PHYSICS AND CHEMISTRY OF SOLID STATE
V. 20, № 4 (2019) p. 432-436

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 20, № 4 (2019) С. 432-436

DOI: 10.15330/pcss.20.4.432-436

UDK 538.9 ISSN 1729-4428

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Structural Features of InPbGaSnCu Molten High Entropy Alloy

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X-ray diffraction method has been carried out to study the structure in the equiatomic InPbGaSnCu high entropy alloy in liquid state. Structure factors and pair correlation functions have been analyzed and used to determine the main structure parameters. Existence of shoulder on right hand side of principal peak and its transformation was the main feature of structure factors. Comparison of structure functions and main parameters obtained from them for multicomponent alloy with ones for constituent elements shown that mixing process is related with formation of structural inhomogeneities in liquid state.

Keywords: high entropy alloys, solid solution, structure factors, short range order.

Article acted received 06.12.2019; accepted for publication 15.12.2019.

Introduction

It is known that fundamental studies on physics of metals are important for development of new materials especially ones with controlled properties. Recently, it was proposed to use a new class of materials, which are known as high entropy alloys (HEA) from substantial concentrations (5 - 35 at. %) of five or more elements. It is assumed that in liquid state such alloys are liquid atomic solutions, which upon cooling transform into multiprincipal element solid alloys. Entropy of such alloys increases due to large number of constituent elements and formation of structure with random atomic distribution which stabilizes the formation of solid solutions and prevents the formation of intermetallic phases during the crystallization. HEAs are characterized high hardness, resistance to temperature disordering, and an increased level of strength characteristics at high temperatures in combination with high oxidation and corrosion resistance. But results of structure studies and physical properties have shown that in most cases the atomic distribution in HEA deviates from atomic solution that leads to decrease of entropy of mixing. It should be noticed in any multi-component alloy in crystalline state beside solid solution can exist intermetallics or/and eutectic phases, which significantly change the properties. From thermodynamic viewpoint the formation of solid solutions phases or intermetallics among another one is the result of interatomic interaction. With increasing of alloying elements amount, the probability of solid solutions formation increases but some amount of intermetallics or eutectic phases can also be formed. It is clear that such structure formation processes are related with structure features before solidification in liquid state.

Currently, HEA are being increasingly studied [1-6]. Structure and physical properties of these alloys are widely studied first of all by X-ray diffraction analysis, scanning electron microscopy and measurement of mechanical characteristics. Therefore HEA are the multicomponent alloys with properties, significantly different from properties of elements, from which they are alloyed.

Among high-entropy metal alloys special attention is attracted by the multicomponent alloys of Al- and Cu-based systems with transition elements (Fe, Co, Ni, etc.), in which formation of a mixture of solid solutions based on bcc and fcc structures with a high level of strength and plastic characteristics take place [7]. Unfortunately the studies of HEA in liquid state are scarce. In this paper, we study the structure of InPbGaSnCu equiatomic alloy in liquid state.

I. Experimental

The structure of melts was studied by using a high-temperature *X*-ray diffractometer for investigation of the metal melts, as was reported in [8]. An incident *CuK*α - radiation beam, monochromatized using a *LiF* crystal, which was installed into the primary beam according to Bragg-Brentano focusing geometry [9]. The accuracy of the measurement of the X-ray scattered intensity was in the range of 2 – 3 %. The temperature was measured and maintained with an accuracy of ±2 K. Intensity curves were corrected on polarization and incoherent scattering [10-13]. After normalization procedure the structural factors (SF) have been calculated at different temperatures [14].

The melting-solidification process has been studied by DSC using equipment interfaced with a computerized data system. The heating of samples was carried up to 1400 K in an inert atmosphere with linear heating mode and heating rate of 20 K/min. The temperature was measured with an accuracy of ± 1 K.

II. Results and discussion

Unfortunately, there are no data on the phase diagrams of multicomponent alloys yet. Therefore, at first it was needed to determine the liquidus temperature for InPbGaSnCu HEA alloy. In present work, by means the DSC method it was established that at temperatures above 940 K the alloy is completely in liquid state (Fig. 1). It is also seen that this melt show the tendency to supercooling.

