Modification of Al-Si-Cu cast alloy

Mária Farkašová
University of Žilina
Faculty of Mechanical Engineering
Slovakia

Eva Tillová
University of Žilina
Faculty of Mechanical Engineering
Slovakia

Mária Chalupová
University of Žilina
Faculty of Mechanical Engineering
Slovakia

The modification effect of hypoeutectic AlSi6Cu4 cast alloy on the microstructure and mechanical properties (tensile strength and hardness) was systematically investigated. The samples were modified by AlSb10 (0 - 10 000 ppm) and studied without and after T6 heat treatment. The results show that the addition of Sb into Al-Si-Cu cast alloy should act as a modifier, so it supposes to change the eutectic Si morphology. However, its effect as a modifier is more inoculation and caused refinement of microstructure, which has led to mechanical properties increasing. Refinement of microstructure could obviously improve the size and distribution of eutectic cells. The eutectic cells are significantly refined in a fully modified eutectic microstructure (more than 1 000 ppm Sb). It can be speculated that the stick-fibrous transition of eutectic Si morphology involving in impurity modification may be independent of the frequency and mode of eutectic nucleation.

Keywords: *Al-Si cast alloy, modification, microstructure, mechanical properties, Si-morphology.*

1. INTRODUCTION

The hypoeutectic Al-Si based alloys are well-known casting alloys with a highly desirable combination of characteristics, such as castability, weldability, low thermal expansion coefficient, good corrosion resistance, and machinability. These properties lead to the application of Al-Si alloys in automotive industry, especially for automotive engines, crankcases, intake manifolds, cylinder blocks, cylinder heads, pistons, cast oil pans and valve lifters [1].

Mechanical properties are principally controlled by the cast structure. Microstructure evolution of hypoeutectic Al-Si alloys during solidification is in two stages: primary dendrite Al-phase formation (α-matrix), and the subsequent eutectic transformation (eutectic Si particles in α-matrix). Based on the Al-Si binary diagram, the volume fraction of Al-Si eutectic in commonly used hypoeutectic Al-Si alloys, such as AlSi7Mg0.3, AlSi9Cu3, AlSi6Cu4, can be more than 50 % [2]. Typically, the Al-Si eutectic accounts for a volume fraction of 50-90 % of these alloys [3].

Therefore, for a given composition (and heat treatment), it is the ability to optimize grain size, eutectic structure, cell size, casting soundness, and the size and distribution of intermetallics that determines the properties. The important influence on the mechanical properties of Al-Si alloys has the morphology of the eutectic silicon [2]. Silicon is a faceted phase and makes the Al-Si eutectic an irregular eutectic. The brittleness of Si-crystals, of course, is the main reason responsible for the poor properties of Al-Si alloys since the large eutectic silicon particles lead to premature crack initiation and fracture in tension conditions. It has been proven that modification of eutectic silicon plays an important role in improving the mechanical properties of hypoeutectic Al-Si alloys. Therefore, many efforts have been made in the modification of casting Al-Si alloys in order to achieve fine silicon phase with beneficial shapes and distribution.

The eutectic silicon in Al-Si alloy can be modified using chemical, quenching, outfield or superheating modification [4-6]. Chemically induced modification results in a fibrous or fine flake-like structure. With small addition of impurity elements such as strontium (Sr), sodium (Na), potassium (K), calcium (Ca) or cerium (Ce), the eutectic Si undergoes a morphological transition from coarse needles/plate-like to fine and globular/fibrous morphology, improving the mechanical properties of Al-Si alloy [7,8]. Elements which produce a refined flake-like structure are antimony (Sb), arsenic (As) and selenium (Se). Of these, only Sr, Na, and Sb produce significant modification at low levels of addition. Thus they are the only elements used widely in industry. Na and Sr produce by far the strongest modifying action at very low levels of addition. Although similar mechanical properties can be achieved by addition of Sb, the effect of Sb on the microstructure of the eutectic differs greatly from that produced by Na or Sr. The addition of Sb refines the Al-Si eutectic to form a fine flake-like structure instead of the fibrous structure produced by Na or Sr [4-6].

Sb is predominantly used in Europe and Japan, and is commonly referred to as a permanent modifier [9]. Unlike Sr and Na, once it is added to the aluminium melt, it remains as a permanent constituent of the aluminium alloy. The modifier is therefore added by the supplier of foundry ingot and does not require any make up addition at the foundry. Some of the advantages of Sb modification are:

- Does not fade.
- Not sensitive to regassing.
- Suitable for parts which are prone to porosity formation.

