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Influence of Molybdenum on the Thermal, Structural Properties and Micro Hardness of AlSi10Mg(Cu) Alloy

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Abstract

This work is dealing with the impact of molybdenum on the structure properties of commercial cast AlSi10Mg(Cu) alloy. The solidification path of AlSi10Mg(Cu) alloy with various content of molybdenum has been investigated using cooling curve techniques. The samples for testing have been poured into permanent steel mold. The content of molybdenum has been varied from 0 to 0.20 wt. %.The desired chemical composition was achieved by adding of master alloy AlMo10 into commercial AlSi10Mg(Cu) alloy. The micro hardness of as cast alloys with different content of molybdenum has been measured. The microstructure and EDX analysis from the casted samples has been carried out. The results show that molybdenum in commercial AlSi10Cu(Mg) alloy precipitate in the interdendritic region isolated in the form of Al(FeMnMoMg)Si rich intermetallic. The increased content of molybdenum increase slightly liquidus temperature, prolonging precipitation of the last eutectic and surprisingly decrease the micro hardness of commercial alloy for approximately 16 %.

Keywords: AlSi10Mg(Cu), Influence of molybdenum, Thermal analysis, Al(FeMnMoMg)Si rich intermetallics, Micro hardness

1. Introduction

The most common aluminium foundry alloys are based on the aluminium-silicon system because of their outstanding properties such as: superior castability, corrosion resistance, good wear properties, good fluidity, low melting point and good machinability. Among them hypoeutectic AlSi10Mg0.3Cu alloys are frequently applied alloys for production of engine automotive parts. The major solidification characteristic of those alloys is the precipitation of two eutectics (primary Al-Si and secondary Al-Si-Cu). Those eutectic structures are mostly responsible for defining the microstructure and mechanical properties of these alloys [1-4]. Information related to formation of various phases during solidification of those alloys are very important for foundry engineers. Those data enable the foundry engineers to ensure that the casting will achieve the desired properties for its intended application after corresponding melting, liquid metal processing, mold filling and heat treatment procedure. Primary alloying elements such as silicon, magnesium and copper are mainly responsible for defining the microstructure and mechanical properties of those alloys [5]. Silicon as a major alloying elements for those alloys is added to improve castability and fluidity, as well as to reduce shrinkage and to give superior mechanical and thermo - physical properties. Magnesium role, as a second major alloying elements, is to improve the strength and hardness of those alloys in as cast and especially after heat treated conditions. Addition of magnesium into AlSi10Mg(Cu) melt improve corrosion resistance, weldability and provide good machinability of this aluminum alloy. Usually, copper is added into Al-Si alloys to improve their mechanical properties in as cast and heat treated conditions. At the same time copper addition has negative impact on the corrosion resistance of those alloys increasing especially their stress corrosion susceptibility as well as making those alloys more prone to shrinkage porosity. Therefore, the content of copper in the investigated alloys have been limited up to maximum 0.30 wt. %. To ensure that cast components have good metallurgical and mechanical properties their as-cast microstructures must be closely monitored. Thermal analysis apparatus is suitable and mostly available foundry tool for such monitoring beside traditional metallographic practice. Thermal analysis is a technique which record the changes of temperatures during solidification time and present them in the form of plot well known as a cooling curve. Any inflection points, slopes or arrested lines observed on the cooling curves are related to the formation of corresponding metallurgical phases [1, 3, 7, 8, 9]. Even thermodynamically week events which cannot be easily detected on the cooling curves are clearly visible on their corresponding first or second derivative curves. Therefore, the first derivative plotted versus time is very often utilized more accurately to describe the solidification path of aluminum foundry alloys [1]. The first derivative physically represents the rate of cooling (solidification) of the test sample. Currently, thermal analysis technique has been regularly applied to monitor the quality of aluminum melt as well as the effectivity of master alloys additions (especially grain refiner and modifier).

