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Influence of structure state of melt on solidification process

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ABSTRACT

Purpose: This work is to establish the physical foundation for searching of new possibilities to improve the properties of metallic alloys by effecting of them in liquid state,- the experimental data on structure of binary alloys with various kind of phase diagram are analyzed. The importance of treatment in liquid state is motivated by existence of inhomogeneous structure in wide temperature range. Analysis of temperature dependencies of structure parameters and physical properties allow to suppose that factors of energetic influence (magnetic field for example) can effect the solidificated alloys not only at phase transitions but also at higher temperatures. In order to choose the influence parameters the information about structure and physical properties temperatures dependences is needed.
Design/methodology/approach: The experimental studies on structure of metallic alloys were carried out by means of X-ray diffraction method and physical properties measurements, devices were constructed to study the influence of magnetic field on alloys structure and solidifications process.
Findings: Metallic alloys show the structure inhomogeneities in liquid state within wide temperature range, besides the thermodynamic and kinetic solidification process,- conditions responsible for the structure and properties of solidificated alloys significantly depend on structural state of melt before crystallization.
Research limitations/implications: The purpose of this paper is bound also to the metallurgical and metrology (build-up eutectic temperature fixed-point cells) problems solutions,- finding of new ways of the check and controlling of process of crystallization of this metal alloys.
Originality/value: Using of magnetic field and other energetic influence can change inhomogeneous structure in order to improve the properties of alloys.
Keywords: Metallic alloys; Structure; Solidification

1. Introduction

Interest to studies of molten alloys is motivated by different reasons. One of them whose importance follows from practical use is the possibility to improve the properties of solidificated alloys by effecting them in liquid state. Most of metallurgical technologies have a liquid state as a starting point in producing of solid materials. Changing the structure in liquid state and the cooling conditions it is possible to obtain the solid materials with different properties including amorphous alloys, whose atomic arrangement shows the lack of long range order. In case of amorphous alloys there is untypical way of solidification when the atomic large scale disordering transfers from liquid state to solid one. Most of technologies in order to improve the properties deal with solid materials. Thermal treatment belongs to them and is in wide use during long time. But the possibilities of this method rich a limit at present time. On that reason the new ways of properties improving should be developed including the treatment in liquid state. There are only few works [1-3] where the treatment of melt is considered from viewpoint of fundamental studies on liquids. Particularly it is shown that overheating of melt promotes the formation of better properties upon solidification.

Successful use of treatment before solidification is impossible without detail studies of structure, thermodynamics and physical-chemical properties in liquid state not near the crystallization point only but also at higher temperatures. In this paper we analyze our results on x-ray diffraction studies and physical properties measurements of liquid metallic alloys with aim to use them for proposals in technologies of melt treatment.

2. Experimental

The structure studies of molten binary alloy with various type of phase diagram were carried out with using of x-ray diffration method, viscosity and electroconductivity measurements. Samples were prepared by melting of ingots of high purity in arc furnace filled with argon. The angular dependence of scattered intensity was obtained by means of high temperature diffractometer The specimen was placed in vacuum chamber filled with pure helium in order to avoid the oxidation. Experimental intensity curves were used for calculation of structure factors and pair correlation functions. In order to obtain the structure parameters (most probable interatomic distance, number of neighbour atoms, size of structural units) these functions were used. Concentration and temperature dependences of these parameters indicate the stability of structure to temperature change and content of doping elements.

For treatment of melts first of all we used the magnetic field and acoustic waves [4]. For studies were chosen the binary and ternary alloys, whose structure significantly differs from ideal atomic solution (Cu-Co, Ni-Pb, Fe-Sn, Co-Sn, Li-Pb, Li-Sn, Bi-Te, In-Ga-Sn, Pb-Sn-Sb, Cu-Pb, Bi-Pb-Te). Among these alloys are ones whose equilibrium phase diagrams reveal the eutectic points, chemical compounds and miscibility gaps [4].

