Structure changes in molten eutectic alloys doped with powder of Ni.

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Abstract. The structure of Sn98.7Cu1.3, Bi99.5Cu0.5 and Sn57.0Bi43.0 eutectic melts admixed with Ni powder has been studied by means of X-ray diffraction method. The structure parameters are analysed and compared with ones for pure liquid alloys. It is shown that Ni-atoms intensively interact with Sn and Bi-ones forming the chemically ordered groups, whose presence is important for structure modification of eutectic. The structure of quenched mixtures of eutectic and Ni-powder reveals the inhomogeneous structure due to incompleteness liquid-solid reactions.

1. Introduction
Eutectic alloys have been widely used during long time. Their low melting temperature is the main characteristic, which motivated the practical use. But in many cases another important parameters are required to be of some definite values. For instance, solder eutectic alloys besides the low melting temperature should posses by high electroconductivity, corrosive resistance and needed mechanical properties. Numerous experimental studies of binary systems with eutectic point in phase diagram including X-ray diffraction, thermodynamic, viscosity measurements and others allowed to draw the conclusion about specific of eutectic melts. Concentration dependencies of parameters obtained from diffraction and physical properties measurements reveal the extremum point, noting that eutectic melt can not be considered in frame of simple solution models [1,2].

Thermodynamic description of most number molten eutectic alloys is based on model of preferred like kind atom interaction [3-5]. According to this model the structure of liquid eutectic consists the clusters An and Bm, where A, B – constituents; n,m – numbers of atoms in clusters. Such kind of atomic distribution occurs in lot eutectic melts that was confirmed by diffraction studies [6].

Comparing of structural data in liquid state with ones obtained for solid ones results the some functional dependence between them. Particularly, the microhomogeneous structure at temperatures not far from melting point transforms into solid state. On that reason it is important to know what is kind of structural units just before solidification and how large is their size. These important parameters depend on temperature and can be changed also by addition of other elements, which is known as modification process.

By mean of modification it is possible to improve significantly the properties of eutectic alloys. Unfortunately there is no completed theory of modification process. On that reason it is of great importance to obtain more of experimental information on influence of admixtures on structure and
properties of eutectic in liquid state. In this paper we propose to use the powder of small size for modification of structure of liquid eutectic.

Binary eutectic alloys Sn$_{98.7}$-Cu$_{1.3}$, Bi$_{43}$-Sn$_{57}$ and Bi$_{99.5}$-Cu$_{0.5}$ were chosen for studies. These alloys are interest first of all as Pb-free solders candidates. The structure changes upon adding of Ni powder of 3 µm size have been studied by means of X-ray diffraction method.

2. Experimental.

Eutectics for investigation were prepared from bismuth, tin, and copper of 99.99% purity by melting in vacuum furnace filled with pure argon. The powder of Ni was added into eutectic melts before quenching on the substrate. The diffraction studies were carried out using a high-temperature diffractometer with a special attachment that allows to investigate the solid and liquid samples at different temperatures up to 1800 K. Cu-K$_{\alpha}$ radiation monochromatized by means of LiF single crystal as a monochromator and Breg-Brentano focusing geometry were used. The scattered intensities as a function of the scattering angle were recorded within the range 1Å$^{-1}$ < k < 7Å$^{-1}$, with different angular step, which was equal to 0.05° within the region of principal peak and 0.5° at rest values of wave vectors. The measuring of scattered intensity was done with accuracy, better than 2%. In order to obtain the more accurate scattered intensities, the scan time was equal to 100 s. The diffracted intensity was recorded using a NaI(Tl) scintillator detector in conjunction with an amplification system. The sample was placed in a rounded cup of 20 mm diameter.

Scattered intensities as functions of scattering angels were recorded and corrected on absorption, anomalous dispersion and incoherent scattering[7].

The structure factors (SF) were obtained from angular dependences of scattered intensities. Pair correlation functions (PCF) were calculated from SF by means of Fourier-transformation [7]. From this functions the main structure parameters – first and second peak positions $k_1$, $k_2$, $r_1$, $r_2$, number of neighbors – Z and first peak height $a(k_1)$ were determined. All these parameters were analyzed by comparing with ones for pure liquid tin.

Microscopic studies were performed using scanning electron microscope.

