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INFLUENCE OF LOW NICKEL CONTENTS ON THE SURFACE TENSION AND DENSITY OF NICKEL–INDIUM MELTS

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The density and the surface tension coefficient of nickel–indium melts with low Ni contents ranging from 0 to 15 at.% have been studied, by using the sessile drop method. Analytic expressions are derived for the temperature dependences of the density and the surface tension coefficient of a melt. Anomalies in the concentration dependences of the density and the surface tension coefficient are revealed. They are supposed to be caused by structural inhomogeneities both near the melt surface and in the melt bulk.

Keywords: density, surface tension, Ni–In molten alloys, cluster structure.

1. Introduction

Surface properties of metallic melts have attracted the attention of researchers for a long time, because they are required to solve a number of important scientific and engineering problems associated with the soldering and welding processes, fabrication of high-purity materials, deposition of coatings, and sintering. Furthermore, the surface properties should be studied from the viewpoint of fundamental sciences – physics of liquid metals, materials science, and physical chemistry of the surface – because the data on surface properties are closely related to the surface structure, interaction forces between atoms, and, hence, thermodynamic parameters of melts.

From the analysis of the literature data concerning the surface tension and the density of binary metallic melts, one can see that, at present, there is no mutual understanding in the theoretical description of the concentration and temperature dependences of those physical parameters. The melts of some systems demonstrate anomalies in the concentration dependences – especially at low contents of one of the com-

ponents – and those anomalies have no unambiguous explanation till now [1–4].

The properties of the melts belonging to the Ni–In system, which can be used as lead-free solders, draw the attention of researchers and, therefore, have to be studied in detail. The application of the alloys of this type as solders stimulates researches of the temperature and concentration dependences of their density and surface tension coefficient, with the relevant research results being directly connected with the soldering.

In this work, the sessile drop method was used to measure the surface tension coefficient and the density of indium melts with the addition of nickel (1.5, 2.5, 3.5, 5, 10, and 15 at.%) in order to establish the influence of Ni atoms on the density and the surface tension coefficient of indium. The experimental researches were carried out at the temperatures $T = T_m$ and 1273 K in the argon environment, which was associated with a high pressure of saturated indium vapor at high temperatures. The profile of a molten drop was registered with the use of a photcamera. The measured profiles were used to determine the density and the surface tension coefficient by calculating the volume of a droplet, its height, and the wetting angle.

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2. Experimental Technique

Experimental specimens were synthesized under a flux in a muffle furnace, in accordance with conditions required by the sessile drop method [5]. High-purity substances (Ni 99.9% and In 99.99%) were used for the synthesis. The phase content was monitored with the help of the micro X-ray spectral analysis. The distribution of elements over the specimen bulk was studied on an electron microscope.

The density was determined by analyzing the drop shape. Assuming that the drop, when at rest on a substrate, has a cylindrical symmetry, each photo of a specimen was used to determine the drop contour as the function $x(h)$ (Fig. 1). Then the specimen volume can be calculated by the formula

$$V = \int_0^{h_{\max}} \frac{\pi}{4} R^2 dh = \int_0^{h_{\max}} \frac{\pi}{4} (x_R - x_L)^2 dh, \quad (1)$$

where x_L and x_R are the abscissae of two points in the drop contour with the same height. Since the measurements were discrete, with the value of dh being equal to the size of one pixel (unity), we obtain

$$V_{pt} = \sum_{i=0}^{i_h \max} \frac{\pi}{4} (x_{R[i]} - x_{L[i]})^2. \quad (2)$$

