STUDIES ON THE INFLUENCE OF AlTi5B1 MODIFIER ON THE STRUCTURE AND PROPERTIES OF AlCuMg ALLOYS

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Abstract
New materials used in various industries require sufficiently high mechanical properties, fine-grained structure and ease of metal forming while minimizing production costs. For this reason, work is being carried out to develop new groups of alloys that make it possible to increase the strength of the obtained components while reducing their weight, and thus reducing production costs. This article focuses on two aluminium-based alloys with different content of alloying additives: copper and magnesium i.e., AlCu3Mg3 and AlCu4.5Mg6, which were produced by metallurgical synthesis. The as-cast alloys were characterized for their basic physical, mechanical and electrical properties and were subjected to structural analysis. In the next stage, the alloys were modified with 100, 500, 1000 and 2000 ppm of titanium and then their hardness, electrical conductivity and density were tested. Samples were also subjected to microstructural analysis. The obtained results allowed to examine the evolution of the AlCuMg alloy properties depending on the content of alloy additives and the amount of used modifier.
Keywords
aluminium, AlCuMg, modifier, AlTiB, casting

Introduction
Modern materials based on aluminium and other metals are faced with ever higher requirements in terms of their functional and operational properties, with a simultaneous tendency to reduce the weight and price of the final products. This is most often achieved by shortening the technological line of their production and reducing material consumption. Obtaining the required material properties is possible both through the development of a new range of alloy grades (determined by the selection of appropriate alloy additives) and the use of the best production technology for a given product and the path of further processing.

The idea and the main assumption of this work was to obtain new varieties of Al-Cu-Mg alloys by casting, constituting a specific combination of the 2XXX series (aluminium - copper) and 5XXX series (aluminium - magnesium) alloys, and to conduct research on the effect of modifier addition on the structure and final mechanical and electrical properties as well as the internal structure of the product. Aluminium-copper alloys (series 2XXX) are a group of materials with high strength properties which are commonly subjected to heat treatment (supersaturation and aging, both natural and artificial). On the other hand, aluminium-magnesium alloys, despite the presence of the solvus line in their phase diagram (which allows for their thermal treatment), are mainly produced as solution-hardened alloys or by cold plastic deformation. The concept of obtaining new, high-strength alloys is therefore a combination of the advantageous properties of Al-Cu and Al-Mg materials. With the selection of the appropriate proportion of Cu and Mg in the alloy and their heat treatment, the new material will have a high set of mechanical properties based on the superposition of precipitation and solution hardening phenomena. The design of new types of materials should be correlated with the appropriate technology of their production.

The classic production technology of profiles made from aluminium alloys which are commonly known and used is based on the process of metallurgical synthesis and refining of liquid metal which allows to cast large-size ingots and cooling process (diameters of ingots are ranging from 200 mm to 300 mm). Next the process of long-term heating of ingots occurs (the so-called homogenization) and following cooling, reheating of the ingots for extrusion and the subsequent process of extruding the bars, homogenization and supersaturation and heat treatment (natural or artificial aging) is used. The alternative technology (proposed for the new group of AlCuMg alloys) is based on the process of metallurgical synthesis and refinement of liquid metal, continuous casting, homogenization annealing and supersaturation and heat treatment (natural or artificial aging). Its use allows for a significant shortening of the production line of products (round profiles) and the elimination of the most expensive process such: heating of ingots before the extrusion process and the extrusion process itself. However, it should be noted that the final product from the extrusion process is characterized by a favourable, fine-grained internal structure, guaranteeing its high strength and ease of processing by metal forming. The structure of cast materials is completely different. For pure metals and alloys, the classic casting structure includes a frozen crystal zone at the surface, a dendritic zone and an equiaxed crystal zone around the axis of the ingot. However, this type of structure is not advantageous due to the low mechanical properties and susceptibility to cracking (during metal forming) of the obtained materials. An effective method of grain refinement and mechanical properties increase, used in practice, and derived from the theory of heterogeneous nucleation, is the control of the crystallization process. It is done by creating an appropriate base for crystal nucleation. Such procedure is called structure modification [1–3]. Increasing the number of grains in the material directly improves the mechanical properties and, what is extremely important, reduces the segregation degree and susceptibility to hot cracking of alloys [4].

