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Chemical Ordering in Ni$_{66,7}$ In$_{33,3}$ Liquid Alloy

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Short range order structure of liquid Ni$_{66,7}$ In$_{33,3}$ alloy has been studied by means of X-ray diffraction method at temperatures 1235; 1260 and 1335 K. Experimental structure factors and radial atomic distribution function are analyzed. It is shown that structure of Ni$_{66,7}$ In$_{33,3}$ in liquid state reveals chemical ordering, like to Ni$_2$In type structure.

Key words: molten alloys, structure of melts, cluster, Ni-based alloys.

Introduction

In-Ni alloys attract the attention or researchers due to their current and potential application in electronics. Phase diagram of In-Ni system consists few intermetallic phases, most of which are stoichiometric (Ni$_3$In, Ni$_2$In, NiIn, Ni$_2$In$_3$ and Ni$_3$In$_7$). High temperature forms of Ni$_2$In and NiIn as well as Ni$_3$In$_9$ are nonstoichiometric. Intermediate Ɛ and β – phases show the maxima in liquidus curve and they are formed from liquid state. Ɛ - phase is Ni$_2$In- based solution and also has hexagonal structure, whereas β –phase reveals CsCl-type structure [1]. As it can be seen from phase diagram these two phases are formed from liquid state and have a most wide homogeneity ranges. Therefore at cooling from liquid state to temperatures, corresponding to solid one there is formation of various phases with chemical ordering of atoms. It should be noted that in this system exists hexagonal Ni$_2$In type structure, which is the characteristic of many alloys (AgAsBa, LiBC, Fe$_2$Sn, MnNiGe$_{1,05}$ etc.). For instance the such kind structure have an alloys, which reveal such phenomena as barocaloric effect, giant negative thermal expansion and show the magnetocaloric properties [2, 3]. This kind structure can be formed not at equilibrium thermodynamic conditions only, but also at producing of polycrystalline ribbons by quenching using the melt-spinning technique [4]. Taking into account these features it is interesting to study how the short range order of this kind structure transforms in liquid state, when temperature decreases down to crystallization point. Besides, there is also more general interest from the viewpoint of liquid intermetallic phases, whose structure understanding is far to be completed and clear.

Both constituent elements of Ni$_{66,7}$ In$_{33,3}$ alloy – Ni and In show significantly different structure factors (SF). Principal maximum position in SF for In is 2,30 Å^{-1}, whereas for liquid it equals to 3,10 Å^{-1}. Therefore one can assume that in case of structure formation of alloy the atomic arrangement of each element should be notably transformed upon alloying not only in solid state, as can be seen from phase diagram, but also in liquid state yet before solidification. Such assumption was confirmed by results on investigation of quenched from liquid state alloys, which shown the formation of Ɛ and β – metastable phases [6].

I. Experiment

The samples for X-ray scattering experiment were prepared from Ni and In with purity of 99.99 %. Quartz capsules with the appropriate amounts of the elements were evacuated, flushed with argon and sealed. After that they were melted and homogenized.

The diffraction measurements were performed in the reflection mode. A primary graphite-monochromator was employed in order to produce monochromatic radiation from X-ray source ($\lambda_{Cu-k\alpha}$= 1,54 Å^{-1}). All the measurements were done under 50 mbar helium pressure to reduce evaporation of melts and to avoid oxidation. The total scattered intensities were recorded within the range 5°<Θ<90° with variables steps. The relative statistical error for the measured points is less than 2 %.

II. Result and Discussion

The SFs for liquids Ni$_{66,7}$In$_{33,3}$ at three temperature

show the profile, significantly different comparing to similar curves for liquid constituent elements – indium and nickel (Fig. 1).They have notably less height and notably larger width. These features exist at three different temperatures and indicate high stability of such short range order to temperature change.

As is seen from Fig. 1 and Table 1 principle peak position in SF for melt lies between corresponding values for liquid nickel and indium indicating that there is no structure like to structure of any constituent elements. If compare model SF, calculated in assumption of preferred like kind atoms arrangement with experimental ones we cannot see the agreement between them. The second model, supposed random atomic distribution also was found to be unable to interpret experimental data. Moreover if such distribution really exists the topologic disordering at heating or ordering at cooling should be observed. In fact the experimental SFs don't show significant temperature dependence that allowed us to suppose that chemical ordering attempts to decrease the effect of temperature on disordering of atomic arrangement.

