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REGION OF GLASS FORMATION IN THE SYSTEM ARSENIC-SELENIUM-TELLURIUM

by

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13. ABSTRACT

Compns. for the type AsX SUBN (X equals Se plus Te) for N equals 0.6, 0.8, 1, 1.5, 2.5, 4, 9, and 20 were prepd. by heating the mixt. of the components in the course of 3 to 4 hr to 700 degrees, holding for 1 hr, heating 5 hr at 950 degrees and subsequent quick cooling in the air to 20 degrees. Glassy melts contg. Te smaller than or equal to 58, As smaller than or equal to 60, and Se smaller than 100 At. percent can be prepd. The region of glass formation in the compn. triangle is bounded in the direction to the As apex by N equals 0.6, in the direction towards the Te apex by a line given by the following corresponding values of N and At. percent Te: 1.5, 48.0; 2.5, 57.1; 4, 48.0; 9, 45.0; 20. 36.9, and on the line Se-Te at 20 At. percent Te. Smaller tendency to crystn. at N equals 1.0 and 2.5 compared to the melts with N equals 1.5 is caused by the presence of As SUB2 X SUB3. The cryst. phase in the glass cryst. and polycryst. melts is formed mainly by Te and As SUB2 Te SUB3. D. and microhardness were detd. for all samples. D. of the glassy melt increases with progressing substitution of Se by Te, the appearance of the cryst. phase, however, causes steep increase in D. The substitution of Se by Te causes increase in microhardness in melts with N equals 0.8, 9, 20. [AP1128504]

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Glass Composition						
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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

REGION OF GLASS FORMATION IN THE SYSTEM ARSENIC-SELENIUM-TELLURIUM

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The highest capacity for glass formation with oxygen analogs is found in elements of groups IV and V of the third and fourth periods of the Periodic System. Combination of these elements leads to the formation of directed paired-electron bonds. Substantial regions of glass formation are obtained when arsenic is combined with sulfur or with selenium and also in the three-component system As–S–Se [1]. When the components in the alloys are replaced with their analogs, standing lower in the Periodic System, the ability of the alloys to form glass is reduced due to the rise in the so-called "metallization" of the chemical bonds. Thus, in the arsenic-tellurium system only alloys of the compositions AsTe and $AsTe_{0.8}$ are obtained in conditions of hardening in air [2], while with more severe hardening an alloy of the composition As_2Te_3 is obtained in the glassy state [3].

With an increase in the number of components in the alloys their ability to form glass is raised; the number of spatially different structural units, which increases in this case, hampers the separation of definite crystalline phases. In this connection we might expect that in alloys of three-component systems containing tellurium the ability to form glass would be higher as compared with binary systems. Actually, comparatively large regions of glass formations are obtained in the systems As–Si–Te [4] and As–Ge–Te [2].

The region of glass formation in the complex system As_2S_3–As_2Se_3–As_2Te_3 was determined in work [5]. In work [6] it was shown that alloys with compositions from As_2Se_3 to $As_2Se_3 \cdot 4As_2Te_3$ can be obtained in the vitreous state along the section As_2Se_3–As_2Te_3.

This work involves determination of the region of glass formation in the system As–Se–Te. To determine the region of glass formation in this system and also for subsequent investigation of the physicochemical properties of glasses of this system we synthesized alloys of 45 compositions (see table).

The alloys were synthesized by vacuum melting from elemental arsenic, tellurium of mark V-3, and selenium of rectifier grade.. Ampules with the charge were heated to 700°C in the course of 3-4 hours and held at this temperature for an hour. Then the temperature was raised to 950°C and the ampules with the melt were held for 5 hours with application of vibration mixing. The melts were cooled by pulling the ampules out of the furnace into the air (air hardening: $950°C \xrightarrow{5\ min} 20°C$). For certain compositions the specimens from parallel melts were synthesized in the flame of a gas-oxygen burner. The properties of the alloys obtained in the two different synthesis conditions were identical within the limits of measurement error.

As the initial materials during synthesis of alloys of the system As–Se–Te we took determined compositions in the As–Se system which were investigated in work [7]; in these compositions selenium was progressively substituted by tellurium. The content of arsenic remains constant.

Table. Data from research on the system As–Se–Te.

