

Transition Metal—Chalcogen Systems, V.:

The Iron—Tellurium Phase Diagram

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With 3 Figures

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The iron—tellurium phase diagram was investigated by thermal, X-ray, and isopiestic measurements up to 1,100 °C. Tetragonal β ($\approx \text{FeTe}_{0.9}$) with a homogeneity range from 45.9 to 48.1 at% Te at 715 °C is stable from room temperature to 844 °C where it decomposes peritectoidally into Fe and rhombohedral high-temperature β' ($\approx \text{FeTe}_{0.9}$). β' decomposes at 914 °C peritectically into Fe and liquid, and at 800 °C by a eutectoid reaction into β and γ ($\approx \text{FeTe}_{1.2}$). γ exists between 809° ($\gamma \rightarrow \beta' + \delta$) and 636 °C ($\gamma \rightarrow \beta + \delta$). The monoclinically distorted NiAs-phase δ decomposes peritectically at 55.2 at% Te and 812 °C into β' and liquid and is stable down to the eutectoid $\delta \rightleftharpoons \beta + \delta'$ at 565 ± 15 °C and 58.8 at% Te. δ is separated from hexagonal NiAs-type δ' by a narrow two-phase region. δ' has a maximum range of homogeneity at 650 °C from 59.2 to 65.1 at% Te and exists between the eutectoid $\delta' \rightleftharpoons \beta + \varepsilon$ at 519 °C and the peritectic $\delta + L \rightleftharpoons \delta'$ at 766 °C. Orthorhombic ε ($\approx \text{FeTe}_{2.0}$) is stable from room temperature to the peritectic $\delta' + L = \varepsilon$ at 649 °C. ε and Te form a degenerate eutectic at 446 °C.

In a continuation of the investigation of transition metal-chalcogen phase diagrams¹⁻⁴ the iron—tellurium system was studied.

The preparation of various iron—tellurium alloys has been described by Moser and Ertl⁵, Brukl⁶, Tammann and Schaarwächter⁷, Oftedal⁸, and Tengnér⁹. A careful X-ray investigation of the entire system was carried out by Grønvald, Haraldsen, and Vihovde¹⁰. These authors found a low solid solubility of Fe in Te and of Te in Fe and reported the existence of four compounds: the tetragonal β -phase, closely related to the PbO (B 10) structure, with a narrow homogeneity range close to 47.3 at% Te, the γ -phase of unknown structure, stable above 750 °C at about 52.5 at% Te, the δ -phase, stable above 488 °C from 58.4 to 60.0 at% Te, with NiAs (B 8) structure having a monoclinic deformation at the iron rich side of the

homogeneity range, and the orthorhombic ε -phase with marcasite (C 18) structure between 66.1 and 67.7 at% Te. (Throughout the present publication the lettering of *Gronvold* et al.¹⁰ for the various phases has been