3. Results and discussion

Analysis of structure factors and pair correlation functions obtained from x-ray diffraction studies of liquid binary alloys allowed us to conclude that most of them have inhomogeneous short range order at temperatures which are close to liquidus curve. Evidence of such kind structure is the deviations of structure parameters, calculated for simple models (random atomic distribution, quasieutectic and chemical compound) from experimental ones. Quantitative description of structural inhomogeneities is not developed to present time in exact form and fractions of each structural units of inhomogeneous atomic distribution can be estimated with low accuracy only. On that reason in some cases the thermodynamic data are also used for more exact description of inhomogeneous short range order.

The existence of inhomogeneous structure of molten alloys is also confirmed by physical properties measurements. For example the concentration dependence of viscosity shows the minimum at concentration corresponding to eutectic point. Contrary in case of chemical compounds this characteristics reveals a maximum point in its dependence. In systems with miscibility gap the viscosity dependence on concentration shows the anomalous behavior near the critical point. Such behavior is due to the significant concentration fluctuations whose result are the structure changes. Maximum and minimum points are also observed in concentration dependences of other physical properties (electroconductivity, density, surface tension etc.)

Taking into account that various kind and size structural units have a some definite thermal stability, the temperature dependence of stucture parameters should display the structure changes. In case of random atomic distribution the distance to first neighbors increases no showing any anomalous behaviour. In similar way change number of neighbor atoms and size of structural units parameters. There is a simple topological disordering of short range order due to increase of atomic motion at higher temperatures. Such behaviour of metallic melts as an ideal solutions is also exhibited in increase of electroresistivity, decrease of density, surface tension and viscosity with heating. In most cases for multicomponent melts there is another temperature dependence of structure parameters and physical properties coefficients.

Particularly the deviation from Arrenius relation is observed in temperature dependence of viscosity. Experimental data (Li-Pb) allowed us to obtain the two different values of activation energy. This indicates the existence of changes of interatomic interaction at some definite temperature.

Therefore the structure in liquid binary metallic alloys depends not only on concentration of their components but also on temperature. It should be noted that temperature dependence of structure parameters suggest no simple topological disordering only but also the change in short range order kind.

Taking into account these facts the existing methods of thermal treatment of melt are based on the supposition that overheating of liquid alloys leads to formation of more homogeneous atomic distribution which can be quenched in solid state.

The model analysis of structure data shows that inhomogeneous structure can be considered as a mixture of different size and kind clusters. Chemical and topological ordering of atoms in clusters changes with temperature as well as their size. Commonly the molten alloys reveal the breaking of structural units with heating and as result their size decreases.

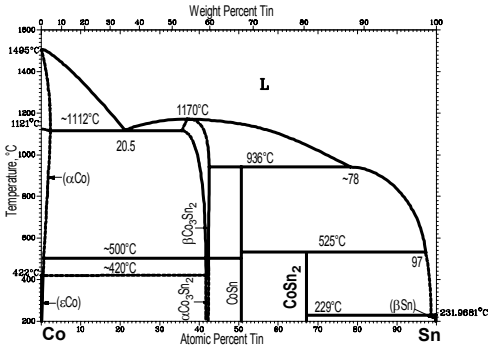

Fig. 1. Co-Sn phase diagram [6]

