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PHASE EQUILIBRIA IN THE Ti–Nb–Ge SYSTEM AT 1170 K

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Summary

Physico-chemical analysis techniques, including studies of microstructure, X-ray phase analysis, electron microprobe, high-temperature differential thermal analysis and measurements of hardness, microhardness and specific electrical resistance, are applied to study the interaction between the components in the Ti–Nb–Ge system. The phase diagram for the Ti–Ge system has been refined. The compound Ti_5Ge_3 melts congruently at 2250 K. The germanides Ti_6Ge_5 and $TiGe_2$ are formed by peritectic reactions at 1920 and 1345 K, respectively. An isothermal section of the Ti–Nb–Ge phase diagram corresponding to 1170 K is constructed and homogeneity regions for ternary niobium and titanium germanide solid solutions are reported. No ternary compounds occur in the system. A polythermal phase diagram section along the quasi-binary $Ti_5Ge_3nNb_5Ge_3$ section is given. The mechanical and electrical properties of a number of alloys are described.

1. Introduction

The purpose of this work was to study phase equilibria in the Ti–Nb–Ge system at 1170 K and some physical and chemical properties of a number of alloys involved.

The interactions between the components in the Ti–Nb and Nb–Ge binary systems have been studied in detail in refs. 1 - 5. The Ti–Ge system has mainly been studied on the titanium side [6 - 8]. The Ti–Nb–Ge phase diagram in the region 0 - 50 mass% Ge at 970 and 1270 K has been studied by Heller [7].

2. Experimental details

Samples studied were alloys prepared using polycrystalline germanium of semiconductor purity (99.99%), vacuum-fusion niobium (99.9%) and titanium from titanium iodide (99.9%). Sample compositions are given in Fig. 1. The alloys were melted in an arc furnace with a non-consumable

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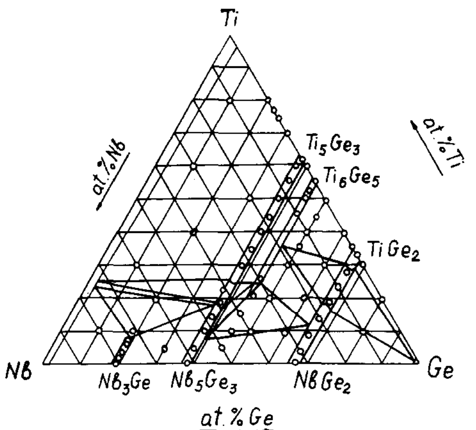

Fig. 1. Compositions of alloys studied and isothermal section of the Ti–Nb–Ge phase diagram at 1170 K.

tungsten electrode in an argon atmosphere. Fused samples were homogenized by annealing and then quenched from 1170 K in ice-cold water.

The isothermal section of the Ti–Nb–Ge phase diagram was determined using the following physico-chemical analysis techniques: microstructural studies, X-ray phase analysis, electron microprobe, high-temperature differential thermal analysis, hardness and microhardness tests and specific resistance measurements at room temperature. The microstructures of the alloys were revealed by etching the specimens with nitric and hydrofluoric acids. X-ray phase analyses were obtained on an FR-552 focusing monochromator using Cu $K\alpha_1$ and Cu $K\alpha_{av}$ lines and germanium as the internal reference. The observed reflections were identified by comparing the patterns with the ASTM catalogue. A "Camebax" micro-analyser was employed to perform local X-ray spectral analyses of samples using titanium $K\alpha$, germanium $K\alpha$ and niobium $L\alpha$ lines. The accuracy of the measurement was 2.5 to 3 relative per cent. High-temperature differential thermal analysis involved repeated heating of samples at a constant heating rate of $80°\ min^{-1}$. Tungsten–tungsten/rhenium (20 at.%) thermocouples were used to register the temperature and were calibrated against aluminium, copper, platinum, palladium and iron as reference substances. Microhardness and hardness were tested by the indentation technique using a diamond square pyramid under loads of 0.98 and 49 N, respectively. Six or more indentation marks were made for each sample. Specific resistance measurements were taken with the help of a four-probe microhead [9].

