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PHASE EQUILIBRIUM IN SYSTEMS MnSe-Bi, $MnBi_2Se_4$-Se

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By methods of physical and chemical analysis we studied two sections (MnSe-Bi, $MnBi_2Se_4$ - Se) of triple system Mn-Bi-Se and their state diagrams were plotted. It was established that the section MnSe-Bi is quasibinary, but $MnBi_2Se_4$-Se is partially quasibinary.

Keywords: *diagram, synthesis, quasibinary, eutectics*

Introduction

There is information on interaction in triple system Mn-Bi-Se in literature [1]. Its authors studied the section MnSe-Bi_2Se_3 by physical-chemical analysis and constructed state diagram, established the formation of two intermediate triple peritectic compounds at ratio of components 1:1 and 1:3 – $MnBi_2Se_4$, $Mn_3Bi_2Se_6$ correspondingly. Syngony was determined and parameters of unit cellof obtained peritectic compounds were calculated.

Information about binary systems which make up triple Mn-Bi-Se is presented in literature [2, 3, 4].

In the system Bi-Se one congruently melting (Bi_2Se_3) and two incongruently melting compounds (BiSe and Bi_2Se) are formed. Bi_2Se_3 melts at 706^0C and has rhombohedral lattice with parameters of a=4,138; c=28,6Å.

Manganese with selenium forms two compounds. MnSe melts congruently at a temperature higher than 1540^0C with polymorphic transformations at 6,50, 850^0C, but the compound $MnSe_2$ melts incongruently. Crystals of MnSe have a cubic lattice of type NaCl, where a=5,46 Å [3].

The system Mn-Bi contains one compound of MnBi. Periods of hexagonal lattice for MnBi are equal to a=4,25; c=6,01Å [4].

For detecting the character of chemical interaction in triple system Mn-Bi-Se we investigated the sections MnSe-Bi and $MnBi_2Se_4$-Se.

The investigation of alloys of the system was conducted by methods of physical-chemical analysis: differential-thermal (DTA), X-ray phase, microstructural (MSA) analyses and by measuring micro hardness. During synthesis of alloys we used: Bi of type Bi-000; selenium rectifier (frequency 99.9998) and manganese– electrolytic. Obtaining of complex selenides of manganese has experimental difficulties due to high reactivity of manganese with container material, that's why synthesis of alloys is conducted in graphitized quartz ampoules pumped off till residual pressure 10^{-3} mm of mercury. Ampoule was heated in one temperature furnace vertical at temperatures 100^0C higher than liquidus with further annealing one month at temperatures 50^0C lower than solidus. Equilibrium was controlled by measuring micro hardness by its unchanged values. Alloys were analyzed by DTA, values of micro hardness, X-ray and MSA analyses.

Section MnSe-Bi

According to the data of DTA in alloys of system MnSe-Bi in manganese-rich region besides endoeffects of liquidus and solidus, effects of corresponding polymorphous conversions of manganese differedon thermograms. They were realized at low temperatures by metatectic reactions at slightly below temperatures than for MnSe. Transformation of γ-MnSe to β-MnSe modification in the system occurs at 780^0C, but in α-MnSe at 550^0C.

