The structure changes in Al$_{0.88}$Si$_{0.12}$ eutectic melt upon addition of Ni.

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Abstract. X-ray diffraction studies of Al$_{0.88}$Si$_{0.12}$ melts admixed with Ni (5, 10, 15 and 20 at% of Ni) were carried out. Experimental scattered intensities were used for calculation the structure factors and pair correlation functions. It is shown that additions of Ni to eutectic alloys transform the atomic distribution in liquid state. Changed in such way the atomic distribution in some respects persists after transition to solid one. Chemically ordered structural units with composition and atomic arrangement corresponding to AlNi and Al$_3$Ni intermetallics can exist as structural units in liquid (Al$_{0.88}$Si$_{0.12}$)$_{1-x}$Ni$_x$ alloys.

1. Introduction  
Eutectic alloys show the long history of their practical application, first of all due to low melting temperature. Now there are more characteristics, that determine the practical importance of these alloys. On that reason it is of interest to study the possibilities of physical properties improvement by different methods: thermal treatment, doping with other elements, etc.

In this work we present the results on structure studies of Al$_{0.88}$Si$_{0.12}$ eutectic melt admixed with Ni. This eutectic alloy is commonly used for producing the various units in machine building industry by casting. The structure and properties of Al-Si alloys have been extensively studied both in solid and liquid state. Nevertheless the influence of other elements on the structure in liquid state just before solidification is unclear yet. We select Ni for doping the Al-Si alloys because this element improves properties of Al-based alloys.

Such studies are interesting from fundamental viewpoint concerning to modification of alloys also. It is unclear what processes take place in liquid state and in what way they continue at cooling in solid state.

2. Experimental  
The samples were prepared in arc melting furnace filled with pure argon. The purity of the initial metals was 99.999%. The diffraction studies were carried out using a high-temperature diffractometer with a special attachment that allows investigating 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 1 Å$^{-1}$ < k < 7 Å$^{-1}$, with different angular step, equal to 0.05° within the region of principal peak and 0.5° at the 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 NaI(Tl) scintillator detector in conjunction with an amplification system. The sample was placed in a rounded cup of 20 mm diameter. Intensity curves were corrected on polarization, absorption and incoherent scattering [1]. After this procedure they were normalized to electron units by Krogh-Moe method [2]. Obtained intensity curves were used to calculate the structure factors (SF) and than the pair correlation function (PCF). The main structure parameters, obtained from SF and PCF, were analyzed.

3. Results and discussion

The structure factor for Al_{0.88}Si_{0.12} eutectic melt is shown at figure 1 with comparison to SF for liquid Al and Si. The main feature of this SF is the splitting of the second peak into two subpeaks. First of them does not correspond to principal peak of liquid Al, but the second one has the position as in liquid Si.

These two facts allowed us to suppose that short range order structure in liquid eutectic melt can not be described by one of simple models: random atomic distribution or the self association model. Therefore one can suppose that some part of Si-atoms is strongly bonded with Al-ones forming in such way the chemically ordered structural units. Small part of Si-atoms bonded via covalent bonds and exists in form of self-associated structural units. With heating the splitted shape of the second peak smears and becomes like SF of typical metallic liquids indicating the dominant role of thermal disordering in atomic rearrangement at higher temperatures. The obtained results on structure of Al_{0.88}Si_{0.12} eutectic melt are in accordance with the other diffraction studies and physical properties measurements [3-5].

Having such kind of a structure, it is of interest to understand how the admixtures will interact with these structural units. In case of Ni, taking into account binary Ni-Si and Al-Ni systems pronouncing the chemical compounds of higher thermal stability [6, 7], one can suppose the increase of tendency to interaction of unlike kind of atoms with addition of Ni. The structure factors for Al_{0.88}Si_{0.12} melts admixed with 5, 10, 15 and 20 at% of Ni are shown at figure 2. The main features of these functions are the shift of principal peak position to large k-values and its significant arise. Also the main maximum becomes more assymetric. Such changes can not be caused by simple diluting of Ni atoms in above mentioned structural units existing in liquid eutectic melt.
In order to clarify how nickel atoms come into structure of liquid melt, the concentration dependencies of parameters, obtained from structure factors and pair correlation functions, have been analyzed. Concentration dependencies of $S(k)$ principal peak position $k_1(x)$ and distance to first neighbors $r_1(x)$ show almost a linear functions (figure 3.). The deviation from such behavior is observed at higher temperatures, particularly at overheating above liquidus temperature for 100 K. Parameter $r_1$ reduces more rapidly then at lower temperatures. The reason of this is that at higher temperatures some part of structural units (clusters) brakes with heating resulting easier mixing of Ni-atoms with Al and Si ones. Concentration dependence of the number of neighbors $Z$ confirms this assumption also, showing small increase of coordination number with content of Ni at lower temperatures and almost unchangeable value at higher ones ($T_L+100K$).

Another parameter which is sensitive to structure change – principal peak height $S(k_1)$ - decreases upon addition of 5 at% of Ni and then slightly increases. Tendency to more significant increase of this parameter appears when content of Ni riches 20 at%. It is known that high values of this parameter are peculiarity for metallic liquids and lower ones are observed in melts, where bonding between atoms becomes partly localized. Consequently the Al$_{0.88}$Si$_{0.12}$ admixed with Ni melts transform their chemical bonding to the formation of chemically ordered microgroups. 3d-band of Ni in order to be completed attempts to take the electrons from Al.

Obtained results allowed us to suppose that chemically ordered structural units with composition and atomic arrangement corresponding to AlNi and Al$_3$Ni intermetallics can exist in liquid
(Al_{0.88}Si_{0.12})_{1-x}Ni_{x} alloys. In order to check this assumption we have calculated the intensity curves by smearing of Al_{3}Ni and AlNi crystalline structure. It can be seen (figure 4), that there is an agreement between principal peak positions. Also the small shoulder on left-hand side lies opposite the sharp maximum for Al_{3}Ni structure. The influence of this compound on structure of admixed eutectic is larger than AlNi one. Therefore the assumption of existence of Al_{3}Ni-like structural units in (Al_{0.88}Si_{0.12})_{1-x}Ni_{x} liquid alloys is reasonable.

![Figure 4](image)

**Figure 4.** The structure factor for liquid (Al_{0.88}Si_{0.12})_{0.8}Ni_{0.2}, Al_{3}Ni, AlNi alloys.

4. Conclusions
The addition of Ni-atoms to Al_{0.8}Si_{0.12} eutectic melt promotes the formation of chemically ordered structural units on the base of Al_{3}Ni chemical compound. The structure and physical properties modification process carried out by addition of Ni atoms has selective features. During this process the atomic distribution significantly changes in clusters with preferred interaction of Al and Si atoms.

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