To recalculate the specimen size into millimeter units, the formula

$$V = \frac{d_C^3}{d_C^3} \frac{mm}{pt} V_{pt} \quad (3)$$

was used, where $d_{C \text{ mm}}$ and $d_{C \text{ pt}}$ are the diameters of a calibration instrument (a graphite cylinder 21.450 mm in diameter) used for the given experiment. Finally, the density was calculated by the formula

$$\rho = \frac{m}{V}. \quad (4)$$

In order to calculate the surface tension coefficient, the height of the drop on the substrate and the wetting angle were measured first. Then the calculation was carried out according to the formula [6]

$$\sigma = \frac{g\rho h^2}{2(1 + \cos(\theta))}, \quad (5)$$

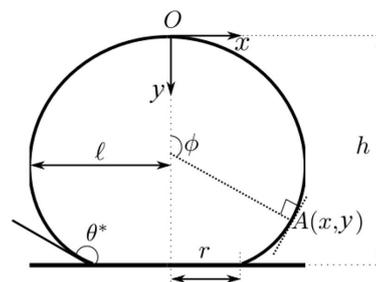


Fig. 1. Specimen coordinate frame

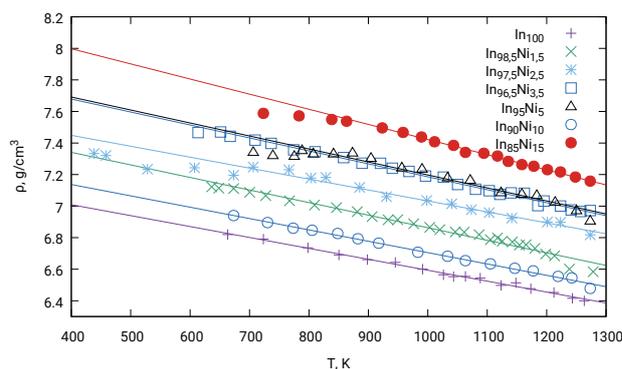


Fig. 2. Temperature dependences of the density for melts of the $\text{In}_{1-c}\text{Ni}_c$ system

where σ is the surface tension coefficient, g the free fall acceleration, ρ the specimen density, h the drop height (see Fig. 1), and θ the wetting angle.

In our case, the wetting angle was determined as the arctangent of the coefficient k in the equation $y = kx + b$, which linearly approximated the contour within an interval of x that corresponded to $h \in [0; \frac{h}{10}]$. To make the calculations more precise, the angle was determined on both drop sides and averaged.

3. Results and Their Analysis

From the results of our experimental researches, the temperature and concentration dependences for the density and the surface tension coefficient were obtained for In–Ni melts. In Fig. 2, the temperature dependences of the melt density are depicted. Their form is typical of metallic melts and has a linear character. As the temperature decreases, the melt density increases. The density of the melts with higher nickel contents are more sensitive to the temperature variation.

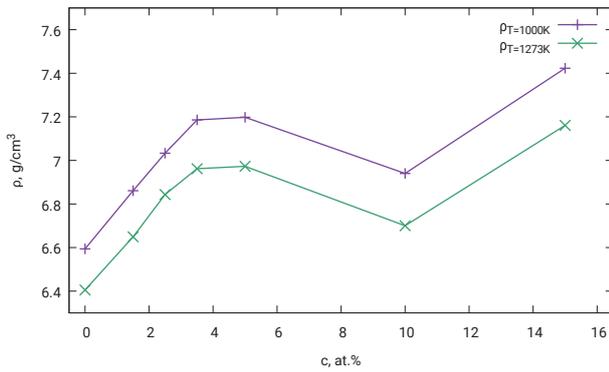


Fig. 3. Concentration dependences of the density

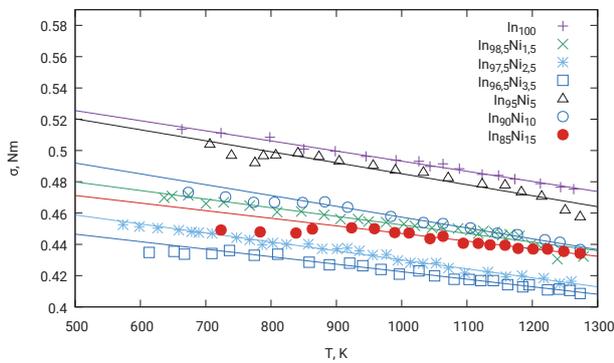


Fig. 4. Temperature dependences of the surface tension coefficient for the melts of the $In_{1-c}Ni_c$ system