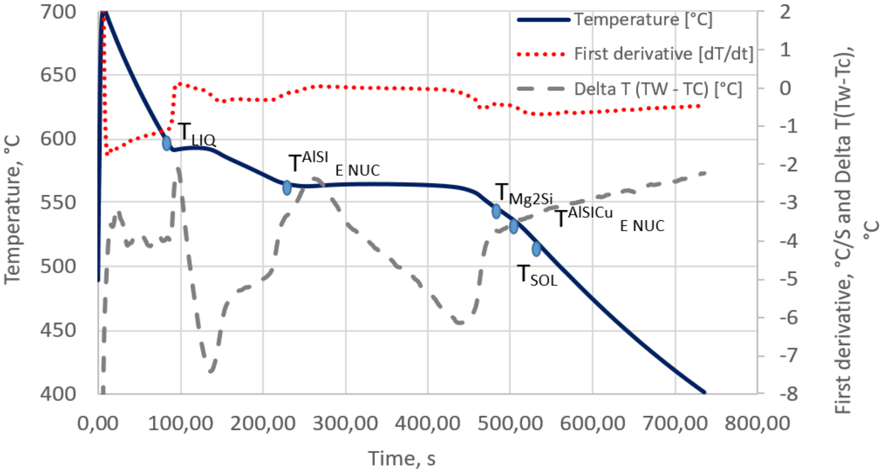

Fig. 1. The cooling curve, its first derivative and delta T curve of AlSi10MgCu alloy. The cooling curve and its first derivative and delta T curves have been obtained applying two thermoelements, one located in center of cup and second close to its wall

The solidification path of commercial AlSi10Mg(Cu) alloy, formation of Mg rich intermetallic as well as primary silicon and secondary copper eutectic phases can be described according to Figure 1, as follows:

1. A primary α-aluminum dendritic network forms around 592°C. The particular temperature depends mainly on the amount of major and minor alloying elements (e.g., silicon, magnesium, titanium, boron) present in the alloy. This precipitation of primary α-aluminium leads to an increase in the concentration of other alloying elements (e.g., silicon, magnesium…) in the residual liquid.
2. At 567°C (the Al-Si eutectic temperature) the eutectic mixture of silicon and α-Aluminium forms, leading to a further localized increase in the magnesium content of the remaining liquid. Various contents of copper, magnesium, zinc and other alloying elements have significant impact on Al-Si eutectic temperature while various contains of silicon does not change considerably this temperature. Addition of modifiers such as strontium or sodium depress this temperature significantly.
3. At the temperature of 547°C, the Mg_2Si rich phase begin to precipitate. This phase has significant impact on the mechanical properties of this alloy in as cast as well as heat treated conditions.
4. By higher content of copper (Cu > 0.10 wt.) the copper rich eutectic phase appears at approximately 530 ºC. In the case when the alloy is modify with strontium, the massive" or "blocky" Al_2Cu phase forms instead of fine Al-Al_2Cu eutectic phase. In the case of AlSi10Mg(Cu) alloy with magnesium content higher than 0.5 wt. % Mg, an ultra-fine $Al_5Mg_8Cu_2Si_6$ eutectic phase can start simultaneously to precipitate at the same temperature.
5. The end of solidification (solidus temperature) has been achieved around 525 °C.

