Th) [2]. "From the X-ray patterns the existence of an additional phase with a composition between $ThNi_5$ and Th_2Ni_5 has to be assumed; however, the thermal and microscopic work failed to indicate unequivocally such a phase" [1].

The results of a detailed crystallographic study [3, 8] of the intermediate phases occurring at room temperature deviate from those of [1] as far as the compositions of the peritectically formed compounds are concerned. Instead of $ThNi_9$, Th_2Ni_5, and Th_2Ni [1], the formulas Th_2Ni_{17} [10.53 at. (31.77 wt.) % Th], $ThNi_2$ (66.42 wt. % Th), and Th_7Ni_3 (90.22 wt. % Th) were suggested, besides $ThNi_5$ and ThNi. Since these new formulas are well founded on crystal-structure determinations (see below), the phase diagram given by [1] was slightly modified [4] to accommodate the new results (Fig. 574).

Age hardening in Ni-rich alloys was observed by [1] and the "room temperature" solubility of Th in solid Ni estimated to be below 0.1 wt. (0.03 at.) %. Previously the data <0.01 wt. % for "room temperature" and <0.05 wt. % for 1000°C had been given [5]. No solubility of Ni in solid Th was found by [1].

Crystal Structures. Th_2Ni_{17} crystallizes hexagonally, with $a = 8.37$ A, $c = 8.14$ A, $c/a = 0.972$, and 38 atoms per unit cell, in a new structural type [3, 8]. $ThNi_5$ was shown [6, 3, 8] to have the hexagonal $CaCu_5$ type of structure, with $a = 4.921$ A, $c = 3.990$ A, $c/a = 0.811$ [6], and $a = 4.97$ A, $c = 4.01$ A, according to [8], who found some evidence that the composition may be variable, with a possible range from $ThNi_5$ to $ThNi_4$. $ThNi_2$ is isotypic with AlB_2 (hexagonal C32) type and has the parameters $a = 3.95$ A, $c = 3.83$ A, $c/a = 0.970$ [3, 8]. ThNi crystallizes orthorhombically, with $a = 14.51$ A, $b = 4.31$ A, $c = 5.73$ A, and 16 atoms per unit cell, in a new structural type [3, 8]. Th_7Ni_3 is hexagonal (isotypic with Th_7Fe_3), with $a = 9.86$ A, $c = 6.23$ A, $c/a = 0.632$, and 20 atoms per unit cell [7, 8].

1. L. Horn and C. Bassermann, *Z. Metallkunde*, **39**, 1948, 272–275; the alloys were melted in Al_2O_3 crucibles in a hydrogen or argon atmosphere; however, Th losses by oxidation could not be fully prevented. All alloys were chemically analyzed, at least for Th. For the sake of clarity not all thermal data were plotted in Fig. 574.
2. Th_2Ni was first claimed to have been prepared by E. Chauvenet, *Bull. acad. belg.*, **1908**, 684.
3. J. V. Florio and R. E. Rundle, *U.S. Atomic Energy Comm., Publ.* ISC-273, 1952; *Met. Abstr.*, **21**, 1954, 526. See also the summary table in J. V. Florio, R. E. Rundle, and A. I. Snow, *Acta Cryst.*, **5**, 1952, 450.
4. The compositions of the peritectic points at 1110 and 1050°C and of the eutectic at 1000°C [91 wt. (72 at.) % Th, according to [1]] were tentatively assumed to lie at somewhat higher Th contents.
5. W. Hessenbruch and L. Horn, *Z. Metallkunde*, **36**, 1944, 145–146.
6. T. Heumann, *Nachr. Akad. Wiss. Göttingen, Math.-Phys. Kl.*, **1**, 1948, 21–26; *Structure Repts.*, **11**, 1947-1948, 59.
7. N. C. Baenziger, *U.S. Atomic Energy Comm., Publ.* AECD-3237, 1948.
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0.0882
1.9118

Ni-Ti Nickel-Titanium

Ni-rich Alloys. The existence of Ni-rich solid solutions was indicated by measurements of conductivity [1, 2]. The constitution of the alloys in the composition range 70–100 wt. % Ni was disclosed by [3] by means of thermal and micrographic analysis. Their findings showed that a Ni-rich solid solution forms a eutectic with the compound $TiNi_3$ (78.61 wt. % Ni; melting point 1378°C) at 83.8 wt. (80.8 at.) %