3. Results and discussion

The phase diagram for the Ti–Ge binary system shown in Fig. 2 was determined using the differential thermal analysis technique. Germanium

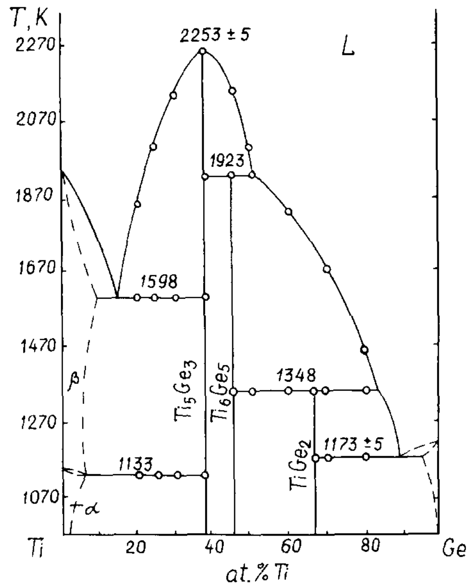

Fig. 2. Phase diagram of the Ti–Ge system.

was found to decrease the titanium polymorphic transformation temperature from 1145 to 1133 K. In the region of 0 to 5 at.% Ge the diagram was drawn using earlier data [6, 7]. A peritectoid reaction β-Ti + $Ti_5Ge_3 \rightleftarrows$ -Ti occurs at 1133 K. The germanide Ti_5Ge_3 and a solid solution of β-Ti form a eutectic at 1598 K and 15 at.% Ge. The compound Ti_5Ge_3 melts congruently, with an open maximum at 2253 K. The system involves two peritectic equilibria: L + $Ti_5Ge_3 \rightleftarrows Ti_6Ge_5$ (1923 K) and L + $Ti_6Ge_5 \rightleftarrows TiGe_2$ (1348 K). A eutectic reaction L $\rightleftarrows TiGe_2$ + Ge occurs at 1173 K and 88 - 90 at.% Ge. The solubility of titanium in germanium is only small. Thus compounds formed in the Ti–Ge system include Ti_5Ge_3, Ti_6Ge_5 and $TiGe_2$; the compounds Ti_3Ge and TiGe were not detected. The X-ray phase and electron microprobe analyses data (Table 1) are also in agreement with the occurrence of the compound Ti_6Ge_5 mentioned in ref. 8. The 1170 K isothermal section of the Ti–Nb–Ge phase diagram is shown in Fig. 1.

Homogeneity regions of ternary solid solutions based on binary compounds occurring in the Ti–Nb–Ge system were found to extend over 10 at.% Ti for Nb_3Ge, 15 - 18 at.% Ti for Nb_5Ge_3, 20 at.% Ti for $NbGe_2$, 37.5 at.% Nb for Ti_5Ge_3, 30 at.% Nb for Ti_6Ge_5 and 2 - 3 at.% Nb for $TiGe_2$.

The data obtained by electron probe analysis have enabled us to refine the lines of phase equilibria for the isothermal section. Precision measurements of lattice parameters have been performed for samples corresponding to the homogeneity regions of ternary solid solutions of binary compounds. The calculation results on the ternary solid solution based on Nb_3Ge are listed in Table 2, those for alloys in the $TiGe_2$–$NbGe_2$ section in Table 3 and those for Ti_5Ge_3–Nb_5Ge_3 alloys in Table 4 and Fig. 3.

