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On the System Ni – S – Te

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The ternary system Ni–S–Te has been examined by X-ray diffraction and metallographic methods and a phase diagram at 600°C is presented. At this temperature about 60 % of the sulfur can be replaced by tellurium in the *fcc* phase $Ni_{3\pm x}S_2$. In the phases $Ni_{3+x}Te_2$ with tetragonal structure, and $NiTe_{0.77}$ with orthorhombic structure about 13 % of the tellurium can be replaced by sulfur. On replacement of tellurium by sulfur in $NiTe_{0.77}$ the lattice constants change continuously and the structure transforms to hexagonal symmetry.

In the phase $NiTe_{1.09}$–$NiTe_2$ with the NiAs–$Cd(OH)_2$ type structure only a small amount of sulfur can be substituted for tellurium. On the other hand tellurium appears insoluble in the NiS (NiAs-structure) and NiS_2 (pyrite structure) phases at 600°C.

Examinations at various temperatures have been performed on alloys containing about 60 at. % nickel. A complete substitution of tellurium for sulfur is possible at higher temperatures in the *fcc* structure.

Lattice constants for some of the phases are presented.

In the *nickel-sulfur* system at 600°C there exists a phase in the range between 37 and 44 at. % sulfur ($Ni_{3\pm x}S_2$) with face-centered cubic structure.[1] The lattice constant increases with increasing nickel content. The hexagonal NiAs-type phase exists between 50.0 and 51.5 at. % sulfur.[2] The nickel disulfide, NiS_2, is of the pyrite structure type.

In addition to the phases mentioned above some low-temperature phases exist: Ni_3S_2 with rhombohedral structure which transforms into the *fcc* high-temperature phase at 555°C,[3] $Ni_{5.87}S_5$[4] with orthorhombic structure [5] between 560°C and 400°C,[3] NiS with rhombohedral structure (millerite-type) below 400°C, and Ni_3S_4 which has a spinel-like structure below 300°C.

In the *nickel-tellurium* system there exists a phase with homogeneity range of 40 to 41 at. % tellurium. On quenching samples in this region the symmetry changes to monoclinic or orthorhombic.[6] High temperature X-ray investigations have shown that the structure is tetragonal (rickardite-type) above 250°C.[7] At 850°C the structure is of the *fcc*-type.[6] A phase with composition $NiTe_{0.77}$ has an orthorhombic structure.[6] At 450°C the homogeneity range with NiAs-$Cd(OH)_2$ structure extends from $NiTe_{1.09}$ to $NiTe_2$.[6]

In the liquid state *sulfur* and *tellurium* are miscible in all proportions.

EXPERIMENTAL

The *nickel* used in this investigation was prepared from "NiO low in Co and Fe" from the British Drug Houses. The oxide was reduced with dried oxygen-free hydrogen at 600°C, and then annealed at 1000°C. Spectrographically pure sulfur and tellurium (99.999 %) were purchased from Johnson, Matthey & Co., and Koch-Light Laboratories, respectively.

The alloys were prepared by fusing calculated quantities of the elements in evacuated silica ampoules, and annealing them for one day at 600°C before quenching in water. Samples rich in sulfur or tellurium were made by adding the calculated amounts of these elements to finely ground samples richer in nickel. Annealing for several days was required to obtain equilibrium in such samples.

The alloys were examined by metallographic techniques and by X-ray powder methods using Guinier type focusing cameras ($CuK\alpha_1$-radiation), and by a 19 cm Unicam high temperature camera.

RESULTS AND DISCUSSION

The compositions of the phases existing in the Ni – S – Te system at 600°C are presented in Table 1. The phases are denoted with capital letters.

Table 1. Phases present in the system Ni – S – Te at 600°C.