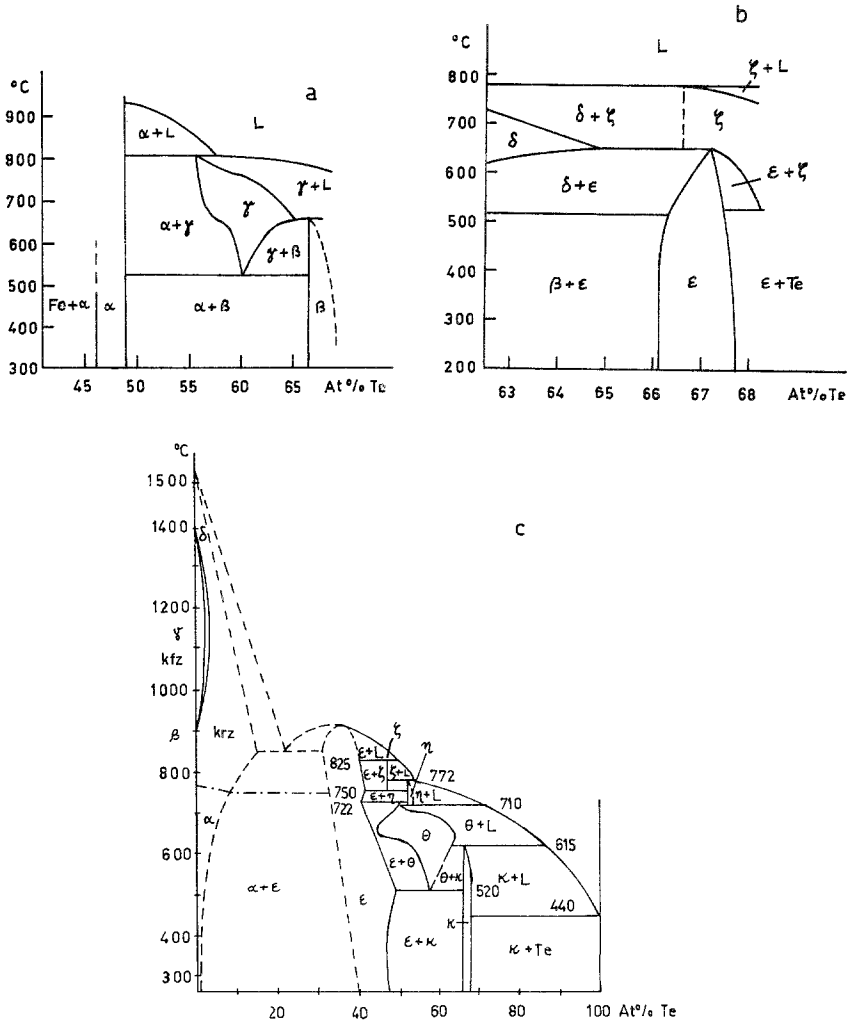


Fig. 1. Iron—Tellurium phase diagram (different lettering). (a) Partial phase diagram of *Chiba*¹¹; (b) Partial phase diagram of *Llewellyn* and *Smith*¹²; (c) Phase diagram of *Abrikosov* et al.¹³

adopted.) Thermal, X-ray, and magnetic measurements by *Chiba*¹¹ confirmed the existence of the three peritectically formed phases β (48.7 at% Te), δ (56 to 65 at% Te) which decomposes eutectoidally at 520°C and 60 at% Te into β and ε , and ε (66.7 at% Te). *Llewellyn* and *Smith*¹² reported the

existence of an additional hexagonal ζ -phase at 66.6 at% Te above 500 °C with an undefined homogeneity range on the Te-rich side. The ϵ -phase was studied by *Dudkin* and *Vaidanich*¹³ and by *Geiderikh*, *Gerasimov*, and *Nikolskaya*¹⁴. The latter authors found by *emf* measurements the peritectic decomposition of ϵ at 640 °C and the eutectoid decomposition of δ at 513 °C. *Leciejewicz*¹⁵ confirmed the structure of the β -phase by neutron diffraction. *Brostigen* and *Kjekshus*¹⁶ determined the phase width of the ϵ -phase at 450 °C as between 66.6 ± 0.2 and 67.4 ± 0.2 at% Te. The solid solubility of Fe in Te was found to be about 0.01 at% Te¹⁷.

Based on thermal, X-ray, and metallographic studies *Abrikosov*, *Dyuldina*, and *Zhdanova*¹⁸ presented a complete phase diagram which is shown in Fig. 1 c together with the partial diagrams of *Chiba*¹¹ (Fig. 1 a) and *Llewellyn* and *Smith*¹² (Fig. 1 b). As can be seen *Abrikosov* et al.¹⁸ found a much wider homogeneity range for the δ -phase, extending from about 45 to 65 at% Te, and an additional high temperature phase at 47–48 at% Te. Recently, *Røst* and *Webjørnsen*¹⁹ reported the existence of a rhombohedral high temperature phase with a homogeneity range from 44.5 to 48.2 at% Te at 845 °C which transforms eutectoidally at 805 °C into the β - and δ -phase.

A comparison of the three diagrams in Fig. 1 reveals major discrepancies. It was therefore decided to reinvestigate the iron—tellurium system using thermal and X-ray measurements. The results were combined with data obtained from isopiestic measurements²⁰ to construct the complete iron—tellurium phase diagram.

