

Phase relations in the ternary Ti-Ni-Cusystem at 800 and 870 degrees C

Citation for published version (APA):

Loo, van, F. J. J., Bastin, G. F., & Leenen, A. J. H. (1978). Phase relations in the ternary Ti-Ni-Cusystem at 800 and 870 degrees C. *Journal of the Less-Common Metals*, 57(1), 111-121. [https://doi.org/10.1016/0022-5088\(78\)90167-4](https://doi.org/10.1016/0022-5088(78)90167-4)

DOI:

[10.1016/0022-5088\(78\)90167-4](https://doi.org/10.1016/0022-5088(78)90167-4)

Document status and date:

Published: 01/01/1978

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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PHASE RELATIONS IN THE TERNARY Ti-Ni-Cu SYSTEM AT 800 AND 870 °C

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(Received April 15, 1977; in revised form June 9, 1977)

Summary

We have investigated the isothermal cross sections through the ternary phase diagram Ti-Ni-Cu at 800 and 870 °C by means of the diffusion couple technique. The results have been corroborated on essential points by the investigation of equilibrated alloys. Use has been made of optical, microprobe and X-ray analyses. The results differ from those mentioned in the literature. For two hitherto undescribed ternary intermetallic compounds X-ray diffraction data are given and crystallographic cell parameters are proposed.

Introduction

One of the topics in our research programme is the acquisition of experimental data on diffusion in ternary metal systems involving the formation of intermetallic compounds. More particularly, we investigate diffusion couples in order to find out (a) the kind and sequence of the intermetallic layers occurring as a function of the choice of the terminal compositions of the couple; (b) the shape and stability of the phase boundaries; and (c) the kinetics of the layer growth. Kirkaldy and coworkers have tried to develop theories on these subjects; experimental data have been published by them [1, 2] and by other investigators [3 - 12]. However, the experimental information is as yet too scarce to verify the various propositions.

Knowledge of the isothermal cross section through the ternary phase diagram is a necessary preliminary to a relevant experimental approach. We selected the model system Ti-Ni-Cu at 800 °C, firstly because of our previous experiments on the binary systems Ti-Ni [13, 14] and Ti-Cu [15], and secondly because Pfeifer *et al.* [16] have published a thorough paper on this phase diagram (see Fig. 1). During the course of the experiments, however, we found that the cross section proposed by Pfeifer *et al.* deviated at some important points from our findings. Since the diffusion layers

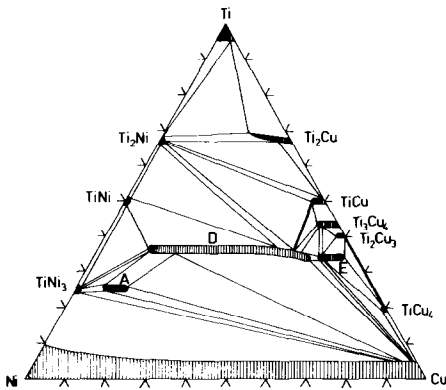


Fig. 1. The cross section through the Ti-Ni-Cu phase diagram at 800 °C, according to Pfeifer *et al.* [16].

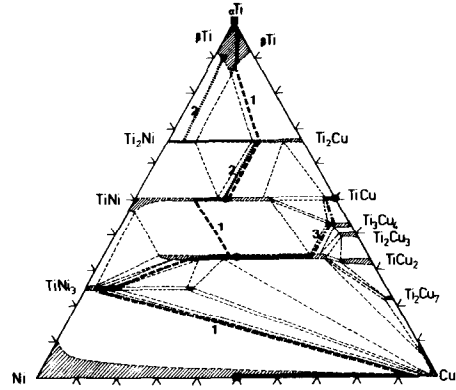


Fig. 2. Measured diffusion paths in the 870 °C cross section. Path 1 is found in the couple α -Ti-NiCu, path 2 in the couple $Ti_{90}Ni_{18}Cu_2$ - $Ti_{50}Ni_{27}Cu_{23}$ and path 3 in the couple TiCu-TiNiCu.

formed at 800 °C were relatively thin and sometimes difficult to analyse, we also investigated the system at 870 °C.

It seems useful to present here the cross sections found by us using the diffusion couple technique and completed by microprobe and X-ray analyses on selected alloys. The data relevant to the study of the diffusion mechanism in ternary metal systems will be presented in a future paper.

The determination of a ternary phase diagram using the diffusion couple technique

Anticipating the specific results of the present investigation, it seems worthwhile to comment upon the use of the diffusion couple technique in investigating ternary phase diagrams.

