Analysis of the phase composition and the structure of aluminum alloys with increased content of impurities

Yu. N. Mansurov, Professor, Deputy Minister¹, e-mail: yulbarsmans@gmail.com
J. U. Rakhmonov, PhD, Research Fellow², e-mail: jovid.rakhmonov@googlemail.com

¹ Ministry of Innovation Development of the Republic Uzbekistan, Tashkent, Uzbekistan.
² University of Quebec at Chicoutimi, Canada.

The development of fundamental knowledge that allows making proper correlation among the chemical composition, structure and properties of non-ferrous alloys is a priority task for the metallurgy of non-ferrous metals and alloys, as this knowledge makes the main contribution to the development of this subject and is a powerful tool for expanding the areas of their application. A variant of the establishment of regularities in metal science is the study of phase equilibria, transformations in the temperature range and compositions of metallic systems. In the scientific literature there is a lot of information on the results of studies of two- and three-component alloys in order to construct equilibrium phase diagrams. However, the non-equilibrium crystallization of alloys, and thus, the non-equilibrium phase diagrams are of greater practical interest from the point of view of industrial production. Taking into account that the compositions of industrial alloys, as a rule, are multi-component, it can be stated that there is no reliable information on multi-component systems in the literature. Industry is interested in the possibility of using alloys with low cost, however, with high performance properties, which is possible in the case of using chemical elements of technical purity, industrial waste or scrap for their preparation. First of all, it concerns aluminum alloys, as the volume of their consumption is the highest among alloys of non-ferrous metals. In addition, the number of applications made of these alloys is continuously growing. The purpose of this paper is to perform a comparative analysis of the non-equilibrium phase diagrams of aluminum-based alloys with an increased content of impurities in comparison with their equilibrium counterparts known from the published scientific literature. In the process of work, equilibrium and non-equilibrium phase diagrams of aluminum with basic alloying elements and the most frequent harmful impurities are constructed.

Key words: aluminum alloys, impurities, structure, phase transformations, phase diagrams, isothermal and polythermal cross sections.

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In accordance with the increasing role of the program of localization of production in the economy, there is a growing need for high-quality alloys of non-ferrous metals, especially aluminum. At the same time, industrial production in the country needs cheaper but high-quality aluminum alloys; this necessitates the development of technologies for processing an increasing amount of scrap and aluminum alloy waste to create commodity products that are not inferior to the world’s analogues. Thus, the improvement of the operational properties of alloys with an increased content of impurities has acquired its relevance. The urgency of the issue is even greater for the regions of Russia, where there is no production of primary aluminum, e.g. the Far East, which is a huge territory with a small population and growing industrial production, and the volume of aluminum alloys used by the enterprises of the region to make finished products is constantly growing. To meet the growing demand for aluminum alloys, technologies that allow processing scrap aluminum are needed. Accordingly, in order to develop new technologies for processing scrap metal, it is necessary first of all to know the phase transformations under real conditions of crystallization of aluminum alloys with a high content of impurities, so that in the future it would be possible to develop methods for neutralizing the harmful effect of impurities and then processing the alloys and fabricating them to produce high-quality, finished products. Considering that industrial production in the regions including those where there is no production of primary aluminum, involves machining the ingots of aluminum alloys in large volumes, then scrap processing of these enterprises and production of quality secondary alloys from it, followed by their implementation in the form of finished products, become an advantageous element of the innovative eco-
In order to create such a production (summarizing the conclusion about the need to process scrap metal and the consequent consequence of it), it should be noted that knowledge of phase transformations in multi-component aluminum-based systems with basic alloying elements and the most harmful impurities, in turn, would allow enterprises to prepare from them quality products, e.g. for automotive or ship-building and ship repair.

The purpose of this work is to construct multi-component phase diagrams of aluminum with basic alloying elements and an increased content of the most harmful impurities for real crystallization conditions in order to ensure the possibility of using aluminum alloy scrap by industry by improving the quality of existing alloys or developing new ones.

To achieve this goal, it was necessary to solve the following tasks:
- to construct non-equilibrium (at high cooling rates) phase diagrams of four-component systems based on aluminum and basic impurities;
- to construct the iso- and polythermal sections (sections) of four-component systems based on aluminum;
- to study phase equilibria and structure of aluminum alloys with basic alloying elements, where improved operational properties are expected.