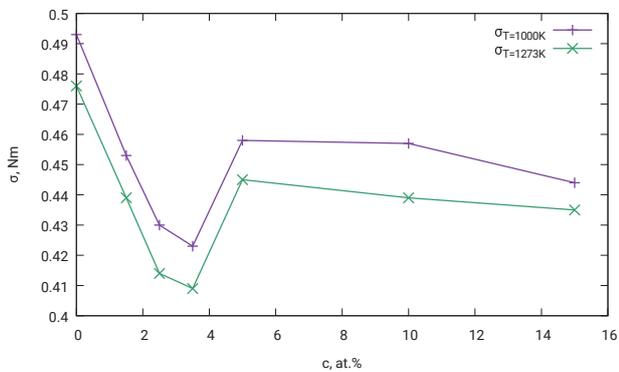


Fig. 5. Concentration dependences of the surface tension coefficient

The concentration dependence of the melt density (Fig. 3) demonstrates an atypical behavior of this parameter in the presence of impurities: the density drastically increases, as the impurity concentration grows from 0 to 3.5 at.%, has a minimum at about 10 at.%, and then starts to increase. Such a be-

havior contradicts the additive law inherent in ideal solutions. Therefore, we may assert that there is a microinhomogeneous distribution of atoms of various kinds in those melts, and the clustering is probable. In this case, we may assume that Ni atoms, whose size is smaller in comparison with that of indium atoms, can penetrate into the voids between the clusters and, in such a way, can increase the melt density. The density reduction can follow from the growth of the role played by the chemical short-range order owing to the dominating interaction between In and Ni atoms, which gives rise to an atomic redistribution in the clusters. Such changes in the liquid state should be studied more carefully with the help of physico-chemical methods and making a smaller content increment.

In Fig. 4, the temperature dependences of the surface tension coefficient are exhibited. They are typical of metal melts and have no anomalies in the examined temperature interval. The decrease of the surface tension coefficient at heating is associated with the fact that the role of the interaction between molecules diminishes, as the temperature grows. As one can see from the plots, the addition of Ni atoms reduces the surface tension coefficient at all Ni concentrations in comparison with pure indium.

In general, the temperature dependences of the density and the surface tension coefficient for examined melts (at $T > T_m$) are well described by the linear dependences $\rho = a_\rho + b_\rho T$ and $\sigma = a_\sigma + b_\sigma T$, respectively. From the analysis of those dependences, one can see that two intervals with different characters of the $\sigma(T)$ dependence can be distinguished in the analyzed concentration interval (see Table). This circumstance allows us to assume that the mecha-

Constants in the temperature dependences of the density and the surface tension coefficient for the melts of the $In_{1-c}Ni_c$ system

c , at.% Ni	a_ρ , g/cm ³	b_ρ , 10 ⁻⁴ g/(cm ³ · K)	a_σ , N/m	b_σ , 10 ⁵ N/(m · K)
0	7.29	-6.92	0.56	-6.47
1.5	7.66	-7.97	0.51	-5.50
2.5	7.73	-6.94	0.49	-5.74
3.5	8.01	-8.21	0.47	-4.80
5	8.02	-8.23	0.56	-6.47
10	7.81	-8.75	0.53	-6.92
15	8.38	-9.58	0.48	-3.71

nism of formation of the surface layer consisting of In and Ni atoms depends on the content of the latter. It should also be noted that the temperature coefficient of the surface tension coefficient is negative ($d\sigma/dT < 0$) in the whole researched concentration interval.