Experimental Procedure

The materials were iron in form of thin sheet (Ferrovac E, Vacuum Metals Corp., Syracuse, USA), powder (Thomas A. Edison, Inc., USA), and wire (0.2 mm diameter, Allied Chemical and Dye Corp., USA), all with a stated purity of 99.9%, and tellurium lumps (ASARCO, New York, USA) with a purity of 99.99, and 99.999% (semiconductor-grade), resp. The iron powder was used for *DTA* and X-ray samples with an Fe content > 50 at%, and the iron wire and the semiconductor-grade tellurium for the isopiestic experiments. Possible surface contamination of tellurium was removed by melting in a closed quartz capsule³ in purified Ar (100 torr) and filtering through pyrex wool by increasing the pressure. The quartz reaction vessels were cleaned with acid (5% HF, 30% HNO₃, rest dist. H₂O), rinsed with distilled water, dried, and degassed. Samples for *DTA* and X-ray measurements (≈ 1.5 g) were weighed on a semi-micro balance to within ± 0.05 mg, those for thermal analyses (≈ 80 g) on an analytical balance to within ± 0.1 mg. The loaded quartz capsules were evacuated to 10^{-3} – 10^{-4} torr, flushed several times with Ti-gettered Ar, and finally sealed in vacuum. Depending on the composition of the alloy the samples were heated for about 15 hrs at 900 to 1,100 °C, then annealed one to three weeks at 600 to 800 °C, and finally furnace cooled. Samples for X-ray measurements were powdered, sealed under vacuum in small quartz ampoules, heat treated at the desired temperature, and then quenched in ice water.

Thermal analyses were carried out with a previously described semi-automatic apparatus³. The quartz containers (≈ 70 mm long, 28 mm O. D.) had in the center a thermocouple tube (4 mm diameter) which was sealed at the lower end and reached close to the bottom of the vessel. A loosely fitting quartz tube protected the thermocouple tube from breaking when the sample solidified. This protection tube did not influence the temperature of the thermal effects. The Pt/Pt-10% Rh thermocouple was calibrated at the freezing points of high purity (99.99%) Cd, Zn, Sb, and Cu²¹.

For the *DTA*-measurements a fully automated apparatus was used¹, employing similar thin walled quartz ampoules for both sample container and neutral reference body. Temperature and temperature difference were measured with Pt/Pt-10% Rh thermocouples, calibrated at the freezing points of Cd, Zn, Sb, and Au.

X-ray measurements were made with a Kristalloflex IV (Siemens, Karlsruhe) using a CoK_α -radiation with Fe filter. Powder patterns were obtained with 57.29 mm diameter Debye-Scherrer cameras, single crystal patterns with specially adapted Debye-Scherrer cameras.

In principle the composition of the samples was calculated from the weight. However, the Fe content of many alloys was also determined analytically. The weighed samples (± 0.05 mg) were dissolved in aqua regia, and excess HNO_3 was removed by repeatedly adding HCl and evaporating. The solution was then diluted with H_2O to a well defined volume. To a measured part of the volume standard acetate buffer solution (pH = 4.62) was added to give a pH = 1.9. The solution was then slowly titrated with 0.05 M *EDTA* with sulfosalicylic acid as indicator²². Analytical values and those calculated from the weight agreed within $\pm 0.3\%$.

Experimental Results and Discussion

The results of the thermal analyses (*TA*) are listed in Tab. 1, the thermal effects obtained by *DTA* in Tab. 2, and the phase boundaries deduced from isopiestic measurements in Tab. 3. These data together with the results obtained from X-ray measurements given in Tab. 4 were used to construct the phase diagram shown in Fig. 2 with the data points in the central part of the diagram omitted for the sake of clarity. The more complicated phase relationships between 40 and 70 at% Te together with the actual experimental points are shown in the partial diagram in Fig. 3.

The solid solubility of Te in Fe was not accurately determined but it appears to be small. X-ray measurements on an isopiestic sample equilibrated at 830 °C with an apparent Te content of about 1.5 at% gave a lattice parameter $a = 2.866$ Å, identical with that of pure α -Fe. This is in sharp contrast to a solid solubility of 18 at% Te at 800 °C reported by *Abrikosov et al.*¹⁸. With increasing Te content the lines due to α -Fe could be observed up to 45 at% Te, accompanied by the lines of another phase which could be unequivocally indexed as belonging to the β -phase. The β -phase has a maximum range of homogeneity at