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Correspondence to: Ing. Mária Farkašová
Faculty of Mechanical Engineering,
Univerzitná 8215/1, 010 26 Žilina, Slovak republic
E-mail: maria.farkasova@fstroj.uniza.sk

Disadvantages of Sb modification include:

- Reacts with Sr and Na reducing the effectiveness of these modifiers.
- Sb is a toxic material and it can react with hydrogen dissolved in the metal.
- Can reduce mechanical properties, particularly in the slower solidifying regions of a casting [9, 10].

There are a number of theories on the mechanism for modification. However, the most accepted theory is that modifiers (and rapid freezing) induce “twinning” in the growing silicon crystals making the crystals change their direction of growth many times resulting in a branched or fibrous structure [2,6].

The present study is a part of a larger research project, which was conducted to investigate and to provide a better understanding microstructure quality control of Al-Si-Cu cast alloys. The main objective of this work was to demonstrate the modification effect by antimony on the mechanical properties, microstructure and structure surface of AlSi6Cu4 cast alloy.

2. EXPERIMENTAL METHODS

Experiments were performed on AlSi6Cu4 cast alloy whose chemical composition is given in Table 1. This alloy has a lower corrosion resistance and it is suitable for high-temperature (up to max. 250 °C) applications (dynamically exposed casts). In Slovak Republic AlSi6Cu4 cast alloy is used first of all for cylinder heads for 1.6 l engines for the automobile Kia Ceed and in the Czech Republic for the automobile Škoda Fabia 1.2 TSI (Fig. 1).

Table 1. The chemical composition (wt. %)

Si	Fe	Cu	Mn	Mg
6.52	0.43	3.88	0.45	0.29
Cr	Ni	Zn	Ti	Al
0.01	0.01	0.46	0.15	base

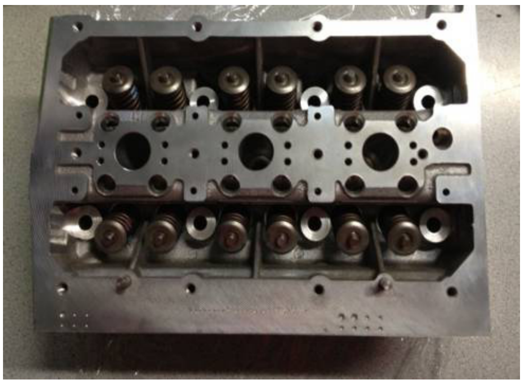


Figure 1. Cylinder heads (Škoda Fabia 1.2 TSI)

Experimental casts were casted in the laboratory of Department of Technological Engineering of University of Žilina (Fig. 2). The melting process and the modification were carried out in a graphite melting crucible in a resistance oven. For the grain refinement process was used refining salt AlCuAB6 and it was carried out while overheating the metal bath to 730 °C ± 5 °C. Antimony was added to the melt in the form of AlSb10 master in the range from 0 to 10 000 ppm under the same technological condition (Table 2). Sb-amount was determined based on the most widely used quantities shown in the literature for Al-Si-Cu based alloys.

Tab. 2 The experimental casts (Sb in ppm)

1	2	3	4	5	6
0	100	300	500	800	1 000
7	8	9	10	11	
1 500	2 000	2 500	3 000	10 000	

Figure 2. Semi products

The semi products - bars were cast, and then machined to produce tensile test samples (ø 14 x 120 mm). The tensile tests were evaluated both in the as-cast state and in a T6 heat treated state [7]. The following heat treatment cycle was applied: solution heat treatment at 505 °C for 6 h, quenching in water at a temperature of 40 °C, and then artificial aging at 170 °C for 8 h and cooled on calm air. The static tensile test was performed for experimental samples in as-cast state and after heat treatment on a tensile machine ZDM 30 at 21 °C according to standard STN EN 10003-1. Values of ultimate tensile strength are determined by the average value of three test bars. Hardness measurement was performed by a Brinell hardness tester (HBW 2,5/62,5/15) with the load of 62.5 kp, 2.5 mm diameter ball and the dwell time of 15 s according to standard STN EN ISO 65061. The Brinell hardness value at each state was obtained by the average of at least six measurements.