TABLE 1

Results of electron microprobe analysis of Ti–Nb–Ge alloys

Alloy composition (at.%)			*Number of phases*	*Phase composition* (at.%)			*Phase*
Ti	*Nb*	*Ge*		*Ti*	*Nb*	*Ge*	
25.0	45.0	30.0	2	25.3	37.9	36.8	Ti_5Ge_3
				25.2	72.6	2.2	(β-Ti + Nb)
20.0	60.0	20.0	2	13.4	67.5	19.1	Nb_3Ge
				22.1	76.2	1.7	(β-Ti + Nb)
10.0	71.0	19.0	1	12.2	67.9	19.9	Nb_3Ge
10.0	30.0	60.0	2	11.0	22.0	67.0	$NbGe_2$
				6.2	55.5	38.3	Nb_5Ge_3
30.0	20.0	50.0	2	33.1	22.1	44.8	Ti_6Ge_5
				16.9	16.6	66.5	$NbGe_2$
20.0	30.0	50.0	2	21.3	34.9	43.8	Ti_6Ge_5
				16.2	16.7	67.1	$NbGe_2$
18.3	15.0	66.7	2	3.9	28.7	67.4	$TiGe_2$
				18.6	13.2	68.2	$NbGe_2$
42.0	—	58.0	2	53.7	—	46.3	Ti_6Ge_5
				34.0	—	66.0	$TiGe_2$
50.0	—	50.0	2	33.7	—	66.3	$TiGe_2$
				54.0	—	46.0	Ti_6Ge_5
55.5	—	44.5	1	55.0	—	45.0	Ti_6Ge_5

TABLE 2

Physico-chemical analyses data on alloys in the region of ternary Nb_3Ge solid solutions (19 at.% Ge)

Composition (at.%)		*Lattice parameters* (nm)	*Specific electrical resistance* (Ω m)	*Microhardness* (MPa)	*Hardness* (MPa)
Ti	*Nb*				
—	81.0	0.5172(1)	64 ± 5	9100 ± 100	8500 ± 100
2.5	78.5	0.5166(1)	82 ± 5	9800 ± 100	8900 ± 100
5.0	76.0	0.5265(1)	79 ± 5	9500 ± 100	8200 ± 100
7.5	73.5	0.5163(1)	69 ± 5	8800 ± 100	7000 ± 200
10.0	71.0	0.5161(2)	120 ± 5	8800 ± 200	5600 ± 300

Alloys of the Ti_5Ge_3–Nb_5Ge_3 section were also studied by differential thermal analysis. The polythermal section shown in Fig. 4 indicates a eutectic nature of interactions between Ti_5Ge_3 ($T_m = 2253 \pm 5$ K) and Nb_5Ge_3 ($T_m = 2433$ K). The non-variant equilibrium is observed at 2083 K. The Ti_5Ge_3–Nb_5Ge_3 polythermal section of the Ti–Nb–Ge phase diagram is quasi-binary.

The mechanical properties (hardness and microhardness) and specific resistance have been studied for a number of Ti–Nb–Ge alloys at room temperature. The microhardness and specific resistance values are listed in Tables 2, 3 and 4. The compound Nb_5Ge_3 and its ternary solid solutions are

TABLE 3

Physico-chemical analyses data on $TiGe_2$–$NbGe_2$ alloys (66.6 at.% Ge)

Composition (at.%)		*Lattice parameters* (nm)		*Specific electrical resistance* (Ω m)	*Microhardness* (MPa)	*Hardness* (MPa)
Ti	*Nb*	*a*	*c*			
33.3	—	0.8588(8)	0.8862(6)	210 ± 20	3000 ± 100	2700 ± 100
		b = 0.5032(3)				
28.3	5.0	—	—	150 ± 20	3300 ± 100	2000 ± 200
23.3	10.0	0.4939(2)	0.6781(2)	145 ± 20	5400 ± 200	3800 ± 300
					3400 ± 100	
18.3	15.0	0.4938(3)	0.6782(5)	110 ± 20	5300 ± 200	4500 ± 200
13.3	20.0	0.4949(1)	0.6785(4)	95 ± 20	5600 ± 100	4900 ± 200
8.3	25.0	0.4957(1)	0.6791(4)	80 ± 10	6300 ± 200	5300 ± 300
3.3	30.0	0.4963(1)	0.6791(2)	110 ± 10	7200 ± 100	6600 ± 200
—	33.3	0.4977(2)	0.6809(3)	80 ± 10	8400 ± 100	7800 ± 100