Phase		Composition range in at. %			Structure
		Ni	S	Te	
Ni		100	0	0	*fcc*-Type
A	$Ni_{3\pm x}(S,Te)_2$	55 – 62.5	17 – 44	0 – 26	*fcc*-Type
B	$Ni_{3+x}(S,Te)_2$	59 – 60	0 – 5	35 – 41	Tetragonal
C		54 – 55.6	0 – 8	38.5 – 44.4	Orthorhombic-hexagonal
D	$Ni_{2-x}(S,Te)_2$	33 – 48	0 – 3	52.2 – 66.6	NiAs-Cd(OH)$_2$-type
E	$Ni_{2-x}S_2$	49.5 – 50	50 – 50.5	0	NiAs-type
F	NiS_2	33.3	66.6	0	Pyrite-type
G	S/Te	0	0 – 100	0 – 100	Liquid (+ vapor)

A survey of the alloys prepared and the phases present at 600°C are given in Table 2 and Fig. 1. In the figure, one-, two-, and three-phase samples are shown as filled, half-filled, and open circles, respectively.

Phase region A. The determination of the boundaries of this phase was based mainly on high temperature X-ray investigations because the phase is not quenchable over the entire range. On quenching from 600°C the structure of the sulfur-rich samples transforms from *fcc* to rhombohedral, whereas in the tellurium-rich area the transformation results in a tetragonal structure (phase B). The *fcc* structure is completely retained by quenching samples No. 11, 12, 13, 23, 25, and 27 from 600°C. In earlier investigations of the systems Ni – S – Se,[4] Ni – Se – Te,[8] and Fe – Ni – Se,[9] no such quenchability of this phase was observed.

Table 2. Compositions of the samples in at. % and phases present at 600°C.

No.	Ni	S	Te	Phases	No.	Ni	S	Te	Phases	No.	Ni	S	Te	Phases
1	65.0	10.0	25.0	Ni+A+B	27	57.0	19.0	24.0	A	53	48.0	1.0	51.0	C+D
2	65.0	17.5	17.5	Ni+A	28	56.5	2.5	41.0	A+B	54	48.0	50.0	2.0	D+E
3	65.0	25.0	10.0	Ni+A	29	56.0	22.0	22.0	B+D	55	47.0	1.0	52.0	C+D
4	65.0	30.0	5.0	Ni+A	30	55.8	5.2	39.0	A+B+C	56	47.0	6.0	47.0	A+D
5	62.0	19.0	19.0	Ni+A	31	55.8	7.3	36.9	A+C	57	46.0	27.0	27.0	A+D+E
6	60.0	0.0	40.0	B	32	55.5	30.0	14.5	A	58	45.0	40.0	15.0	D+E
7	60.0	5.0	35.0	B	33	56.4	0.0	43.6	C	59	44.0	28.0	28.0	D+E
8	60.0	10.0	30.0	A+B	34	55.0	12.5	32.5	A+C	60[a]	42.0	2.0	56.0	D+E
9	60.0	15.0	25.0	A+B	35	54.5	3.0	42.5	C	61[a]	42.0	3.0	55.0	D+E
10	60.0	17.5	22.5	A	36	54.5	5.5	40.0	C	62	42.0	29.0	29.0	D+E
11	60.0	20.0	20.0	A	37	54.5	10.5	35.0	A+C	63[a]	41.0	4.0	55.0	D+E
12	60.0	25.0	15.0	A	38	54.5	14.5	31.0	A+C+D	64	40.8	29.6	29.6	D+E+F
13	60.0	30.0	10.0	A	39	54.5	30.0	15.5	A+D	65	37.4	15.6	47.0	D+E
14	60.0	31.2	8.8	A	40	54.5	35.5	10.0	A+D+E	66	36.0	5.0	59.0	D+E
15	60.0	32.5	7.5	A	41	54.5	40.0	5.5	A+E	67	35.4	17.6	47.0	D+E+F
16	60.0	33.7	6.3	A	42	53.5	5.6	40.9	D+E	68	35.0	7.8	57.2	D+E
17	60.0	35.0	5.0	A	43	53.0	13.0	34.0	A+D	69	33.3	2.6	64.1	D
18	60.0	37.5	2.5	A	44	53.0	30.0	17.0	A+D	70	33.3	5.0	61.7	D+F
19	60.0	40.0	0.0	A	45	52.5	7.5	40.0	A+C+D	71	33.3	10.0	56.7	D+F
20	59.0	5.6	35.4	A+B+C	46	52.5	40.0	7.5	A+D+E	72	33.3	33.3	33.3	D+F
21	58.5	2.5	39.0	B+C	47	52.0	24.0	24.0	A+D	73	33.3	65.2	1.5	D+F
22	58.2	18.0	23.8	A	48	50.0	5.0	45.0	A+C+D	74	22.5	47.5	30.0	D+F+G
23	58.0	21.0	21.0	A	49	50.0	25.0	25.0	A+D	75	22.5	54.6	22.9	F+G
24	57.9	12.6	29.5	A+B+C	50	50.0	49.0	1.0	A+D+E	76	21.2	60.0	18.8	F+G
25	57.4	21.3	21.3	A	51	50.0	50.0	0.0	E	77	20.0	20.0	60.0	D+F+G
26	57.0	16.0	27.0	A+C	52	49.0	25.5	25.5	A+D+E	78	18.7	5.6	75.7	D+G
										79	18.0	9.0	73.0	D+F+G