The microstructure of experimental casts was studied using an optical microscope Neophot 32 and scanning electron microscope (SEM) VEGA LMU II linked to the energy dispersive X-ray spectroscopy (EDX analyser Brucker Quantax). Metallographic samples were produced from selected tensile specimens (after testing). The specimens for microscopic analysis by optical and electron microscopy were prepared by standard metallographic procedures (hot mounting in bakelite, wet ground on SiC papers, DP polished with 3 μm diamond pastes, finally polished with commercial fine silica slurry STRUERS OP-U and etched by 0.5 % HF).

Some samples were also deep-etched for 15 s in HCl solution in order to reveal the 3D-morphology of the eutectic silicon [2, 11]. The specimen preparation procedure for deep-etching consists of dissolving the aluminium matrix in a reagent that will not attack the eutectic components. The residuals of the etching products should be removed by intensive rinsing in alcohol. The preliminary preparation of the specimen is not necessary, but removing the superficial deformed or contaminated layer can shorten the process. Colour etching (by Weck-Al) was used to highlight the eutectic cells [2,12]. Quantitative metallography [13, 14] was carried out on an Image Analyzer NIS - Elements 3.0 to quantify eutectic cells size.

3. RESULTS AND DISCUSSIONS

The effect of Sb-amount to tensile strength is shown in Fig. 3. The figure shows that increasing the amount of the modifying element Sb increases ultimate tensile strength too, but no very. The increase of ultimate strength is weekless. To increase the ultimate tensile strength of not heat-treated alloy AlSi6Cu4 to about 5 to 10 %, is the most appropriate amount of Sb in the range from 1000 to 2500 ppm. A remarkable increase in the strength is observed in heat treated samples (cca 82 %). Tensile strength - R_m for alloy modified with 1 000 ppm Sb (probably it will by optimal amount) increases from 219 MPa to 417 MPa. Higher amount of modifier (above 1 500 ppm Sb) has led to a decrease of ultimate tensile strength.

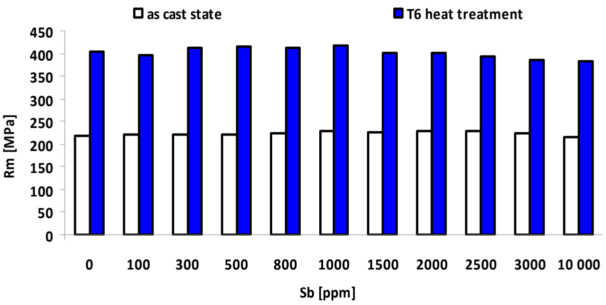


Figure 3. Effect of Sb-modification on the tensile strength

Fig. 4 shows the relation between the amount of Sb-modifier and Brinell hardness value in as cast state and after T6 heat treatment. Results of hardness are comparable with results of tensile strength. The as cast unmodified specimens have hardness value approximately 103 HBW and after heat treatment till 146 HBW. HBW for samples modified by optimal amount - 1 000 ppm Sb increases to 153 HBW. In over-modified casts was observed decreasing of hardness (samples with 10 000 ppm - 138 HBW).

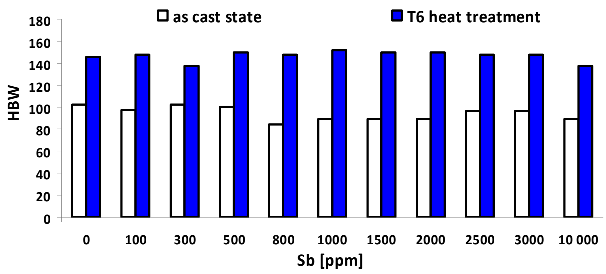


Figure 4. Effect of Sb-modification on the Brinell hardness

The best mechanical properties were observed in the alloy modified with 1 000 ppm Sb (probably it will by optimal amount) after heat treatment – was measured tensile strength - R_m cca 417 MPa and Brinell hardness 153 HBW.

Mechanical properties (tensile and hardness) of AlSi6Cu4 cast alloy mainly depend on the distribution of the α-grains, shape and size of eutectic silicon and morphology and size of intermetallic phases in the interdendritic region.

The Structure of hypoeutectic AlSi6Cu4 cast alloy without Sb is composed by α-matrix, eutectic (Si particles in α-matrix) and many Cu- and Fe-rich intermetallic phases - Fig. 5.