SFs at different temperatures show somewhat untypical for metallic melts profile (Fig. 2). One can see that principal peak shows asymmetry and hump, which slightly transform with temperature variation, whereas the position of principal peak is in fact unchangeable (Fig. 4a). It means the medium distances between atoms in clusters in InPbGaSnCu HEA don't change with heating. More sensitive to temperature is second maximum, which shows the smearing at heating. Comparison of SFs for multicomponent melt with ones for liquid constituent elements shows the interesting features (Fig. 3). Particularly position of first peak and its height for liquid alloy are different significantly than such parameters for liquid copper. As we can see position of this peak for liquid HEA is rather close to one of liquid indium and tin than for other components of alloy. Besides, this maximum has less pronounced asymmetry and shoulder, which are observed in SF for liquid Ga and Sn.

The second maximum of multicomponent melt is also notably shifted comparatively to corresponding maximum of Cu. Therefore the structural features of copper are not observed in structure of melt and it allows to support that all atoms of this element are diluted in atomic matrix of other elements.

Another parameter obtained from SF, which is commonly considered as measure of atomic packing density is the height of principal peak (Fig. 4b). This

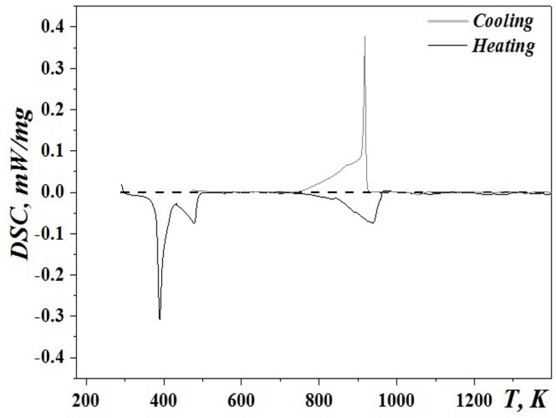

Fig. 1. DSC curves of InPbGaSnCu HEA.

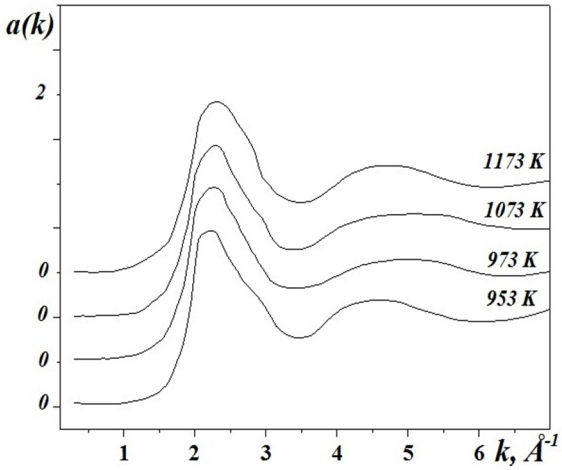

Fig. 2. SFs InPbGaSnCu HEA at different temperatures

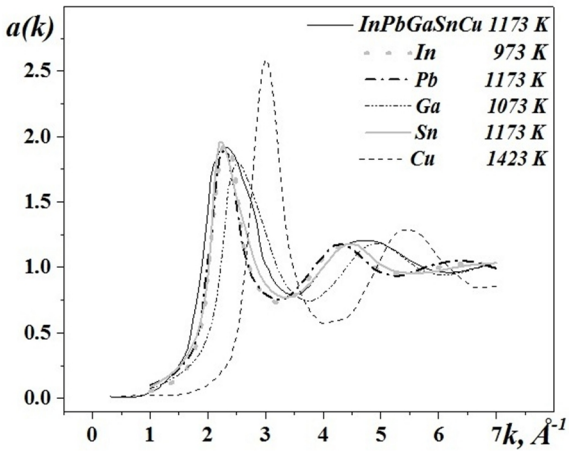

Fig. 3. SF InPbGaSnCu HEA compared with SFs pure components.

