Probing microscopy and other methods in the investigation of aluminium alloys

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Abstract. The work is devoted to the study of the surface of anti-friction aluminium alloys. The influence of alloying elements and heat treatment on the physical and mechanical properties of the surface, its thermal conductivity, and electrical conductivity was estimated. It is shown that the addition of a number of elements (Pb, Bi, Cd, and In) to the base alloy Al-5Si-4Cu and subsequent heat treatment lead to an increase in physical and mechanical properties (so, the greatest hardness value has an alloy with cadmium). Thermal conductivity at the macrolevel was estimated from the measurement of electrical conductivity; it is shown that doping and heat treatment in most cases bring to a little change of these parameters. A complex method of microscopy (scanning electron microscopy with elemental analysis and scanning probe microscopy) was used to study the surface of the samples. Various modes of scanning probe microscopy were used: topography, spreading currents, and surface temperature were measured independently. It is shown that the values of electrical conductivity and thermal conductivity measured at the microlevel are correlated well enough. A significant heterogeneity in the surface thermal conductivity of the cast sample is found, which correlates with the corresponding phase composition of the impurities.

1. Introduction

It is known that aluminium alloys have a wide range of applications. One of the directions is their use as bearing materials in mechanical engineering. This is due to their lower cost compared to expensive bronze, which is often used in these units. At the same time, aluminium alloys have performance properties comparable to those of bronze [1-4]. This is achieved by alloying several elements, including low-melting metals (in particular, tin, lead, bismuth, cadmium, etc.), which makes it possible to improve the characteristics of the material and vary them in a wide range. The principle of operation of bearings based on these alloys is that under unfavourable friction conditions, a soft phase component (low-melting elements) is released onto the surface of the solid matrix, which plays the role of a lubricant that protects the base material from destruction.

This work is devoted to the study of alloys of the Al-Si-Cu-X system, where X is a low-melting element. Based on the calculations and results obtained earlier [5-7], a base composition based on Al-5% Si-4% Cu was taken.

The structure (primarily, the surface topography) was studied by electron and probe microscopies. The study of properties at the macrolevel was carried out by standard methods – Brinel hardness tests.
and electrical conductivity. Probe microscopy was also used to study the complex properties of the surface at the micro level – electrical conductivity and thermal conductivity. Note that the thermal conductivity is the most important characteristic of the alloy, which determines its working properties. However, it is often difficult to measure this value. It is known, however, that in many cases this parameter correlates with conductivity, which is easy to measure. Based on this, the tasks of this work were also independent measurements and establishing a correlation between these parameters.

The general aim of the work was to study the influence of individual elements and heat treatment on the structure and properties of the alloys.

2. Materials and methods

2.1. Alloys

The model alloys based on the basic composition of the Al-5% Si-4% Cu system were studied. The elements were chosen for the following reasons: copper was introduced for hardening, and its 4% concentration was taken close to the limiting solubility of this metal in an aluminium solid solution. Silicon, used to improve casting properties, is taken in an amount of 5%; while achieving the best balance between mechanical and technological properties.

At the first stage of the work, low-melting metals Bi, Cd, In, and Pb were added to the alloy base and the influence of each of these elements on the mechanical, heat-conducting, and tribological properties of the material was investigated. At the second stage, similar alloys based on the base system were investigated, but with the addition of tin taken in an amount of 4%; this concentration corresponds to the content of this element in branded aluminium antifriction alloys. Selected fusible elements, which proved to be the best at the first stage of the experiment, were added to this system (Al-5%Si-4%Cu-4%Sn).

The obtained samples were examined in the cast (initial) state, and also after heat treatment (HT). It is known that the best for mechanical properties is the globular morphology and it is necessary to strive for maximum spheroidization of all the particles that make up the composition [8]. The structures of alloys of similar compositions were studied by the authors in previous works [6, 7, 9]. Thus, it was shown that for analogous alloys, the optimal mode of maintenance was heating to 500°C followed by quenching in water. This regime leading to an improvement in the structure - the spheroidization of phases and the dissolution of copper in an aluminium solid solution - has been chosen in the present study.