Beside major alloying elements (Si, Mg, Cu…) which have significant impact on the solidification path of AlSi10Mg(Cu) alloy, there are also some other elements present in the small amount that can change considerably solidification path of this alloy [2, 4, 10]. Strontium is one of these elements, normally added to aluminum melt in order to modify the morphology of the Al-Si eutectic and improve its mechanical properties [3, 5, 8, 9]. Despite the fact that those major and minor alloying additions provide alloy with good mechanical properties, this alloy still lacks high mechanical properties application for a new generation of engines. It is well know that some elements such as: Zr, Cr, Ni, Co, Mn, Mo, V and so on are added into aluminum melt in order to improve mechanical properties of base alloy, especially their tensile strength at room and elevated temperatures [11, 12, 13, 14, 15, 16]. From this group of element, molybdenum is nominated to be further in this work investigated. Until recently, this alloying element is not so often used as addition in AlSi10Mg(Cu) cast alloy. From the available literature is well known that molybdenum added into AlSi10Mg(Cu) alloy can enhance the transformation of detrimental β-Fe rich phases into less harmful α-Fe rich intermetallic phase [12]. According to L. C. Modolfo [13] molybdenum is sporadically added in aluminum alloys up to 0.30 wt.% mostly as a week grain refiner. In this work, molybdenum is selected to be added into AlSi10Mg(Cu) alloy in order to identify its potential to improve structural and mechanical properties of this alloy. From the available literature [13, 14, 15, 16] it is well known that molybdenum has slow diffusivity in aluminum matrix as well as good potential for formation of Al_3Mo thermodynamically stable intermetallic. The solid solubility of molybdenum into aluminum is according to Figure 2 about 0.20 wt. % at 660 °C and decrease with decreasing temperature, being about 0.02 wt. % at 560 °C. This binary system is characterized by a peritectic reaction that take place at 660 °C from about 0.10 wt. % molybdenum. Therefore, this element forms intermetallic compound, (Al_5Mo) in the interdendritic region during solidification and on that way contributes to better mechanical properties at room and elevated temperature. According to [14], molybdenum addition at low level (up to 0.30 wt. %) into $AlSi_7Mg_{0,3}Cu_{0,5}$ alloy can form a large amount of stable Al-(Fe,Mo)-Si intermetallic. Those stable intermetallics precipitated during solution treatment of the $AlSi_7Mg_{0,3}Cu_{0,5}$ alloy, were responsible for the good mechanical properties of this alloy at elevated temperature. Based on their obtained results, mechanical properties such as: YS, UTS and elongation at 300 °C of the Mo-containing alloy were increased by ~ 25, 15 and 35 % respectively, compared to the base alloy.

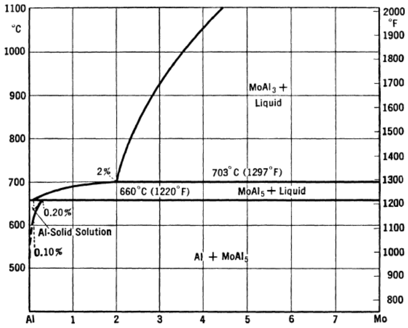

Fig. 2. Part of the binary Al-Mo binary equilibrium phase diagram [13]

O.B. Ifanyi and coworkers [15] in their work indicated that addition of chromium and molybdenum from 0.55 to 5.0 wt. % into AlSi12 alloys increased the hardness and tensile properties of investigated alloy. They found that chromium addition contributed stronger to hardening of investigated alloy than the same addition of molybdenum. The main aim of this work was to characterize the influence of molybdenum on the microstructure evaluation and room temperature micro hardness of the AlSi10Mg(Cu) alloy.

2. Experimental part

2.1. Materials

Commercial aluminum alloy AlSi10Mg(Cu) was melted in the Striko melting furnace and degassing and liquid metal processing has been run in the Balzer electrical holding furnace. The melt temperature in holding furnace was set up at 750 +/- 7 °C and during all experiments have been kept constant. The melt was degassed applying a nitrogen carried inert gas for 12 minutes. The assessment of the melt quality has been done using reduced pressure device. Molybdenum levels (0.10, 0.15 and 0.20 wt. %) has been adjusted by the addition of the AlMo10 master alloy at 750 °C. In order to ensure a stable temperature of the alloy and the complete dissolution of the AlMo10 master alloy, samples from each of the baths were started to be cast 20 minutes after the melt treatment by gas nitrogen was completed. The chemical composition of investigated alloys have been determined applying Spectrolab LAVM12 (Table 1). All alloy compositions in this paper are given in wt. %.