Ni and 1287°C (Fig. 575). The solid solubility of Ti in Ni was found to decrease from 10.8 wt. % Ti at 1287°C to 3.3 wt. % Ti at 850°C. By lattice-parameter measurements and microexamination, [4] found higher solubilities, namely, 11 wt. (13.2 at.) % Ti at 1150°C and 8 wt. (9.6 at.) % Ti at 750°C (Fig. 575). Lattice parameters of

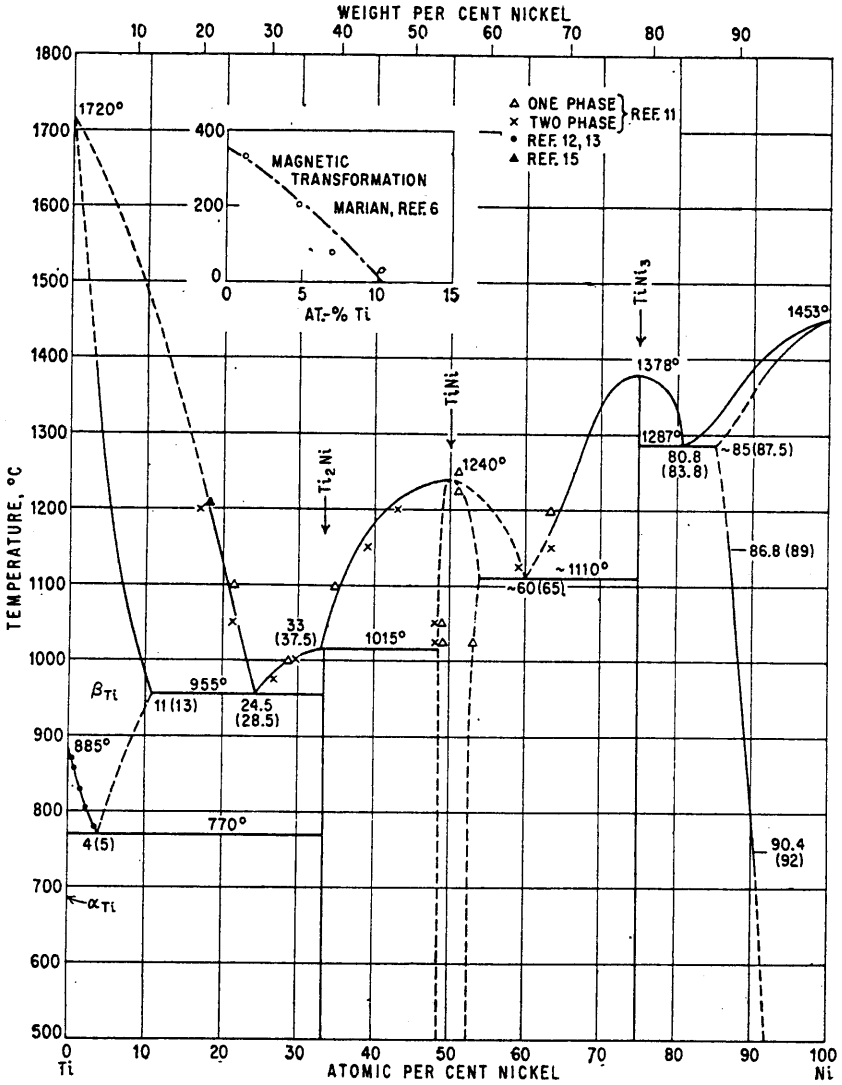

Fig. 575. Ni-Ti. (See also Fig. 575*a* and Note Added in Proof.)

(Ni)-phase alloys were also measured by [5] (up to 3 at. % Ti). The Curie-point temperature vs. composition curve determined by [6] is shown in the inset of Fig. 575.