Table 1. *Thermal Effects by TA*

Composition at% Te	Liquidus	Solidus	Invariant arrests °C				Other effects
39.55	—	—	914;	843;	—	—	—
41.95	—	—	914;	844;	—	—	—
45.90	—	—	915;	842;	—	—	—
46.95	—	—	914;	—	—	—	808–830
48.35	—	—	915;	—	800;	—	808
50.00	901	—	811;	805;	798;	—	516;
50.95	891	—	811;	809;	800;	{ 636 h 635 c	519;
51.65	888	—	812;	810;	800;	{ 638 h 635 c	519;
52.95	862	—	813;	809;	800;	{ 638 h 635 c	519;
53.95	840	—	811;	808;	800;	{ 637 h 633 c	518;
54.90	817	—	812;	809;	—	{ 637 h 633 c	519;
55.35	812	—	—	—	—	{ 638 h 634 c	519;
56.55	809	799	—	—	—	{ 636 h 632 c	519;
58.00	808	781	—	—	—	{ 632 h 618 c	519;
59.05	802	—	—	—	765;	—	519;
59.95	797	759	—	—	766;	—	517;
60.20	795	760	—	—	768;	—	520;
61.25	788	747	—	—	766;	—	518;
62.45	779	721	—	—	766;	—	518;
64.50	765	—	—	—	—	—	520;
65.40	757	—	—	—	649;	—	520;
67.95	739	—	—	—	649;	447;	—
69.95	725	—	—	—	648;	445;	—
75.05	674	—	—	—	649;	447;	—
76.80	665	—	—	—	649;	446;	—
79.95	650	—	—	—	—	448;	—
81.50	637	—	—	—	—	447;	—

750 °C of about 2.5 at% with the Te-rich boundary at 48.5 at% Te. This phase boundary could be quite well delineated above 650 °C using isopiestic data, but the position of the Fe-rich boundary is less certain. One isopiestic data point at 830 °C gave a value of 46.0 at% Te, and other, more indirect isopiestic evidence suggested that the Fe-rich boundary changes but little down to about 700 °C (45.9 at% Te). The composition of the β -phase is thus in very good agreement with the homogeneity range 46.1–48.7 at% Te found by *Chiba*¹¹ and in general

Table 2. *Thermal Effects by DTA*

Composition at% Te	Liquidus	Invariant arrests °C		Other effects
36.7	—	912;	847;	—
37.5	—	912;	849;	—
39.9	—	913;	848;	—
44.1	—	913;	846;	—
45.8	—	912;	844;	—
46.0	—	915;	—	—
46.5	—	915;	—	820–840
47.0	—	914;	—	802–828
47.5	—	914;	—	801–823
47.6	—	915;	—	800–820
65.8	754	649;	517;	—
65.9	755	652;	521;	—
72.0	704	648;	—	446;
84.4	617	—	—	446;
89.8	593	—	—	445;
94.9	551	—	—	447;

Table 3. *Phase Boundaries from Isopiestic Experiments*

Composition at% Te	Temperature of the tieline °C	Composition at% Te
1.5 (α -Fe/ α -Fe + β)	833	46.0 (α -Fe + β / β)
46.5 (β / β + β')	825	47.4 (β + β' / β')
46.2 (β / β + β')	841	46.6 (β + β' / β')
48.9 (β' / β' + γ)	801	55.2 (γ + δ / δ)
47.9 (β / β + γ)	682	57.0 (γ + δ / δ)
48.3 (β / β + γ)	707	56.3 (γ + δ / δ)
48.5 (β / β + γ)	747	55.5 (γ + δ / δ)
48.5 (β / β + γ)	754	55.4 (γ + δ / δ)
58.8 (δ / δ + δ')	650	59.2 (δ + δ' / δ')
58.8 (δ / δ + δ')	669	59.2 (δ + δ' / δ')
58.8 (δ / δ + δ')	685	59.2 (δ + δ' / δ')
58.8 (δ / δ + δ')	690	59.2 (δ + δ' / δ')
58.8 (δ / δ + δ')	715	59.3 (δ + δ' / δ')
58.8 (δ / δ + δ')	725	59.3 (δ + δ' / δ')
58.8 (δ / δ + δ')	732	59.4 (δ + δ' / δ')
58.8 (δ / δ + δ')	742	59.4 (δ + δ' / δ')
56.3 (δ / δ + L)	804	58.2 (δ + L / L)
55.7 (δ / δ + L)	809	56.7 (δ + L / L)
55.4 (δ / δ + L)	811	56.2 (δ + L / L)
65.1 (δ' / δ' + ϵ)	634	67.4 (δ' + ϵ / ϵ)

accord with the approximate value of 47.3 at% Te given by *Grønvold* et al.¹⁰, but differs from the value reported by *Røst* and *Webjørnsen*¹⁹ who placed the stability range between 42.8 and 44.5 at% Te at 845 °C. X-ray measurements on a single crystal formed in a sample with 46.5 at% Te after four weeks at 800 °C, confirmed for β the tetragonal

