5   Reactions with Tellurium

The phase diagram of the W–Te system as proposed by [1] and redrawn by [2] is shown in **Fig. 119**. The orthorhombic (space group Pmmn) ditelluride has been identified as the only intermediate phase [3 to 5], see the reviews [6 to 8]. The formation of WTe_4 as a thin coating on tungsten in Te melts at high temperatures (>700°C) is assumed in [9]. The solubility of W in Te is low (<0.3 at%), as microscopic studies show [3].
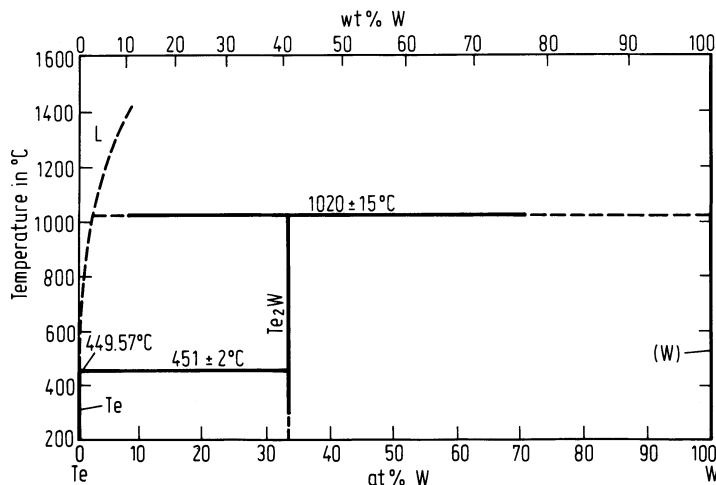

Fig. 119.   Phase diagram of the W–Te system
according to [1, 2].

Metallic gray WTe_2 was obtained by heating stoichiometric mixtures of the elements in evacuated and sealed quartz ampules. The mixture was first fired for 10 to 15 h at 600 to 700°C, then remixed by shaking, and again fired for another 10 to 15 h at 1000 to 1200°C. Single crystals can be prepared by adding a few mg of iodine (or bromine) and transporting the product in a thermal gradient from 900 to 700°C [5]. The direct synthesis from elemental mixtures in heated, closed quartz tubes has also been used repeatedly as a preparation method [3, 4, 10, 11].

The thermal decomposition of WTe_2 in a vacuum of $(1 \text{ to } 2) \times 10^{-2}$ Torr starts at 600 to 620°C and goes to completion at 800 to 850°C [10].

Alloying of tungsten with tellurium in vacuum starts at 640°C [10]. According to [9], the attack by Te vapor at elevated temperatures is minimal. A weight increase was noted between 700 and 800°C, but on further heating to 945°C the weight decreased, and, upon cooling the sample, a thin coating peeled off which was assumed to be WTe_4 [9].

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6   Reactions with Polonium

Tungsten did not react with polonium vapor at up to 700°C [1]. This is to be expected considering the already rather low reactivity of tellurium towards W [2].

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7   Reactions with Boron

Phase Diagram

The phase diagram of the W–B system as proposed by [1] and redrawn by [2] is shown in **Fig. 120**. It is mainly based on the work of [3]. For earlier phase diagrams, see [4, 5, 69]. For the W–B system as a special case of the ternary systems W–B–M (M = Y, La, Ce, Pr, Gd, and Er), see [6]. A calculation of the W–B phase diagram was attempted [79], see also [80] for the thermochemical data.

The identity of the most B-rich intermediate phase has not been definitely established, see, e.g. [10]. Formulas close to WB_4 [7 to 9, 11 to 13, 39, 65, 67, 69] and to WB_{12} [5, 14 to 16] were proposed; the formula $W_{2-x}B_9$ (x ~1/6) was postulated [76]. W_2B_5 has been reported to be the phase richest in B [17 to 22, 24, 25, 32, 33, 77]. Carbon impurities cause decomposition of WB_{12} into W_2B_5 and boron carbide [5, 16]. WB_4 forms W_2B_5 and disappears when heated with 8 wt% C for 1 h at 1400°C [7]. For the influence of C on the phase relations at high B contents, see also [31]. The existence of the phases W_2B_3 [20, 25], W_3B_4 [20, 25], and WB_2 [20, 25 to 28, 73, 74] (see also [11, 30]) has not been confirmed. The monoboride WB occurs in two modifications (α and β) [29, 31, 70]. A low-temperature modification of W_2B_5 prepared from WO_2 and B and reportedly stable at temperatures below 1300 to 1500°C was described [71]. This finding conflicts with other reports [17, 72].