_3Ni, δ-Al_3CuNi to θ-Al_2Cu and γ-Al_7Cu_4Ni, with corresponding increase in the mass fraction of these phases. Increasing amount of these phases is most effective in improving the dimensional stability in terms of the CTE at high-temperature exposure.
- With the increase of Cu content in the piston Al-Si alloy, hardness properties increased to 138 HB. The room temperature tensile strength improved from 274 to 297 MPa with retained elongation. At the elevated temperature the tensile strength of both alloys is similar at 110–113 MPa with almost two-fold increase elongation at the higher Cu content. Primary Si particles dominantly contribute to the mechanical properties at room temperature including hardness and tensile strength, while high temperature properties are attributed to thermally stable phases.
- Increased high-temperature ductility may facilitate forging of these alloys.

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References

[1] Zuo L, Yu FX (2012) DC Casting, Deformation and Strengthening of Al-Si Alloys. Materials Science Forum, 706-709:186-193.

[2] Yu S-B, Kim M-S (2016) Microstructure and High Temperature Deformation of Extruded Al-12Si-3Cu-Based Alloy. Metals, 6(2):32.

[3] Manasijevic S, Radisa R, Markovic S, Acimovic-Pavlovic Z, Raic K (2011) Thermal analysis and microscopic characterization of the piston alloy AlSi13Cu4Ni2Mg. Intermetallics, 19(4):486-492.

[4] Asghar Z, Requena G, Zahid GH, Rafi Ud D (2014) Effect of thermally stable Cu- and Mg-rich aluminides on the high temperature strength of an AlSi12CuMgNi alloy. Materials Characterization, 88:80-85.

[5] Xu C, Jiang Q, Yang Y, Wang H, Wang J (2006) Effect of Nd on primary silicon and eutectic silicon in hypereutectic Al–Si alloy. Journal of alloys and compounds, 422(1-2):L1-L4.

[6] Hernandez-Sandoval J, Garza-Elizondo GH, Samuel AM, Valtiierra S, Samuel FH (2014) The ambient and high temperature deformation behavior of Al-Si-Cu-Mg alloy with minor Ti, Zr, Ni additions. Materials and Design, 58:89-101.

[7] Li Y, Yang Y, Wu Y, Wang L, Liu X (2010) Quantitative comparison of three Ni-containing phases to the elevated-temperature properties of Al–Si piston alloys. Materials Science and Engineering: A, 527(26):7132-7137.

[8] Farkoosh AR, Javidani M, Hoseini M, Larouche D, Pekguleryuz M (2013) Phase formation in as-solidified and heat-treated Al–Si–Cu–Mg–Ni alloys: Thermodynamic assessment and experimental investigation for alloy design. Journal of Alloys and Compounds, 551:596-606.

[9] Backerud L, Chai G, Tamminen J (1990) Solidification characteristics of aluminum alloys. Vol. 2. Foundry alloys. American Foundrymen's Society, Inc, :266.

[10] ASTM Standards (2015) B557-15, Standard Test methods for tension testing wrought and cast aluminum-and magnesium-alloy products, ASTM International, West Conshohocken, PA.

[11] Belov N, Eskin D, Avxentieva N (2005) Constituent phase diagrams of the Al–Cu–Fe–Mg–Ni–Si system and their application to the analysis of aluminium piston alloys. Acta materialia, 53(17):4709-4722.

[12] Yang Y, Yu K, Li Y, Zhao D, Liu X (2012) Evolution of nickel-rich phases in Al–Si–Cu–Ni–Mg piston alloys with different Cu additions. Materials & Design, 33(1):220-225.

[13] Eskin DG (2003) Decomposition of supersaturated solid solutions in Al–Cu–Mg–Si alloys. Journal of Materials Science, 38(2):279-290.

[14] Lasa L, Rodriguez-Ibabe JM (2002) Characterization of the dissolution of the Al2Cu phase in two Al–Si–Cu–Mg casting alloys using calorimetry. Materials Characterization, 48(5):371-378.

[15] Zeren M (2007) The effect of heat-treatment on aluminum-based piston alloys. Materials & design, 28(9):2511-2517.

[16] Mohamed AMA, Samuel FH, kahtani SA (2013) Microstructure, tensile properties and fracture behavior of high temperature Al–Si–Mg–Cu cast alloys. Materials Science and Engineering: A, 577:64-72.

[17] Qian L, Kobayashi T, Toda H, Goda T, Wang Z-g (2002) Fracture toughness of a 6061Al matrix composite reinforced with fine SiC particles. Materials Transactions, 43(11):2838-2842.