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Titanium was used as the first modifier for aluminium and its alloys. The addition of Ti increases the melting point to 665 °C. This effect is essential for the nucleation and growth of solid aluminium grains. The titanium additives are introduced by aluminium master alloys containing numerous crystals of the TiAl3 compound. From the relationships depicted in the Al-Ti phase diagram, a Ti-rich metal in contact with aluminium may start to solidify at a temperature that is above the melting point of the base alloy. Hence, the first solid phase nucleation will start near the surface of the AlTi3 particle [5]. Nevertheless, there is a disadvantageous phenomenon in the process - the decomposition of TiAl3 particles, which leads to the disappearance of the grinding effect and it is necessary to supply the process with high amounts of master alloys to maintain this effect. Therefore, intensive research led to the creation of Al-Ti-B master alloys. Most of the titanium in modern modifiers is present as TiB2, which is practically insoluble in molten aluminium, so high amounts of such master alloys are not necessary. When it is used, there is also a long-lasting fragmentation effect [6]. In industrial practice, research was also carried out on the use of Al-B alloys as a substance disintegrating the structure [7]. It turned out that AlB2 is a very efficient modifier, but it dissolves readily in aluminium, where it reacts with titanium and strontium in the alloy. Additionally, it deteriorates the susceptibility of the alloys to metal forming, causing their brittleness [8]. Further research led to the observation that TiB2 particles also had some disadvantages. They are quite thick and tend to agglomerate, which creates many quality problems with the final products. This contributed to the development of Al-Ti-C master alloys. Even though TiC particles are smaller and less prone to agglomeration than TiB2, they have not gained such widespread use as TiB2. The main reason was their low efficiency [7,9]. The above-mentioned problem of modification of aluminium and its alloys is described in the literature. However, there are no in-depth analyses of the behaviour of the material after casting, with a high content of such alloys as Cu and Mg, and thus constituting the research material that is the subject of this study. On this basis, a decision was made to test the influence of the most promising structure modifier (according to the authors) [6] - the effect of AlTi5B1 master alloy modification on the properties and structure of AlCuMg alloys dedicated to the continuous casting process and direct processing by metal forming (mainly die forging) and machining.

**Methods**

Melting, metallurgical synthesis and casting of individual alloys were carried out in order to obtain materials for testing. First, the material for casting was prepared, both in the form of pure aluminium and alloy additives such as pure magnesium (100%), AlCu50% master alloy and AlTi5B1 structure modifier. The base material (99.7% pure aluminium) in the form of pieces was placed in a crucible mounted in an induction furnace, which was heated to a temperature of 740 °C. After the pure aluminium was melted, the alloying additives (Mg and AlCu50%) were introduced into each crucible. Next metal was thoroughly mixed and left in the furnace for another 10 minutes.
After melting and mixing the components, Desydral (in the amount of 0.5% of the feed weight) was added using a special graphite lance to degas the alloy. The liquid metal refining process took 3 minutes in total. In the final stage of alloying, the alloy was refined with argon gas (refining time of 5 minutes). The exact amounts of the input materials, master alloys, modifiers and refining agents used are shown in Table 1.