(1) № п. п.	(2) Химический состав	(3) Содержание, ат. %			X = (Se + Te)	(4) Плотность (d) г/см³	(5) Микротвердость (H), кг/мм²	(6) Примечание
		As	Se	Te				
1	2	3	4	5	6	7	8	9
1	$AsSe_{0.48}Te_{0.12}$	62,5	30,0	7,5	$AsX_{0.6}$	4,678	113	Стекло (7)
2	$AsSe_{0.36}Te_{0.24}$	62,5	22,5	15,0		5,01	146	Стекло
3	$AsSe_{0.30}Te_{0.30}$	62,5	18,7	18,8		4,957	171	Стекло
4	$AsSe_{0.18}Te_{0.42}$	62,5	11,2	26,3		5,09	161	Стекло
5	$AsSe_{0.12}Te_{0.48}$	62,5	7,5	30,0		5,13	142	Стекло
6	$AsSe_{0.06}Te_{0.54}$	62,5	3,7	33,8		5,331	—	$As_2Te_3 > As_2Te_3$ + стекло (7)
	$AsSe_{0.8}$ [7]				$AsX_{0.8}$	4,55	66	
7	$AsSe_{0.64}Te_{0.16}$	55,6	35,5	8,9		4,025	128	Стекло (7)
8	$AsSe_{0.48}Te_{0.32}$	55,6	26,6	17,8		4,592	149	Стекло
9	$AsSe_{0.40}Te_{0.40}$	55,6	22,2	22,2		4,955	157	Стекло
10	$AsSe_{0.24}Te_{0.56}$	55,6	13,3	31,1		5,18	163	Стекло
11	$AsSe_{0.16}Te_{0.64}$	55,5	8,9	35,5		5,234	162	Стекло
12	$AsSe_{0.08}Te_{0.72}$	55,6	4,4	40,0		5,335	163	Стекло
	$AsTe_{0.8}$ [2]					5,421	173	Стекло
	AsSe [7]				AsX	4,53	139	Стекло
13	$AsSe_{0.8}Te_{0.2}$	50,0	40,0	10,0		4,715	155	Стекло (7)
14	$AsSe_{0.6}Te_{0.4}$	50,0	30,0	20,0		4,918	148	Стекло
15	$AsSe_{0.5}Te_{0.5}$	50,0	25,0	25,0		5,026	156	Стекло
16	$AsSe_{0.3}Te_{0.7}$	50,0	15,0	35,0		5,206	160	Стекло
17	$AsSe_{0.2}Te_{0.8}$	50,0	10,0	40,0		5,297	164	Стекло
18	$AsSe_{0.1}Te_{0.9}$	50,0	5,0	45,0		5,307	166	Стекло
	AsTe [2]					5,453	161	Стекло
	$AsSe_{1.5}$ [7]				$AsX_{1.5}$	4,55	156	Стекло (7)
19	$AsSe_{1.2}Te_{0.3}$	40,0	48,0	12,0		4,773	142	Стекло
20	$AsSe_{0.9}Te_{0.6}$	40,0	36,0	24,0		4,973	140	Стекло
21	$AsSe_{0.75}Te_{0.75}$	40,0	30,0	30,0		5,070	146	Стекло
22	$AsSe_{0.45}Te_{1.05}$	40,0	18,0	42,0		5,209	147	Стекло
23	$AsSe_{0.3}Te_{1.2}$	40,0	12,0	48,0		5,371	148	Стекло
24	$AsSe_{0.15}Te_{1.35}$	40,0	6,0	54,0		6,103	—	As_2Te_3 кристалл (8)
	$AsSe_{2.5}$ [7]				$AsX_{2.5}$	4,53	133	Стекло (7)
25	$AsSe_{2.0}Te_{0.5}$	28,6	57,1	14,3		4,763	123	Стекло
26	$AsSe_{1.5}Te_{1.0}$	28,6	42,8	28,6		5,013	130	Стекло
27	$AsSe_{1.25}Te_{1.25}$	28,6	35,7	35,7		5,123	127	Стекло
28	$AsSe_{0.75}Te_{1.75}$	28,6	21,6	49,8		5,328	128	Стекло
29	$AsSe_{0.5}Te_{2.0}$	28,6	14,3	57,1		5,425	134	Стекло
30	$AsSe_{0.35}Te_{2.15}$	28,6	10,0	61,4		5,510	--	Стеклокристалл (9)
31	$AsSe_{0.25}Te_{2.25}$	28,6	7,1	64,3		6,146	--	As_2Te_3 + Te + стекло (7)
	$AsSe_4$ [7]				AsX_4	4,45	105	Стекло (7)
32	$AsSe_{3.2}Te_{0.8}$	20,0	64,0	16,0		4,735	169	Стекло
33	$AsSe_{2.4}Te_{1.6}$	20,0	47,9	32,0		5,061	105	Стекло
34	$AsSe_{2.0}Te_{2.0}$	20,0	40,0	40,0		5,126	117	Стекло
35	$AsSe_{1.6}Te_{2.4}$	20,0	32,0	48,0		5,270	122	Стекло
36	$AsSe_{1.2}Te_{2.8}$	20,0	24,0	56,0		5,509	—	Te кристалл (8)
	$AsSe_9$ [7]					4,35	65	Стекло (7)
37	$AsSe_{7.2}Te_{1.8}$	10,0	72,0	18,0		4,764	90	Стекло

