INFLUENCE OF CHEMICAL COMPOSITION AND HEAT TREATMENT OF AlSi6Cu4 ALLOY ON THE UTILIZATION OF COPPER STRENGTHENING EFFECTS

MARKO GRZINCIC
Illichmann Castalloy, Member of ALICON Group
Zarnovica, Slovakia

DOI:10.17973/MMSJ.2016_03_201567

e-mail: grzincicm@illichmann.sk

The paper presents deals with a quantification of intermetallic phases rich in copper in the alloy AlSi6Cu(X) with a variable content of copper, modified with strontium and during thermal treatment age hardening in artificial or natural way. It concerns variables occurring in the common industrial practice. The rate of solidification, thermal treatment regime and other elements of the alloy chemical composition were not be variated. Microhardness measurements related to a condition of 27 samples. Substructural TEM analysis characterizes the copper alloying condition of the structure matrix. Copper as a hardening element was identified by EDX analysis. Important process and material factors appealing to resultant mechanical properties of the alloy were identified, and the factors having a minimal effect were eliminated.

KEYWORDS
Al-alloys, thermal treatment, hardening, intermetallic, Cu-phase

1. INTRODUCTION

Copper content in casting aluminium alloys based on silumines hardenable by copper ranges commonly from 1% to 4%. It concerns common, usually secondary, alloys for gravity casting which contain higher percent of harmful elements, especially iron. Copper as well as magnesium is the precipitating element in silumines [Bäckerud 1986]. During the thermal treatment, it improves strength of the casting material. When solidifying in a mould, copper is separated in the form of intermetallic phases that do not improve the casting mechanical properties. Any intermetallic phases never improve mechanical properties of Al-alloy. Identification of the creation of intermetallic phases during the solidification is possible with thermal analysis [Apelian 1984, Argyropoulos 1983, Kierkus 1999]. During the standard thermal treatment, at first the casting is heated to temperature making the copper dissolution possible. The duration of time of dissolution is fundamental because the longer duration of time, the larger volume of copper is dissolved. However, it is the energy-intensive process, and hence a compromise duration of time is chosen. Once the copper is soluted, the casting must be cooled-down suddenly (critical quenching velocity) in order to avoid a repeated creation of copper rich intermetallic phase. The aim of the presented paper is to improve the casting mechanical properties in alternative way, not to use the solution annealing. Copper is a self-hardening element; some producers chose a natural age hardening, very favourable for economic reasons. The artificial age hardening, when the casting must be again heated to the given temperature and the duration of time ranges within hours, is more economic-intensive, but still significantly cheaper way to improve mechanical propertis.

The higher copper content means the alloy higher price. Therefore, it is desirable to have the lowest effective concentration. Thermal treatment is the energy-intensive process and any process time reduction or even the heat treatment leaving out result in great financial benefits. Modification by strontium is the metallurgical process aiming to improve the material ductility [Crossley 1966, Garat 1992, Sigworth 1983, Wang 1995]. However, strontium often occurs in intermetallic compounds and hence it was variated in experiments as well [Djurdjevic 1999].

The paper describes the experiment with three variables as well as results of possible material analyses. The aim is to evaluate effects of factor combinations that occur commonly in casting operations [Doty 1996].

2. EXPERIMENTAL WORK, RESULTS AND THEIR ANALYSIS

Tab. 1 describes the experiment matrix when the alloy chemical composition was changed – copper content ranged from 1 weight % to 4 weight %. The liquid alloy was modified by strontium to 140 ppm or it did not modified at all, and some samples had aged naturally, and some of them artificially. The samples, marked with AA (*artificial aging*), are treated by artificial aging at 180°C within 4 hours, i.e. it concerns thermal treatment T5. The samples, marked with NA (*natural aging*), aged naturally within 7 months. Altogether 27 samples were prepared. All samples were casted under the same conditions of solidification (thermoanalysis steel cup with massive bottom to increase solidification velocity; area for identification 5mm distance from bottom surface and in sample axis), and the base metal chemical composition was equal as well.