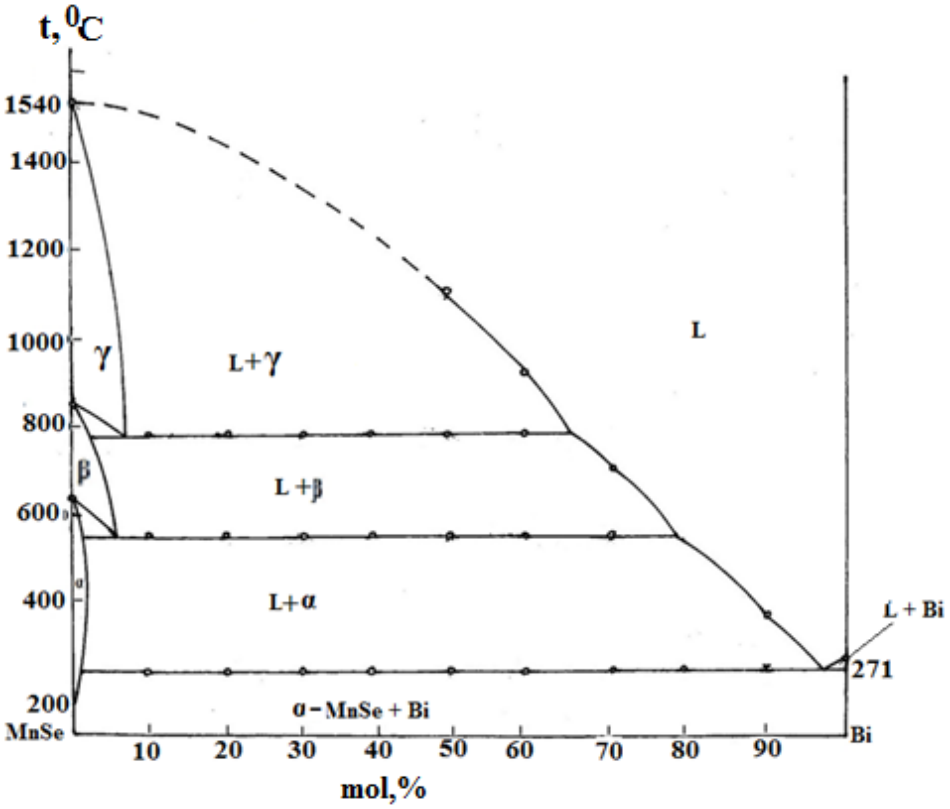

Fig.1. State diagram of the system MnSe-Bi

Table 1

Results of thermal analysis and measurement of micro hardness of alloys of section MnSe-Bi

Content, mol%		Thermal effects, ^{0}C	Microhardness, kG/mm^2	
MnSe	Bi		Dark phase MnSe	Light phase Bi
95	5	200, 550, 780	140	not measured
90	10	240, 550, 780	140	not measured
85	15	240, 550, 780	145	90
80	20	240, 550, 780	149	90
70	30	240, 550, 780	149	92
60	40	240, 550, 780	149	92
50	50	240, 550, 780	140	92
40	60	240, 550, 780, 90	140	90
30	70	240, 550, 700	140	90
20	80	240, 550	not measured	90
10	90	240, 300	not measured	90
5	95	240, 300	not measured	90
2,5	97,5	240, 280	not measured	90
-	100	275	not measured	90

At the range of concentration 10 mol% of MnSe only two effects are fixed in alloys, the higher one conforms to liduidus, but the other one corresponds to eutectic equilibrium and has similar stopping temperature at 250^0C (content of eutectic 98 mol% Bi).

MSA data show the existence of two phases. Determination of microhardness of alloys showed that two rows of values were obtained: 140 kG/mm^2 (MnSe) and 90 kG/mm^2 (Bi). According to the results of thermal analysis state diagram of MnSe-Bi was plotted (Fig.1).

State diagram was confirmed by the data on determination of microhardness, MSA and X-ray analysis. Liquidus of the section MnSe-Bi consists of two branches of initial crystallization of phases. The section MnSe-Bi is quasibinary section of triple system Mn-Bi-Se and is related to eutectic type.

Section $MnBi_2Se_4$-Se

For the purpose of determining coordinates of nonvariant points in quasitriple system MnSe-Bi_2Se_3-Se the section $MnBi_2Se_4$-Se was studied. On the basis of physical-chemical analysis phase diagram of the system $MnBi_2Se_4$-Se was plotted (Fig. 2).

In the table 2 the results of thermal analysis and measurement of microhardness of alloys of the system $MnBi_2Se_4$-Se are presented. Characteristics of section $MnBi_2Se_4$-Se is the fact that it cannot be named quasibinary, since the composition of liquid phase in the crystallization process of alloys is mixed. All alloys of the section are crystallized at temperature of triple peritectics, as result of four-phase reaction:

$$L + Mn_3Bi_2Se_6 \rightleftarrows MnBi_2Se_4 + Se$$

both initial phases L and $Mn_3Bi_2Se_6$ are fully spent. That's why below isotherms at 160^0C, which is a solidus of the section, we observed only two phases of $MnBi_2Se_4$ and selenium, microhardness of which corresponds to 100 kG/mm^2 ($MnBi_2Se_4$) and 60kG/mm^2 (Se) (table 2). Liquidus of section consists of two branches of initial crystallization phases of $Mn_3Bi_2Se_6$ and Se. Isotherm at 190^0C and monovariant curve (42-50 mol % Se) correspond to release of double eutectics of $Mn_3Bi_2Se_6$ + Se monovariant curve (0-42 mol % Se) conforms to three-phase peritectic reaction which are observed in alloys.

