170/18

ARCHIWUM ODLEWNICTWA
Rok 2006, Rocznik 6, Nr 18 (2/2)
ARCHIVES OF FOUNDRY
Year 2006, Volume 6, N° 18 (2/2)
PAN – Katowice PL ISSN 1642-5308

THE STRUCTURE OF LIQUID EUTECTIC AS A GOWERNING FACTOR IN CRYSTALLIZATION PROCESSES

W. PROKHORENKO [a] [1,3], S. MUDRY [b] [2], S. PROKHORENKO [c] [1],
A. BYLICA [d] [3], J. NAVOTSKA [e] [1]

[1] National University « Lvivska Politechnika » 12 Bandera str., Lviv, 79646, Ukraine
[2] Lviv National I.Franko University. 50 Dragomanov str., Lviv, 79005, Ukraine
[3] Rzeszowian University 16C Rejtana str.; Rzeszow 35959, Poland

ABSTRAKT

The structure of Ga-In-Sn eutectic melt has been studied by means of x-ray diffraction method. The structure factors and pair correlation functions are analyzed. It is shown that inhomogeneous structure exists within some temperature range and can be changed by outside energetic influence.

Key words: Ga-In-Sn, structure factor, crystallization processes, liquid eutectic.

Gallium-based eutectic melts are interesting due to their promising using as a coolants in nuclear power stations, as a matrix for ferrocolloide composite systems and as a termosensitive elements in sensors and temperature reference points. Now these alloys are already used as a low temperature Pb-free solders. Besides Ga-based alloys, revealing a low temperature of phase transition and semimetal properties are suitable materials for studying of governing by crystallization processes. It should be noted, that analysis of crystallization processes commonly is not considered with connection to the structural-thermodynamical state of melt, what is no absolutely correct.

In this paper we present the results on x-ray diffraction studies of short range order in liquid Ga-In-Sn eutectic melt at different temperatures. Early we have obtained the structure data for these melt at temperature somewhat higher than crystallization point [2].

The structure studies were carried out with using of difractometer whith horizontal

[a] *prof., dr. hab. inż* *vprokhor@polynet.lviv.ua vprokhor@univ.rzeszow.pl*
[b] *prof., dr. hab.* *rus@icmp.lviv.ua*
[c] *dr.* *vprokhor@polynet.lviv.ua sprokhorenko@wp.pl*
[d] *prof., dr. hab., inż* *bylica@polynet.lviv.ua*
[e] *post-grad* *navotska@wp.pl*

axis of honiometer and Bregg-Brentano focusing geometry. The chamber of diffractometer was filled with pure helium in order to avoid the oxidation of sample during experiment. The temperature of specimen was measured with accuracy ±2K. Scattered intensities were recorded within scattering angles range 20°-140° with step 0,01° in maxima regions and 0,05° at other angles.

The total structure factors (SF) calculated from intensity values at different scattering angles for Ga-In-Sn liquid eutectic alloy are shown in *Fig.1*. These SF are compared with SF for liquid components – In, Ga and Sn. In order to analyse the structure of this melt we have estimated the positions of first and second maxima as well as heights of principal peaks.

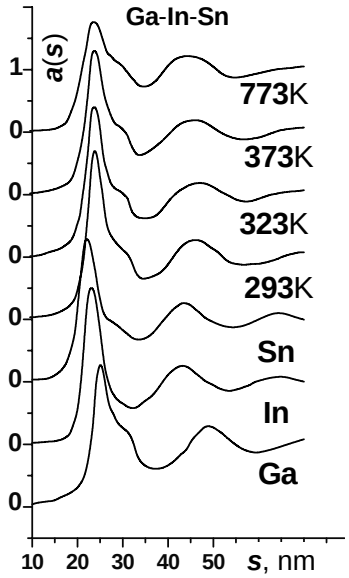

Fig. **1**. Structure factors of liquid eutectic Ga-In-Sn alloy

It can be seen that SFs for Ga-In-Sn eutectic melt are more similar to one for liquid Ga then for other elements. The comparison of main structure parameters including the existence of shoulder confirms that similarity. Nevertheless one can not suggest that short range order in liquid eutectic melt is the same as in liquid Ga. As was shown early in our work [2] the structure of this eutectic melt is inhomogeneous. In this work we focus the attention on the temperature stability of observed inhomogeneities.

Most probable interatomic distances r_1 and r_2 as well as number of neighbours Z were determined from pair correlation functions. These functions were calculated from SF by means of Fourier transformation. In order to study the temperature change of structure we analyzed the temperature dependence of main structure parameters obtained from SF and pair correlation functions. One can see that some shift of principal peak position in SF to small values of wave vector is observed. This maximum decreases it's height and becomes of more width. Such behavior is the evidence of thermal disordering which results in decrease of structural units size and packing density. It should be noted, that near crystallization temperature the structure changes are more drastic that at following heating.

Some features are observed also in temperature dependence of first and second interatomic distances (*Fig.2a*). As follows from figure the r_1 and r_2 parameters increase with temperature. besides, the last shows the significant increase near malting temperature. At higher temperatures this parameter is about unchangeable. Therefore the changes of these parameters are no in accordance what is the evidence of inhomogeneities influence on temperature dependence of structure.