Another feature of experimental SF is the presence of small shoulder of left hand side of principal peak, whose position is close to the main maximum of SF for liquid In. Therefore one can suppose that structure of $Ni_{66,7}In_{33,3}$ melt is inhomogeneous and consists at least of two kind structural units, one of which are In-like clusters. In order to confirm this supposition we have interpreted the principal maximum profile as additive sum of two – Gaussian like curves. One of them, which is located at lower wave vector values has a position about 2,0 $Å^{-1}$ that is significantly less then for liquid In (Fig. 2). Therefore the supposition on existence of small clusters of In was not confirmed. Taking into account the tendency to chemical ordering due to preferred interaction of unlike kind atoms, which follows from results of thermodynamic measuremenrts, according to which integral enthalpy of mixing shows large negative value [4], we have compared the positions of diffraction peaks and their relative intensities for Ni_2 In type structure with maxima positions in SF for liquid $Ni_{66,7}$ $In_{33,3}$ alloy (Fig. 1). As is seen there is a good agreement between them.
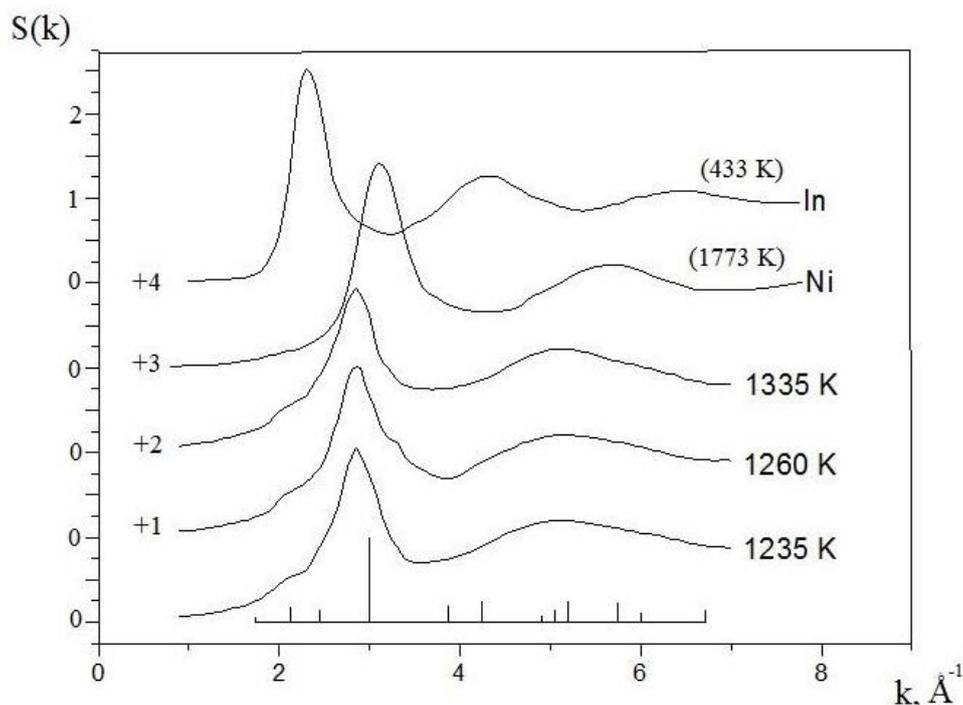

Fig. 1. Structural factor of the melts and diffraction reflexes of the compound Ni_2In.

Table 1

Structure parameters of $Ni_{66,7}In_{33,3}$, In and Ni liquid alloys

Melts	T, K	k_1, $Å^{-1}$	k_2, $Å^{-1}$	k_2/k_1	r_1, Å	r_2, Å	r_2/r_1	Z_{min}	Z_{sym}
$Ni_{66,7}In_{33,3}$	1235	2.85	5.15	1.81	2.69	4.72	1.75	12.1	10.4
$Ni_{66,7}In_{33,3}$	1260	2.84	5.15	1.81	2.66	4.66	1.75	11.2	10.2
$Ni_{66,7}In_{33,3}$	1335	2.85	5.15	1.81	2.69	4.72	1.75	10.2	9.7
Ni	1773	3.10	5.70	1.54	2.53	4.70	1.86	11.6	
In	433	2.30	4.32	1.88	3.23	6.10	1.89	11.6	

k_1. k_2- principal and second peak positions in SF;

r_1.r_2- distances to first and second neighbor atoms;

Z - number of neighbor atoms.