[a] The observations are probably not representative for equilibrium conditions at 600°C (see text).

Table 3. Lattice constants of the high temperature *fcc* phase $Ni_{3\pm x}(S,Te)_2$, (Phase A).

Sample No.	Composition	Lattice constant, Å	Examination conditions
19	$Ni_{.60}S_{.40}$	5.230	X-ray 580°C
15	$Ni_{.600}S_{.325}Te_{.075}$	5.303	X-ray at 470°C
13	$Ni_{.60}S_{.30}Te_{.10}$	5.262	Quenched from 600°C
12	$Ni_{.60}S_{.25}Te_{.15}$	5.322	Quenched from 600°C
11	$Ni_{.60}S_{.20}Te_{.20}$	5.374	Quenched from 600°C
10	$Ni_{.600}S_{.175}Te_{.225}$	5.480	X-ray at 600°C
8	$Ni_{.60}S_{.10}Te_{.30}$	5.55	X-ray at 700°C
6	$Ni_{.60}Te_{.40}$	5.76	X-ray at 900°C
29	$Ni_{.56}S_{.22}Te_{.22}$	5.287	Quenched from 600°C
5	$Ni_{.62}S_{.19}Te_{.19}$	5.419	

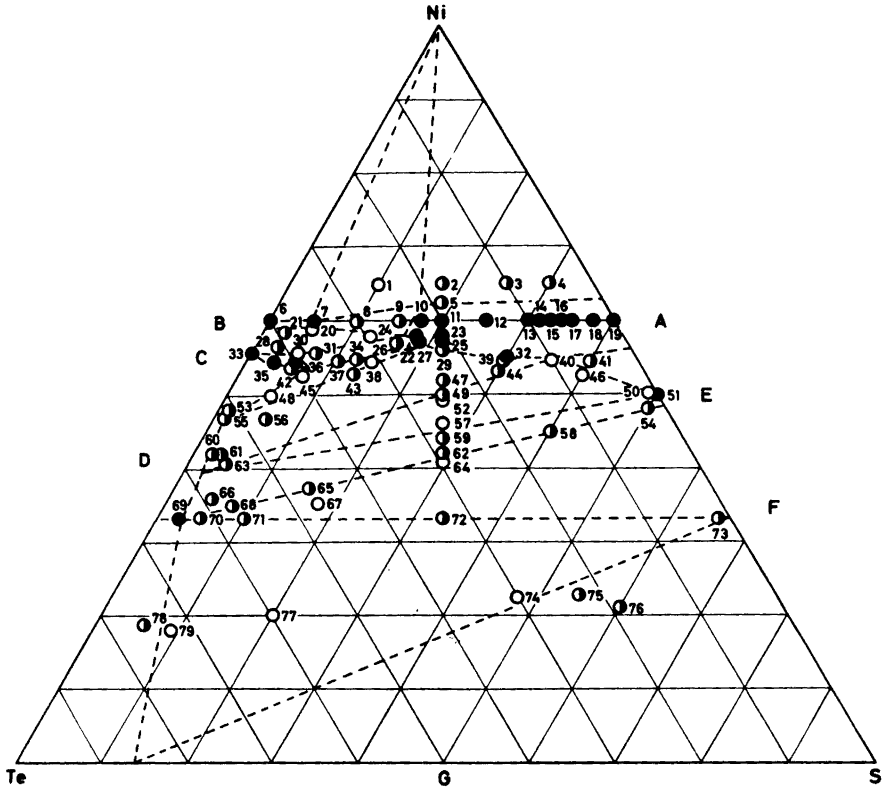

Fig. 1. Ternary plot of compositions in at. %. Filled, half-filled and open circles represent the presence of one, two and three phases, respectively. The phase boundaries are shown as broken lines. The phases are denoted with capital letters.

In the cubic phase a complete mutual exchange of sulfur and tellurium atoms is possible at elevated temperature, and also an appreciable variation of the nickel/chalcogen ratio is observed. Lattice constants of this phase, measured at different temperatures, are listed in Table 3.

As one would expect, the increasing substitution of tellurium for sulfur leads to a successive increase in the lattice dimension. Since no superstructure lines appear in the X-ray photographs, sulfur and tellurium atoms are probably randomly distributed over the chalcogen positions.