For binary systems, the method has proved to be advantageous relative to the classical methods using equilibrated alloys [13, 14, 17 - 21]. The underlying principle is that all the concentrations which are found in the diffusion zone after annealing must belong to single-phase regions in the binary equilibrium diagram at the temperature in question. The concentration values on both sides of the phase boundaries are the coexisting equilibrium values for the two phases. Deviations from these values as mentioned by Eifert *et al.* [22] have never been found in our laboratory. Of course, obvious precautions have to be taken: the diffusion process must not be impeded, *i.e.* the diffusion coefficients shall be a function of the concentration only, and during cooling of the couple no alterations may occur in the diffusion zone.

For ternary systems the problem is more intricate. In this case, we can analyse the concentration-penetration curves of the various elements in the

diffusion zone and plot these values as a so-called diffusion path in a triangular isothermal cross section of the phase diagram. In Fig. 2 three examples of these paths from the present work are shown. The drawn parts of the path are the measured concentrations in a diffusion couple and represent single-phase regions. The shaded areas are concentration gaps and, in this case, represent two-phase fields. Theoretically, concentration gaps corresponding to three-phase fields are also possible [1, 23]. Obviously, a large number of diffusion paths is necessary in order to construct a complete isothermal cross section. This is possible only by changing the terminal compositions of the couple.

Allowance should be made for the fact that two-phase fields can manifest themselves in several ways in the diffusion couple [1, 23].

(1) If the diffusion path follows a tie line in a two-phase field, a planar interface and accessory concentration gap will occur in the couple. The concentrations at both sides of the interface are in equilibrium.

(2) If the diffusion path cuts the tie lines, a locally equilibrated columnar two-phase layer is produced. Layers containing isolated precipitates of other phases, or non-planar interfaces may also occur. The stability of such a diffusion path in relation to the annealing time is still a matter for investigation.

In the present work, in order to be sure of thermodynamic equilibrium circumstances, we have used only those couples in which single-phase layers bounded by planar interfaces have been produced. In fact, this condition was met by the majority of the couples.

Experimental procedure

We have used in this investigation Ti bar of purity 99.97 wt.% (M.R.C.), Ni bar of purity 99.99 wt.% (M.R.C.) and Cu bar of purity 99.99 wt.% (Halewood Chemicals).

The various binary and ternary alloys have been prepared by repeated argon arc melting, after which they were homogenised at 800 or 870 °C for at least one week in sealed evacuated silica capsules.

Diffusion couples have been made by solid state resistance welding of the mechanically polished slices in a modified arc furnace, as described earlier [13]. During this process no diffusion layer was formed. The couples were heated in sealed evacuated silica capsules at 800 or 870 °C for times varying between 16 and 900 h.

After diffusion annealing, the couple was embedded, ground and polished parallel to the diffusion direction and, in most cases, etched with a mixture of 10% H₂O₂, 5% HF and 85% H₂O. After that, it was examined microscopically and often subjected to microprobe analysis. In one case the couple was ground perpendicular to the diffusion direction in order to subject the polished and etched diffusion layers to X-ray diffraction analysis.

X-ray diffraction analysis was also performed on a number of annealed alloys, on polished and etched cross sections of the alloys as well as on powdered samples.

In the following section we consider these analytical techniques in more detail.

Analytical techniques

Optical microscopy

In the microscope investigation of the couples and alloys, the use of polarised light turned out to be of tremendous value. Experience has shown that each phase can be determined unambiguously by its specific colour transitions, even in very thin layers or small precipitates.

Layer thicknesses were measured using a calibrated filar micrometer eyepiece.

Microprobe analysis

Concentration-penetration curves have been recorded using an S.E.M. II A electron probe microanalyser (A.E.I., England). In order to transform the measured X-ray intensities into concentrations, use was made of the Ziebold-Ogilvie method [24]. Applied to a binary system A-B, this method leads to the empirical relation

$$\frac{1 - K_A}{K_A} = A_{AB}^A \frac{100 - N_A}{N_A} \quad (1)$$

where K_A is the relative X-ray intensity of element A, *i.e.* the net X-ray intensity obtained from an alloy divided by the net intensity of the pure metal standard A, N_A the concentration of element A in mol.% in that alloy and A_{AB}^A an experimentally determined constant. We have verified many times in our laboratory that this empirical method leads to good results, accurate to better than ± 1 mol.% [25].

An extension to ternary systems is possible, but leads to concentration-dependent values for the constant A. Applied to the system Ti-Ni-Cu, one finds

$$A_{\text{TiNiCu}}^{\text{Ti}} = \frac{A_{\text{TiNi}}^{\text{Ti}} N_{\text{Ni}} + A_{\text{TiCu}}^{\text{Ti}} N_{\text{Cu}}}{N_{\text{Ni}} + N_{\text{Cu}}} \quad (2)$$

and analogous equations for $A_{\text{TiNiCu}}^{\text{Ni}}$ and $A_{\text{TiNiCu}}^{\text{Cu}}$. Substitution of eqn. (2) in eqn.(1) leads to expressions for the concentrations of the elements, which depend only on the binary A_{ij}^i values and the experimentally determined relative intensities K_i . A computer programme was written in order to convert these intensities into concentrations.

