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Transition Metal—Chalcogen Systems, VI: The Zirconium—Tellurium Phase Diagram

Hanna Sodeck, Helga Mikler, and **Kurt L. Komarek** *

Institute of Inorganic Chemistry, University of Vienna,
A-1090 Vienna, Austria

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In the binary Zr—Te system isopiestic, thermoanalytical, and X-ray studies were carried out. The results were combined with data from literature to construct a partial phase diagram. Tetragonal Zr_5Te_4 exists at 44.4 at % Te. Hexagonal ZrTe (WC structure) with a composition between 49 and 50 at % Te is found from 723 to 1,273 K. NiAs-type $Zr_{1-x}Te$ has a range of homogeneity above 1,273 K from 52.0 to 66.6 at % Te, and at 973 and 723 K from 57.0 to 66.6 at % Te. Within this range the NiAs-type structure transforms into the $Cd(OH)_2$-type structure. At 60 at % Te $Zr_{1-x}Te$ has a melting point of about 1,970 K. At 75 at % Te monoclinic $ZrTe_3$ is found which decomposes peritectically at 903 K. At 778 K orthorhombic $ZrTe_5$ transforms into liquid and $ZrTe_3$, and at 712 K $ZrTe_5$ forms a eutectic with Te.

(Keywords: Chalcogen phases; Isopiestic vapor pressure; Thermoanalysis; X-ray)

Übergangsmetall—Chalcogen-Systeme, 6. Mitt.: Das Zirkonium—Tellur-Phasendiagramm

Im binären Zr—Te-System wurden isopiestische, thermoanalytische und röntgenographische Untersuchungen durchgeführt. Die Resultate wurden mit Literaturdaten kombiniert und ein partielles Phasendiagramm aufgestellt. Tetragonales Zr_5Te_4 existiert bei 44.4 At % Te. Hexagonales ZrTe (WC-Struktur) mit einer Zusammensetzung zwischen 49 und 50 At % Te ist zwischen 723 und 1273 K beständig. $Zr_{1-x}Te$ mit NiAs-Struktur hat oberhalb 1273 K einen Homogenitätsbereich von 52.0 bis 66.6 At % Te, bei 973 und 723 K einen solchen von 57.0 bis 66.6 At % Te. Innerhalb dieses Bereiches geht die NiAs-Struktur in die $Cd(OH)_2$-Struktur über. $Zr_{1-x}Te$ mit einer Zusammensetzung von 60 At % Te hat einen Schmelzpunkt von etwa 1,970 K. Bei 75 At % K. wurde monoklines $ZrTe_3$ gefunden, welches bei 903 K peritektisch zerfällt. Bei 778 K reagiert orthorhombisches $ZrTe_5$ zu $ZrTe_3$ und Schmelze, bei 712 K bildet $ZrTe_5$ mit Te ein Eutektikum.

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Introduction

In a continuing series of studies of transition metal—chalcogen phase diagrams[1–5] the zirconium—tellurium system was investigated by X-ray diffraction, thermal analysis, and isopiestic vapor pressure measurements.