Liné and Huber [1] suggest a crystal structure for the *fcc* high temperature phase of Ni_3S_2 in which four sulfur atoms occupy a fourfold position, whereas six nickel atoms are distributed on two fourfold positions, leaving a number of vacant metal positions. This structure type is in accordance with the observed increase of the lattice constants with increasing nickel/chalcogen ratio (*cf.* Table 3, samples 29, 11, 5).

High temperature X-ray studies of phase A gave an approximate value of the temperature at which it begins to decompose on cooling. Results for some

Table 4. Decomposition temperature of phase A on cooling, and phases present just below the decomposition temperature.

Sample	Composition	Decomp. temp. of phase A, °C	Phases just below decomp. temp.
19	$Ni_{.600}S_{.400}$	555 [a]	Rb [b]
18	$Ni_{.600}S_{.375}Te_{.025}$	500	A+Rb
15	$Ni_{.600}S_{.325}Te_{.075}$	400	B+Rb
13	$Ni_{.600}S_{.300}Te_{.100}$	400	B+Rb
12	$Ni_{.600}S_{.250}Te_{.150}$	425	A+B
10	$Ni_{.600}S_{.175}Te_{.225}$	600	A+B
8	$Ni_{.600}S_{.100}Te_{.300}$	700	A+B
6	$Ni_{.600}T_{.400}$	850	A+B

[a] Determined by Rosenqvist.[3]
[b] Rb: Ni_3S_2 rhombohedral low temperature modification.

samples containing 60 at. % nickel are listed in Table 4. Above these temperatures the *fcc* structure is assumed to exist up to the melting temperature which is just below 800°C for Ni_3S_2[3] and approximately 1025°C for Ni_3Te_2.