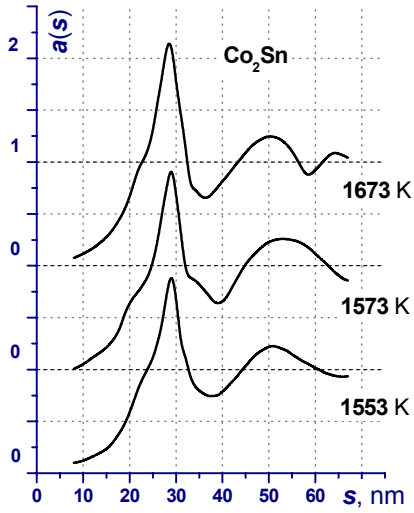

Fig. 2. Temperature dependence of structure factors for Co_2Sn liquid alloy

Such a decomposition of a liquid alloy on cluster scale leads to the formation of solution with random atomic distribution. In order to obtain the some definite structure before solidification a very slow cooling should be performed. But in real metallurgical conditions, which are far from equilibrium ones to reach a needed slow cooling is in fact impossible and upon solidification the crystallite size is a function of cooling rate. It is known also that during solidification at thermodynamic conditions, which are far from equilibrium ones the clusters can form the fractal structure [7]. Sometimes it is needed to avoid the formation of such kind structure or contrary to effect it on different stages of process. In such case the effect of magnetic field or ultrasonic waves applied on melt can be useful in order to change the size of clusters and other structure parameters. In this way can be changed such parameter of fractals as a fractal density. Results on studying of magnetic field influence on structure of Bi-Mn and Ni-Pb eutectic melts shown that such the field promotes the increase of ordering degree. This increase is more significant in case when among components of molten alloy are ferromagnetic elements. Therefore the effecting by magnetic field and ultrasonic waves of melt can be carried out at different temperatures and it allows to obtain the such kind structure which can not be formed at equilibrium crystallization. Besides the magnetic field and ultrasonic waves the effecting of melt can be also carried out by another kind of energetic influence which posses the ability to change the size of clusters and their structure.

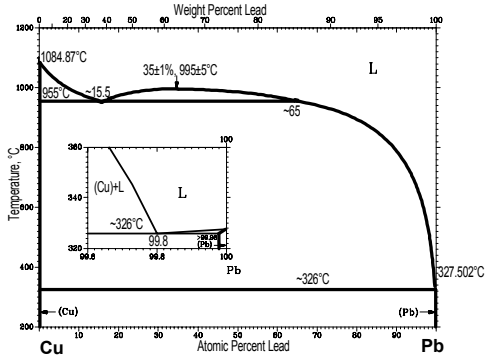

Fig. 3. Cu-Pb phase diagram [6]

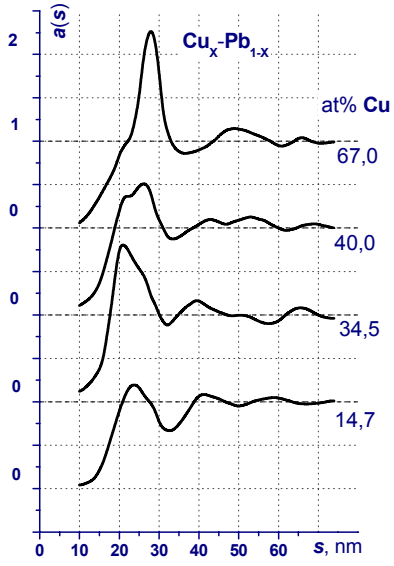

Fig. 4. The structure factors of $Cu_X Pb_{1-X}$ liquid alloys

The Co-Sn binary alloys are chosen to illustrate the existence of inhomogeneous structure in liquid state. There is a strong interaction between unlike kind atoms what is displayed in large negative value of enthalpy of mixing and existence of chemical compounds in phase diagram (Fig.1). One of them forms from liquid state and others are the result of peritectic reactions. The components of this system significantly differ in structure parameters. The concentration dependence of structure parameters as well as physical properties coefficients show the extreme points. The results on X-ray diffraction studies indicate the significant changes at the concentration corresponding to Co_2Sn chemical compound. The structure factors for Co_2Sn liquids alloys are shown in Fig.2. As it can be seen there are the significant changes of atomic arrangement on temperature.