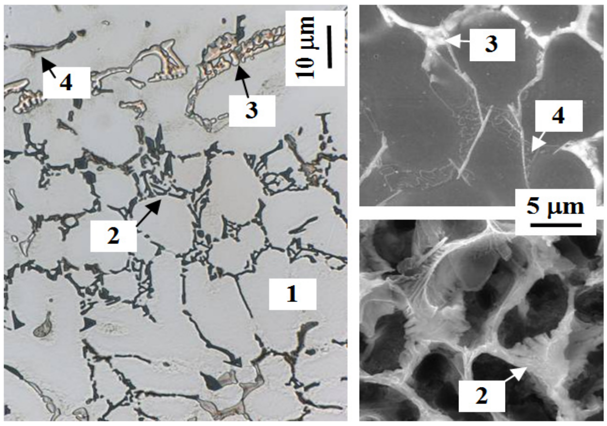


Figure 5. Microstructure of AlSi6Cu4 alloy, etch. 0.5 HF (1 - α-matrix, 2 - eutectic Si, 3 - Cu-phases, 4 - Fe-phases)

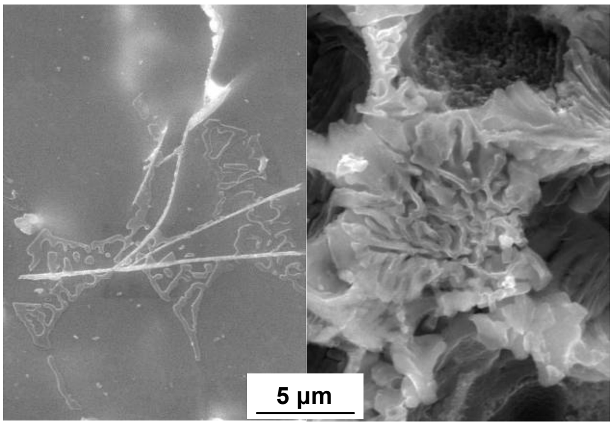
Commercial Al-Si alloys contain significant amounts of iron, which plays an important role in the nucleation of the eutectic Si in these alloys. Relatively high iron contents (0.43 % Fe) promote the formation of the Fe-rich needles Al_5FeSi (β-phase). In unmodified hypoeutectic AlSi6Cu4 alloy, eutectic Si nucleates on these β-phases (Fig. 5) before the nucleation of α-matrix and this results in free growth of silicon into the eutectic liquid with its typical plate-like morphology [15]. On the other hand, in chemically modified hypoeutectic Al-Si alloys, the growth of the β-phase is halted resulting in a large number of equiaxed α-grains nucleating before nucleation of Si and hence silicon is forced to grow in between the α-grains acquiring a fibrous, flake-like morphology. This growth pattern is aided by silicon’s ability to twin easily and growth proceeds with the twin plane re-entrant edge (TPRE) mechanism [13, 14].

Fig. 6 shows SEM microstructure and three-dimensional morphology of the eutectic Si in as-cast AlSi6Cu4 alloy without, whit 1 000 and 10 000 ppm Sb. The microstructure seen in Fig. 6a reveals fine, but still plate-like eutectic silicon. It is obvious in Figures 6a, 6b that the fine eutectic Si platelets decrease more and more in size after addition of Sb and changes morphology from compact plate-like to stick or fibrous. Si-particles in samples with 10 000 ppm coarsens probably as a result of over-modification (Fig. 6c).

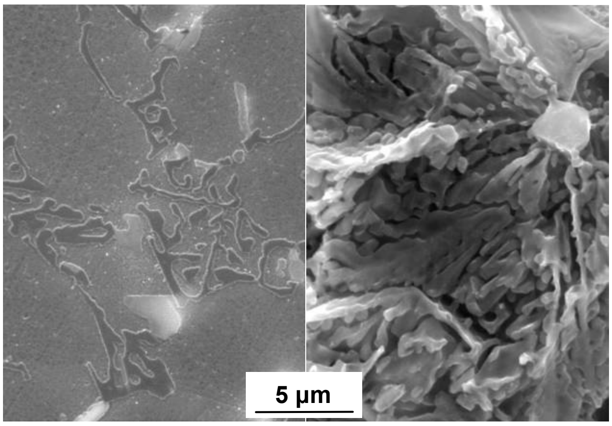
Morphology of eutectic Si in all heat treated samples (Fig. 7) was observed as rounded particles. After deep etching we observed fragmentation of fine compact Si-plate-like phase and its transformation to fine sticks-like phase (Figures 7a, 7b, 7c).