Alloy + Cu	Sr content	No.-Sample			
		1	2	3	4
AlSi6Cu1	140 ppm Sr	AA	AA	NA	NA
AlSi6Cu2		AA	AA	NA	NA
AlSi6Cu3		AA	NA	–	–
AlSi6Cu4		AA	NA	–	–

Alloy + Cu	Sr content	1	2	3	4
AlSi6Cu1	0 ppm Sr	AA	AA	NA	NA
AlSi6Cu2		AA	AA	NA	NA
AlSi6Cu3		AA	AA	NA	NA
AlSi6Cu4		AA	NA	NA	–

Tab. 1. Survey of variable factors and identification of samples, AA (artificial aging)_NA (natural aging)

Alloy AlSi6Cu1 with 140 ppm Sr				
Marking sample	1AA	2AA	3NA	4NA
HV 0,02	63	64	54	54
Alloy AlSi6Cu2 with 140 ppm Sr				
Marking sample	1AA	2AA	3NA	4NA
HV 0,02	69	69	62	62
Alloy AlSi6Cu3 with 140 ppm Sr				
Marking sample	1AA	2NA	–	–
HV 0,02	78	70	–	–
Alloy AlSi6Cu4 with 140 ppm Sr				
Marking sample	1AA	2NA	–	–
HV 0,02	81	77	–	–
Alloy AlSi6Cu1 without Sr				
Marking sample	1AA	2AA	3NA	4NA
HV 0,02	64	64	53	53
Alloy AlSi6Cu2 without Sr				
Marking sample	1AA	2AA	3NA	4NA
HV 0,02	69	70	62	62
Alloy AlSi6Cu3 without Sr				
Marking sample	1AA	2AA	3Na	4Na
HV 0,02	77	77	70	70
Alloy AlSi6Cu4 without Sr				
Marking sample	1AA	2NA	3NA	–
HV 0,02	81	73	73	–

Tab. 2. Average values HV0.02

2.1 Microhardness measurements

The microhardness of α-phase was measured for the all produced samples. Fifty values were measured for each sample, and the indicate values spread was about 12 HV0.02. Average values for each analysed sample are given in Table 2.

Results achieved from microhardness measurements of α-phase (matrix) can be resumed into the points as follows:

1. Presence of **Sr do not influence microhardness values of α-phase** (matrix). It is no difference in values of this property between samples containing Sr and samples without Sr.
2. In accordance with theoretical laws of precipitation strengthening of alloy based on Al-Cu, the samples **containing the lowest amount of Cu** (i.e. the samples with 1 % Cu) have **the lowest values of α-phase strengthening**. On the other hand, the samples **containing the highest content of Cu** (i.e. the samples with 4 % Cu) have **the highest α-phase strengthening**.
3. **Higher values of α-phase microhardness** of the samples, subjected to artificial aging at 180 °C/4 h, are connected probably with a presence of **GP zones** as well as Θ-phase.
4. **Thermal treatment** using artificial aging **does not result in any noticeable improvement of the α-phase strength** represented by HV0.02 values compared with the α-phase strength of the samples that aged naturally – T4.
5. **The hardening effect**, i.e. a proportional difference between α-phase microhardness of the samples aged naturally (100 %) and the samples after artificial aging, **is dependent on Cu content only** not at all on Sr presence or absence, Table 3.
6. **Hardening effect** is very low, and it comes down, if Cu content is reduced, which indicates an ineffective thermal treatment (missing solution annealing).

Alloy	Hardening effect v %
AlSi6Cu1	≈ 19
AlSi6Cu2	≈ 11
AlSi6Cu3	≈ 11
AlSi6Cu4	≈ 5

Tab. 3. Hardening effect

2.2 TEM-analyses

Substructural analysis were realized for the alloy AlSi6Cu4, the sample 1AA with 140 ppm Sr. To the sample substructure is specific a presence of separated Θ' phase having acicular shape in planes $\{100\}_\alpha$ ca 80 % as well as of GP zones ca 20%, Fig. 1. This structure character is typical of a breakdown stage of a supersaturated solid solution α in the system Al-Cu at higher temperatures when the GP zone is already transformed to Θ' phase. This stage breakdown (where both Θ' phase and GP zones occur) of the supersaturated solid solution α provide maximum strength at higher temperatures, namely from standpoint of precipitation strengthening. A density of Θ' phase as well as GP zones is very low, which indicates α- phase insufficient alloying.

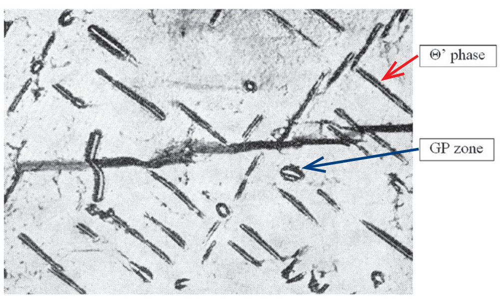


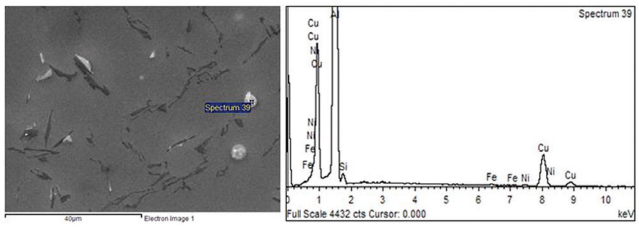
Fig. 1. Substructure of the sample 1AA, magnified 120.000 x

2.3 EDX-Analyses

An equipment INCAx-sight of the company Oxford connected to SEM – JEOL JSM 7000F was used for EDX analyses [Grzincic 2014]. The samples were analyzed in the regime SEI at beam voltage 15 KV. Forty EDX analyses were carried out for each sample.