parameter decreases with temperature increasing that is the evidence of topological disordering of atomic distribution due to increasing of atomic free volume. Such dependence is typical for metallic liquids including

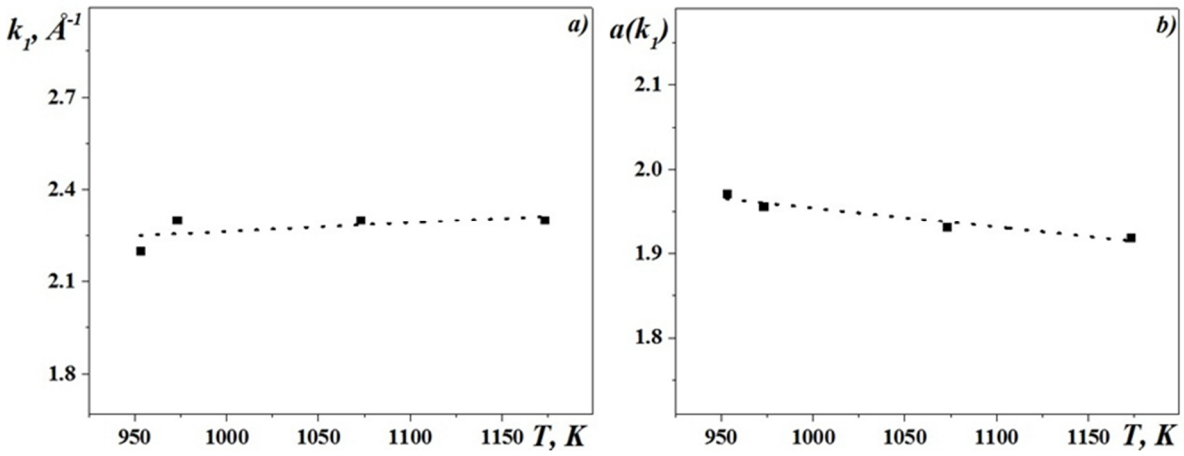

Fig. 4. Temperature dependence principal peak position (a) and principal peak height (b) InPbGaSnCu HEA.

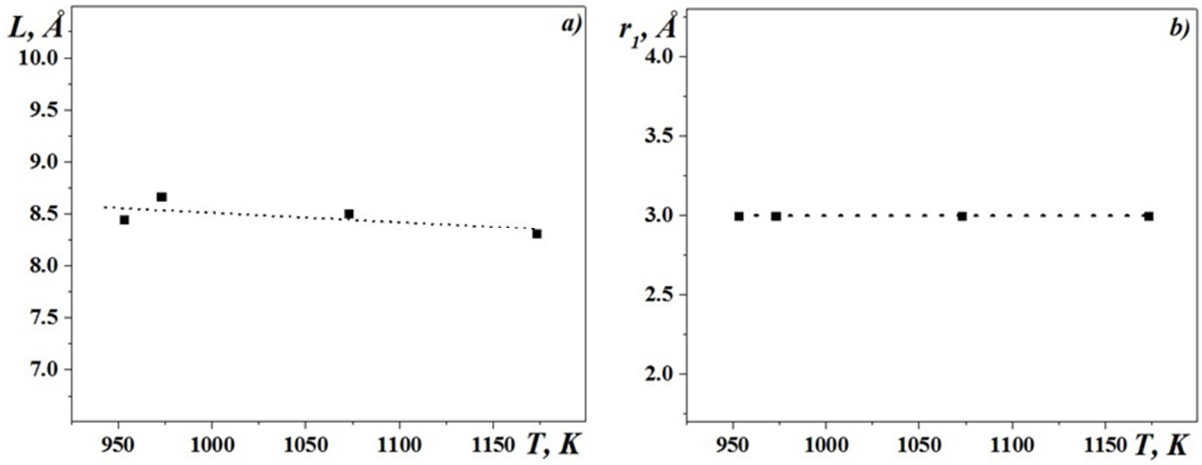

Fig. 5. Temperature dependence of cluster's size (a) and distance to neighbor atoms (b) in molten $In_{20}Pb_{20}Ga_{20}Sn_{20}Cu_{20}$ alloy.

pure liquid metals and is related with negative thermal expansion coefficient [15].