TABLE 4

Physico-chemical analyses data on Ti_5Ge_3–Nb_5Ge_3 alloys (37.5 at.% Ge)

Composition (at.%)		*Lattice parameters* (nm)		*Specific electrical resistance* (Ω m)	*Microhardness* (MPa)	*Hardness* (MPa)
Nb	*Ti*	*a*	*c*			
62.5	—	1.0163(1)	0.5140(1)	190 ± 30	10400 ± 200	9500 ± 100
57.5	5.0	1.0160(2)	0.5126(2)	260 ± 50	11600 ± 100	9900 ± 100
52.5	10.0	1.0150(4)	0.5117(3)	190 ± 40	10700 ± 100	9200 ± 100
47.5	15.0	1.0144(2)	0.5111(2)	160 ± 30	8900 ± 100	7300 ± 200
42.5	20.0	1.0143(2)	0.5109(2)	190 ± 30	8400 ± 100	6400 ± 200
		0.7642(5)	0.5265(5)		5900 ± 100	
37.5	25.0	—	—	380 ± 30	8300 ± 100	6100 ± 200
		0.7646(2)	0.5264(5)		6000 ± 100	
32.5	30.0	0.7633(3)	0.5258(5)	360 ± 30	7800 ± 100	7000 ± 100
27.5	35.0	0.7624(2)	0.5255(3)	330 ± 30	9800 ± 100	7600 ± 200
25.0	37.5	0.7625(2)	0.5252(3)	360 ± 20	11100 ± 100	8300 ± 200
22.5	40.0	0.7608(2)	0.5246(2)	350 ± 20	11500 ± 100	8600 ± 200
17.5	45.0	0.7605(1)	0.5244(2)	330 ± 30	11900 ± 100	8900 ± 100
12.5	50.0	0.7589(2)	0.5237(3)	300 ± 20	11300 ± 100	8800 ± 100
7.5	55.0	0.7585(2)	0.5234(3)	270 ± 40	11000 ± 100	8300 ± 200
2.5	60.0	0.7568(1)	0.5230(2)	210 ± 30	10100 ± 100	7300 ± 100
—	62.5	0.7563(2)	0.5228(2)	240 ± 40	9500 ± 100	6600 ± 100

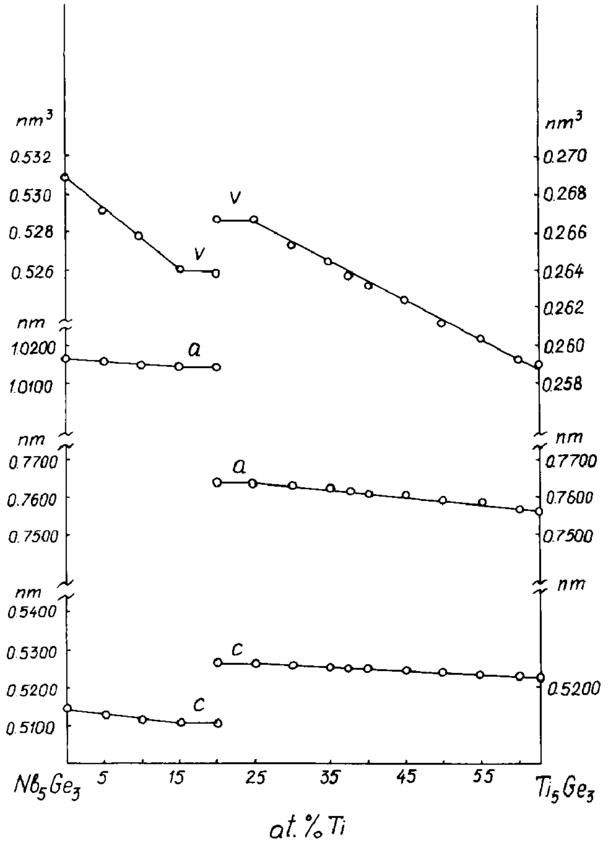

Fig. 3. The dependence of crystal lattice parameters on alloy compositions for the Ti_5Ge_3–Nb_5Ge_3 section.