2.2. Physical and mechanical properties

With the use of modern experimental methods, the physical and mechanical properties of the alloys of the Al-Si-Cu-X system, in particular, their hardness and electrical conductivity, were studied. The Brinell hardness was measured using the standard method in accordance with GOST 9012-59 on the Nemesis 9000 universal hardness tester with the following parameters: ball diameter 2.5 mm, load on the indenter was 612.9 N, and holding time 20 s. The electrical conductivity of the samples was investigated with a VE-26NP vortex structuroscope. The principle of operation of a structuroscope is based on the method of eddy currents using the phase method for processing the signal of an overhead eddy current transducer. The measuring range of the device is 5-62 MSm/m. The relative error is 2%.

2.3. Microscopy

Investigation of topography: electron microscopy was carried out on a scanning electron microscope (SEM) "Quanta-650" with an X-ray spectral microanalyzer EDAX. The regime of secondary electrons with an accelerating voltage of up to 25 kV was used. Samples were studied before and after HT. Studies at the nanoscale were carried out using various methods of scanning probe microscopy (SPM). The study of topography was carried out using the Smart SPMTM microscope (manufactured by AIST-NT). The tapping mode (resonance frequency 250 kHz) was used, cantilevers (probes) of the fpN10 series with the tip curvature radius of 20 nm were used. A special feature of the work was the investigation of the same selected areas of the surface by both methods of microscopy – SEM and
SPM. For doing it, i.e. for reliable identification of the investigated regions, the "reference method" was used – the investigated region of the surface was accurately labelled with marks [9].

Investigation of the properties of the surface of alloys was carried out using the Ntegra Prima SPM (NT-MDT). Preliminary measurement of the surface relief was carried out in a contact and semi-contact modes. At the same time, a map of the surface spreading current and the thermal conductivity of the samples was measured.

When measuring the spreading current between the sample surface and the probe, a constant voltage of up to 10 V was supplied and a current was measured for different points of the surface.

The thermal conductivity was estimated with the aid of a scanning thermal microscopy (STM) using a special probe, the end of which was a resistor to which a voltage of a predetermined value was applied. The temperature of the probe was measured by the change in its resistance built into the arm of the Winston bridge. To determine the thermal conductivity of the surface, the probe is first heated to a certain temperature, which changes when interacting with the surface. In conditions of a sufficiently slow scan, when transient processes can be neglected, the change in probe temperature will vary inversely with the thermal conductivity of the material in the region of its contact with the surface. Thus, the temperature difference recorded in this case provides information on the heat-conducting properties of the samples.

3. Results and discussion
For all samples, the surface structure and its change as a result of HT were studied. The influence of HT on the physical and mechanical properties of alloys was also evaluated.

In addition, at the second stage of research for alloys containing tin, new methods of studying surface properties, including additional modes of SPM, were used. In this case, the electrical conductivity and thermal conductivity were measured independently.

It should be noted that at the first stage the thermal conductivity was estimated from the electrical conductivity measured at the “macro level” using the known dependence; at the same time, their correlation was assumed on the basis of the literature data. At the second stage, these parameters were measured by SPM modes independently at the micro level and their correlation was shown.

3.1. Microscopic examination of the surface of Al-Si-Cu-X system
The complex method of microscopic studies [9] was used to study the initial surface of experimental aluminium alloys, both in the cast and HT state. The use of SEM made it possible to study the structure of experimental alloys and to estimate the effect of HT on its change. Figure 1 demonstrates the obtained SEM images of the initial surface of the samples (with additives of low-melting elements) in the cast (virgin) and HT state.

Studies have shown (Fig. 1) that all alloys are close in structure and contain in their composition two similar phases: compound Al$_2$Cu and eutectic Al-Si. They are distinguished by low-melting phase components – Pb, Bi, Cd, and In. It was also found that heat treatment led to the spheroidization of the phase constituents of the alloys.

The complex method of microscopic research used in the work included the joint use of various methods of electron and probe microscopy. Thus, the same surface regions were studied by the SEM and SPM methods. For this purpose, special markers (benchmarks) were applied to the surface, which made it possible to isolate and analyse the necessary area. This approach made it possible to obtain topographic images with elemental composition (both over the entire surface and in selected regions), and also to estimate the surface relief. Such a complex technique was applied to the study of all experimental alloys. As an example, the results obtained for a sample of the Al-5Si-4Cu-1Cd alloy in a cast (initial) and HT state are presented in Figure 2: they are given as SEM images with element analysis and SPM images, with corresponding 3D images. Table 1 shows the chemical composition of the selected regions.
Figure 1. SEM images of the initial surface of new model aluminium alloys with additives (indicated above): (a) in the cast; (b) in the heat-treated state.