### Materials and Methods

Model aluminum alloys with an increased content of impurities, scrap and waste, as well as standard secondary alloys based on aluminum were used in the work.

Alloys were prepared in a laboratory electric resistance furnace with silicate by heaters. The weight of each melted material was 2 kg, for which the charge was pre-calculated. Aluminum of technical purity, Al – 10% Fe, Al – 5% Ni, Al – 7.5% Mn, Al – 5% Co based master alloys were used as charge materials, the remaining elements were introduced into the melt in pure form. The temperature of heating of the alloys maintained at the range of 720–740 °C, since at high temperatures volatilization of the fusible impurities and, most importantly, the main alloying elements and an increased content of the most harmful impurities, in turn, would allow enterprises to prepare from them quality products, e.g. for automotive or ship-building and ship repair.

The analysis of non-equilibrium crystallization of aluminum alloys of 3- and 4-component systems containing iron and silicon is carried out, since they are considered to be the most harmful impurities in foundry aluminum alloys. In general, crystallization of alloys within the primary crystallization region (Al) is considered here, which, however, does not prevent the proposed method from being applied to other alloys. Copper and magnesium were chosen as the main alloying elements (not counting silicon as the main alloying element), because aluminum alloys containing these elements are the most commonly used alloy groups [5–8].

\[ \text{Al} - \text{Cu} - \text{Fe} - \text{Si system}. \]

Following the most probable variant of the equilibrium diagram of this system, it can be seen that in most industrial siluminis (5–12% Si, up to 6% Cu, up to 1% Fe), iron is a part of the AlFeSi phase, which does not participate in peritectic reactions. Therefore, the phase composition of alloys in the solid state in the presence of copper in the cast state corresponds to the equilibrium (Al) + (Si) + AlCu + AlFeSi.

With lower silicon and higher copper concentrations, two peritectic transformations occur:

\[ L + \text{Al}_8\text{Fe}_2\text{Si} \rightarrow (\text{Al}) + \text{Al}_4\text{FeSi} + \text{Al}_7\text{FeCu}_2; \]
\[ L + \text{Al}_7\text{FeCu}_2 \rightarrow (\text{Al}) + (\text{Si}) + \text{Al}_4\text{FeSi}, \]

incomplete completion of which, can lead to the presence of “superfluous” phases of AlFeSi and AlFeCu2 in the cast structure.

With increasing iron concentration and decreasing silicon, the probability of the formation of AlFeCu and AlFe phases is increased, and as a result of suppression of peritectic transformations, the following reactions are expected to occur:
$L + Al_3Fe \rightarrow (Al) + Al_8Fe_2Si + A_{16}(FeCu)$;
$L + A_{16}(FeCu) \rightarrow (Al) + Al_8Fe_2Si + Al_7FeCu_2$.

In accelerated solidification in metallic molds, as in the $Al – Fe – Si$ system, formation of the $Al_8FeSi$ equilibrium phase is suppressed in quaternary alloys containing 2–3% $Fe$ and 2–3% $Si$, resulting in non-equilibrium crystallization, which leads to non-equilibrium phase composition of cast alloys: $(Al) + (Si) + Al_2Cu + Al_8Fe_2Si$. This has a positive effect on the mechanical properties, since the morphology of the $Al_5FeSi$ phase is more favorable than the morphology of the $Al_3FeSi$ phase. The results obtained correspond to the results of [9–11].

$Al – Fe – Mg – Si$ system.

As follows from the equilibrium phase diagram of this system [1–2], there are four $Fe$-containing phases in the aluminum angle: $Al_8Fe; Al_8Fe_2Si; Al_5FeSi$ and $Al_8FeMg_3Si_6$, which can crystallize primarily or through various eutectic and peritectic reactions. Primary crystals of the first phase are usually found only at silicon concentrations of less than 3% and iron content greater than 2%, and the latter at a concentration of $Si > 7\%$. $Mg > 1\%$, and $Fe < 0.5\%$. As in the $Al – Fe – Si$ ternary system, an increase in the cooling rate substantially narrows the region of primary crystallization of the $Al_3Fe$ phase. In alloys with an increased content of magnesium, as follows from the equilibrium phase diagram of $Al – Fe – Mg – Si$, the presence of iron and irrespective of the silicon concentration, only one iron-containing phase, $Al_3Fe$, can be formed.

