Development of methods for determining the density of low-melting metals

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Abstract. Features of the formation and development of scientific research in the laboratory of physics of interfacial phenomena in ChISU named after L.N. Tolstoy in the 1970-1980s of the last century are considered in this paper. Particular attention is paid to the development and improvement of various methods for measuring the density of liquid metals and alloys. We determined the contribution of ChSU scientists in the study of metals and alloys properties and gave a scientific assessment of the obtained results. The development of methods and techniques for measuring the density of liquid metals and alloys went in two directions. Primarily, we took significant steps towards improving the accuracy of density measurements. The instruments were designed in which the accuracy of measuring density and, in particular, the temperature coefficient of density was significantly increased. Foremost, this concerns advanced pycnometers and areometers designed in ChSU laboratories. The instruments received inventor’s certificates, and they were awarded the bronze medal of the Exhibition of Achievements of National Economy in 1977. The second direction improving the measuring technique of the metal properties is characterized by instrument designing for the joint measurement of physico-chemical properties in the same thermal vacuum conditions. Both areometers and pycnometers were used to determine density in these instruments.

1. Introduction

Density is an important structurally sensitive characteristic of thermodynamic systems. Knowing the exact values of density allows determining the specific and molar volume, and through them, judging the size of atoms and molecules, the degree of their interaction in melts. It is believed that accurate data on the melt density, in some cases, can provide more information about the structure and melt formation. Problems of reliable measurement of density values sometimes come to the fore in the measuring equipment design in various fields of modern science and technology.

In this regard, the issues associated with the development of new and improvement of existing methods for measuring the density of liquids and solids have been and are still relevant over the past decades [1-4]. Since the 70s of the last century, scientific studies of physico-chemical and surface properties of liquid metals and their alloys have been carried out in the laboratory of physics of interfacial phenomena at ChISU under the leadership of Kh.I. Ibragimov. Herewith, certain success was achieved both in the development of new methods for measuring physico-chemical properties, and in the enhancement of existing instruments and techniques. The surface properties and density of a large number of pure metals and their binary and ternary systems were studied experimentally using designed methods and devices. These results are widely used as reference data in various fields of human activity. However, the designed instruments and their specifications are scattered across various sources, not
properly systematized, and not subjected to critical analysis. In this paper, we have set the task to begin complex and extensive work with a critical analysis of instruments and methods for measuring the density of liquids developed in our laboratory. We hope this work will be continued in the future.

2. Materials and methods

As emphasized above, in our laboratory, the physico-chemical properties (including density) of liquid metals and alloys were mainly studied. A distinctive feature of these objects is that they are actively oxidized in the air. Following this, the measurement of physico-chemical properties must be carried out in a vacuum or in an inert environment. This creates great difficulties in studying the concentration dependence of the physico-chemical properties of binary, in particular, multicomponent systems. Separate arrangements of alloys and measurements of their properties are associated with a laborious and lengthy procedure for preliminary preparation of the device for each measurement separately. On average, it takes 3 to 5 days to prepare the device and measure the density temperature dependence of one alloy. At the same time, expensive metals and materials are used wastefully. In this regard, the development of devices and techniques that allow increasing the experimental research productivity while maintaining the achieved measurement accuracy is of particular interest.

The issue of joint measurement of the surface tension, density, and electron work function under the same thermal vacuum conditions has been solved for a long time at Kabardino-Balkarian State University (mainly based on the big drop method), and in the laboratory of ChISU (mainly based on the maximum pressure method in a drop). Before proceeding with the description of the instruments, it is necessary to first dwell on fundamentally new versions of devices and techniques. The latter are aimed at improving the accuracy and productivity of experimental studies of the concentration dependence of the metals and alloys’ density.

Thus, the development of new and improvement of existing methods for measuring density went towards increasing the experiments’ productivity, while maintaining the achieved accuracy, as well as towards increasing the accuracy of individual reference measurements. New devices and techniques were developed on the basis of pycnometric and areometric methods for measuring density. We will consider them separately.