Figure 2. Image of the surface of the alloy Al-5Si-4Cu-1Cd: (a), (d) SEM images; (b), (e) 2D SPM topography image; (c), (f) 3D SPM topography image; (a), (b), (c) cast and (d), (e), (f) after HT.
The obtained results indicate that the SEM and SPM images of the surface correlate well and substantially complement each other. We note that on SEM images, silicon in the matrix is seen very poorly (this is due to the proximity of atomic numbers of silicon and aluminium), while the use of SPM makes it possible to obtain additional information [9], so these elements are well separated on the SPM picture. So, the joint use of two methods makes it possible to estimate the parameters of the relief of irregularities on the surface and the spatial geometry of the alloy.

Additional information on the phase composition of the multicomponent alloy was obtained by mapping. Figure 3 shows the distribution of chemical elements of the Al-5Si-4Cu-1Cd alloy in a cast and HT state.

![Figure 3. Map of the individual elements distribution on the surface of the alloy Al-5Si-4Cu-1Cd: (a) in the cast, (b) in the HT state.](image-url)
The location of the alloying elements could be estimated from Figure 3. Thus, during the HT, the silicon phase becomes more globular, and its amount varies insignificantly compared with the cast state. The soft phase (Cd) is spheroidized after annealing (i.e., assumes a rounded shape). The number of Al₅Cu₇ phase inclusions becomes significantly less than in the cast state, which is due to their partial dissolution (in Al-matrix). It is also indicated by the analysis of the elemental composition in Table 3 (the content of copper in the matrix increases to 3.84% by mass).

Thus, it is shown that HT at 500°C, followed by quenching in water, changes the structure of the alloy. The joint use of SEM and SPM methods allows qualitative evaluating structural and phase changes.

### 3.2. Investigation of physico-mechanical properties of Al-Si-Cu-X system

The strength properties of aluminium alloys are usually indicated by the value of hardness, and thermal conductivity is one of the most important characteristics for antifriction alloys. This is due to the need for maximum heat dissipation from contact surfaces during friction. To determine the thermal conductivity, measurements were made of the specific electric conductivity of alloys, since there is a correlation between these characteristics. Using the equation \( y = 5.64 \cdot x + 23.43 \), where \( x \) is the experimental value of the SES, given in Refs. [10,11], the value of the thermal conductivity of the four-component alloys was calculated. To compare and evaluate the effect of each fusible element separately on the mechanical and thermal conductive properties, the obtained values of the physical and mechanical properties of the investigated alloys were compared with the values of the base alloy Al-5% Si-4% Cu.

Table 2 shows the measured values of the hardness of alloys, the conductivity, and the corresponding values of the thermal conductivity of alloys in the cast (initial) state and after HT.

| Alloy      | Hardness, HB | Electrical Conductivity, MSm/m | Thermal conductivity, Wt/(m·K) |
|------------|--------------|--------------------------------|--------------------------------|
|            | Cast         | After HT | Cast         | After HT | Cast         | After HT |
| Al-5Si-4Cu | 71.1 ± 0.8   | 77.9 ± 0.1 | 23.4         | 22.9     | 155.4        | 152.6    |
| Al-5Si-4Cu-1Bi | 69.2 ± 0.8   | 101.6 ± 0.8 | 20.7         | 20.5     | 140.2        | 139.1    |
| Al-5Si-4Cu-1Cd | 68.7 ± 0.8   | 141.7 ± 0.9 | 20.5         | 19.8     | 139.1        | 135.1    |
| Al-5Si-4Cu-1In | 67.7 ± 0.1   | 124.1 ± 1.8 | 20.4         | 19.9     | 138.5        | 135.7    |
| Al-5Si-4Cu-1Pb | 68.9 ± 1.4   | 111.2 ± 0.5 | 20.1         | 19.7     | 136.8        | 134.5    |