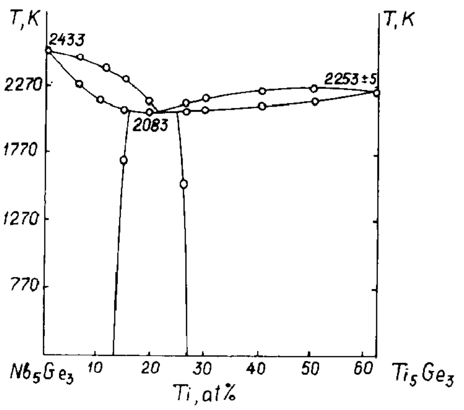

Fig. 4. Polythermal Ti_5Ge_3–Nb_5Ge_3 section of the phase diagram.

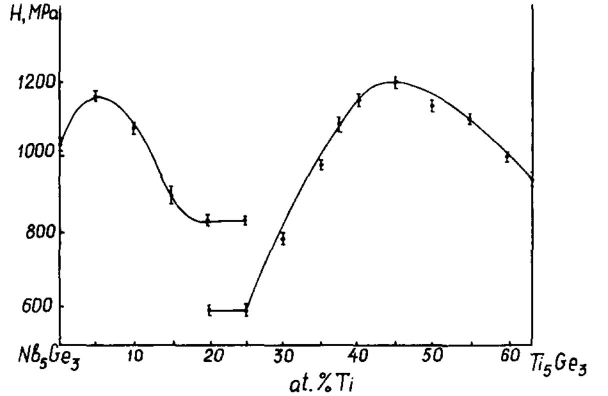

Fig. 5. Microhardness as a function of composition for Ti_5Ge_3–Nb_5Ge_3 alloys.

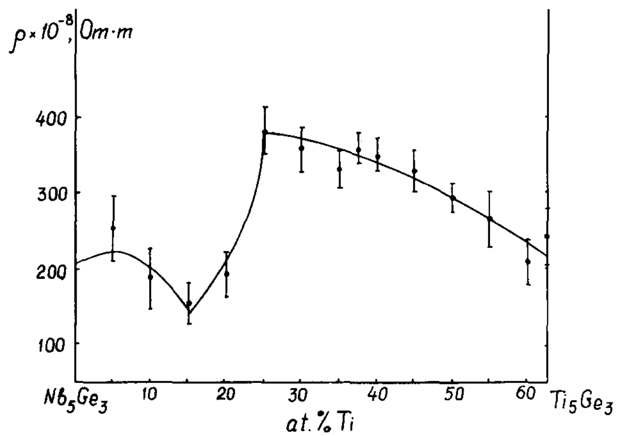

Fig. 6. Specific resistance as a function of composition for Ti_5Ge_3–Nb_5Ge_3 alloys.

characterized by high microhardness values. Niobium admixtures increase the microhardness of the Ti_5Ge_3-based alloys. The concentration dependence of microhardness for Ti_5Ge_3–Nb_5Ge_3 alloys is given in Fig. 5. Inflection points occur at phase region boundaries; in the two-phase region each phase is characterized by a constant microhardness value, while doping Nb_3Ge with titanium causes an increase in microhardness. Ti–Nb binary alloys show reduced microhardness values which increase with the addition of germanium.

Shown in Fig. 6 is the specific resistance *vs.* composition dependence for Ti_5Ge_3–Nb_5Ge_3 alloys. When the third component concentration is increased, the specific resistance of Ti_5Ge_3-based alloys increases and that of Nb_5Ge_3 solid solutions decreases. Within the homogeneity regions of compounds $NbGe_2$ and Nb_3Ge, the values of specific resistance vary insignificantly. Addition of niobium, however, enhances the resistance of the alloys in the composition region of the $Ti_{6-x}Nb_xGe_5$ solid solutions.

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