Over a modification occurs in AlSi6Cu4 alloy when modifier is present in the amount of 1 500 ppm Sb to cause its formation as AlSb compound (Fig. 8).

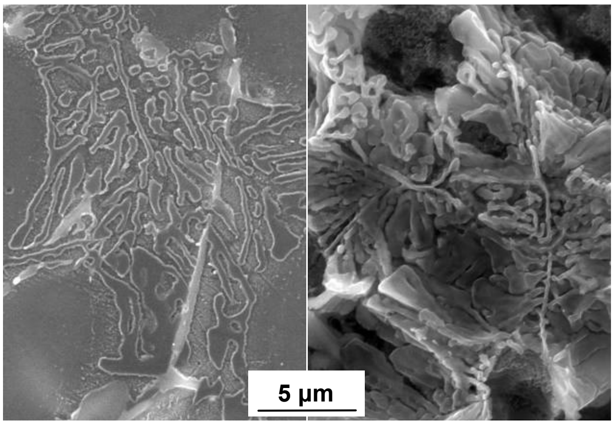
The additions of Sb to AlSi6Cu4 cast alloy give rise to a transformation of the eutectic silicon phase; however the result was not as dramatic as we attended (e.g. as modification with Sr or Na).



a) unmodified



b) modified by 1 000 ppm Sb

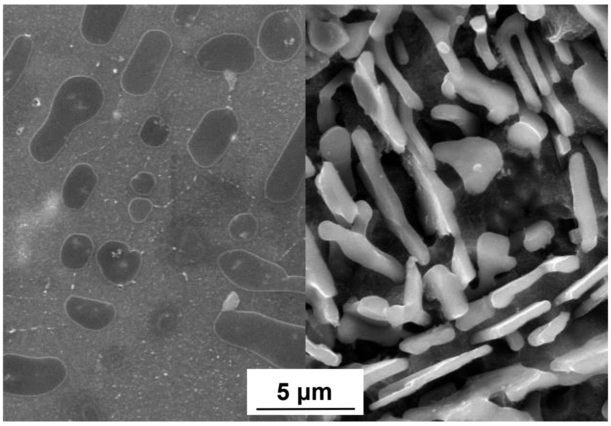


c) modified by 10 000 ppm Sb

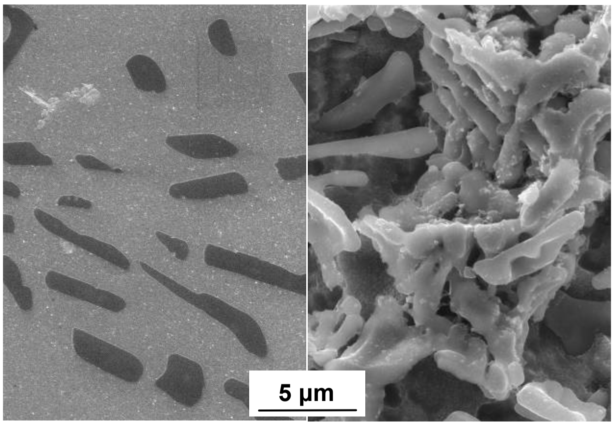
Figure 6. Morphology of eutectic Si, as cast state, etch. 0.5 HF/deep etch., SEM

Therefore were observed eutectic cells (Fig. 9). The concept of eutectic cell originates from the gray cast-iron [4]. For the Al-Si alloy, the eutectic cell in Al-Si alloy should be considered the eutectic Si as well as branches from one eutectic nucleus together with the coupled-growth eutectic Al phases. It is widely accepted that the eutectic Si phase is the "leading phase" in the growth, which is a successive framework in a eutectic cell. Therefore, the morphology of eutectic cell depends upon the growth of eutectic Si phase in each aspect [13, 14].