2.2. Samples for structural analysis

All samples for testing have been poured into permanent steel mold (Figure 3). Sample for microstructure characterization were cut from test bars and prepared applying standard metallography procedure by grinding and polishing using Struers equipment. Representative areas of the cast samples (bars) were investigated using optical microscope Leica DMI 5000 DM. Magnifications up to 500x was used to investigate the microstructures. The mold temperature at the start of pouring was kept constant within the temperature range from 195 °C to 210 °C during the whole experiment.

Table 1.
Chemical composition of the alloys (wt. %)

Alloy	Si	Fe	Cu	Mn	Mg	Ti	Sr	Zn	Mo
Charge 1	9.99	0.32	0.22	0.32	0.37	0.080	0.0157	0.056	0.0005
Charge 2	9.87	0.31	0.21	0.31	0.37	0.080	0.0156	0.056	0.10
Charge3	9.90	0.33	0.21	0.30	0.37	0.095	0.0148	0.070	0.16
Charge4	9.80	0.32	0.21	0.29	0.37	0.090	0.0150	0.070	0.20

Fig. 3. The shape of the steel mold for collecting test samples

2.3. Thermal analysis

Sample with mass of approximately 250 g were poured into coated stainless steel cup. The height of the cup was 60mm, while diameters were 45 and 55mm at the bottom and at the top respectively. The weight of the test cup was 50g. Two calibrated N type thermocouples protected with steel tubes were inserted into the aluminum melt and applied to collect the solidification temperature between 750 and 400 °C. During each trials, one thermocouple was located into center while second was located close to the wall of the thermal analysis cup. The deepest position of both thermocouples from the bottom of the crucible were kept always at the constant height of 20 millimeters. Accuracy of the thermocouples were ± 0.10 °C. The data for Thermal Analysis was collected using a high-speed National Instruments data acquisition system linked to a personal computer. Throughout the all experiments, the sampling rate was 5 data per second. The cooling conditions were kept constant during all experiments at approximately 0.15 °C/s. The cooling rate has been calculated as the ratio of the temperature difference between liquidus and solidus temperature to the total solidification time between these two temperatures. Each thermal analysis trial was repeated two times. Consequently, a total of 8 cooling curves were gathered.

3. Results and discussion

3.1. As cast microstructure

The as cast microstructure of two AlSi10Mg(Cu) alloys (with and without molybdenum) has been illustrated in Figures 4 and 5. It is clear from both Figures that dominant phases in both microstructures are primary α-Al dendrites and primary Al-Si eutectic phase. The alloy without molybdenum addition contains the small amount of iron rich phases. The addition of 0.15 wt. % molybdenum into AlSi10Mg(Cu) alloy slightly change the microstructure of a new alloy. However, no significant differences in the size of Secondary Dendrite Arm Spacing (SDAS) is observed in the microstructures of those two alloys as Table 2 indicates. According to Figure 5, addition of 0.15 wt. % molybdenum results in the formation of a new Al(FeMnMoMg)Si rich intermetallic phase. The new phase with polygonal plate form and gray color has been mostly located inside α-Al matrix. The EDX analysis, shown in Table 3 and the phases has been illustrated in Figure 6.