Particularly the left hand side of principal maximum shows the shoulder, which transforms with temperature change. Subsidiary maximum exists also between first and second maxima and its height changes with temperature. It can be seen from figure that width of principal peak changes in anomalous way. At the first two temperatures in fact it is the same whereas at last temperature it increases. The similar dependence is observed also in temperature dependence of pair correlation functions. All these changes in structure factors and pair correlation functions were analyzed by comparing of structure parameters, calculated from pair correlation functions with model values. Taking into account the results on interpretation of structure data the conclusion about significant influence of Co_2Sn-like atomic ordering on structure of alloys within wide concentration range can be drawn. It was founded that maximum fraction of such chemically ordered groups corresponds to chemical compound in phase diagram and rapidly decreases with departure from stochiometric composition. It should noted that similar features of short range order are also observed in other binary alloys, whose phase diagrams reveal the existence of chemical compounds. But as follows also from thermodynamic analysis the thermal stability of chemically ordered atomic arrangement is higher in systems which show the sharp maximum in liquidus curve. This characteristic reach a higher value if the electronegativity difference is significant. For example in Li-Pb liquid alloys the Li_4Pb-like structural units show the high thermal stability although the maximum in liquidus curve is not very sharp. To molten alloys with such feature belong also systems with semiconductor properties such as Tl-Te, Tl-Se, Ge-Te and others.

Therefore the inhomogeneous short range order exists in wide temperature range upon melting of Co_2Sn compound. Analysis of this temperature dependence allowed us to conclude that Co_2Sn – like atomic arrangement is a main feature of structure. The Co_2Sn clusters partly dissociate with heating forming the structural units with random atomic distribution. Taking into account these facts we can suppose that influence of magnetic field as well as other outside energetic factors on melt will be different at various temperatures. Particularly upon decomposition of Co_2Sn chemical compound Co atoms will show the faster self-association under applied magnetic field than at under common conditions. With heating the ability of magnetic field to promote the formation of like kind atoms groups reduces due to influence of thermal disordering. On other hand, as it was founded from model analysis of structure data, the fraction of Co_2Sn – associates is small, the influence of magnetic field is supposed to be negligible. We also assume that applying of high frequency acoustic waves will help in breaking of Co_2Sn –associates. Similar behaviour we predict in other binary systems, whose equilibrium phase diagrams show the existence of chemical compounds, which consist ferromagnetic element.

Another kind of inhomogeneities in liquid state is pronounced in binary alloys, whose phase diagrams reveal the miscibility gap. Alloys of Cu-Pb system belong to them (Fig.3.) The structure factors, obtained for melts of different content of Pb at temperatures 5K above liquidus curve show the significant changes with concentration (Fig.4). It can be seen that principal maximum transforms its profile showing the increase of shoulder on its left hand side with increase of Pb content. For melts containing 34,5 and 45at.% of Cu principal maximum can be considered as superposition of two subsidiary maximum corresponding to similar maxima of structure factors for Cu and Pb. There the inhomogeneous structure of these alloys consist the clusters of like kind atoms. We suppose that in this case the grinding of structural units can be promoted by acoustic waves treatment. In order to confirm it the experimental studies should be carried out.

4. Conclusions

Metallic alloys show the structure inhomogeneities in liquid state within wide temperature range. Besides the thermodynamic and kinetic conditions, the structure and properties of solidificated alloys significantly depend on structural state of melt before transition to solid one. Using the magnetic field and other energetic influence promote the change of inhomogeneous structure in order to improve the properties of alloys. During the influence by magnetic field the clusters of ferromagnetic atoms should increase their order Influence by acoustic waves is supposed to promote the change in size of structural units.

More complicated kind of structure inhomogeneities occur in liquid binary alloys whose phase diagrams show the both chemical compounds and miscibility gap (Fe-Sn, Ga-Te, Ca-Se eth). In this case the structure and physical properties reveal the significant chances with temperature. On order to obtain a random atomic distribution the molten alloys should be overheated to comparatively high temperatures. Taking into account a such structural features one can suppose that outside energetic influence will be useful in treatment of melt.

The intermediate case of structural inhomogeneities was founded in melts with eutectic points in phase diagram. Nevertheless within some temperature range most of them reveal the structural units this preferred interaction of like kind atoms. Therefore the melt of such kind will also sensitive to outside energetic influence and can be improved in this way upon solidification.

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