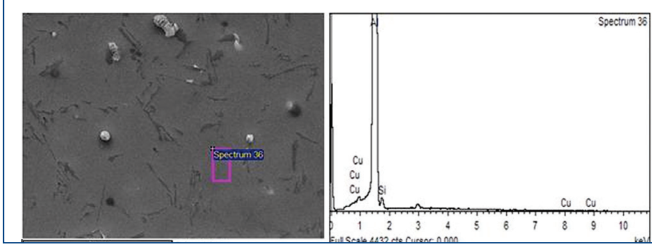
Results achieved from EDX analyses can be resumed into the points as follows:

1. **All samples** in α-phase (matrix) **comprise irregular-shaped bright particles** based on intermetallic phase **$CuAl_2$. A prospective solution annealing process might dissolve them under certain conditions.**
2. α-phase of all samples is alloyed with Cu heterogeneously (irregularly). Consequently, a different α-phase strengthening occurs within a dendritic cells. In this way, it is possible to explain **a great spread of the achieved HV 0.02 values**.
3. α-phase (matrix) of not a single one sample was not alloyed with the alloying element in amount with witch the alloy was alloyed. Even though the samples were small, a solidification rate was not fast enough.
4. **Just the smaller part of the alloying element Cu took a share in precipitation processes, α-phase strengthening.**



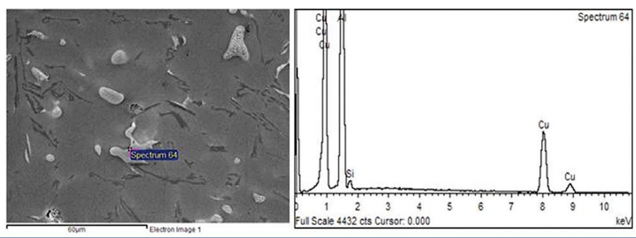
Al	Si	Fe	Ni	Cu
76.67	1.70	0.41	0.47	20.74

Fig. 2. Alloy AlSi6Cu1 with 140 ppm Sr, artificially aged; EDX of chosen particles [weight %]



Al	Si	Cu
97.84	1.65	0.51

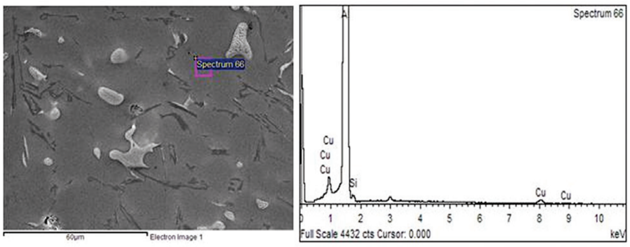
Fig. 3. Alloy AlSi6Cu1 with 140 ppm Sr, artificially aged; EDX matrix, [weight %]



Al	Si	Cu
54.43	1.63	43.94

Fig. 4. Alloy AlSi6Cu4 with 140 ppm Sr, artificially aged; EDX of chosen particles [weight %]

Fig. 2 to 5 show a representative documentation of EDX spot and area analyses. In every Figure the results of EDX analysis in K spectrum as well as in weight percent are given. Fig. 2 documents the presence of irregular white particles with high Cu content – particles based on $CuAl_2$. Fig. 3 and 5 provide low alloying of α-phase (ca 50 %) with the alloying element copper. Fig. 4 and 5 document the enormous amount of (dissolved) white particles with high Cu content based on $CuAl_2$.