In a preliminary report *Hahn* and *Ness* [6] mentioned the existence of the phases $ZrTe_3$ (monoclinic), $ZrTe_2$ (hexagonal CdJ_2-structure), ZrTe (hexagonal NiAs-structure), Zr_4Te_3 (tetragonal) and Zr_3Te_2 (hexagonal WC-structure), and commented on the pyrophoric nature of alloys with less than 50 at % Te. *McTaggart* and *Wadsley*[7] prepared the compounds $ZrTe_3$, $ZrTe_2$, Zr_2Te_3, and ZrTe by direct synthesis or by stepwise thermal decomposition with structures in agreement with *Hahn* and *Ness*[6]. *Bear* and *McTaggart*[8] described the chemical, *McTaggart*[9] the electrical properties of these compounds[7]. In a more detailed publication[10] Zr_3Te_2 was assigned a range of homogeneity between 33.33 and 42.86 at % Te; between 44.44 and 68.75 at % Te another wide range of homogeneity was found which included the phases ZrTe (NiAs) and $ZrTe_2$ (CdJ_2). The *a*-axis was practically constant over the entire range but the *c*-axis showed a distinct maximum at 58.33 at % Te. Subsequent investigations[11,12] revealed that Zr_4Te_3 was actually ZrSiTe. *Brattås* and *Kjekshus*[13] prepared a new tetragonal compound, Zr_5Te_4, by arc-melting. They also found a hexagonal phase with WC-structure between 49 and 50 at % Te, obviously identical with the "Zr_3Te_2" compound of *Hahn* and *Ness*[6,10]. A careful determination of the lattice parameter of $ZrTe_3$[14] showed the compound to be stoichiometric. More recently *Furuseth et al.*[15] found that $ZrTe_3$ exists in two variants with a mirror image type relationship between them. Formation of these variants was explained by the growth kinetics from the gas phase. *Gleizes* and *Jeannin*[16] determined the range of homogeneity of the nonstoichiometric "$ZrTe_2$" phase, prepared at 800 °C, to be between 59.18 and 63.34 at % Te; they could not obtain stoichiometric $ZrTe_2$. Since the X-ray pattern of the alloy with 58.18 at % Te showed superstructure lines, the authors concluded that no continuous transition exists between the NiAs- and the CdJ_2-structure. The change in lattice parameter was explained by Zr atoms occupying Te vacancies. The break in the *c*-axis versus composition curve at 61.54 at % Te was supposed to coincide with the complete filling of the Te vacancies, and additional Zr atoms were to be inserted between the layers. *Jenkins*[17] calculated on the basis of theoretical and experimental relative intensities a structural model with Zr and Te vacancies for the concentration ranges 50 to 60 at % Te and 60 to 66.7 at % Te between 600 and 817 °C. The alloys were sensitive to air and exhibited in this temperature range a two-phase region between 41.2 and 56.6 at % Te, supposedly a mixture of hexagonal Zr_4Te_3 and a superstructure of ZrTe or $ZrTe_2$. The hexagonal phase $Zr_{1+t}Te_2$ [$Cd(OH)_2$ structure; $Zr_{1+t}Te_2 = Zr_{1-x}Te$] was synthesized by *Brattås* and *Kjekshus*[18] at 800 °C from the elements and its range of homogeneity determined to be 60.0 to 65.5 at % Te. Single crystals at the Te-rich phase boundary could be obtained by a chemical transport reaction. Additional diffraction lines at Te contents < 60.6 at % Te were interpreted as being due to a doubling of the c-axis or spiral dislocations formed during crystal growth. The orthorhombic compound $ZrTe_5$ was prepared at 450 °C from the elements by *Furuseth, Brattås, and Kjekshus*[19].

Judging by the more recent investigations[13, 14, 17, 18] there are five different compounds, Zr_5Te_4, ZrTe, $Zr_{1-x}Te$, $ZrTe_3$, and $ZrTe_5$, in the phase diagram. To further elucidate the phase relations in the system X-ray studies were carried out between 30 and 90 at % Te, phase boundaries were determined by isopiestic measurements, and some liquidus—and transition temperatures were obtained by thermoanalytical methods.

Experimental Procedure

Starting materials were semiconductor-grade Te lumps with 99.999 % Te (ASARCO, New York, U.S.A.), Zr powder with about 99.9 % Zr (Metallwerke Plansee, Reutte, Austria) which showed only diffraction lines of Zr, and 0.02 mm thin reactorgrade Zr foil (Wah Chang Corp., Oregon, U.S.A.). The ThO_2 crucibles were purchased from ZIRCOA Refractories (Solon, Ohio).

Preliminary experiments revealed that ThO_2 crucibles were best suited for the preparation of Zr—Te alloys. Zr foil, cleaned in acetone, wrapped in Mo foil and annealed, was put into MgO-, Al_2O_3-, ZrO_2-, and ThO_2-crucibles, resp. It was then sealed into evacuated quartz ampoules and heated about 24 h at 1,273 K. Foil kept in MgO-, Al_2O_3-, and ZrO_2-crucibles became brittle, in the ThO_2-crucible it remained ductile. Especially in isopiestic experiments the ThO_2 crucibles turned dark through and through at temperatures above 873 K but no reaction with the sample was observed. On quenching most ThO_2 crucible shattered to pieces.