Table 1. Mass of each input material used in the metallurgical synthesis process

| Alloy                  | Mass of individual input materials [g] |
|------------------------|----------------------------------------|
|                        | Al  | Mg  | AlCu50 | AlTi5B1 | Desydral |
| AlCu3Mg3               | 250 | 7.5 | 15     | 0       | 1.36     |
| AlCu3Mg3 + 100 ppm Ti  | 250 | 7.5 | 15     | 0.55    | 1.36     |
| AlCu3Mg3 + 500 ppm Ti  | 250 | 7.5 | 15     | 2.73    | 1.36     |
| AlCu3Mg3 + 1000 ppm Ti | 250 | 7.5 | 15     | 5.45    | 1.36     |
| AlCu3Mg3 + 2000 ppm Ti | 250 | 7.5 | 15     | 10.90   | 1.36     |
| AlCu4.5Mg6             | 230 | 10.4| 27.6   | 0       | 1.34     |
| AlCu4.5Mg6 + 100 ppm Ti| 230 | 10.4| 27.6   | 0.54    | 1.34     |
| AlCu4.5Mg6 + 500 ppm Ti| 230 | 10.4| 27.6   | 2.68    | 1.34     |
| AlCu4.5Mg6 + 1000 ppm Ti| 230 | 10.4| 27.6   | 5.36    | 1.34     |
| AlCu4.5Mg6 + 2000 ppm Ti| 230 | 10.4| 27.6   | 10.72   | 1.34     |

Afterwards, the crucibles were removed from the furnace, mixed again to homogenize the material in volume and poured into a crucible with an internal diameter of 40 mm and a height of 120 mm. The material in the form of ingots was obtained, from which samples were cut for further tests. As a result, alloys with the following chemical composition were obtained: AlCu3Mg3 and AlCu4.5Mg6. Obtained castings were analysed for their basic physical, mechanical and electrical properties, which allowed to obtain information about the properties of these alloys in the state after casting and before modification (reference material). The other part of the castings obtained by metallurgical synthesis was modified with titanium in the form of AlTi5Bi master alloy with Ti 100, 500, 1000 and 2000 ppm. Fig. 2 shows the process of metallurgical synthesis of castings.
Finished ingots made of AlCuMg alloys were tested for physical, mechanical and electrical properties after casting and after modification. Before starting the tests, samples were cut from the central part of each casting and polished with sandpaper with a grain size of 500, 800, 1200, 1500, 2000, respectively.

The hardness tests were carried out using the Brinell method. Analysis was carried out on an INNOVATEST model NEXUS 3000 hardness tester with a ball with a diameter of 2.5 mm and at a given load 31.25 kg. Five prints were made on each of the samples.

After the hardness test, electrical conductivity was measured on the same samples, 10 measurements were made on each of the samples. The electrical conductivity was measured with a Sigtastest model 2.069 meter, using the eddy current method.

Another study which was carried out was the measurement of the casting density, based on the Archimedes law, the density was determined using the following relationship:

$$\rho = \frac{m_p}{m_p - m_w} (\rho_w - \rho_p) + \rho_p$$

where:
- $\rho$ – density of the tested material [g/cm$^3$],
- $m_p$ – mass of the tested sample in the air [g],
- $m_w$ – mass of the tested sample in the water [g],
- $\rho_p$ – air density [g/cm$^3$],
- $\rho_w$ – the density of distilled water at a certain temperature [g/cm$^3$].

Density of distilled water was determined based on tabular data which links it with test temperature. The obtained final density result was the average of five individual measurements.

As part of the work, microstructural tests were also carried out using the Olympus GX 51 light microscope equipped with digital image recording.
Results and discussion

At the first stage of the research, the Brinell hardness measurements were carried out on AlCu3Mg3 and AlCu4.5Mg6 alloys in the state immediately after casting and after modification with titanium. The results of hardness measurements are presented in Fig. 3.

![Fig. 3. Brinell hardness for samples with different titanium content. Source: Authors'](#)

The AlCu3Mg3 and AlCu4.5Mg6 alloys in the condition after casting have Brinell hardness of 72.5 and 76 HBW, respectively. Mechanical properties of the examined alloys in the as-cast state show significant increase in the hardness compared to alloys described in the literature. According to the research results presented in [10], AlCu alloys with the content of copper addition at the level of 2% and 4% by weight show a hardness of 37 and 47 HBW respectively, while the AlCu4.5 alloy in the state after casting reaches a hardness value of 57 HBW [11]. AlMg alloys with a level of magnesium 3% and 6% have hardness of 58 and 60 HBW respectively [12]. The obtained results of hardness measurements of the tested AlCuMg alloys are at a satisfactorily high level already at the casting stage.