It is known, that complicated process of structure homogenization in melt during heating should be displayed in temperature dependence of thermodynamical functions especially in configuration entropy value (S_{CONF}), which can be calculated with using of

pair correlation function [3]. We have calculated this function and compared it with temperature dependence of number of neighbors Z (*Fig.2b*). Function $S_{CONF}(T)$ increases slightly within range from melting temperature up to 100K above it and then rapidly decreases with following heating. Similar behavior is also observed in temperature dependence of Z parameter. Moreover the position of maximum in both dependences is the same. Therefore it is possible to suggest that in temperature range $T_{melt} \div (T_{melt}+100K)$ the breaking of clusters occurs, but the total fraction of them in melt is unchangeable. With following heating the structure changes are different due to more intensive influence of thermal disordering on cluster size and their distribution.

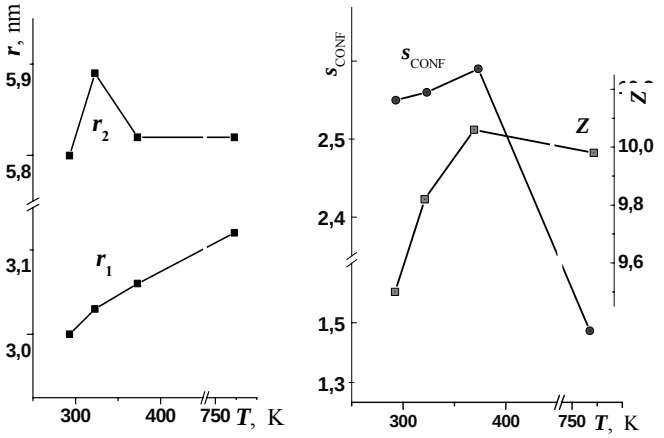

Fig. 2. Temperature dependences of structure parameters of eutectic alloys Ga-In-Sn temperature dependence
*Fig.***2a** (r_1, r_2); *Fig.***2b** (r_1, r_2);

The existence on nonequilibrium and inhomogeneous structure can be used in order to govern by crystallization process in eutectic melts.

Flemings [4] was the first who proposed to use the magnetic hydrodynamical mixing (MHD) in order to obtain the tixotropic materials. The idea of method is the breaking of dendrite at crystallization front by flowing liquid metal. Commonly this flow is generated by magnetic field. It is important that in this case as at effecting by other factors of influence, one can consider the formation of small dispersed structure as a result of created already conglomerates. In other words under the treatment by filed is the solid-liquid mixture.

We propose to use the outside influence on the melt only and to effect the structure at different temperatures above the melting point. The wide range of inhomogeneous structure existence allowed us to suppose that upon such treatment the structure of eutectic melts can be modificated.

Analysis of structure data for eutectic melts allowed us to suppose that outside energetic influence can change at first the size of clusters and their arrangement in matrix, formed by randomly distributed atoms. The size of such clusters in eutectic melts is about 1nm to 10nm near the crystallization temperature. The decrease of such size with temperature is not linear dependence and shows the anomalous behavior attributed to transition from one nonequilibrium state of liquid to another. The departure of structural and thermodynamical state of melt from equilibrium should be accounted in casting

technologies in order to obtaine the solidificated materials of high quality.

Comparing the melt with solid one allows to consider the influence of defects on melting process. Solid alloys including eutectic ones consist various defects such as vacancies, impurities, dislocation and disclinations. When the concentration of such defects reach some critical value the crystal shows the thermodynamical and structural nonstability and as result the failure (mechanical or thermal) occurs. On other hand the self-organization processes in eutectic melt before crystallization also are connected with some "defects" which can be "transferred" into solid. Such "defects" are connected with size of clusters and their structure. Clusters as a nanoscale structural units have no complete definition, but in melts they are considered as a dynamical ordered atomic groups which are in equilibrium with disordered part of structure. Just the existence of inhomogeneous atomic arrangement in liquid eutectic melts gives a possibility to govern the structural and thermodynamical state before crystallization.

REFERENCES

[1] V. Y. Prokhorenko, V. V. Roshchupkin, M. A. Pokrasin, S. V. Prokhorenko,and V. V. Kotov. *Review - Liquid Gallium: Potential Uses as a Heat-Transfer Agent*, High Temp. 38, 954- 968 (2000)

[2] Lutsyshyn T. *The structure of diluted metallic solutions with limited solubility in solid state.* Thesis. Lviv-2005 (in Ukrainian)

[3] EI Kharkov, VI Lysov, V.Eu. Fedorov. *Thermodynamic of Metals*. Kuiv, 1982. (in Russian)

[4] Flemings M.C. *Bechawiour of metals and alloys in the semisolid state*. //Metall Trans A 22A, -1991, -4, -p.957-981

[5] Braszczynski J. *Teoria procesów odlewniczych*. –Warszawa: Państwowe wydawnictwo naukowe. -1989

[6] Prokhorenko S., Bylica A., Prokhorenko V. *Thermal, sound and magnetic treatment of melts with the purpose of improvement of the quality of casting*. Journal Solidification of Metals and Alloys. - 2000. - Vol.2, №43. - P. 479-486.

[7] Taran Yu., Mazur V. *The structure of eutectic alloys*. Moscow. 1978 (in Russian)

STRUKTURA CIEKŁEJ EUTEKTYKI JAKO ISTOTNY CZYNNIK W PROCESIE KRYSTALIZACJI

STRESZCZENIE

W pracy przedstawiono wyniki porównawczych badań stukturalnych eutektycznego stopu Ga-In-Sn. Uzyskane wyniki potwierdziły występowanie w tym stopie struktur niehomogenicznych w szerokim zakresie temperatury oraz możliwość zmiany takich struktur przez zewnętrzne oddziaływanie energetyczne.

Recenzował: Prof. Edward Fraś