Zr—Te alloys which were not used immediately had to be stored in argon atmosphere since on exposure to air the crystalline samples turned into X-ray amorphous powder. Samples between 30 and 71 at % Te were especially reactive; after a few weeks the X-ray pattern showed only rather weak lines, and after three months lines were completely absent. Coarse crystalline, Te-rich samples proved to be more stable. Isopiestic specimens between 53 and 66 at % Te were obtained as a very fine crystalline powder and decomposed rapidly. Only isopiestic specimens with about 75 at % Te could be used for X-ray work. Even when a Zr—Te alloy, prepared at some higher temperature, was exposed only shortly to air before annealing at some other temperature, its X-ray pattern would show only a few weak lines, and frequently lines of ZrO_2

could be observed. It was therefore necessary to prepare new samples for each measurement. The following procedure was used: The weighed components (1 to 1.5 g total weight) were filled into ThO_2-crucibles (10 mm high, 10 mm diameter, 1 mm wall thickness) which were placed into quartz capsules. After repeated evacuation and backfilling with argon the capsule was sealed under a vacuum of 10^{-2} Pa. It was then heated at 1,273 K for about 14 days in a resistance furnace, without opening annealed for another two to four weeks at the desired temperature, and finally quenched in ice water. The ampoules were opened in argon, the specimen passed through a sieve and stored in an argon-filled desiccator over silica gel. X-ray measurements were made with a Kristalloflex IV (Fa. Siemens, Karlsruhe, BRD) with a Cu K_α-radiation with Ni filter. The specimens were sealed under Ar in thin quartz capillaries, and powder patterns were obtained with 57.29 mm diameter Debye-Scherrer cameras.

Differential thermal analyses were carried out in a previously described apparatus[1]. The samples (about 3 g) and the neutral reference material (99.9% Cr) were sealed in evacuated quartz capsules. The optimal heating and cooling rates were about 3°/min. The Pt/Pt-10% Rh thermocouples were calibrated under the same exerimental conditions at the melting points of Cd, Zn, Sb, and Ag. Liquidus temperatures of Zr—Te alloys were determined in a furnace (Metallwerke Plansee, Reutte, Austria) consisting of a directly heated vertical tungsten tube which contained a tungsten boat with the sample placed on a support. The changes of the sample could be observed with a calibrated micropyrometer through the port hole of the W tube which was closed by a quartz window. During the experiment the furnace was kept under a slight positive Ar pressure. Since only coarse crystalline Zr—Te samples were available, melting point determinations proved to be difficult.

Isopiestic experiments were performed as previously described[20]. Because of the reactivity of Zr the samples were placed into ThO_2 crucibles to avoid direct contact with the quartz crucibles. After equilibration the Te-rich boundary of the NiAs- like structure $Zr_{1-x}Te$ and the composition of $ZrTe_3$ could be obtained from a plot of sample composition versus sample temperature. A detailed description and evaluation of the isopiestic experiments will be published later.

Results and Discussion

The delineation of the phase diagram at elevated temperatures on the Zr-rich side up to 70 at% Te proved to be difficult, since thermoanalytical methods did not produce useful results due to the reaction between the Zr metal and the quartz vessel. Also as mentioned above the Zr-rich isopiestic specimens were X-ray amorphous. The partial phase diagram shown in Fig. 1 is therefore based mainly on X-ray diffraction experiments with alloys prepared by direct synthesis from the elements and annealed at 1,273, 973, and 723 K, resp. The lattice constants of the pure elements were for Zr $a = 3.23_4$ Å, and $c = 5.11_4$ Å, and for Te $a = 4.45_6$ Å, and $c = 5.92_5$ Å. In addition to the pure components the five compounds Zr_5Te_4, ZrTe, $Zr_{1-x}Te$, $ZrTe_3$, and $ZrTe_5$ could be verified, but no other phases could be found.