Table 4. *X-Ray Phase Studies in the Iron—Tellurium System*

Composition at% Te	Annealing Temp., °C	Phases	Composition at% Te	Annealing Temp., °C	Phases
0.5	886	α -Fe	56.0	742	$\delta + \gamma$
1.5	858	α -Fe	56.4	595	$\delta + \beta$
37.5	900	α -Fe + β	56.6	750	$\delta + \gamma$
44.1	900	α -Fe + β	57.4	595	$\delta + \beta$
45.8	715	β	57.8	715	δ
46.4	900	β	57.9	540	$\delta' + \beta$
46.5	800	β	57.9	580	$\delta + \beta$
47.5	800	β	57.9	715	δ
47.7	900	β	58.9	595	$\delta + \delta'$
47.9	900	β	58.9	720	$\delta + \delta'$
48.0	800	β	58.7	540	δ'
48.0	860	β	59.7	715	δ'
48.1	715	β	59.8	715	δ'
48.5	836	β	60.0	715	δ'
51.7	620	$\beta + \delta$	60.4	595	δ'
51.7	645	$\beta + \gamma$	60.6	715	δ'
51.7	715	$\beta + \gamma$	61.8	715	δ'
51.7	775	$\gamma + \beta$	62.6	715	δ'
51.7	793	γ^*	63.0	683	$\delta' + \varepsilon$
51.7	808	γ^*	63.3	647	$\delta' + \varepsilon$
53.1	715	γ^*	64.0	640	$\varepsilon + \delta'$
53.1	793	γ^*	64.7	640	$\varepsilon + (\delta')$
53.1	808	γ^*	67.6	637	ε
55.7	750	$\gamma + \delta$	—	—	—

* Some β might be present, since two weak diffraction lines of γ coincide with two strong lines of β .

symmetry with the space group P4/nmm. The lattice parameters $a = 3.82$ and $c = 6.28$ Å are in very good agreement with the results obtained by *Grønvold* et al.¹⁰ on a sample at the Fe-rich boundary, i.e. $a = 3.823_0$ and $c = 6.276_7$ Å. At 844 °C (845 °C¹⁹) the β -phase with 46.1 at% Te decomposes most probably by a peritectoid reaction into Fe and the high temperature β' -phase. However, it is also possible that the nonvariant reaction at 844 °C is a eutectoid and that there is a congruent transformation point between β and β' with a maximum

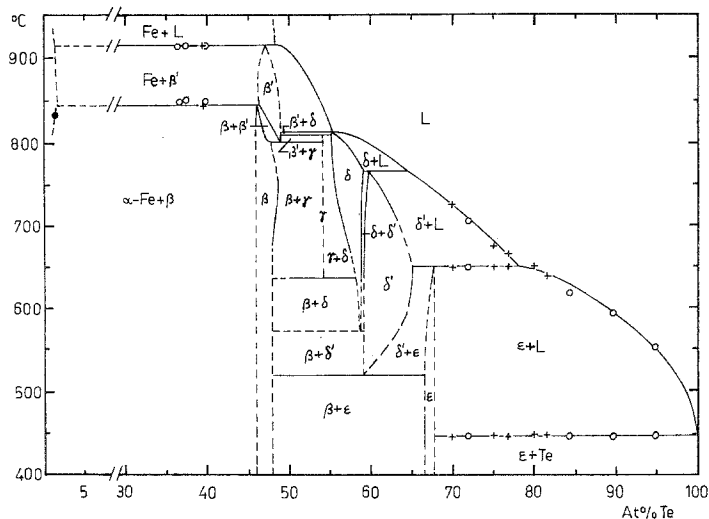


Fig. 2. Complete $T-x$ diagram of the iron—tellurium system. + = T/A experimental points, o = DTA experimental points; ● = phase boundaries from isopiestic experiments

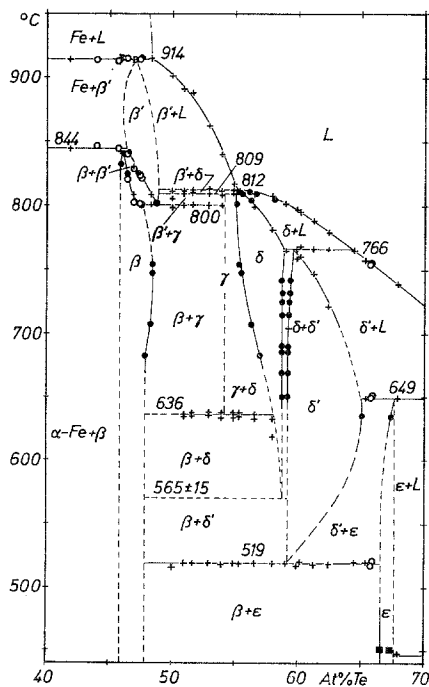


Fig. 3. Partial $T-x$ iron—tellurium phase diagram. + = T/A experimental points, o = DTA experimental points; ● = phase boundaries from isopiestic experiments; ■ = phase boundaries by Brostigen and Kjekshus¹⁶