KEY: (1) No.; (2) Chemical composition; (3) Content, at. %; (4) Density (d), g/cm^2; (5) Microhardness (H), kg/mm^2; (6) Remarks; (7) Glass; (8) crystal; (9) glass-crystal; (10) Cr. solid solution.

Table (continued)

1	2	3	4	5	6	7	8	9
38	$AsSe_{5,1}Te_{3,5}$	10,0	51,0	35,0	[illegible]	5,015	102	Стекло (7)
39	$AsSe_{4,5}Te_{4,5}$	10,0	45,0	45,0		5,147	107	Стекло
40	$AsSe_{3,6}Te_{5,4}$	10,0	36,0	54,0		5,596	—	Te кристалл (8)
	AsSe[illegible] [7]				[illegible]	4,2[illegible]	52	Стекло (7)
41	$AsSe_{15,5}Te_{4,0}$	4,8	73,5	15,4		4,590	52	Стекло
42	$AsSe_{12,4}Te_{4,0}$	4,8	55,4	39,9		5,017	91	Стекло
43	$AsSe_{10,5}Te_{10,5}$	4,8	46,2	46,2		5,450	-	Se_xTe_y кристаллы (8)
44	Se_4Te	0	80,0	20,0	[illegible]	4,674	76	Стекло (7)
45	$Se_{2,33}Te$	0	70,0	30,0		5,266	—	Кр. твердый раствор (20)

The compositions of the obtained vitreous and glass-crystalline alloys, the atomic % content of components in them, the total content of chalcogen in the alloys (X), their density, and their microhardness are presented in the table. The composition of separated crystalline phases obtained by X-ray phase analysis is also shown for alloys of the glass-crystal type.

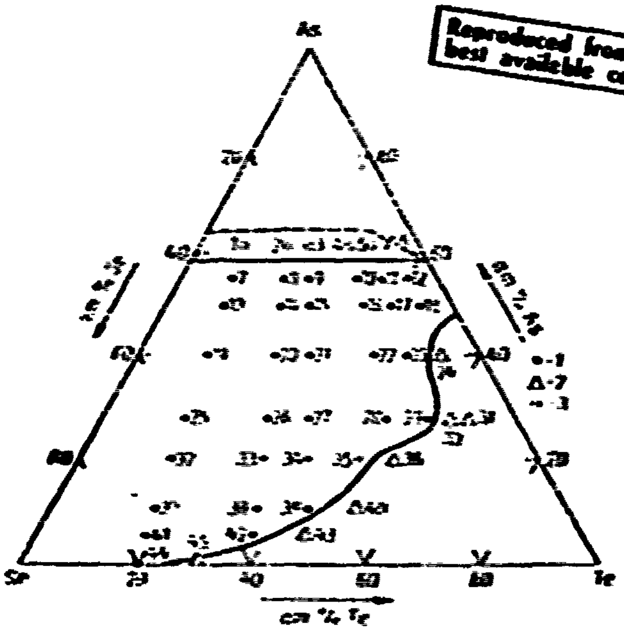

Fig. 1. Glass formation region in the system As-Se-Te. 1 - glass; 2 - glass-crystal; 3 - glass with nonuniform composition.