The concentration dependence of the surface tension coefficient, $\sigma(c)$, has a minimum at the Ni concentration $c \approx 3$ at.% (see Fig. 5). We may suppose that such a behavior is associated with a non-uniform distribution of nickel atoms in the melt and with the change of the ratio between Ni concentrations at the specimen surface and in the specimen bulk, when a larger amount of nickel is added. At a low content of nickel atoms, which try to fill their $3d$ shell with electrons from indium atoms, they are arranged in microvoids in the liquid indium structure near the surface and diminish attraction between indium atoms. However, the number of such voids is confined, so that, as the content of Ni atoms grows further, they are forced to diffuse into the bulk or to form associations near the specimen surface, which results in an increase of the surface tension.

The experimentally observed dependence can be described in the framework of the Butler model [7]. For calculations, the equation

$$\sigma = \sigma_1 - \frac{RT}{\omega} \ln(Fc) \quad (6)$$

can be used, where σ_1 is the surface tension coefficient for component 1 (in our case, it is indium) at a selected temperature, $R = 8.31$ J/(K mol), T the temperature, ω an area occupied by one mole of the mixture, F the ratio between the activities near the surface and in the bulk, and c the impurity concentration. Nevertheless, for the description to be correct, it is necessary to introduce a dependence of the activity ratio on the impurity concentration. After calculations, we obtain a dependence shown in Fig. 6. One can see that it has rather a good agreement (both qualitative and quantitative) with the experiment (curve 1 in Fig. 6). However, as is evident from Fig. 7 (curve 1), the model does not agree with experimental data at concentrations exceeding 5 at.%. In this case, we should use different coefficients in Eq. (6) (curves 2 in Figs. 6 and 7). However, new approximations do not satisfactorily describe the experiment at concentrations $c \lesssim 5$ at.%.

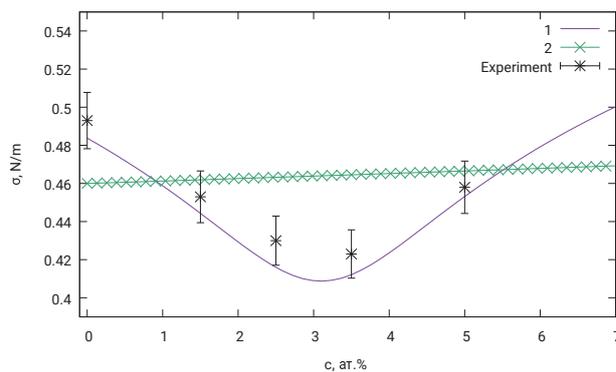


Fig. 6. Concentration dependence of the surface tension coefficient for the melts of the $\text{In}_{1-c}\text{Ni}_c$ system calculated in the concentration interval (0÷5) at.% Ni

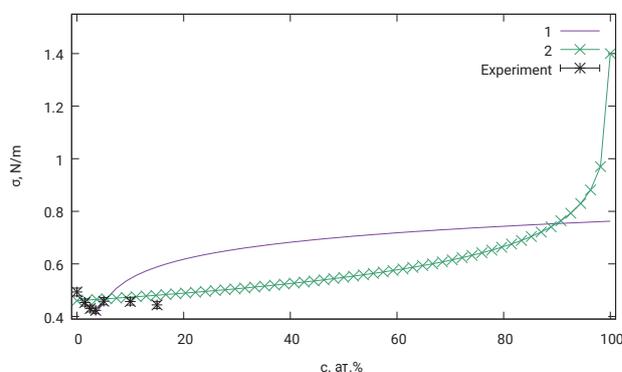


Fig. 7. The same as in Fig. 6, but in the whole concentration interval (0÷100) at.% Ni

The results of measurements obtained for the surface tension coefficient and the density were supplemented with structural researches, by using the electron microscopy method and the X-ray study of the phase composition.

The results of electron microscopy researches (Fig. 8) testify to the presence of In_3Ni_2 microcrystals chaotically arranged in a pure indium matrix over the specimen volume. The dimensions of crystals that are visible at a 500-fold magnification vary from 8 to 20 μm .

The presence of this compound was also confirmed by the data obtained at the X-ray phase analysis (Fig. 9). The results obtained within this method enabled us to calculate the dimensions of nanocrystals: $d = 12$ nm for In and $d = 9$ nm for In_3Ni_2 .