Half–height width is a parameter, which is related with structural ordering too and can be used for calculation of mean size of structural units (clusters). For multicomponent $In_{20}Pb_{20}Ga_{20}Sn_{20}Cu_{20}$ alloy mean size of structural units is in fact unchangeable with temperature that is the evidence of high temperature stability of such kind structure within investigated temperature range (Fig. 5a).

For more detailed information about the structure of InPbGaSnCu equiatomic high entropy melt SFs were used to calculate pair correlation functions (PCFs). These functions were used to determine the most probable distance to neighbor atoms. As we can see this parameter is unchangeable with heating that confirms the assumption pointed out above from analysis of temperature dependence of principal peak position in SF (Fig.5b). Comparing the values this structure parameter with ones for constituent elements (Table 1) we can see a good agreement with XRD data (Fig. 6).

Identification of diffraction peaks shown that upon solidification mainly exist two kind atomic solutions: Pb-based solutions and Sn-based ones. Diffraction pattern reveals also the unidentified small peaks which supposed to be caused by existence of stable and metastable chemically ordered clusters. Certainly that cooling rate is not large enough to consider the structures in solid and liquid state as absolutely identical, but it is correct to determine the main tendencies at structure formation process of multicomponent high entropy alloys.

Obtained results allowed us to suppose that there are two dominant tendencies at formation of multicomponent $In_{20}Pb_{20}Ga_{20}Sn_{20}Cu_{20}$ HEA. On other hand, the tendency to formation of self-associated atomic groups is less pronounced. If analyze the binary phase diagrams, existing in this multicomponent system we can note that

Table 1

The most probable distance to neighbor atoms in melts at temperature near the melting point

Melt	r_1, *Å*	*T, K*
In	3.15	433
Pb	3.30	613
Ga	2.80	473
Sn	3.25	523
Cu	2.50	1423
InPbGaSnCu	3.00	1173

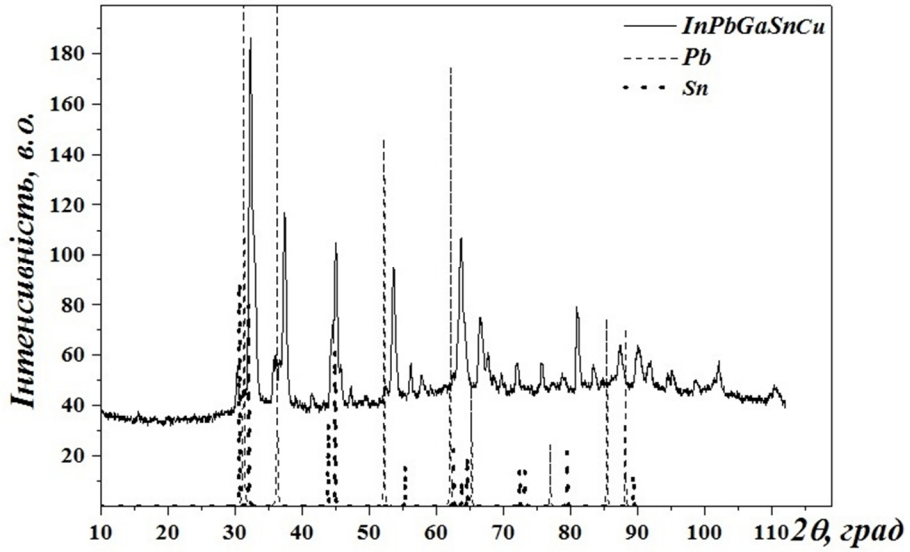

Fig. 6. XRD patterns of $In_{20}Pb_{20}Ga_{20}Sn_{20}Cu_{20}$.

many of them are of eutectic type and two of them (Ga-Pb, and Cu-Pb) show the miscibility gap in liquid state. On the other hand, Cu-atoms attempt to interact with ones of Sn, In and Ga forming the intermetallic phases, which decrease entropy too. Therefore we have structural inhomogeneities in liquid state, which exist not only before solidification but also at higher temperatures.