temperature close to 848 °C and 46 at% Te. The β' -phase with 47 at% Te decomposes peritectically at 914 °C (920 °C¹⁹) into Fe and liquid with 48.35 at% Te. According to *Abrikosov* et al.¹⁸ the phase with the highest Fe content has a congruent melting point of 910 °C. Between 914 °C and about 1100 °C no further thermal effects could be observed in the alloys indicating that the liquidus curve Fe + L/L must rise very steeply. The isopiestic experiments²⁰ point to a noticeable range of homogeneity for the β' -phase which at 870 °C extends from less than 46.1 to about 47.9 at% Te. At 845 °C *Røst* and *Webjørnsen*¹⁹ reported for β' a homogeneity range from 44.5 to 48.2 at% Te. The two-phase region between β' and β is clearly delineated by thermal effects between 800 and 844 °C in alloys with 46.5, 46.95, 47.0, 47.5, 47.6, and 48.35 at% Te, and by isopiestic equilibrium curves²⁰. However, attempts to identify the β' -phase by X-ray measurements at room temperature failed. Samples annealed at 900 °C and quenched showed the same X-ray patterns (β) as those heat treated at 715 °C, leading to the conclusion that β' transforms so rapidly on cooling that it cannot be retained by quenching. *Røst* and *Webjørnsen*¹⁹ were able to identify β' by high temperature X-ray measurements and to determine its structure as rhombohedral. At 800 °C (805 °C¹⁹) β' with 48.9 at% Te decomposes by a eutectoid reaction into β and γ . The thermal effect due to the eutectoid can be observed in all alloys from 48.35 to 53.95 at% Te but not up to the phase boundary of the δ -phase. Furthermore, X-ray patterns of samples with 51.66 and 53.10 at% Te, heat treated at 807 °C and quenched, and of an alloy with 51.66 at% Te, heat treated at 840 °C and quenched, showed diffraction lines mostly due to the γ -phase. From all this evidence we concluded that β' decomposes into β and γ , and not into β and δ , as reported by *Røst* and *Webjørnsen*¹⁹.

An alloy with 53.1 at% Te, heat treated at 715 °C, gave an X-ray pattern which could be indexed as the γ -phase, reported by *Grønvald* et al.¹⁰. The γ -phase has a composition of about 54.2 at% Te, possibly with a narrow homogeneity range between 54 and 55 at% Te, and it is stable between 636 and 809 °C. *Grønvald* et al.¹⁰ placed the γ -phase at about 52.4 at% Te and around 750 ± 30 °C. At 809 °C γ decomposes into β' and δ , and at 636 °C into β and δ . Both thermal effects are weak; the arrest at 809 °C could be observed in alloys from 50.00 to 54.90 at% Te, the arrest at 636 °C from 50.95 to 58.00 at% Te. The latter arrest showed some thermal lag: on heating (h) it was about 40 °C higher than on cooling (c). Between 640 and 790 °C two-phase regions containing γ could be clearly identified by X-ray measurements: between 51 and 52 at% Te $\beta + \gamma$, between 55 and 56 at% Te $\gamma + \delta$. With increasing annealing temperature the diffraction lines of the γ -phase

become noticeably stronger which might indicate a broadening of the homogeneity range between 720 and 800 °C. An alloy with 51.7 at% Te, annealed at 620 °C, showed only diffraction lines of the β - and δ -phase.