However, in industrial $Al – Mg$ alloys with $Fe$ and $Si$ impurities containing less than 6% $Mg$ and obtained by casting into metallic molds, an $Al_8Fe_2Si$ phase is often formed, which, like in the case of the $Al – Fe – Si$ ternary system, can be explained by the influence of the rate of crystallization. The larger the $V_c$, the greater the probability of formation of the $Al_8Fe_2Si$ phase, which can be illustrated by the example of the liquidus projection of the quadruple phase diagram (Fig. 1), in which the dashed line shows the shift of the boundary of the double eutectic reaction $L \rightarrow (Al) + Al_3Fe$ to the $Al – Mg$ side with growth of $V_c$ (from the DNOPI line to the $D' – N – I'$ line). The results on the study of the four-component diagram of the $Al – Fe – Mg – Si$ state correspond to those published in [12–14].

$Al – Fe – Cu – Si$ system.

Following the most probable version of the equilibrium diagram of this system, it can be seen that in most industrial siluminins (5–12% $Si$, 0–6% $Cu$, 0–1% $Fe$), iron forms part of the $Al_8FeSi$ phase, which does not participate in peritectic reactions. Therefore, the phase composition of alloys in the solid state in the presence of copper in the cast state corresponds to the equilibrium $(Al) + (Si) + Al_3Cu + Al_7FeSi$.

With a lower silicon and higher copper contents, two peritectic transformations can occur: $L + Al_8FeSi \rightarrow (Al) + Al_8FeSi + Al_7FeCu_2$ and $L + Al_7FeCu_2 \rightarrow (Al) + (Si) + Al_7FeSi$, the incomplete completion of which may lead to the presence in the cast structure of “superfluous” phases of $Al_8Fe_2Si$ and $Al_7FeCu_2$.

With increasing iron concentration and decreasing silicon, the probability of $Al_8(FeCu)$ and $Al_3Fe$ phases increases due to suppression of peritectic transformations: $L + Al_3Fe \rightarrow (Al) + Al_8Fe_2Si + Al_8(FeCu)$ and $L + Al_8(FeCu) \rightarrow (Al) + (Si) + Al_8Fe_2Si$. In accelerated solidification in metallic forms, as in the $Al – Fe – Si$ system, formation of the $Al_8FeSi$ equilibrium phase is suppressed in quaternary alloys containing 2–3% $Fe$ and 2–3% $Si$, resulting in non-equilibrium crystallization, which leads to non-equilibrium phase composition of cast alloys: $(Al) + (Si) + Al_3Cu + Al_8Fe_2Si$. This positively affects the mechanical properties, since the morphology of the $Al_8Fe_2Si$ phase is more favorable than the morphology of the $Al_3FeSi$ phase. The results obtained during the study of the $Al – Fe – Cu – Si$ phase diagram correspond to [15–18].

$Al – Fe – Ni – Si$ system.

Analysis of nonequilibrium crystallization in this system is of practical importance, since, on the other hand, nickel is a part of a number of industrial alloys, in particular piston silumin, and on the other hand, the presence of several peritectic reactions has a strong influence on the structure.

As a rule, nickel is introduced into alloys to form a triple compound $Al_8FeNi$, which positively affects the characteristics of heat resistance. In order for the negative effect of this phase on plasticity to be minimal, the inclusion of the $Al_8FeNi$ phase should have a favorable morphology.
globular or skeletal. Such a morphology can be achieved in the case of the formation of this phase in the eutectic reaction. On the other hand, iron should not form other phases with needle-shaped morphology, in particular Al$_3$Fe and Al$_5$FeSi. It should be noted here that the ratio of Fe:Ni = 1:1 turns out to be sufficient only for alloys containing less than 5–6% Si, and with a higher silicon content there is a danger of formation of primary or eutectic needles of the Al$_3$FeSi phase. The structures of three alloys, which contain 1.7% of Fe and 1.7% of Ni, show a strong influence of silicon on the morphology of Fe-containing phases (Fig. 2). To explain this, it is proposed to use the variant of the equilibrium diagram of the state of Al – Fe – Ni – Si with allowance for the suppression of peritectic transformations.

Of the three non-variant peritectic transformations occurring in the given system, the most important for silumin is the reaction of $L + Al_5FeSi \rightarrow (Al) + (Si) + + Al_5FeNi$, the failure of which leads to the presence of an “excess” phase of Al$_5$FeSi in the structure.