The method has been applied on eleven ternary calibration alloys. All results were within ± 2 mol.% of the weighed-in values; in nine of them the deviation was less than 1 mol.%.

The method can be employed for analysing homogeneous alloys as well as for recording concentration-penetration curves in diffusion couples. In the latter case, this was done by taking point counts at intervals of $2.5 \mu\text{m}$ on a trace parallel to the diffusion direction. Care must be taken that the three concentration measurements take place at exactly the same spots on the trace.

X-ray diffraction

In order to identify the various intermetallic compounds and to determine their lattice parameters, X-ray diffractometry with standard goniometer speed and recording sensitivity has been carried out using Cu or Fe K_α radiation. However, since we came across hitherto unknown compounds, we have tried to measure as accurately as possible the position and intensity of very weak reflections which are overlooked in standard diffractograms.

We have, therefore, lowered the scanning speed of our Philips PW 1050 goniometer to $0.02^\circ \text{min}^{-1}$ by using the normal step-scanning device PW 1063. The time constant was extended to an appropriate value of 50 s by inserting an electronic device representing that time constant into the connecting cable between the output ratemeter and the input recorder. With very weak reflections the average background intensity can be a number of times higher than the net peak intensity, so a continuously adjustable zero suppression of 0 - 100% f.s.d. proved advantageous. Because of the properties of the ratemeter output circuit, the switching on of the zero suppressor could be combined with a doubling of the recording sensitivity, resulting in a

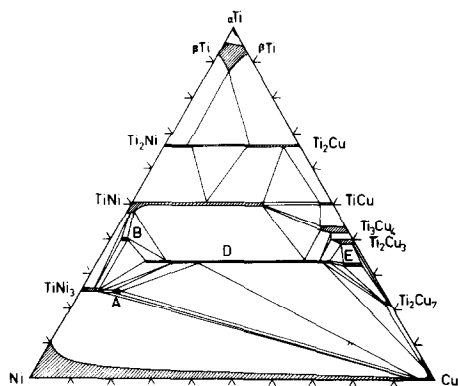


Fig. 3. The cross section through the Ti-Ni-Cu phase diagram at 800 °C, according to our measurements.

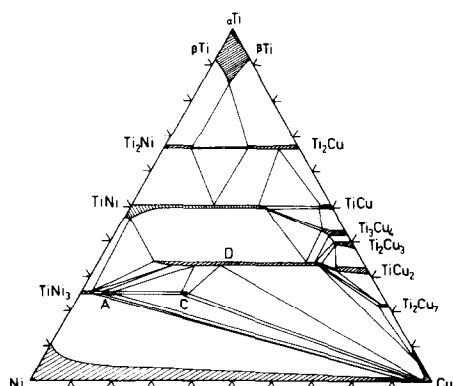


Fig. 4. The cross section through the Ti-Ni-Cu phase diagram at 870 °C, according to our measurements.

TABLE 1

Types of couples, together with the developed single-phase layers at 800 and 870 °C