At a nickel content of 60 at. % the minimum transition temperature of phase A is about 400°C. Below this temperature equilibrium exists between phase B and the rhombohedral Ni_3S_2. The solubility of tellurium in the rhombohedral phase seems to be negligible, since even sample 18 with only 2.5 at. % tellurium contains two phases, both in the high temperature examinations and after cooling slowly. Nor was any difference observed between lattice constants of the rhombohedral phase in sample 18 and in stoichiometric Ni_3S_2. On the contrary, when the samples were quenched from 600°C the rhombohedral phase was present in samples containing up to 7.5 at. % tellurium, and moreover, an appreciable increase of the lattice constants was observed, *i.e.* from $a = 4.083$ Å, $\alpha = 89.46°$ for Ni_3S_2 to $a = 4.155$ Å, $\alpha = 90.0°$ for sample 15, $Ni_{.600}S_{.325}Te_{.075}$. This suggests that tellurium is dissolved in the rhombohedral phase Ni_3S_2 in the quenched samples. The structure is obviously metastable in this case.

The phase B. High temperature X-ray photographs of Ni_3Te_2 confirm that the structure changes from monoclinic to tetragonal (phase B) rickardite-type structure. The latter is stable up to at least 750°C. At 850°C the structure is of the *fcc*-type, whereas equilibrium exists between the phases A and B at 800°C. Sulfur can be substituted for tellurium in phase B and this solubility increases appreciably with decreasing temperature. At 60 at. % nickel the maximum solubility of sulfur is about 5 at. % at 600°C (sample 7), 10 at. % at 500°C (sample 8), according to X-ray high temperature investigations, and 15 at. % (sample 9) after slow cooling to room temperature. At nickel contents of less than 60 at. % still more sulfur can be substituted for tellurium in slowly cooled samples.

The lattice constants at 600°C of the tetragonal structure were measured for two samples:

No. 6, Ni_3Te_2: $a = 3.865$ Å, $c = 6.033$ Å;
No. 7, $Ni_{.60}S_{.05}Te_{.35}$: $a = 3.854$ Å, $c = 5.978$ Å.

On quenching of sample 7 the structure changes to orthorhombic symmetry with lattice constants $a = 3.772$ Å, $b = 3.793$ Å, and $c = 6.043$ Å.

The phase C. In the orthorhombic phase with composition approximately $NiTe_{0.77}$ partial substitution of sulfur for tellurium is possible. By this substitution the structure transforms to a hexagonal type, as is also the case when selenium is substituted for tellurium.[8] In the ternary region of phase C a certain variation of the nickel/chalcogen ratio is possible. The lattice constants measured on some quenched samples are given in Table 5.

Table 5. Lattice constants of phase C measured on samples quenched from 600°C.

Sample No.	Composition	Lattice constants			Structure
		a	*b*	*c*	
33	$Ni_{.564}Te_{.436}$	3.912	6.872	12.38	Orthorhombic
35	$Ni_{.545}S_{.030}Te_{.425}$	3.827	6.755	12.31	Orthorhombic
36	$Ni_{.545}S_{.055}Te_{.400}$	3.852		12.22	Hexagonal
37[a]	$Ni_{.545}S_{.105}Te_{.350}$	3.814		12.19	Hexagonal

[a] Two phase sample.

The phase D. In the binary nickel-tellurium system the phase region with NiAs-$Cd(OH)_2$ type structure has an extension from $NiTe_{1.09}$ to $NiTe_2$.[6] Only small amounts of sulfur can replace tellurium in this phase. In the nickel-rich part of the phase the maximum content of sulfur is about one at. % whereas in the tellurium-rich part about three at. % sulfur can be present.

The phases E and F. The phase region E with NiAs-type structure has a homogeneity range of 50 – 51.5 at. % sulfur.[2] No substitution of tellurium for sulfur was found in this phase. Nor could any solubility of tellurium be observed in the pyrite type phase NiS_2 (phase F).

The ternary phase diagram at 600°C. In the ternary phase diagram in Fig. 2 the extensions of the homogeneity ranges are shown, and tie lines indicate the equilibrium conditions in the two phase regions. The directions of the tie lines were largely determined by comparing the lattice dimensions of samples near the phase limits with those of the same phase in two- and three-phase samples. This method is rather sensitive when there is a considerable variation in the lattice constants along the phase limits. Such variations occur for the phases A and D in the present study.