In alloys with more than 50 at% Te another invariant arrest at 812 °C could be observed. It became stronger with increasing Te concentration and is due to the peritectic decomposition of δ into β' and liquid. By extrapolating the $\beta' + L/L$ liquidus and the peritectic line the peritectic composition was found to be 55.2 at% Te. By a similar extrapolation of the $\gamma + \delta/\delta$ and $\delta/\delta + L$ phase boundaries we obtained the composition of δ at the peritectic temperature as 55.1 at% Te, which would indicate that the NiAs-phase in the Fe-Te system does not have a congruent melting point. Chiba¹¹ found the peritectic temperature at 805 °C and the composition of δ at about 56 at% Te. Isopiestic equilibrium curves between 650 and 750 °C indicated that the monoclinically distorted NiAs δ -phase is separated from the hexagonal NiAs δ' -phase by a small two-phase region which extends at 730 °C from 58.8 to 59.3 at% Te. X-ray photographs taken from an alloy with 58.9 at% Te, annealed at 720, 600, and 580 °C, showed both δ and δ' together. However, in an X-ray pattern of the same alloy, annealed at 550 °C, diffraction lines of δ were absent, and a sample with 57.9 at% Te, heat treated at 540 °C, contained β and δ' . It can therefore be assumed that the homogeneity range of δ becomes very narrow and that δ transforms at 58.8 at% Te and 565 ± 15 °C into β and δ' by a eutectoid reaction. The absence of a thermal arrest at the eutectoid can be explained by the similarity of δ and δ' and by the closeness in composition of the two phases at the eutectoid temperature. The δ' -phase (59.6 at% Te) undergoes a peritectic decomposition at 766 °C into δ (59.05 at% Te) and liquid (62.45 at% Te). At 519 °C δ' decomposes by a eutectoid reaction into β and ϵ . Indirect isopiestic evidence places the eutectoid composition between 58 and 60 at% Te. The eutectoid reaction at 519 °C undercools considerably (up to 30 °C) and a reliable temperature could only be obtained from heating curves. This also explains the lower value of 488 ± 2 °C found by Grönvold et al.¹⁰ for the eutectoid. Other values reported for the eutectoid temperature and composition are: 520 °C, 60 at% Te¹¹; 513 °C, 57.5 at% Te¹⁴; 520 °C, 58 at% Te¹⁸.

The NiAs-phase has a maximum range of homogeneity between 55.1 at% Te at 812 °C to 65.1 at% Te at 649 °C but monoclinically distorted δ is definitely separated from hexagonal δ' by a narrow two-phase region. It was, however, not possible to determine the phase boundaries by X-ray measurements since Fe-rich δ and Te-rich δ' could not be retained by quenching. Alloys annealed in the one-phase field and quenched with a Te-content less than ≈ 57 at% Te contained

$\gamma + \delta$, with a Te-content more than ≈ 63 at% Te $\delta' + \epsilon$. This explains the rather narrow range of homogeneity from 58.4 to 60.0 at% Te obtained by *Grønvald* et al.¹⁰ from X-ray measurements. These authors also observed that the structure showed a monoclinic distortion which disappeared with increasing Te-content and became hexagonal at 60 at% Te without a two-phase region between them. *Chiba*¹¹ determined the phase boundaries of the NiAs field by heat capacity measurements and found a homogeneity range from 56 (805 °C) to 65 at% Te (660 °C), in good agreement with our results. The maximum stability

Table 5. *Lattice Parameters of the NiAs-Phase in the Iron—Tellurium System*

Composition at% Te	Lattice Parameters		
	a , Å	c , Å	c/a
59.7	3.827	5.642	1.474 ₃
59.8	3.823	5.643	1.476 ₁
60.0	3.818	5.651	1.480 ₁
60.4	3.813	5.653	1.482 ₆
60.6	3.808	5.660	1.486 ₃
61.8	3.780	5.666	1.498 ₉
62.6	3.775	5.673	1.502 ₈

range of 45 to 63 at% Te at 650 °C given by *Abrikosov* et al.¹⁸ is obviously too large.

X-ray photographs of samples with 57.8 and 57.9 at% Te, annealed at 715 °C, showed pure δ with the following lattice parameters: $a = 3.86$, $b = 6.66$, $c = 5.64$ Å; $\beta = 90.2^\circ$. The only reflections found were those with $h + k = 2n$. The lattice parameters of an alloy with 58.4 at% Te as reported by *Grønvald* et al.¹⁰ are in good agreement: $a = 3.846$, $b = 6.661$, $c = 5.641$, $\beta = 90.20$. Between 59.7 and 62.6 at% Te X-ray photographs of alloys annealed at 715 °C showed pure δ' . The concentration dependence of the lattice parameters and of the c/a ratio in this range is given in Table 5. With increasing Te content the a -parameter decreases, and c and c/a increase, similar to the behavior in the Co—Te system⁴. The lattice parameters, reported by *Grønvald* et al.¹⁰ for an alloy with 60 at% Te ($a = 3.816_2$ Å, $c = 5.654_8$ Å, $c/a = 1.482$), agree well with our results. The data of *Abrikosov* et al.¹⁸ indicate hexagonal symmetry for all alloys from 45 to 63 at% Te and differ considerably from our values.