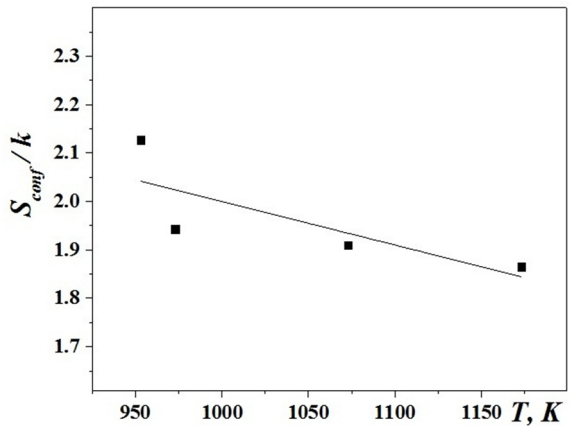

Fig. 7. Temperature dependence configuration entropy of $In_{20}Pb_{20}Ga_{20}Sn_{20}Cu_{20}$.

Table 2

Calculated values of configurational entropy at temperatures near the melting points

Melt	S_{conf}/k	*T, K*
In	1.29	573
Pb	2.00	613
Ga	0.89	473
Sn	1.17	523
Cu	0.42	1423
InPbGaSnCu	2.13	953

Multicomponent liquid alloy can be considered as composite system, consisting atomic solution as matrix and embedded clusters with preferred interaction unlike kind atoms. Taking into account the results on XRD-studies it is possible to suppose that due to residual covalent bonds in liquid tin and gallium some part of self-associated atomic groups on the base of these elements can also exist in multicomponent melt.

It is that presence of such clusters changes the entropy and first of all its main contribution – configurational entropy. We have calculated this thermodynamic function according formula:

$$\frac{S_{conf}}{k} = -2pr_0 \int_0^{\infty} r^2 g(r) \ln[g(r)] dr$$

where k – is Boltzmann's constant, ρ_0 – mean atomic density, r is a distance from any atom to another one, $g(r)$ – pair correlation function.

It is known this function is a measure of topologic ordering in atomic arrangement. Configuration entropy S_{conf} has the higher value near melting point and slowly decreases with heating (Fig. 7).

Such behavior is caused mainly by topological disordering and decreasing of chemical short range order in clusters with intermetallic – like structure. Configurational entropy have been calculated also for constituent elements of alloy with assumption that multicomponent melt can be considered as effective one component liquid. Such assumption is motivated by the fact that most of atoms of multicomponent melt form the atomic solution. (Table 2).

As it is seen from the table liquid HEA has a higher value of configurational entropy, whereas for liquid Cu it reveals minimum value. That allows to conclude that on that reason the total entropy of melt upon mixing of In, Pb, Ga, Sn and Cu will be increased.

Conclusions

Structure of equiatomic InPbGaSnCu molten alloy has another structure than one of each any constituent element. XRD-data showed that this melt can be considered as a mixture of Pb-based and Sn-based solid solutions, in which clusters with intermetallic – like structure are embedded. General features of such structure persist with heating, but some topologic disordering occurs. In assumption of effective one-component liquid the experimental pair correlation functions were used for calculation of configurational entropy of mixing, which for InPbGaSnCu equiatomic melt is higher than one for constituent elements.

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Структурні особливості високоентропійного розплаву InPbGaSnCu

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Для дослідження структури високоентропійного еквіатомного розплаву InPbGaSnCu був застосований метод дифракції Х-променів. Отримано і проаналізовано структурні фактори (СФ) і парні кореляційні функції (ПКФ). Ці функції використовувались для визначення головних структурних параметрів. Відзначено, що на правій вітці головного піку СФ спостерігається плече, трансформація якого є головною особливістю структури розплаву. Порівняння структурних параметрів розплаву з відповідними величинами складових компонент сплаву показало, що процес змішування супроводжується утворенням структурних неоднорідностей в рідкому стані.

Ключові слова: високоентропійні сплави, твердий розчин, структурний фактор, ближній порядок.