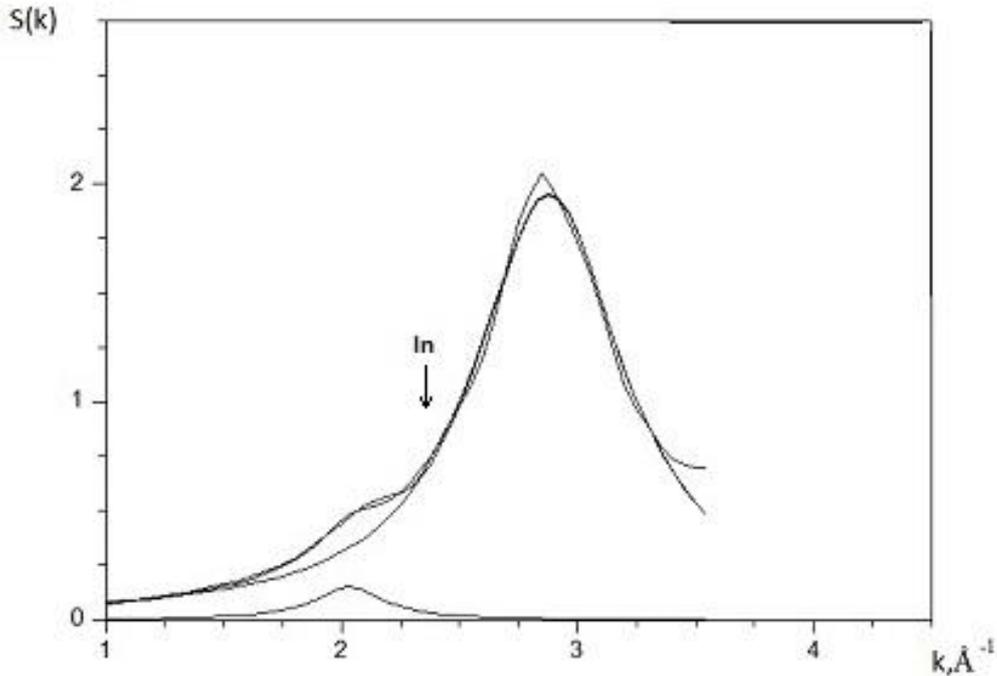**Fig. 2.** Interpretation of the principal maximum profile of SF $Ni_{66,7}In_{33,3}$ at 1235 K as additive sum of two – Gaussian like curves.
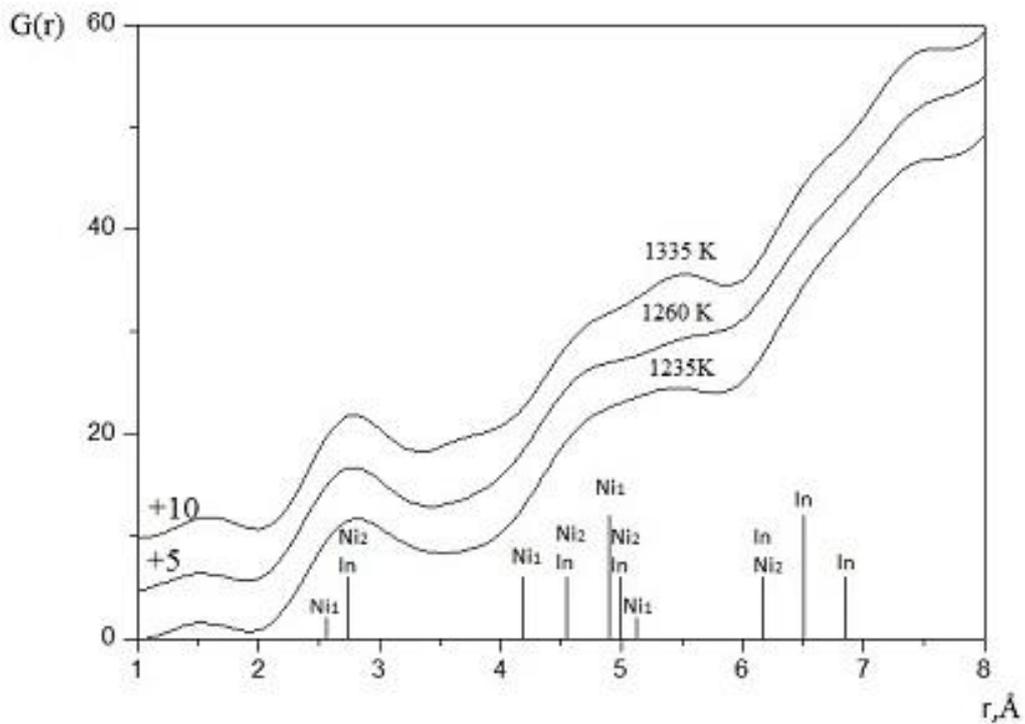