The compositions of the vitreous and glass-crystalline alloys are plotted in the concentration triangle in Fig. 1 and the region of glass formation in the system As–Se–Te is marked. From Fig. 1 it is clear that replacement of selenium by tellurium facilitates crystallization of the alloys. However, this tendency toward crystallization in the three-component system As–Se–Te is substantially more weakly expressed than in the binary system As–Te. This is indicated by the large glass-formation region in the As–Se–Te system. Up to 58 at. % tellurium and up to 60 at. % arsenic can be introduced into the composition of the vitreous alloys. As in the As–Se–S system, the glass formation region in the As–Se–Te system is displaced in the concentration triangle toward the side with predominating contents of selenium.

The maximum capacity for glass formation with tellurium is found in alloys with commensurate contents of arsenic and selenium (from $AsSe_{0.8}$ to AsSe). In those selenides which contain 20 at. % or less arsenic the ability to form glass with tellurium is noticeably reduced, while up to 20 at. % tellurium can be introduced into the composition of the elementary vitreous selenium; however, a further increase in the tellurium content leads to the formation of crystalline solid solution. The greatest ability to form glass with tellurium in alloys with commensurate contents of arsenic and selenium indicates that selenium is not the only glass-former in this system. The appearance of more complex structural units in the melt also favors glass formation.

In alloys of the composition $AsX_{0.6}$, 33 at. % selenium (out of 37.5 at. %) can be substituted by tellurium. During the synthesis of alloys with the composition $AsX_{0.6}$ the formation of a small encrustation containing crystalline arsenic is observed on the inner surface of the ampule. Thus the actual composition of the obtained vitreous alloys differs from the composition of of the initial charge. Vitreous alloys of indeterminant composition are singled out by a broken line in the region of glass formation (Fig. 1).

In agreement with literature data, along the As_2Se_3–As_2Te_3 ($AsX_{1.5}$) section 52 at. % of the selenium (out of 60 at. %) is substituted by tellurium. The increased crystallization capacity of the alloys along this section as compared with the $AsX_{1.0}$ and $AsX_{2.5}$ sections is apparently connected with the fact that As_2Se_3 and As_2Te_3 are individual compounds.

Tellurium and the arsenic telluride As_2Te_3 are the basic crystalline phases which can be singled out in glass-crystal and polycrystalline alloys. In the glass-crystalline alloy No. 6, enriched with arsenic, crystalline arsenic is separated. In alloy No. 43, which has a dominant content of chalcogens, it is apparently their solid solutions which are separated.

Fig. 2. Nature of the change in density of alloys as a function of the arsenic content. a – $AsSe_x$; b – $As(Se_{0.8}Te_{0.2})_x$; c – $As(Se_{0.6}Te_{0.4})_x$; d – $As(Se_{0.5}Te_{0.5})_x$; e – $As(Se_{0.2}Te_{0.8})_x$; f – $As(Se_{0.2}Te_{0.8})_x$.

Designation: г/см^3 = g/cm^3.

The density of the glasses was measured with a hydrostatic balance; microhardness was measured on the PMT-3. The density of the obtained vitreous alloys is increased linearly with substitution of selenium by tellurium. Crystallization of the alloys is accompanied by a sharp nonlinear increase in density. In the binary system As–Se the density of the vitreous alloys varies unevenly. The maximum value of density in the As–Se system was obtained for the stoichiometric compound As_2Se_3 (line a on Fig. 2) [7]. As selenium is substituted by tellurium in the vitreous alloys the nature of the change in their density as a function of arsenic content becomes ever smoother, virtually linear (lines b→f, Fig. 2); there is a sharp deviation from linearity for alloys which are partially crystallized.

The microhardness of the glasses in the system As–Se–Te varies within the limits 80–170 kg/mm^2. When selenium is substituted by tellurium in the vitreous alloys of the composition $AsX_{1.5}$, $AsX_{2.5}$, and AsX_4 the microhardness remains virtually unchanged. The virtual invariability of microhardness during substitution of selenium by tellurium over the section As_2Se_3–As_2Te_3 was indicated in work [5]. In vitreous alloys enriched both with arsenic ($AsX_{0.8}$, AsX) and chalcogen (AsX_9, AsX_{20}) the microhardness is increased noticeably as selenium is substituted by tellurium. The nature of the change in microhardness as a function of arsenic content in vitreous alloys shows virtually no differences from the change in density.

Conclusion

1. The region of glass formation was determined in the system As–Se–Te. It was shown that up to 58 at. % tellurium and 60 at. % arsenic can be introduced into the composition of the vitreous alloys.

2. The nature of the dependence of density and microhardness of the obtained vitreous alloys on the ratio and content of their components was established.

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