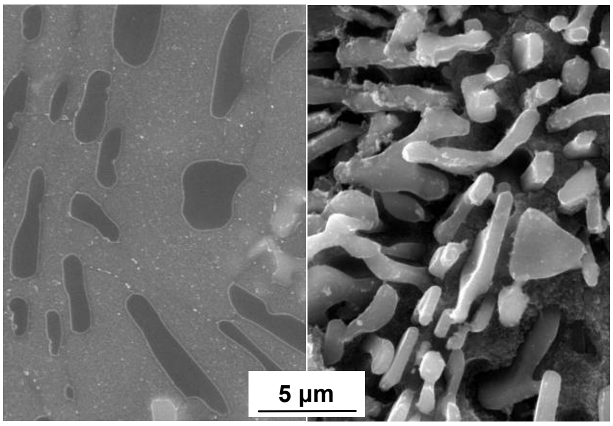
Al-Si alloys without any grain refiner addition have the maximum grain size (220 µm) [15]. Sb-modification decreases the size of eutectic cells,



a) unmodified



b) modified by 1 000 ppm Sb



c) modified by 10 000 ppm Sb

Figure 7. Morphology of eutectic Si after heat treatment, etch. 0.5 HF/deep etch., SEM

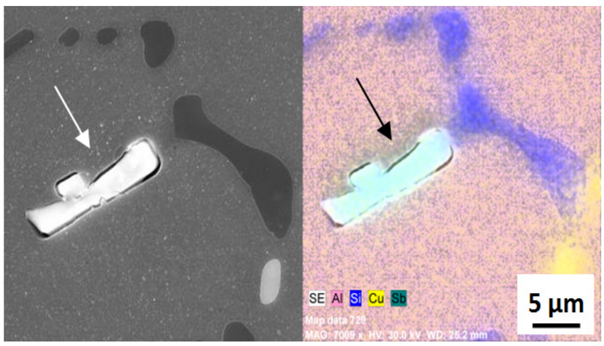


Figure 8. Morphology of eutectic Si after heat treatment, etch. 0.5 HF/deep etch., SEM

but increases their number (Fig. 9, Fig. 10). The size of eutectic cells decreases from 156 μm (0 ppm Sb) to 84 μm (1 000 Sb) what's 84 %. Next decrease of eutectic cells between 1500 ppm and 10 000 ppm is nerveless. It is likely that, the effect of Sb addition is possible to characterize rather than modifier as refiner.

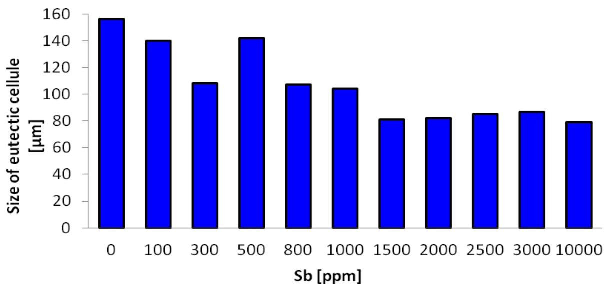
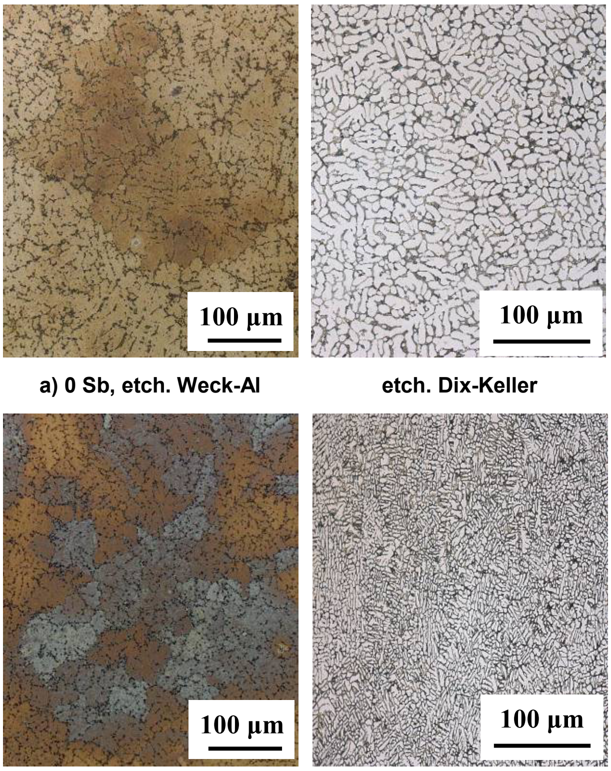