**Industrial silumin, doped with copper (“cuprous”)**

Silumin containing copper (up to 8%), which are produced in the enterprises of the region, are considered. According to the concentration of silicon (4–13%), most alloys are related to pre-eutectic. A structure close to eutectic has only silumin AK12M2. To analyze the phase composition of most alloys in the T4 state, one should use the Al – Si – Cu – Fe – Mg system state diagram. Only high-purity alloys can be analyzed for the quaternary Al – Si – Cu – Mg system and, even more rarely, for the ternary Al – Si – Cu system. The phase composition of the aluminum matrix after aging (especially in the T7 regime) can be analyzed to a considerable extent from the diagrams of Al – Si – Cu and Al – Si – Cu – Mg. In the presence of manganese, some information can be extracted from the corresponding multicomponent phase diagrams, which have by now been poorly studied. To analyze structures in the cast state, one should use nonequilibrium phase diagrams.

The AK5M2 alloy is characterized not only by a soft restriction on impurities (in particular, iron up to 1.3%, zinc up to 1.5%), but also by a large interval of the content of alloying elements, especially copper (1.5–3.5%) and magnesium (0.2–0.8%). This makes it easier to prepare using mixed scrap and waste. Silumin AK5M2 — one of the most common, because of its low cost, castings from it are used mainly in the cast state. As in the copper-bearing silumine AK5M, the basic structural constituents of the alloy are a solid solution based on aluminum (Al) and a eutectic based on aluminum and silicon, or rather several different ones, including multiphase eutectics, which include, in addition to (Si), various phases containing Fe, Mn, Cu, Mg and other elements. Depending on the particular composition, the microstructure can vary greatly.

At a low content of manganese, iron (and its amount, as a rule, is not lower than 1%) is mainly included in the composition of the β-phase. Conversely, if the concentration of manganese is closer to the upper limit, needle-like inclusions of the β-phase are practically not encountered, since all iron binds to the Al$_{15}$(FeMn)$_3$Si$_2$ phase. Moreover, it is possible for the primary crystals of this phase to form, especially when cast into the ground. The number of phases of Al$_2$Cu, Al$_5$Cu$_2$Mg$_6$Si$_x$ and Mg$_2$Si is much larger than in the AK5M alloy. Zinc, as a rule, is fully included in the composition of aluminum solid solution. When the alloy is heated, globular particles of the silicon phase are formed. In this case, not all of the magnesium and copper can dissolve in the solid solution, as follows from the section of the aluminum-silicon-copper-magnesium phase diagram at 10% Si and 500 °C (Fig. 3). In the microstructure of heated and cooled castings, magnesiu-containing phases (Al$_5$Cu$_2$Mg$_6$Si$_x$, Mg$_2$Si and Al$_5$FeMg$_3$Si$_6$) can often be detected.

Alloy AK5M2 is made from recycled materials. It has satisfactory casting properties and corrosion resistance. In the AK5M4 alloy, the copper content is approximately equal to the silicon content, so the volume fraction of the copper-containing phase, in addition to the silicon phases, is greater than the other phases. A significant part of copper (up to 1.5%) when casting is part of a solid solution based on aluminum, which makes this silumin more hard compared to those previously considered. It has a wide range of concentrations on the alloying components, more admits the content of impurities and is mainly prepared from scrap. Depending on the ratio of Fe and Mn, iron can be included in one of two phases: β or Al$_{15}$(FeMn)$_3$Si$_2$. These phases have a needle or ske-
letal structure, respectively. Magnesium is mainly present in the \( \text{Al}_6\text{Cu}_2\text{Mg}_8\text{Si}_5 \) phase.

Recommended for casting in metal molds castings are heated by quenching, which causes crushing, spheroidization and kaogulation of eutectic silicon plates. Partially dissolve in a solid aluminum solution of the particle \( \text{Al}_6\text{Cu}_2\text{Mg}_8\text{Si}_5 \), mainly the phase \( \text{Al}_6\text{Cu}_2\text{Mg}_8\text{Si}_5 \) disappears. A strong increase in hardness after aging after quenching provides the formation of secondary precipitates of phases \( \text{Al}_6\text{Cu}_2\text{Mg}_8\text{Si}_5 \), \( \text{Mg}_2\text{Si} \), \( \text{Q} \) (\( \text{Al}_6\text{Cu}_2\text{Mg}_8\text{Si}_5 \)) and \( \text{S} \) (\( \text{Al}_2\text{CuMg} \)). Naturally, the relative elongation in this case decreases almost to zero, therefore, the guaranteed level of strength (\( \sigma \)), even in the T6 state, is rather modest (200 MPa).