Fig. 3. Maxima positions in experimental function of radial distribution of atoms compared with distances to nearest atoms in crystalline Ni_2In.

We have compared also maxima positions in experimental function of radial distribution of atoms with distances to nearest atoms in crystalline Ni_2In (Fig. 3). One can see that there is a good correlation between them. Therefore, distances Ni-Ni and Ni-In atoms are most pronounced in atomic distribution function, calculated from experimental SF. Another kind distances In-In is not in accordance with maxima in experimental function of atomic distribution.

We have estimated also the difference in atomic radii of constituent elements. For indium values of atomic, covalent and ionic radii respectively (0.166; 0.144 and 0.081nm) prevails the corresponding values for nickel (0.124; 0.115; 0.069 nm). Therefore r_{In}/r_{Ni} ratios are about 1.3. But, taking into account that liquid $Ni_{66}In_{33,3}$ alloy show metallic behavior [4] the such ratio will be more correct in our case if use the values of metallic radii. These parameters we have determined as half

distances to neighbor atoms r$_1$, which were estimated from pair correlation functions. Therefore values of metallic radii ratio was found to be 1,28 and is almost the same that for other kind radii, determined for solid state. The electronegativity difference for binary In-Ni system is small and equals to 0.1. Such values of these parameters allowed us to suppose that there are conditions for formation of heterocoordinated short range order with dense atomic distribution.

Such features as well as existence of wide homogeneity range for Ɛ–phase in phase diagram allowed us to suppose that before solidification the molten alloy attempts to create the pre-crystallization conditions for this phase formation, in which upon crystallization content of indium is somewhat higher than in crystalline Ni$_2$In hexagonal structure. On that reason inhomogeneous structure of melt transforms its atomic distribution just before transition into solid state that results the formation of slight deviation of composition in clusters than should be in Ni$_2$In-like structural units. We can also conclude that wide inhomogeneity range of β-phase is related with above mentioned features of short range order structure in liquid state.

Conclusions

Liquid Ni$_{66,7}$In$_{33,3}$ alloy has an atomic distribution, whose main feature is existence of chemical ordering of atoms, which support the high thermal stability of structure. Short range order structure in liquid state has similar characteristics than crystalline Ni$_2$In cell. Atomic distribution in molten Ni$_{66,7}$In$_{33,3}$ suppose insignificant its transformation upon solidification, when the formation of ε - phase occurs.

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Хімічне впорядкування в розплаві Ni$_{66,7}$In$_{33,3}$

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Методом Х-променевої дифрактометрії досліджено структуру ближнього порядку розплаву Ni$_{66,7}$In$_{33,3}$ за температур 1235; 1260 і 1335 К. Проаналізовані експериментальні структурні фактори та функція радіального розподілу атомів. Показано, що структура розплаву Ni$_{66,7}$In$_{33,3}$ є мікронеоднорідною, основними структурними одиницями якої є хімічно упорядковані кластери та самоасоційовані групи атомів In.

Ключові слова: розплави, ближній порядок, кластер, сплави на основі нікелю.