Figure 9. Relation between amount of Sb and size of eutectic cells on samples after heat treatment T6



a) 0 Sb, etch. Weck-Al **etch. Dix-Keller**

b) 10 000 ppm, etch. Weck-Al **etch. Dix-Keller**

Figure 10. Size of eutectic cells on samples after heat treatment

On the basis of classical solidification theory [3,4, 13], grain size, on one hand, depends on the number of potentially efficient nuclei in the melt, and, on the other hand, is determined by the nucleation rate. Firstly, with the refinement of primary dendrite α-phases (Fig. 10), it could influence both the distribution of nuclei for eutectic and the concentration in the liquid near the dendrite-liquid interface prior to the coupled growth of α- and eutectic Si phase.

Secondly, some unknown potent nuclei for eutectic Si phase are easily activated in the undercooling melt, i.e., the number of eutectic nuclei is increased in unit time and unit volume of melt. Obviously, the time for meeting of grains or of loping solute fields is shortened due to the increase of nucleus density, which restricts the growth of the eutectic cells in the time and space. Combining the results and analysis, it can be concluded that the evolution of primary dendrite α-phases affects remarkably the size, shape and distribution of eutectic cells.

Eventually, an important issue needs further to be clarified, is the modification mechanism of eutectic Si. Up to now, two predominant modification operating mechanisms have been put forward for explaining the modification behaviour of eutectic Si [3, 13]. The first, the effective nuclei for eutectic Si in melt are removed by modification elements based on the phenomenon of increased nucleation undercooling, consequently, the solid-liquid eutectic interface advances at higher growth rate. The second, the interface structure of eutectic Si phase-liquid is changed by the modification elements based on the observation of high density growing twins, which would transform the growth manner of eutectic Si. The eutectic cells are refined significantly in a fully modified eutectic microstructure, as shown in Fig. 6. It can be speculated that the stick-like transition of eutectic Si morphology involving in impurity modification may be independent of the frequency and mode of eutectic nucleation.

4. CONCLUSION

The effect of Sb-modification in AlSi6Cu4 aluminium cast alloy on themicrostructure, mechanical properties and structure surface was investigated and the following conclusions could by drawn:

Sb-modifier should act as a modifier, so it supposes to change the eutectic silicon morphology. However, its effect as a modifier is not as significant as we have expected. Sb affects the Si-morphology nerveless. Its effect was more inoculating and caused refinement of microstructure what has led to mechanical properties (such as tensile strength) increasing. After T6 heat treatment tensile strength for alloy modified with 1 000 ppm Sb increases from 219 MPa to 417 MPa and hardness from 103 HBW to 143 HBW.

Refinement of microstructure could obviously improve the size and distribution of eutectic cells. This indicates that the evolution of primary dendrite α-phases affects remarkably the following eutectic nucleation and growth. The eutectic cells are refined significantly in a fully modified eutectic microstructure (more than 1 000 ppm Sb - Fig. 9). It can be speculated that the stick-like transition of eutectic Si morphology involving in impurity modification may be independent of the frequency and mode of eutectic nucleation. 1 000 ppm Sb reduces the size of eutectic cells about 84 % by improving the nucleation.

ACKNOWLEDGMENT

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МОДИФИКАЦИЈА Al-Si-Cu ЛИВЕНЕ ЛЕГУРЕ

Марија Фаркашова, Ева Тилова, Марија Шалупова

Утицај модификација на микроструктуру и механичке особине (затезна чврстоћа и тврдоћа) подеутектиктичког AlSiCu 4 ливеног алуминијума је систематски истражен. Узорци су модификовани додавањем AlSb10 (0 - 10 000 ppm) и утицај је проучен без и након примене третмана T6 топлотне обраде. Резултати показују да додавање Sb у Al-Si-Cu ливене легуре делује као модификатор, па се претпоставља да долази до промена Si морфологије. Модификатор је изазвао пречишћавање микроструктуре, што је довело до промене механичких особина. Префињеност микроструктуре може побољшати очигледно величину и дистрибуцију еутектиктичих ћелија. Еутектиктичке ћелије су знатно префињене у потпуно модификованој еутектичкој микроструктури (више од 1 000 ppm Sb). Може се претпоставити да штап-влакнасте транзиција еутектичке Si морфологије и укључивање нечистоћа модификације су независни од учесталости и начина еутектичке нуклеације.