[7] reported that, besides $TiNi_3$, two additional compounds exist, TiNi (55.06 wt. % Ni) and Ti_2Ni (37.99 wt. % Ni). These phases were identified by X-ray investigations. In 1941, [8] carried out thermal (in the region 50–80 wt. % Ni) and roent-

genographic work and published a phase diagram in which the results of [3] (between 70 and 100 wt. % Ni) were adopted. It was shown that (*a*) the TiNi-$TiNi_3$ eutectic occurs at approximately 66 wt. (61.3 at.) % Ni and 1100°C, (*b*) the phase TiNi is formed by a peritectic reaction at 1270°C (cf. below), and (*c*) TiNi has a certain undetermined range of homogeneity. It should be mentioned that the titanium used by [8] was only 95 wt. % pure and that the alloys were melted in Pythagoras, or corundum, crucibles. Between 0 and 54 wt. % Ni the diagram of [8] was hypothetical.

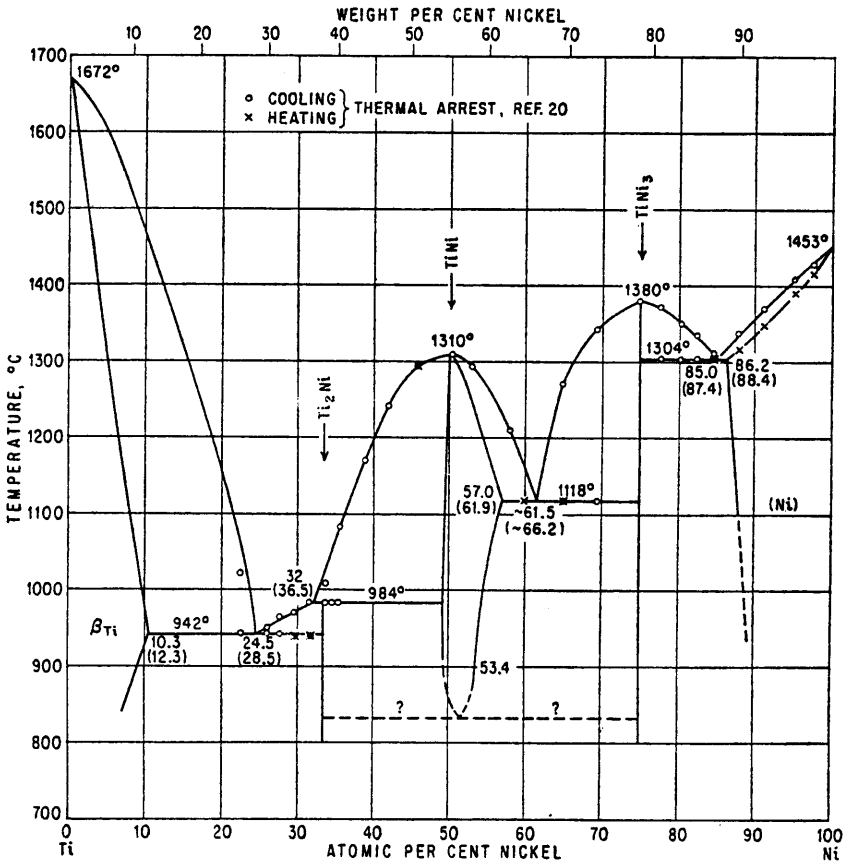

Fig. 575*a*. Ni-Ti. (See also Fig. 575.)

Ti-rich Alloys. The first attempt to reveal the phase relationships in the Ti-rich alloys was made by [9], using Mg-reduced titanium-base alloys prepared by powder-metallurgy methods. Their tentative diagram, as obtained by micrographic analysis, shows the eutectoid at about 7.3 wt. (6.0 at.) % Ni and approximately 765°C; the β_{Ti} phase, with 12 wt. (10 at.) % Ni, forms a eutectic at 33 wt. (28.7 at.) % Ni and about 965°C with an intermediate phase.

According to unpublished work by [10] on Mg-reduced titanium-base alloys, the eutectoid point would be located (by extrapolation) at 7 wt. (5.8 at.) % Ni and 765°C.

[11] have studied the system in the range 0–68 wt. % Ni with iodide titanium–base alloys by metallographic, X-ray, and melting-point methods. Their results are

incorporated in Fig. 575 and indicate that there is a eutectic at about 28.5 wt. (24.5 at.) % Ni, a peritectic melt at approximately 37.5 wt. (33 at.) % Ni, and a maximum melting point at the composition TiNi. The data of [8], which were interpreted to indicate the peritectic formation of the TiNi phase, were shown to be incorrect. The phase TiNi was proved to have a certain range of homogeneity. The composition of the eutectoid was given as 6.2 wt. (5.1 at.) % Ni, and the maximum solubility of Ni in α-Ti as <0.2 wt. %.