2.1 Pycnometric methods

The simplest pycnometer used to determine the density was characterized by the presence of a single capillary tube. This fact created a number of inconveniences due to the capillary tube narrowness, which made it difficult to fill the pycnometer reservoir with metal. Besides, we did not manage to remove the gas bubbles formed between the walls of the pycnometer and the liquid metal during heating. To solve this problem, the authors [7] have developed a two capillary vacuum pycnometer.

Further research showed that together with the solution of one issue, the next occurs after using this device. Namely, the use of two capillaries leads to sensitivity decrease of the device and a density change. On the other hand, the temperature measurement interval in these devices is relatively narrow, which does not allow measuring density in a wide temperature range. Reasoning from this fact, a new vacuum single capillary pycnometer was developed combining the high accuracy of a single capillary pycnometer and the convenience of a two capillary pycnometer [8]. An important feature of a new single capillary pycnometer is the ability to select a capillary with smaller diameter, which significantly affects the measurement accuracy.

With the extension of experimental research objects, in particular, seeing the study of two and three-component systems it became necessary to expand the capabilities of existing pycnometers. Among other factors, the need to expand the range of the pycnometric method application for studying density arose. This problem was solved by the authors [9] who proposed a device for measuring the liquid melts density of binary systems in a wide concentration range with a two capillary pycnometer. A distinctive feature of this device is that the presence of a dosing tube makes it possible to prepare alloys of new concentrations and measure the temperature dependence of their density without opening the device and without violating the thermal vacuum conditions in it.
Figure 1. Two capillary vacuum pycnometer.

Figure 2. Single capillary vacuum pycnometer

Figure 3 demonstrates the device. It consists of a two capillary pycnometer 1, microburette 2, and bins for metal 3-7

Figure 3. Pycnometer for studying the concentration and temperature dependence of the density of liquid metal melts.

2.2 Areometric methods
The transition of the experimental research process to a more complex level, associated with the need to study structurally complex systems, justified and predetermined the need for further improvement and the creation of new devices for determining the density and surface properties of metals and multicomponent melts. For these purposes, the pycnometric density measurement method was not always suitable. In particular, when measuring the properties of toxic metals (mercury, thallium, lead), the disadvantages of the pycnometric method appeared. For instance, when measuring density with a pycnometer at the end of the experiment, it is necessary to determine the metal mass before and after measurements, which requires certain skills in working with toxic materials. Under these conditions,
areometers deprived of the above disadvantages, are more preferable. However, available areometers were practically unsuitable for extremely precise measurements. This happened because when measuring the density with an areometer, it was necessary to take into consideration the effect of wetting the glass, the areometer is made of, by the metal under study. In particular, it was required to measure the wetting angle in parallel and take into account its effect. On the other hand, the thermal expansion of the glass, from which the areometer is made, when measuring in a wide temperature range (several hundred degrees) has a noticeable effect on the measured density value, especially on the density temperature coefficient. It should be borne in mind that KBSU scientists successfully solved the first task. They used a capillary outlet and measured the wetting angle by the difference in metal levels in a narrow and wide tube, which, in turn, gave consideration to the effect of capillary forces on the measured density value. The second problem of taking into account the effect of glass thermal expansion, the areometer is made of, was solved in our laboratory [10]. After this improvement, areometric devices began to be widely used to measure the density of liquid metals and alloys, not only in our laboratories, but also far beyond the country borders.

Figure 4 shows a device for density measurement with an areometer with constant weight and tungsten ballast, designed in the ChISU laboratory [11]. A significant advantage of this device in comparison with a vacuum pycnometer is that it provides an opportunity to measure the density of metal alloys directly in the device.