The titanium modification of the AlCu3Mg3 alloy results in an increase in the hardness of the alloy, reaching the highest hardness for a Ti-modified sample in the amount of 2000 ppm, which is a 13% increase in hardness compared to the sample after casting. Slightly lower hardness in relation to the casting hardness was recorded for the AlCu3Mg3 sample enriched with the modifier in the amount of 100 ppm (69 HBW - hardness decrease by 5%), which may be caused by different structure in relation to other samples or local porosity of the material. Modification with titanium in the amount of 500 and 1000 ppm increased the hardness in relation to the casting by 1 and 7% respectively.

AlCu4.5Mg6 alloy has a hardness of 76 HBW in the as cast state. Hardness is increasing with increasing the amount of modifier. The highest hardness has a sample with the addition of a modifier in the amount of 2000 ppm – 83.1 HBW (hardness increase by 9% compared to the alloy before modification). The addition of titanium in the amount of 100 and 1000 ppm increased the hardness of the alloy by 3 and 4%, respectively. Modification of titanium in the amount of 500 ppm decreased the hardness in relation to casting by approx. 1%.

The results of the electrical conductivity tests of AlCuMg alloys in the as-cast state and after modification with various titanium contents are shown in Fig. 4.
As a result of modification of AlCuMg alloys, a decrease in their electrical properties was observed. The AlCu3Mg3 alloy generally has better electrical properties than the AlCu4.5Mg6 alloy, both as-cast as well as after modification. It is related to the lower content of copper and magnesium alloying additives, which reduce the electrical properties of the material.

The AlCu3Mg3 alloy in the as-cast condition shows electrical conductivity of 22 MS/m. The lowest level of electrical properties was obtained when the alloy was modified with titanium in the amount of 500 ppm (18.8 MS/m) and 2000 ppm (18.9 MS/m) which results in a decrease of the electrical conductivity of the alloy by 15 and 14 % respectively.

Before modification, the AlCu4.5Mg6 alloy shows electrical conductivity of 17.3 MS/m, decreasing in electrical properties to the level of 15.1 MS/m for the modification with titanium in the amount of 2000 ppm (a decrease in electrical conductivity by 13%). It is directly related to the increase in the number of grain boundaries in the material. Modifier addition reduces the electrical conductivity of the casting by 5% (100 ppm Ti), 10% (500 ppm Ti) and 8% (1000 ppm Ti).

As part of the research, the density of the samples was also measured. Results are shown in Fig. 5.

The density of the tested castings before modification was 2.68 g/cm$^3$ for the AlCu3Mg3 casting and 2.62 g/cm$^3$ for the casting with a higher content of alloy additives (AlCu4.5Mg6).

In case of AlCu3Mg3 alloys, the density does not change significantly with increasing titanium content, oscillating around 2.68-2.69 g/cm$^3$. In case of the AlCu4.5Mg6 alloy, there is a noticeable variation between individual samples. The highest density has a sample with a titanium content of 2000 ppm equal to 2.70 g/cm$^3$, and the
smallest density has a sample directly after casting – 2.62 g/cm³, which proves the beneficial effect of the modification treatment on reducing the porosity of the castings.

Industrial AlMg alloys dedicated for metal forming have density in the range of 2.64-2.69 g/cm³ [13]. 2XXX series aluminium alloys show a slightly higher density at the level 2.75-2.84 g/cm³ [13]. According to the literature data, the density of AlCu alloys with the addition of copper in the amount of 2% and 4% by weight is at the level of 2.72 and 2.77 g/cm³ respectively, and the alloy density increases with increasing copper content [10]. The introduction of the modifier to the examined AlCuMg alloys allows to obtain a density which for the tested alloys is similar to pure aluminium (2.70 g/cm³), therefore conclusion is that these products do not show significant porosity [13].