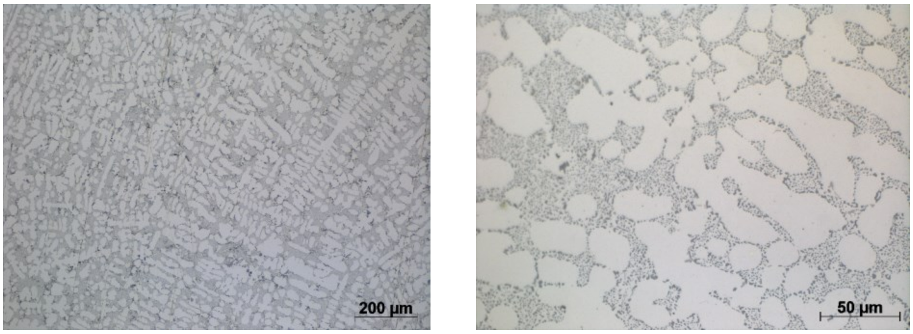

Fig. 4. The as cast microstructure of AlSi10Mg(Cu) alloys

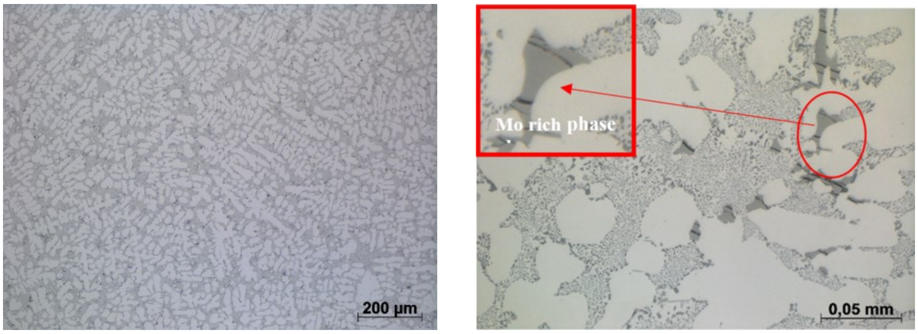

Fig. 5. As cast microstructure of AlSi10Mg(Cu)Mo

Table 2.
Effect of Molybdenum addition into AlSi10Mg(Cu) on the size of the SDAS

Alloy	SDAS, µm
AlSi10Mg(Cu)	16.9
AlSi10Mg(Cu) + 0.10 wt.% Mo	16.8
AlSi10Mg(Cu) + 0.15 wt.% Mo	17.6
AlSi10Mg(Cu) + 0.20 wt.% Mo	17.2

Table 3
The chemistry of the Al(FeMnMoMg)Si rich intermetallic listed in wt. %

Element	Weight %			
	EDX Point 4	EDX Point 5	EDX Point 6	Analyzed Area
Al	71.38	73.08	73.2	71.2
Si	10.47	10.06	10.3	10.27
Fe	4.8	4.69	4.74	5.11
Mn	4.42	4.29	4.24	4.61
Mo	3.33	3.3	2.86	3.16
Mg	1.03	1.1	1.07	1.07

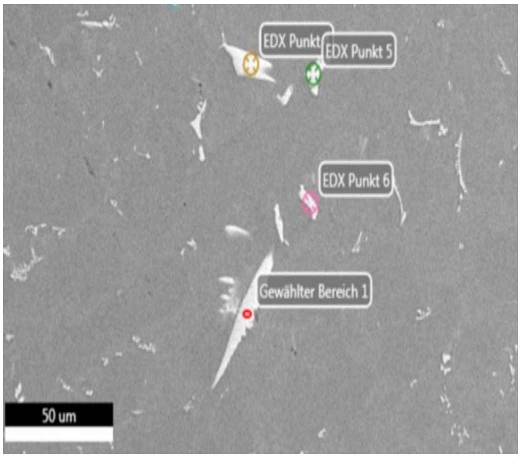

Fig. 6. Al(FeMnMoMg)Si rich intermetallic phase

3.2. Thermal analysis

Figure 7 shows two first derivative curves of the AlSi10Mg(Cu) alloy with and without molybdenum addition plotted versus solidification temperature. Two main differences can be recognized observing the shape of those two curves. It looks that addition of molybdenum move primary solidification of α-Aluminum phase (liquidus temperature) to slightly higher temperature. The AlSi10Mg(Cu) alloy without molybdenum addition started to solidify at approximately 592°C, while addition of 0.15 wt.% of molybdenum moved the start of primary precipitation to 594°C. The observed undercooling (ΔT = Tmax – Tmin) at cooling curves without and with molybdenum was 1.7°C and 0.5°C respectively. All of those previously mentioned indicates that molybdenum addition should have potential to reduce the grain size of primary precipitated α-Aluminum phase.