The device structurally consists of a measuring tank 1 and an auxiliary tank 2, interconnected by pipes 3 and 4. Equilibrium during “swimming” in the melt is achieved with the help of the ballast placed in the areometer body and a guide tube 5.

Despite certain advantages, this device also had a significant drawback, namely, it did not consider the effect of capillary forces. We introduced a constructive innovation into the device in order to solve the issue. The measuring chamber was supplemented with a special capillary outlet of a known radius (Figure 5).

Thus, taking into account the capillary outlet, the formula, determining the density, was obtained:

\[ \rho = \frac{P_0}{g(V_0 + \pi r^2 h - \pi r R \Delta H)} \]

where \( P_0 \) - mass of the areometer in vacuum; \( g \) - gravity acceleration; \( V_0 \) - volume to a specified mark; \( r \) - areometer rod radius; \( h \) - distance from the liquid level in the areometer chamber to the specified mark on the rod; \( R \) - capillary outlet radius; \( \Delta H \) - difference in liquid levels in the capillary outlet and the chamber.
An areometric device was also used in research in which two areometers with different masses and volumes were applied to account for the action of capillary forces. Figure 6 demonstrates the device.

![Figure 6. Density measuring devices with two areometers: 1,2- tubes through which melt is poured into tanks 5; 4,6- ballasts; 5,3,7- rods; 8,9- guide tubes.](image)

The device was worked out by the areometric method, in which one areometer was applied to determine the density concentration dependence (Figure 7). Structurally, it differed from the areometer shown in Figure 1 by the fact that a U-shaped volume-calibrated microburette is included in its design. The latter allows preparing alloys of different compositions without opening the device itself.

We have worked out and used a device that structurally includes two areometers to determine the concentration dependence of density. The device consists of an areometric reservoir 1 with guide tubes 2, and areometers 3 and 4, two volume-calibrated microburettes 5 and 6, and reservoirs 7 and 8 (Figure 8).

![Figure 7. Areometric device for determining the concentration dependence of density [13].](image)

![Figure 8. Areometric device with two areometers to determine the density dependence on composition [13].](image)

As the number of components in the melts increased, the devices for determining the concentration dependence of the density of the given systems were also improved. Thus, a device with two areometers
was worked out to define the density of multicomponent systems, and it became possible to measure the wetting angles with glass alloys (Figure 9).

Figure 9. A device for determining the concentration dependence of the density with an improved areometer [14].

4. Results
Therefore, a comparative analysis of the devices and density measurement techniques developed in the ChSU laboratories has been carried out by two main methods: pycnometric and areometric. The advantages and disadvantages of both methods have been revealed, the effective use areas of the developed devices have been defined. We have found out that:

The pycnometric method and devices based on density measurement by this method have certain advantages over others. The main advantages of pycnometric density measurement include high accuracy of density measurement, the possibility of multiple measurements, which can significantly reduce the random error, the ability to conduct an experiment in a deep vacuum without the presence of foreign gases:

- the need to make a pycnometer from a transparent vacuum-tight material (glass or quartz). The requirements are caused by the visualization inevitability of the metal meniscus in the capillary;
- relatively narrow temperature range of density measurements (on the bottom, the temperature range is limited by the melting temperature of the studied metal, and on the top, by the softening temperature of glass or quartz the pycnometer is made of);
- the need to weigh the studied metal before and after measurements.

5. Conclusion
We have defined that the areometric method and devices based on it allow studying the density dependence of metals and melts on temperature and composition with high accuracy. However, it should be noted that in order to gain highly accurate results, it is required to take into account the influence of the wetting angle and thermal expansion of the areometer on the obtained experimental results. The advantages of areometers include:

- sufficiently high measurement accuracy (no more than 0.2%);
- lack of necessity to measure the studied metal mass (it is enough to know the exact value of the mass and radius of the areometer rod);
- the possibility of their effective use in combined devices. The strategic mission of the development of the tourist and recreational complex of the coastal zone of the seas within the
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