Zr-rich samples quenched from 1,273 K contained up to about 40 at % Te a mixture of Zr and Zr_5Te_4, the phase richest in Zr. At 44.4 at % Te pure Zr_5Te_4 was obtained. Its X-ray pattern could be indexed as body-centered tetragonal with the lattice parameters $a = 10.76_1$ Å, and $c = 3.83_9$ Å, in good agreement with the data of *Brattås* and *Kjekshus*[13], $a = 10.763$ Å, and $c = 3.840$ Å. Since the lattice parameters did not change with composition, Zr_5Te_4 must have a very narrow homogeneity range. Between 47 and 49 at % Te Zr_5Te_4 was found together with hexagonal ZrTe, and between 50 and 52 at % Te ZrTe together with hexagonal $Zr_{1-x}Te$ (NiAs-structure). Above 1,273 K Zr_5Te_4 was found to coexist with $Zr_{1-x}Te$. For an alloy with 48 at % Te a liquidus temperature of about 1,870 K was observed.

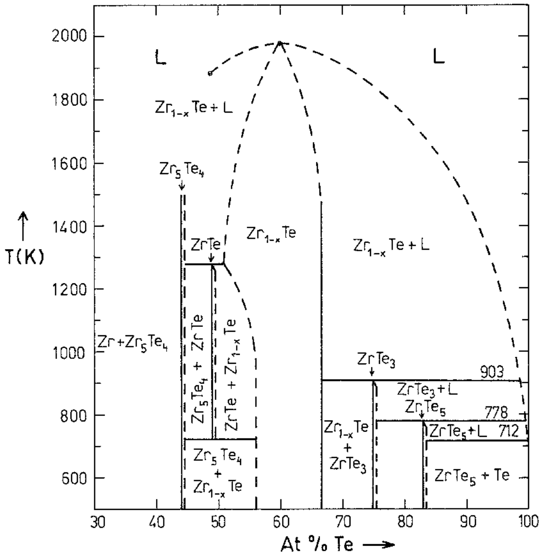

Fig. 1. Partial phase diagram of the Zr—Te system

At 973 K up to about 49 at % Te the alloys were a mixture of Zr_5Te_4 and ZrTe. Near 50 at % Te pure ZrTe was obtained so that its stoichiometry with no appreciable range of homogeneity can be placed between 49 and 50 at % Te. ZrTe has the hexagonal WC-structure with the lattice parameters $a = 3.76$ Å and $c = 3.86$ Å, again in good agreement with the data in the literature[13], $a = 3.763$ Å and $c = 3.862$ Å. Between 50 and 57 at % Te the samples were a mixture of ZrTe and $Zr_{1-x}Te$. In this concentration range the X-ray patterns could be evaluated only with great difficulties due to the dark background and the similarity of the structures.

After a heat treatment of about four weeks at 723 K the alloys between 45 and 50 at % Te showed only the pattern of the $Zr_{1-x}Te$ phase. Although Zr_5Te_4 should also be present it is in this range below the limit of detectability by X-ray diffraction. However, since the lattice parameters of $Zr_{1-x}Te$ were constant in this concentration range, a two phase region is indicated, presumably up to about 57 at % Te.

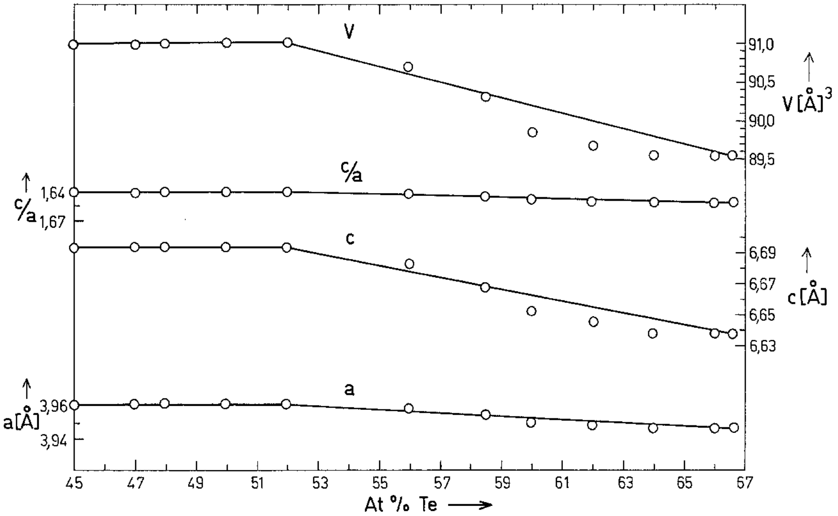

Fig. 2. Lattice parameters of $Zr_{1-x}Te$ (NiAs-like-structure)

After shorter annealing times diffraction lines of ZrTe could sometimes be detected. ZrTe is therefore a high temperature phase existing only between about 723 K and 1,273 K.