It should be pointed out that there is a certain discrepancy between the phase diagram and the phases observed in quenched samples 60, 61, and 63. In these samples traces of phase E were observed, whereas investigations of the other samples in this region strongly indicate that an equilibrium exists between the phases A and D at 600°C. The traces of phase E are probably

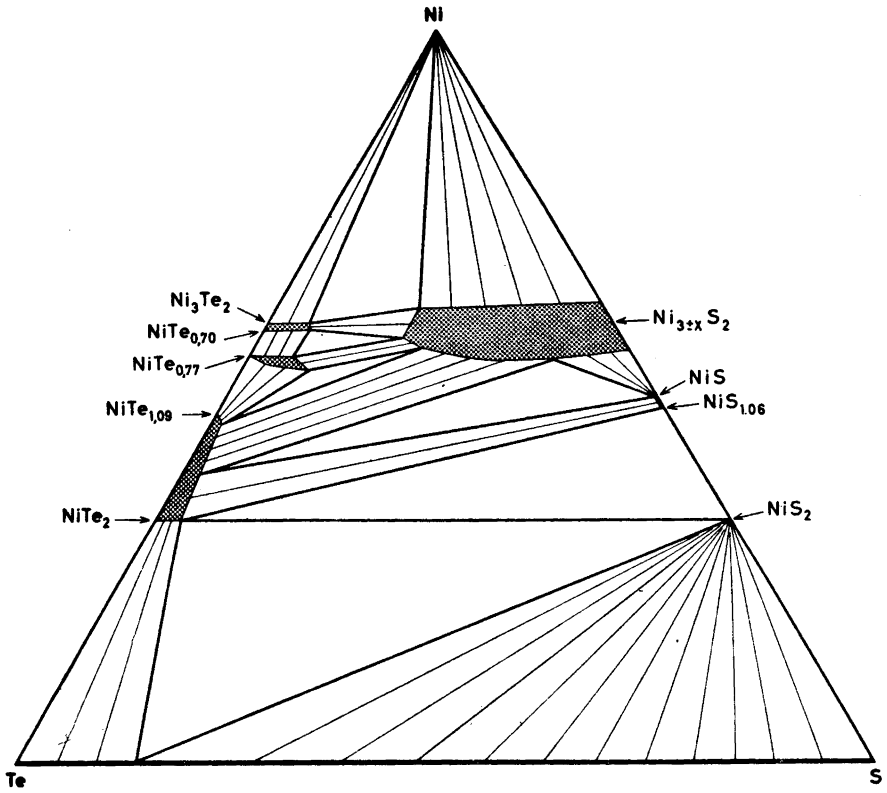

Fig. 2. Isothermal phase diagram at 600°C of the condensed system Ni–S–Te. Single-phase fields are shown as heavy lines or shaded fields, two-phase fields are indicated by tie lines and three-phase fields by open triangles.

formed during the quenching. By means of high temperature X-ray methods only phase D could be observed in these samples. This method is, however, less sensitive than the Guinier method, and it is reasonable to assume that the samples contain two phases at 600°C.

The equilibrium conditions at 600°C for the Ni–S–Te system presented in Fig. 2 concern the condensed state. The vapor pressure of the liquid S–Te phase at 600°C varies from 6 mmHg for pure tellurium to about 6 atm. for pure sulfur. The S/Te-ratio is therefore assumed to be greater in the vapor than in the liquid state. This introduces an error in the determination of the tie lines limiting the three-phase area between the phases D, F and the liquid G. This error is, however, assumed to be negligible because the liquid in the three-phase region is rich in tellurium and therefore the vapor pressure must be rather low. Moreover, the amount of each sample (about 1 g) was relatively large compared to the volume (about 1 cm^3) of the silica tubes in which the samples were annealed.

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