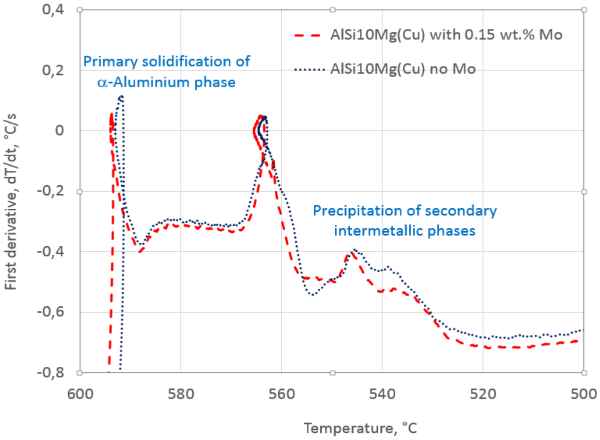

Fig. 7. First derivatives of two cooling curves of AlSi10Mg(Cu) alloys with and without molybdenum addition

Another difference has been related to the precipitation of secondary intermetallic phases (magnesium and copper rich phases). The changes in shapes of two first derivative curves during the last stage of solidification indicated that different amount of phases precipitated during solidification of those two alloys. In both curves the Mg_2Si intermetallic phase start to precipitate at almost the same temperature (~ 549°C), while the addition of molybdenum depressed the start of precipitation of AlSiFeMgCu (~ 541°C without molybdenum) Al(FeMnMoMg)Si intermetallic phase rich on molybdenum at ~ 538°C. At the same time as Figure 6 illustrates the new molybdenum rich phase precipitated in the larger temperature interval (~28°C) than the phase without molybdenum (~ 20°C).

3.3. Micro hardness

The micro hardness of the alloys was measured using an QNESS_Q10M hardness tester with following parameters.

The hardness testing was carried out on the as-cast samples. Indentations were performed on the polished surface with a load of 50 gr using a Micro Vickers equipment. The result was measured with the lens with 40x* magnification.

Table 4.
Impact of Molybdenum on the micro hardness of AlSi10Mg(Cu) alloy

Alloy	Micro hardness, HV 0,05
AlSi10Mg(Cu)	89
AlSi10Mg(Cu) + 0.10 wt.% Mo	82
AlSi10Mg(Cu) + 0.15 wt.% Mo	75
AlSi10Mg(Cu) + 0.20 wt.% Mo	75

According to Table 4, addition of Molybdenum up to 0.20 wt. % results in the slight depression of the micro hardness. The reason might be in the slow diffusion of molybdenum into α-Al matrix of alloy with higher concentration of silicon [14]. It looks that molybdenum together with magnesium, manganese, iron and silicon form intermetallic phases and on that way decrease the content of magnesium in the α-Al matrix consequently causing decrease the hardness of alloy with higher molybdenum content.

4. Conclusions

Experiments have been carried out to observe the effect of molybdenum additions between 0 and 0.20 wt. % on the structural properties and micro hardness of cast AlSi10Mg(Cu) alloy. It was found that addition of molybdenum into AlSi10Mg(Cu) alloy slightly change the solidification paths of this alloy. Those changes are related to the beginning and the end of solidification. Higher amount of molybdenum increases the liquidus temperature for approximately 2 °C and at the same time depress the precipitation temperature of molybdenum rich internmetallic for approximately 3 °C. Molybdenum addition up to 0.20 wt. % forms a coarse plate like molybdenum rich intermetallics, which precipitates in the interdendritic region of aluminum matrix. Addition of Molybdenum up to 0.20 wt. % results in the slight depression of the micro hardness.

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