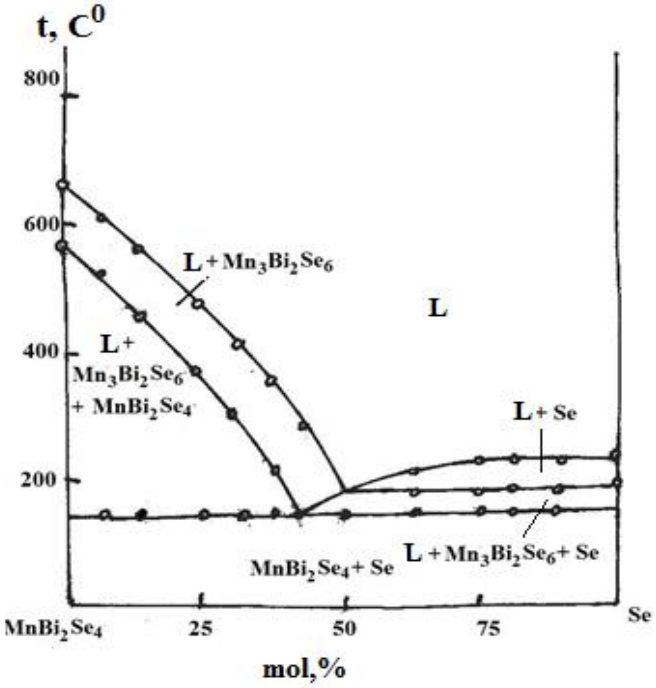

Fig. 2. State diagram of the system $MnBi_2Se_4$-Se

Table 2

Results of thermal analysis and measurement of microhardness of alloys of section $MnBi_2Se_4$– Se

Content, mol%		Thermal effects, ^0C	Microhardness, kG/mm^2	
$MnBi_2Se_4$	Se		$MnBi_2Se_4$ dark phase	Se Light phase
100	-	590	100	not measured
95	5	160, 500, 600	100	not measured
90	10	160, 550, 575	105	not measured
80	20	160, 410, 500	109	60
70	30	160, 300, 490	100	60
60	40	160, 210, 300	100	60
50	50	160, 190, 190	100	60
40	60	160, 190, 200	100	60
30	70	160, 190, 205	100	60
20	80	160, 190, 205	100	60
10	90	160, 190, 210	not measured	60
5	95	160, 190, 205	not measured	60
-	100	220	100	60

Solubility on the basis of initial components was not practically established. By this way the section MnSe-Bi is quasibinary, but $MnBi_2Se_4$-Se is partially quasibinary section of triple system Mn-Bi-Se.

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MnSe-Bi, $MnBi_2Se_4$-Se SİSTEMLƏRİNDƏ FAZA TARAZLIQLARI

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Fiziki-kimyəvi analiz metodları ilə Mn-Bi-Se üçlü sisteminin iki MnSe-Bi, $MnBi_2Se_4$–Se kəsikləri tədqiq olunmuş və onların hal diaqramları qurulmuşdur. Müəyyən olunmuşdur ki, MnSe-Bi kəsiyi kvazibinar, $MnBi_2Se_4$– Se kəsiyi isə qismən kvazibinardır.

Açar sözlər: *diaqram, sintez, kvazibinar, evtektika*

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМАХ MnSe-Bi, $MnBi_2Se_4$-Se

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Методами физико-химического анализа исследованы два разреза (MnSe-Bi, $MnBi_2Se_4$ - Se) тройной системы Mn-Bi-Se и построены их диаграммы состояния. Установлено, что разрез MnSe-Bi квазибинарный, а $MnBi_2Se_4$–Se частично квазибинарный.

Ключевые слова: *диаграмма, синтез, квазибинарный, эвтектика*