Al	Si	Cu
96.48	1.21	2.31

Fig. 5. Alloy AlSi6Cu4 with 140 ppm Sr, artificially aged; EDX of matrix [weight %]

3. CONCLUSIONS

The hardening effect could be evaluated by measurement of microhardness of α-phase (matrix). The thermal treatment using artificial aging improves appreciable strength of the alloy with low Cu content; this effect is reduced, if Cu content grows, in concrete terms the hardening effect is falling from 19% to 5 %, if Cu content grows from 1 % to 4 %. Growing Cu content improves the hardening effect of α-phase matrix. If 3 % Cu is added (base material with 1 % Cu), the thermally not treated alloy hardens nearly by 28 % and the artificially aged alloy by 39 %. All samples, without regard to Cu content and Sr presence, contain a large amount of dissolved intermetallic phase $CuAl_2$. It is the result of conditions of the casting solidification as well as of absence of a solution annealing. All samples show a high heterogeneity of dissolved Cu in the matrix within one dendritic cell, which leads to the great spreads of HV0.02 values – dendritic cells are hardened heterogeneously. The content of dissolved Cu in α-phase is only 50 % of the alloying element amount. Conscious the crucial impact of copper content on the price of the alloy, it is hereby offering also the economic effect of chemical composition optimization. Higher copper content than 2 % do not have a fundamental importance on the mechanical characteristics of the material and in practice it is practically chosen as a certain insurance policy of minimum importance. A huge potential of the thermal treatment follows from it clearly, should succeed in solving most of copper in the case of the thermal treatment with solution annealing [Grzincic 2013]. Strontium does not influence α-phase microhardness. Simultaneously, it is necessary to pay attention to a satisfactory solidification rate at all areas of the casting, where maximum possible mechanical properties are expected. Of course, mechanical properties of the material of casted silumines are influenced by many other factors, e.g. by morphology of iron intermetallic phases, content, size and morphology of impurities or porosity characteristic [Caceres 1999].

REFERENCES

[Apelian 1984] Apelian, D., et al. Assessment of Grain Refinement and Modification of Al-Si Foundry Alloys by Thermal Analysis, AFS Transaction 161, 1984, pp 297-307.

[Argyropoulos 1983] Argyropoulos, S., et al. The Quantitative Control of Modification in Al-Si Foundry Alloys Using a Thermal Analysis Technique, AFS Transaction 27, 1983, pp 351-358.

[Bäckerud 1986] Bäckerud, L., et al. Solidification Characteristics of Aluminum Alloys, 2. edition, AFS/SKANALUMINIUM, Oslo (1986).

[Caceres 1999] Caceres, C. H., et al. The Effect of Cu Content on the Level of Microporosity in Al-Si-Cu-Mg Casting Alloys, Scripta Materialia, year 40, 1999, pp 631-637.

[Crossley 1966] Crossley, P.B. and Mondolfo, L. F. The Modification of Aluminum Silicon Alloys, Modern Casting, year 49, 1966, pp 53-64.

[Djurdjevic 1999] Djurdjevic, M., at al. The Effect of Strontium on the Microstructure of the Aluminum-Si and Aluminum-Cu Eutectics in the 319 Aluminum Alloy, International Journal of Cast Metals Research, No. 12, 1999, pp 67-73.

[Doty 1996] Doty, H. W., Samuel, A. M., Samuel, F. H. Factors Controlling the Type and Morphology of Cu-Containing Phases in the 319 Aluminum Alloy, 100th AFS Casting Congress, Philadelphia, USA, 20.–23. 4. 1996, pp 1–30.

[Garat 1992] Garat, M., et al. State of the Art Use of Sb, Na and Sr Modified Al-Si Casting Alloys, AFS Transaction 146, 1992, pp 821-832.

[Grzincic 2013] Grzincic, M. and Lukac, I. Optimization of the Solution Annealing Treatment of the AlSi10Mg(Cu) alloy. Manufacturing Technology, 2013, year 13, No. 4, pp 455-458.

[Grzincic 2014] Grzincic, M. and Lukac, I. Identification of Intermetallic Phases in the Alloy AlSi6Cu4, Manufacturing Technology, 2014, year 14, No. 2, pp 166–160.

[Kierkus 1999] Kierkus, W. T. and Sokolowski, J. H. Recent Advances in Cooling Curve Analysis: A New Method of Determining the ‹Base Line› Equation, AFS Transactions (1999).

[Sigworth 1983] Sigworth, G. K. Theoretical and Practical Aspect of the Modification of Al-Si Alloys, AFS Transaction 66, 1983, pp 7–16.

[Wang 1995] Wang, L. and Shivkumar S. Strontium Modification of Aluminum Alloy Casting in the Expendable Pattern Casting Process, Journal of Material Science, 1995, No. 30, pp 1584–1594.

CONTACT

Dr. Marko Grzincic
Illichmann Castalloy Ltd., Member of ALICON Group
Partizanka 81, 966 81 Žarnovica, Slovakia
tel: +421 456 830 342
e-mail: grzincicm@illichmann.sk
www.alicongroup.co.in