3. Results and discussion

It is clear that mixture of melt and solid powder should transit to equilibrium state by means of diffusive process. Depending on tendency to chemical interaction between constituents of eutectic and elements of powder, temperature, powder size, time of solid-liquid reaction and other factors such mixture attempts to form the homogeneous phase with other properties.

In fig.1. the diffraction patterns for Sn$_{98.7}$-Cu$_{1.3}$+Ni mixture solidificated on Ni substrate are shown. The increase of Ni-powder content in Sn$_{98.7}$-Cu$_{1.3}$+Ni mixtures promotes the reduce of mean interatomic distance. Consequently the formation of more compacted structure with structural units of less size is the result of such modification. The cooling of eutectic melts and their crystallization was carried out also in magnetic field applied. As follow from analysis of diffraction patterns the sizes of crystallites becomes less in case of magnetic field.
Fig. 1. Diffraction patterns for Sn$_{98.7}$Cu$_{1.3}$+Ni mixture solidified on Ni substrate (a – H=0; b – H=360kA/m)

Diffraction patterns for Bi$_{99.5}$Cu$_{0.5}$+Ni mixtures are shown in fig.2. It can be seen that phase contents of contact and opposite sides of substrate are different.
Contact size consists Bi$_3$Ni intermetallic and pure bismuth. Opposite side also has this intermetallic phase, but its fraction is less, whereas the content of Ni is larger. Therefore Bi-atoms which attempt to interact with Ni ones rearrange its distribution. Some part of them interact with Ni-powder, another – with Ni-substrate.

Fig 2. Diffraction patterns for Bi$_{99.5}$Cu$_{0.05}$ eutectic alloy(a) and for Bi$_{99.5}$Cu$_{0.05}$+15at%Ni mixtures(opposite(b) and contact(c) sides of substrate).

Fig 3. Structure factors of liquid (Bi$_{99.5}$Cu$_{0.05}$)$_{1-x}$Ni$_x$ molten alloys.
The similar behavior is also observed for Sn$_{57}$Bi$_{43}$ eutectic melt. The addition of Ni-powder leads to rearrangement of atomic distribution due to formation of intermetallic compounds covering Ni-powders.

In order to understand the processes of structure formation in these mixtures they were also investigated not only quenching but also at higher temperatures when liquid and solid phase coexist. In fig 3 are shown the structure factors of liquid Bi$_{99.5}$Cu$_{0.05}$ admixed with different content of Ni powder. As it can be seen the SFs show the typical profile no revealing the crystalline-like peaks. This allows noting that Ni-powder is diluted completely in eutectic matrix. The change of SF principal peak profile and appearance of shoulder on its right hand side is attributed to change in interatomic bounding. In our case one can suppose that between Ni and Bi atoms exists strong chemical interaction. Atomic distribution in chemically ordered structural units has been determined by comparing of experimental structure factors with ones calculated according to model of disordered crystalline cel (Fig 4). From this figure follows that experimental SFs are more similar to ones calculated on the base Bi$_3$Ni chemical compound. Consequently, the due to formation of chemically ordered Bi$_3$Ni-like clusters the modification of eutectic structure occurs.

Fig.4. Experimental structure factors for (Cu$_{0.005}$Bi$_{0.995}$)$_{0.85}$Ni$_{0.15}$ and intensity curves calculated according to model of disordered crystalline cell.

Nevertheless there is difference in structure of Bi$_{99.5}$Cu$_{0.05}$ +Ni liquid alloys and quenched solid ones. In quenched alloys some part of Ni-powder is not completely diluted in Bi$_{99.5}$Cu$_{0.05}$ eutectic melt and due to that the structure becomes more inhomogeneous. Besides changing the duration and temperature of eutectic + powder mixture it is possible to vary the size of powder which remains when reactions is finished (Fig 5). In such way the formation of nanoscale structural units can be carried out.
4. Conclusions.

The addition of Ni-powder to Sn$_{98.7}$Cu$_{1.3}$ eutectic melt promotes the reduce of mean interatomic distances. The size of crystallites becomes less in case of crystallization of Sn$_{98.7}$Cu$_{1.3}$+Ni mixtures in magnetic field. In the case of Bi$_{99.5}$Cu$_{0.05}$ eutectic melt, Bi-atoms attempt to interact with Ni ones rearrange its distribution. Changing the duration and temperature of eutectic + powder mixture it is possible to vary the size of powder which remains when reactions is finished.

5. References.

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