Hence, the formation of In-based clusters on the basis of intermetallide In_3Ni_2 in the solid state and

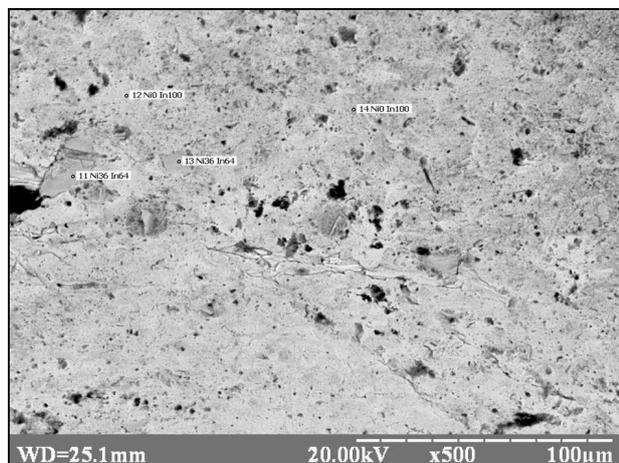


Fig. 8. Microstructure of the indium-nickel alloy with a Ni content of 10 at.% obtained on an electron microscope

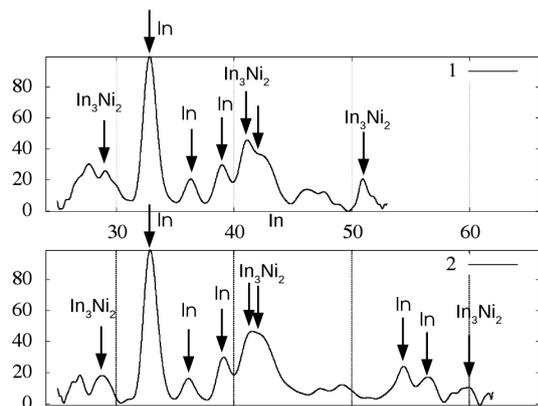


Fig. 9. Diffraction patterns of crystallized alloy (10 at.% Ni): for the material at the melt–gas interface (1), for the material at the melt–substrate interface (2)

with various dimensions testifies to a tendency toward clustering in the melt [8]. The tendency to a situation, where the interaction between atoms of different kinds dominates, results in the formation of a micro-heterogeneous structure containing clusters of various types, structures, and dimensions. As a result, the temperature and concentration dependences of the density and the surface tension coefficient change.

4. Conclusions

Using the method of sessile drop, the temperature dependences of the density and the surface tension coefficient are studied for indium–nickel melts with low nickel contents. Linear dependences of examined pa-

rameters, which are typical of metal melts, are obtained. Atypical concentration dependences of the density and the surface tension coefficient are revealed, which can be explained by a change of the impurity concentration at the surface or a change of the ratio between the impurity activities near the surface and in the bulk of the specimen.

Electron microscopy and X-ray phase analyses of the internal structure of specimens are carried out as well. The researches on an electron microscope revealed the formation of In_3Ni_2 compound with various crystal sizes. This result is confirmed by the X-ray phase analysis. The data obtained are used to calculate the dimensions of the crystals formed in the melt after its crystallization.

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ВПЛИВ МАЛИХ КОНЦЕНТРАЦІЙ НІКЕЛЮ НА ПОВЕРХНЕВИЙ НАТЯГ ТА ГУСТИНУ ІНДІЮ

Резюме

Методом лежачої краплі досліджено густину та поверхневий натяг збагачених індієм розплавів системи нікель–індій з різним вмістом нікелю в межах 0–15 ат.%. Отримано аналітичні вирази для температурних залежностей густини та коефіцієнта поверхневого натягу. Виявлено аномалії на концентраційних залежностях густини та поверхневого натягу, причиною яких припускаються структурні мікронеоднорідності як на поверхні, так і в об'ємі розплавів.