**Hardness.** According to the results given in Table 2, it can be seen that the addition of low-melting metals into the Al-5% Si-4% Cu alloy does not greatly affect the hardness values of the samples in the cast (initial) state, which is approximately 70 HB. After HT for all alloys, the hardness increases; this is primarily due to the dissolution of nonequilibrium excess phases containing copper. It should be noted that the addition of low-melting elements in a small amount to experimental alloys subjected to maintenance increases the hardness values to 100-140 HB, which is 40 to 75% higher than that of the base alloy. The greatest value of hardness after HT (142 HB) has an alloy with cadmium, and the lowest one has an alloy with bismuth (102 HB). This difference is probably due to the various effects of these additives on the process of nucleation and isolation of the hardening phase in aging (θ-Al₅Cu₇).

**Electrical conductivity and thermal conductivity.** Table 2 also shows the effect of HT on the change in the specific electrical conductivity (SEC). It is known that SEC of aluminium increases with decreasing impurities [8]. In our case, SEC is reduced by the elements that enter the solid solution after the HT (such alloying additives as Cu and Si). Low-melting metals are practically insoluble in Al, but they to a small extent reduce the value of the SEC. Proceeding from the assumption of the existence of a correlation between electrical conductivity and thermal conductivity, the addition of alloying elements has the same effect on the aluminium alloy – reducing the value of thermal conductivity.
conductivity. It should be noted that all experimental alloys have a higher electrical conductivity, and, consequently, thermal conductivity than bronze BrO4TS4S17 (the value of the SEC is 11.7 MSm/m). To a large extent, this is explained by the fact that the electrical conductivity of copper is significantly reduced, when there is even a very small amount of impurities.

3.3. Complex microscopic investigation of the surface of initial samples of the Al-Si-Cu-Sn-X system

In the second part of the work, the alloy of Al–5% Si–4% Cu–4% Sn system with addition of tin was taken as the basis, to which selected fusible elements were added based on the results obtained. The presence of a low-melting component in the investigated alloys corresponds to the content of this additive in branded aluminium alloys and allows us to consider that an alloy of the composition Al-5%Si-4%Cu-4%Sn (up to 0.5% Pb, Bi, and Cd) should have a sufficiently high level of operational (tribological) properties. Lead and bismuth, as well as tin, in the alloy serve to reduce friction and provide resistance to scoring under dry friction or lubrication conditions. In addition, at the first stage it was found that cadmium could affect the hardness. The results of hardness measurements are shown in Table 3.

Table 3. Results of the hardness test of alloys under study

| Alloy                  | Hardness, HB |
|-----------------------|--------------|
| Al–5Si–4Cu–4Sn–(0.5Bi-0.5Pb-0.5Cd) | 72.7 ± 0.9    |
| Al–5Si–4Cu–4Sn–(0.5Bi-0.5Pb)    | 71.2 ± 1.5    |
| After HT               | 129.2 ± 1.6   |
| After HT               | 125.4 ± 1.2   |

It can be seen that the HT significantly increases the strength and hardness. Cadmium in this case also slightly increases the hardness of the alloy.

Using the example of Al-5Si-4Cu-4Sn (0.5Bi-0.5Pb) sample (without cadmium), the effect of HT on the structure as well as the thermal and conductive properties of the alloy was also evaluated. The results of comparative microscopic studies of an alloy of this composition – cast (initial) and after HT (500 °C), are shown in Figure 4.

It can be seen that the methods used complemented each other: as in the first stage, the SPM made it possible to visualize elements that are difficult to distinguish on SEM images, and also to estimate the spatial geometry of individual phase components [9]. It can be seen that, just as in the first case, the spheroidization of particles, the phase constituents of the alloy, takes place at HT.

To study the conductive properties of the surface, new SPM techniques have been applied at this stage. Of particular interest here is the possibility of directly measuring the thermal conductivity map and correlating it with a map of the independently measured electrical conductivity of the samples.

Figure 5 shows the obtained images of the same sample in the cast and HT state: the relief images and the temperature map are shown.

The higher temperature of the probe corresponds to the lighter areas in the image and qualitatively indicates their lower thermal conductivity. In Figure 5, it is possible to isolate the relief areas (phase 1), at which the probe temperature is virtually the same as the matrix (solid phase inclusions - Al2Cu or Al-Si), i.e. their thermal conductivity is the same. In the areas indicated by 2 (soft phase component Sn-Pb-Bi), the probe has the highest temperature, i.e. in these places there is the greatest thermal resistance at heat exchange. In other areas, the temperature of the probe is intermediate, but higher than the temperature of the matrix.