The hexagonal $Zr_{1-x}Te$ compound with NiAs-type structure is the only phase in the Zr—Te system with an appreciable range of homogeneity. At 1,273 K pure $Zr_{1-x}Te$ was found to exist between 52 and 66.6 at % Te, at 973 K and at 723 K between 57 and 66.6 at % Te. At 1,273 K Zr-rich $Zr_{1-x}Te$ is in equilibrium with Zr_5Te_4, and at 973 K with ZrTe. At 723 K $Zr_{1-x}Te$ was also observed in X-ray patterns in the range between 45 and 57 at % Te but the presence of the second phase, Zr_5Te_4, could not be ascertained. X-ray patterns of alloys with less than 60 at % Te contained some weak additional lines already observed by other authors[16,18] which did not belong to the NiAs structure. However, these lines could be indexed by doubling the c-axis. For alloys between 45 and 57 at % Te these weak lines disappeared when the samples were annealed at 723 K. For an alloy with 60 at % Te a melting point of about 1,970 K was observed. The Te-rich phase boundary of $Zr_{1-x}Te$ according to both X-ray diffraction of samples prepared from the elements and the isopiestic concentration-temperature curves is situated at 66.6 at % Te.

For the determination of the concentration dependence of the lattice parameters of $Zr_{1-x}Te$ only those X-ray films were used which contained pure $Zr_{1-x}Te$. Samples quenched from 1,273 K showed between 52 and 66.6 at % Te a decrease of the lattice parameters with increasing Te-content as can be seen in Fig. 2. The a-axis decreases from 3.962 Å at 52 at % Te to 3.947 Å at 66.6 at % Te, and the c-axis from 6.693 Å to 6.637 Å. The lattice parameters of the alloys between 45 and 52 at % Te were constant, indicative of a two-phase region. *Brattås* and *Kjekshus*[18] found at 1,073 K a range of homogeneity of the $Zr_{1-x}Te$ phase between 60 and 65.5 at % Te with "a" decreasing from 3.9810 Å to 3.9524 Å, and "c" from 6.700 Å to 6.625 Å.

Between 67.2 and 74 at % Te the X-ray patterns showed the two phases $Zr_{1-x}Te$ and $ZrTe_3$. At 75 at % Te single-phase monoclinic $ZrTe_3$ was obtained with the lattice parameters $a = 5.89$ Å, $b = 3.93$ Å, $c = 10.10$ Å, and $\beta = 97.8°$ which were in good agreement with the data in the literature[7,10,14]. An alloy with 72 at % Te contained thread-like single crystals of $ZrTe_3$. DTA-experiments at 75 and 80 at % Te gave an arrest at 903 K which was interpreted as the peritectic decomposition of $ZrTe_3$. In isopiestic experiments $ZrTe_3$ was found at 75 at % Te between 873 K and 896 K, and was identified by X-ray diffraction; around 80 at % Te X-rays revealed the two-phase region $ZrTe_3$—$ZrTe_5$. A sample with 83.3 at % Te, prepared at 723 K consisted of orthorhombic $ZrTe_5$ with the lattice parameters a = 3.99 Å, b = 14.50 Å, and c = 13.73 Å, in good agreement with the results of *Furuseth et al*[19]. At 90 at % Te $ZrTe_5$ was observed together with Te. DTA-measurements gave the peritectic decomposition of $ZrTe_5$ at 778 K, and the eutectic between $ZrTe_5$ and Te at 712 K (melting point of pure Te 725 K). All the results are incorporated in the partial phase diagram shown in Fig. 1.

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