Alloys with compositions between 65.4 and 76.8 at% Te show an arrest at 649 °C, corresponding to the peritectic decomposition of ϵ into δ' and liquid. Other values for the peritectic temperature reported

in the literature are 660 °C¹¹, 640 °C¹⁴, and 615 °C¹⁸. The homogeneity range of ϵ could not be well established but at 500 °C it seems to extend from 66.6 to 67.8 at% Te, in agreement with the range 66.6–67.4 at% Te at 450 °C found by *Brostigen* and *Kjekshus*¹⁶. An isopiestic point at 67.4 at% Te and 634 °C suggests that at the peritectic temperature ϵ contains an excess of Te. The X-ray photograph of an alloy with 67.55 at% Te, annealed at 633 °C, showed only lines of orthorhombic ϵ with the lattice parameters $a = 6.26$, $b = 5.25$, and $c = 3.87$ Å. The values are in good agreement with the more accurately determined lattice parameters of stoichiometric ϵ of *Brostigen* and *Kjekshus*¹⁶. ϵ and solid Te participate in a eutectic reaction at 446 °C with a liquid phase containing practically only tellurium.

The present work confirms the phases β , γ , δ , and ϵ found by *Grønvold* et al.¹⁰, and the high-temperature phase β' , observed by *Røst* and *Webjørnsen*¹⁹. The additional high temperature phases reported by *Llewellyn* and *Smith*¹² and *Abrikosov* et al.¹⁸ could not be found. The phase diagram has a general similarity to the partial diagram of *Chiba*¹¹ but it differs in many details from the diagram proposed by *Abrikosov* et al.¹⁸.

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References

- ¹ *K. L. Komarek* and *K. Wessely*, *Mh. Chem.* **103**, 896 (1972).
- ² *K. L. Komarek* and *K. Wessely*, *ibid.* **103**, 923 (1972).
- ³ *K. O. Klepp* and *K. L. Komarek*, *ibid.* **103**, 934 (1972).
- ⁴ *K. O. Klepp* and *K. L. Komarek*, *ibid.* **104**, 105 (1973).
- ⁵ *L. Moser* and *K. Ertl*, *Z. anorg. allg. Chem.* **118**, 271 (1921).
- ⁶ *A. Brukl*, *Mh. Chem.* **45**, 471 (1924).
- ⁷ *G. Tammann* and *K. Schaarwächter*, *Z. anorg. allg. Chem.* **167**, 401 (1927).
- ⁸ *I. Oftedal*, *Z. phys. Chem.* **132**, 208 (1928).
- ⁹ *S. Tengnér*, *Z. anorg. allg. Chem.* **239**, 126 (1938).
- ¹⁰ *F. Grønvold*, *H. Haraldsen*, and *J. Vihovde*, *Acta Chem. Scand.* **8**, 1927 (1954).
- ¹¹ *S. Chiba*, *J. Phys. Soc. Jap.* **10**, 837 (1955).
- ¹² *J. P. Llewellyn* and *T. Smith*, *Proc. Phys. Soc. [London]* **74**, 65 (1959).
- ¹³ *L. D. Dudkin* and *V. I. Vaidanich*, *Fiz. Tverd. Tela* **2**, 1526 (1960); *Soviet Phys.-Solid State (Engl. Transl.)* **2**, 1384 (1961).
- ¹⁴ *V. A. Geiderikh*, *Ya. I. Gerasimov*, and *A. V. Nikolskaya*, *Dokl. Akad. Nauk SSSR* **137**, 1399 (1961); *Proc. Acad. Sci. USSR. Chem. Sect. [Engl. Transl.]* **137**, 349 (1961).
- ¹⁵ *J. Leciejewicz*, *Acta Chem. Scand.* **17**, 2593 (1963).

- ¹⁶ G. Brostigen and A. Kjekshus, *Acta Chem. Scand.* **24**, 1925 (1970).
¹⁷ S. A. Abakarov, G. B. Bagdadyev, and P. Sh. Dazhayev, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **6**, 1169 (1970).
¹⁸ N. Kh. Abrikosov, K. A. Dyuldina, and V. V. Zhdanova, *Khalkogenidy* **2**, 98 (1970); *Chem. Abstr.* **75**, 91874a (1971).
¹⁹ E. Røst and S. Webjørnsen, *Acta Chem. Scand. A* **28**, 361 (1974).
²⁰ H. Ipser and K. L. Komarek, to be published.
²¹ W. F. Roeser and S. Lonberger, *Natl. Bur. Std. (U.S.), Circ. No. 590* (1956).
²² A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd ed. London: Longmans, Green and Co., 1966. p. 415.

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