Alloy AK5M4 is made from recycled materials. It is designed as a high-temperature alloy for the manufacture of pistons for pumps, brake equipment, etc. With almost the same properties as the AK5M7 alloy, it contains less copper, and as a result its output volume is doubled almost to replace the AK5M7 alloy. This alloy is made from recycled materials. It is used for the manufacture of pistons of tractor and automobile engines. Recently, the refractory alloy AK5M7 is replaced with the AK5M4 alloy.

The alloy AK8M3, except for silicon and copper, does not contain other alloying elements, but it admits a large number of impurities, including Fe up to 1.3% and Mg to 0.45%. This makes the alloy convenient for its preparation from recycled materials. However, unlike the most common secondary silumin AK5M2, the choice of raw materials for the AK8M3 alloy is more limited, in particular because of the relatively low magnesium content.

The AK9M2 alloy is characterized by a wide range of alloying elements and a large tolerance for impurities, so it is mainly prepared from recycled materials. Its microstructure is close to the microstructure of the latter, differing in detail: a smaller amount of the \( \text{Al}_6\text{Cu}_2 \) phase and the possible presence of magnesium silicide, as well as the quaternary \( \text{Al}_8\text{FeMg}_3\text{Si}_6 \) compound. However, in general, the structure is dominated by eutectic silicon particles and needle-like inclusions of the \( \beta \) phase. After heating for quenching under the T6 regime, complete or partial fragmentation and spheroidization of the Si phase occurs and almost complete dissolution of the Cu and Mg-containing phases. The AK9M2 alloy has good casting properties and an average level (for the cast state) of the mechanical properties.

Typical microstructures of industrial silumines are shown in Fig. 4.

Fig. 3. Isothermal sections of the state diagram \( \text{Al} - \text{Si} - \text{Cu} - \text{Mg} \) at 8% Si:
\( a \) — solid lines — \( 500 \) °C; \( b \) — dashed — \( 200 \) °C

Fig. 4. Typical structures of cuprous silumin (casting in chill mold), SM:
\( a \) — AK5M (A); \( b \) — AK5M7 (L); \( c \) — AK8M3 (T6); \( d \) — AK9M2 (T6)

In the alloy AK12M2, unlike other silumines, iron is not an admixture, but a doping element in an amount of 0.6–1.0%. According to the phase diagram of \( \text{Al} - \text{Si} - \text{Fe} \), at this concentration, most of the \( \beta \)-phase is included in the triple eutectic \( \text{Al} - (\text{Si}) - \beta \), which is the main structural constituent of the alloy.

The alloy is recommended for obtaining shaped castings of complex shape by injection molding, which provides favorable (dispersed) morphology of the eutectic phases, as well as a sufficiently high copper content in (Al).
Such a structure makes it possible to obtain comparatively high mechanical properties in the state T1 ($\sigma > 260$ MPa, $\delta > 1\%$). With silicon content closer to the upper limit, primary crystals (Si) can be found in the structure. The AK12M2 alloy is usually not subjected to heat treatment for quenching, although such treatment can significantly increase ductility. This alloy is produced mainly from primary materials, although recently the volume of its production from scrap and waste has been increased. It is used at the enterprises of the automobile industry, including for the manufacture of pistons. The results of this study, obtained in accordance with the purpose and tasks of this paper, supplement the results obtained by the authors [8–18].

Conclusions

1. On the basis of the study of phase transformations of aluminum-based alloys with basic impurities and doping elements crystallized under nonequilibrium conditions, sections of phase diagrams are constructed that allow optimizing their structure and properties.

2. Based on the study of phase diagrams, their sections and sections, variants of optimization of the composition of the produced alloys or production of new ones at enterprises of the real sector of the economy are proposed. The phase diagrams, their sections and cross sections are constructed for real conditions for the crystallization of aluminum alloys with Mg, Cu, Si, Fe, Ni, Mn and other elements to improve the efficiency of using aluminum alloy scrap by industry by improving the quality of existing alloys or developing new ones.

3. In the paper, non-equilibrium (at high cooling rates) diagrams of the state of four-component systems are constructed; iso- and polythermic sections (sections) of four-component systems based on aluminum with basic alloying elements and the most common impurities are constructed; phase equilibria and the structure of model and industrial alloys are studied.

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References