On the HT sample, the probe temperature distribution is more homogeneous (Fig. 5d). A higher temperature corresponding to a lower thermal conductivity is observed only on impurities localized mainly at the boundaries of the phase-Al-Si, the inclusions of which have an oval shape. The thermal conductivity of the Al-Si phase does not differ much from the thermal conductivity of the matrix. Another phase (Al2Cu) is not observed, since at HT, copper dissolves in the Al matrix.

A comparison of the thermal conductivity maps and the surface conductivity of the cast sample is shown in Figure 6. The same section was scanned at first in the thermal microscopy mode, and then in the surface conductivity mode (current measurement).
Figure 4. The surface image of the Al-5Si-4Cu-4Sn- (0.5Bi-0.5Pb) alloy: the SEM image of (a) cast, (c) after the HT; Squares indicate the areas of the SPM study; SPM image (2D) (b) cast, (d) after HT.

Figure 5. SPM images of the topography of the sample Al-5Si-4Cu-4Sn- (0.5Bi-0.5Pb): (a) cast and (c) HT alloys; a map of the deviation of the probe temperature from the nominal value: (b) cast and (d) HT alloys.

A comparison of Figures 6b and 6c shows that there is no complete correspondence between the thermal conductivity of the surface and its electrical conductivity. Indeed, there are sections, which thermal conductivity and electrical conductivity are smaller (denoted by 1) or roughly equal to (denoted by 2) those of the matrix, which qualitatively agrees with the Wiedemann-Franz law for metals. However, there are areas, which thermal conductivity is much lower than the thermal conductivity of the matrix, but the electrical conductivity is much higher (region 3). There may be several reasons for this. Thus, a special feature of the measurements of the samples under study is that the aluminium surface is covered by a nonconducting oxide, the thickness of which most likely depends on the local composition of the sample. Therefore, it is difficult to obtain high-quality images in the contact scanning regime and to correlate the heat-conducting properties of the surface with its electrical conductivity.
Figure 6. SPM images of the surface of the cast sample Al-5Si-4Cu-4Sn-(0.5Bi-0.5Pb):
(a) topography (17x17 μm²); (b) map of the probe temperature deviation from the
nominal value (17x17 μm²); (c) is a spreading current distribution map (18x18 μm²).

In addition, the heat exchange depends on the contact area of the probe and the surface, which can
lead to the influence of the relief on the measured probe temperature, for example, at the extremum
points of the relief. Also, the reason for this behaviour can be related to the peculiarity of the phase
composition of individual sections. In general, this question requires more detailed study.

However, in most cases, for the measured samples there is a correlation between electrical
conductivity and thermal conductivity. All these results indicate the prospects of using the electrical
methods for studying the surface properties of alloys.

4. Conclusion
It has been found that the addition of even a small amount of low-melting elements to the base alloy
Al-5Si-4Cu and subsequent heat treatment have a significant effect on the mechanical properties of the
material. Physico-mechanical properties increase for the alloy having cadmium with the highest
hardness value. The thermal conductivity during alloying changes insignificantly; the addition of
elements somewhat reduces this index.

Study of the surface by the complex method of scanning probe microscopy has shown that the
separately measured values at the microlevel of the electrical conductivity and thermal conductivity
correlate qualitatively.

Substantial inhomogeneity of the surface thermal conductivity of the cast sample is established,
which correlates with the corresponding phase composition of impurities.

It is shown that the temperature treatment of the sample leads to a more uniform surface thermal
conductivity; the phases with a lower thermal conductivity are concentrated at the boundaries of
phases with a higher thermal conductivity.

On the whole, the results obtained show that the use of "electric methods" and scanning thermal
microscopy is promising for studying the surface properties of alloys.

Acknowledgments
This work was supported by the Russian Scientific Foundation, project no. 14-19-01033-P (study of
topography and elemental composition of the surface) and grant of the President of the Russian
Federation MK-871.2018.8 (no. AAAA-A18-118080290023-0) (study of electrical properties of the
surface). The authors are grateful to N.A. Belov (MISiS) for providing samples.

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