Structural tests were also carried out on the prepared samples. They included the analysis of the microstructure using an optical microscope. The obtained microstructures are shown in fig. 6-9.

![Microstructure of AlCu3Mg3 alloy before modification.](image)

Fig. 6. Microstructure of AlCu3Mg3 alloy before modification.

*Source: Authors’*

![Microstructure of AlCu3Mg3 alloys modified with various titanium content.](image)

Fig. 7. The microstructure of AlCu3Mg3 alloys modified with various titanium content: a) 100 ppm b) 500 ppm c) 1000 ppm d) 2000 ppm. *Source: Authors’*
Fig. 8. Microstructure of AlCu4.5Mg6 alloy before modification.

Source: Authors’

Before modification AlCuMg alloys had a classic casting structure, the distribution of grains in the cross-section was rather irregular and their size reached a few or even several millimetres. The addition of the modifier in the amount of 0.1% resulted in significant grain fragmentation in the ingots to a diameter of about 0.1-0.2 mm. Such a small amount of modifier contributed to the satisfactory refining effect of the ingot structure. Increasing the titanium content in the alloy contributed to the reduction of the grain diameter by approx. 0.1 mm and less for 500 - 1000 ppm Ti. The addition of titanium in the amount of 2000 ppm led to a very fine fragmentation of the structure of the ingot. The grains had a diameter of approx. 0.05 mm and less. The tested scope of titanium addition in castings has a positive effect on the structure and grain diameter reduction. The obtained grain size
corresponds to products extruded from aluminium alloys [14,15].
The modification treatment contributed to the transformation of the structure from columnar grains (dendrites) to equiaxed grains as well as to the reduction of grain size (with a simultaneous increase in their amount), which improves their ease of metal forming and contributes to a reduction in costs and improvement of production efficiency [4]. Reducing the grain size in ingots is one of the strengthening mechanisms according to the Hall-Petch relationship [16]:

\[ \sigma_p = \sigma_0 + k d^{-1/2} \]

where:
- \( \sigma_p \) – yield point,
- \( \sigma_0 \) – constant,
- \( k \) – constant,
- \( d \) – average grain size.

Increasing the number of grains because of the modification treatment contributes to a direct improvement of mechanical properties (low for pure aluminium) and a reduction in the degree of segregation and susceptibility to hot cracking of the alloys.

**Impact**

There is a constant market demand for new products obtained from new types of alloys in innovative, cost-effective manufacturing technologies. This is especially true within non-ferrous metals market where year-to-year there is an intensive substitution of extremely expensive copper products with products based on aluminium and its alloys. Various AlCuMg alloys subjected to tests constitute a specific combination of the 2XXX AlCu series and the 5XXX AlMg series. These alloys will have up to 10% higher mechanical properties (after heat treatment) than the current alloys of the 2XXX series. This type of product (round cast profile) with higher properties, used for products obtained in the further processing by die forging or machining, will allow for direct replacement of some of the existing alloys and partial reduction of weight and dimensions ("slimming") of the final products, since the "slimmed-down" product, thanks to its higher strength properties, will be characterized by a load capacity comparable to the products currently used. Limiting the mass of the product brings measurable economic benefits (lower product price) resulting from lower material costs of production. It should also be remembered that the profiles currently used for the die forging process and machining are made of 2XXX, 5XXX series alloys, which are obtained in traditional technology - the extrusion process and a number of accompanying operations that are energy and material consuming (the issue of production waste). The proposed technology of continuous casting of products from new varieties of AlCuMg alloys will therefore allow for a partial reduction of the product price also at the production stage.