[12] determined the $\beta_{Ti}/(\alpha + \beta)$ boundary up to 3.6 at. % Ni by measuring the hydrogen pressure in equilibrium with an extremely dilute solution of hydrogen in Ti-rich (iodide titanium base) alloys as a function of temperature. His boundary (Fig. 575) deviates considerably from those presented by the other investigators [9–11]; however, after this boundary has been rechecked at one composition [13] by both the hydrogen method and microscopic observations on quenched alloys [14], there remains little doubt that it is the correct one. The $\beta_{Ti}/(\beta + Ti_2Ni)$ boundary, investigated by [9–11], should, therefore, be redetermined.

[15] described methods for determining liquidus points of reactive alloys; the point found for an 18.2 at. % Ni alloy is plotted in Fig. 575.

Crystal Structures. Ti_2Ni possesses a f.c.c. translation group [7, 16], with a = 11.333 A [16] and approximately 96 atoms per unit cell. [17] suggested the Fe_3W_3C ($E9_2$) type of structure.

The compound TiNi has the CsCl (B2) type of structure [7, 16, 20, 21], with a = 3.013 A [20], a = 3.015 A [21]. [16] found that TiNi decomposes, upon annealing for 10 days at 800 or 650°C, into Ti_2Ni and $TiNi_3$; however, this could not be corroborated by [11] (48 hr, 750°C). See Note Added in Proof.

The structure of $TiNi_3$ forms the hexagonal $D0_{24}$ prototype [18, 16, 19]. The lattice constants are a = 5.1010 A, c = 8.3067 A, c/a = 1.6284 [19].

Note Added in Proof. The phase boundaries above 900°C of the entire system have been carefully redetermined by [20]. In Fig. 575*a*, the results of thermal analysis are plotted. The Ti-rich portion of the diagram as well as the extent of the (TiNi)-phase field was worked out by microscopical methods. As regards the (Ni) solvus line, which was found by microscopic work to be in good agreement with that proposed by [4] (Fig. 575), [20] assume that "the true solubility curve would show a greater decrease at low temperatures than the straight line in [Fig. 575*a*], although the latter represents the structures found after annealing for 500 hr at 1050°C." Precision lattice parameters of the intermediate phases as well as the (Ni) phase are given in [20]. In corroboration of the results of [16], the TiNi phase was found to decompose into Ti_2Ni + $TiNi_3$ at lower temperatures.

In an X-ray study, [22] found the limiting solubility of Ti in solid Ni to be 10 at. %.

The formation and subsequent decomposition of metastable phases (such as retained β, α') in Ti-Ni alloys containing up to 11 at. % Ni have been studied by [23].

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1.4581
0.5419

Ni-Tl Nickel-Thallium

Figure 576 shows the phase diagram worked out by [1] using thermal analysis and microscopic examination. According to the length of the thermal arrests at 1387°C, the monotectic horizontal extends from 3 wt. (0.9 at.) Tl to practically 100% Tl. The existence of a (Ni) primary solid solution is also indicated by the depression of the magnetic-transformation temperature of Ni on addition of Tl.

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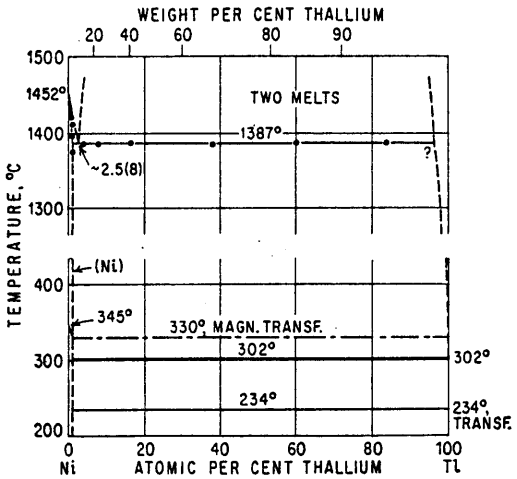

Fig. 576. Ni-Tl