After assuming market prices of pure metals such as aluminium, copper and magnesium, as well as knowing the costs of acquiring metallurgical master alloys (AlCu50 and AlTi5B1), taking into account employee costs, electricity, heat treatment and other costs determined based on conversations with entrepreneurs from the industry casting and metal forming of non-ferrous metals, it can be estimated that the cost of producing 1 kg of profile extruded from the currently used 2XXX series alloys is approximately 10.7 PLN/kg. The production of the same amount of profile from the new range of AlCuMg alloys based on the continuous casting technology will reduce this price to approximately 9.85 PLN/kg. Additionally, the production costs can be reduced by about 13% (to the level of 8.7 PLN/kg) in case of using 80% of the total input for the foundry process as the input material of qualified waste materials (scrap). Obviously, the amount of scrap can be increased up to 95%, which will additionally reduce the cost of manufacturing the product.

The reduction in the price and the fact that the final forging or machined parts can be slimmed down by about 5-10% (which will result in a reduction in the material consumption of the product) allows to state that the work covered by this study a significant impact and a favourable economic effect. It also allows for the management of a large part of waste scrap from non-ferrous metals.

**Conclusions**

The basic physical, mechanical, electrical and structural properties on a micro scale were tested on new aluminium-based alloys with various contents of copper and magnesium alloying additives, which underwent a structure modification treatment. Modification with the use of inoculants is aimed at changing the form of the
casting structure - from the classic casting structure to a fine-grained and uniform structure over the entire cross-section of the ingot. This type of alloy structure has a positive effect on the mechanical properties and the ease of metal forming processes. Analysing the results obtained in the experimental tests, a significant influence of the addition of the structure modifier in the form of titanium on the mechanical, electrical and structural properties of Al-Cu-Mg alloys is noticeable.

The hardness of the alloys after casting reaches a higher value for the alloys with a higher content of AlCu4.5Mg6 alloying additives than for the AlCu3Mg3 alloys. The addition of titanium significantly increased the hardness of the castings after the modification in relation to the hardness of the alloy after casting. After the Brinell hardness test, the highest increases were obtained for titanium content of 2000 ppm for both the AlCu3Mg3 alloy (13% increase) and the AlCu4.5Mg6 alloy (9% increase in hardness). Generally, a greater impact on the hardness of the alloy because of modification with titanium with different additive content was observed for the AlCu3Mg3 casting. The hardness increase is higher than for the analogous modification variants in case of the AlCu4.5Mg6 alloys. The hardness test being the measure of the mechanical properties of the casting clearly indicates the positive effect of the modifier on the increase in strength properties of AlCuMg alloys.

The electrical conductivity of the alloys in the as-cast condition reaches the level of 22 MS/m for the AlCu3Mg3 alloy and 17.3 MS/m for AlCu4.5Mg6 alloy. The modification treatment contributed to the decrease in the electrical properties of the alloys, the highest decrease to 18.8-18.9 MS/m (14-15% of the electrical conductivity value before modification) was recorded for the modification of the AlCu3Mg3 alloy with titanium in the amount of 500 and 1000 ppm. The decrease in electrical properties of 13% was observed after modification of the AlCu4.5Mg6 alloy with titanium in the amount of 2000 ppm. According to the literature data, the addition of titanium, even in small amounts, reduces the electrical properties of aluminium, which is also confirmed by the results of the research.

The study of the density of the alloys before and after the modification showed no significant differences for both alloys, reaching the same density level for the AlCu3Mg3 alloy with different titanium content, while for the AlCu4.5Mg6 alloy there was a slight differentiation in the density levels of ~ 0.08 g/cm³ which proves the positive effect of the modification on reducing the porosity of the alloy. The density of AlCuMg alloys enriched with titanium is similar to that of pure aluminium, which proves the beneficial effect of the modification treatment on reducing the porosity of the castings.

To sum up, the tested alloys already at the casting stage have high mechanical properties, which will be even higher after applying heat treatment. The use of the structure modifier allows for their additional increase and most importantly, the reduction of the average grain size to the size known from traditionally used extruded products. Their advantage is that they are obtained in the continuous casting technology, which means that they will be significantly cheaper than those currently offered on the market. Additionally, they can be made from aluminium scrap, which may further reduce the price of the final product.

Conflict of interest
There are no conflicts to declare.

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