No.	Type	Phases at 870 °C	Phases at 800 °C
1	α -Ti-Ni	β -Ti, Ti ₂ Ni, TiNi, TiNi ₃	β -Ti, Ti ₂ Ni, TiNi, TiNi ₃
2	α -Ti-Cu	β -Ti, Ti ₂ Cu, TiCu, Ti ₃ Cu ₄ , Ti ₂ Cu ₃ , TiCu ₂ , Ti ₂ Cu ₇	β -Ti, Ti ₂ Cu, TiCu, Ti ₃ Cu ₄ , Ti ₂ Cu ₃ , Ti ₂ Cu ₇ N.A.
3	α -Ti-Ni ₃ Cu	β -Ti, Ti ₂ Ni, TiNi, D, A, TiNi ₃	β -Ti, Ti ₂ Cu, TiNi, D, A, TiNi ₃
4	α -Ti-NiCu	β -Ti, Ti ₂ Cu, TiNi, D, A, TiNi ₃	N.A.
5	α -Ti-NiCu ₃	β -Ti, Ti ₂ Cu, TiCu, TiNi, D	N.A.
6	Ni-TiCu	TiNi ₃ , A, D, E(=TiCu ₂), Ti ₂ Cu ₃ , Ti ₃ Cu ₄	TiNi ₃ , A, D, E, Ti ₂ Cu ₃ , Ti ₃ Cu ₄
7	Ni-Ti ₃ Cu ₄	TiNi ₃ , A, D, E(=TiCu ₂), Ti ₂ Cu ₃	N.A.
8	Ni-Ti ₂ Cu ₃	TiNi ₃ , A, D, E(=TiCu ₂)	N.A.
9	Ni-TiCu ₂	TiNi ₃ , A, D	N.A.
10	Ni-Ti ₂ Cu ₇	TiNi ₃ , A, D, Cu	TiNi ₃ , A, D, Cu
11	Cu-Ti ₂ Ni	D, TiNi	N.A.
12	Cu-TiNi	D	D
13	Cu-TiNi ₃	A	N.A.
14	TiNi-TiCu	D, Ti ₃ Cu ₄	D, Ti ₃ Cu ₄
15	TiNi-Ti ₃ Cu ₄	N.A.	D
16	Ti ₂ Ni-Ti ₃ Cu ₄	N.A.	TiNi, TiCu
17	TiNiCu-Ni ₃ Cu	C, A, TiNi ₃	A, TiNi ₃
18	TiNiCu-NiCu	C, A, TiNi ₃	A, TiNi ₃
19	TiNiCu-Ni ₄ Cu ₆	C, A, TiNi ₃	N.A.
20	TiNiCu-Ni ₂ Cu ₈	C, A	N.A.
21	TiNiCu-NiCu ₉	C	N.A.
22	TiNiCu-Cu	-	-
23	TiNiCu-Ti ₂ Cu ₇	-	-
24	TiNiCu-TiCu ₂	-	-
25	TiNiCu-Ti ₂ Cu ₃	E(=TiCu ₂), Ti ₂ Cu ₃ , Ti ₃ Cu ₄ (!)	E(="TiCu ₂ " = Ti ₂ Cu ₃ + Ti ₂ Cu ₇)
26	TiNiCu-Ti ₃ Cu ₄	E(=TiCu ₂), Ti ₂ Cu ₃	E
27	TiNiCu-TiCu	Ti ₃ Cu ₄	N.A.
28	TiNiCu-TiNi ₃	A	A
29	TiNiCu-TiNi	-	N.A.
30	Ti ₆₀ Ni ₂₇ Cu ₂₃ - α -Ti	Ti ₂ Cu, β -Ti	N.A.
31	Ti ₅₀ Ni ₂₇ Cu ₂₃ -TiCu	D, Ti ₃ Cu ₄	N.A.
32	Ti ₅₀ Ni ₂₇ Cu ₂₃ -Ti ₆₀ Ni ₁₈ Cu ₂	Ti ₂ Cu, Ti ₂ Ni	N.A.
33	Ti ₆₀ Ni ₂₇ Cu ₂₃ -Ti ₆₈ Ni ₁₆ Cu ₆	Ti ₂ Cu	N.A.
34	Ti ₂₂ Ni ₇ Cu ₄ -TiNi	N.A.	N.A. B

For the designation of the various phases see Figs. 3 and 4; N.A. means not analysed; - means no layer formed.

TABLE 2

Phases present in equilibrated alloys according to microprobe analysis

Alloy	Phases present at 870 °C	Phases present at 800 °C
Ti ₂₅ Ni ₆₅ Cu ₁₀	A + C	N.A.
Ti ₂₅ Ni ₄₉ Cu ₂₆	C + D + Cu	A + D + Cu
Ti ₃₁ Ni ₈ Cu ₆₁	N.A.	Ti ₂ Cu ₇ + D + E
Ti _{33.5} Ni _{6.5} Cu ₆₀	E(=TiCu ₂) + Ti ₂ Cu ₃	N.A.
Ti ₃₅ Ni ₅₉ Cu ₆	TiNi ₃ + TiNi + D	TiNi ₃ + B + D
Ti ₃₈ Ni ₈ Cu ₅₄	N.A.	D + Ti ₂ Cu ₃ + Ti ₃ Cu ₄
Ti ₃₈ Ni ₄ Cu ₅₈	N.A.	E + Ti ₂ Cu ₃
Ti ₄₀ Ni _{56.5} Cu _{3.5}	N.A.	B
Ti ₄₅ Ni ₈ Cu ₄₉	N.A.	TiNi + TiCu + Ti ₃ Cu ₄
Ti ₆₀ Ni ₁₆ Cu ₂₄	TiNi + Ti ₂ Cu	TiNi + Ti ₂ Cu
Ti ₆₀ Ni ₂₃ Cu ₁₇	TiNi + Ti ₂ Ni + Ti ₂ Cu	TiNi + Ti ₂ Ni + Ti ₂ Cu
Ti ₆₅ Ni ₁₀ Cu ₂₅	TiNi + Ti ₂ Cu	N.A.
Ti ₇₅ Ni _{12.5} Cu _{12.5}	β -Ti + Ti ₂ Ni + Ti ₂ Cu	β -Ti + Ti ₂ Ni + Ti ₂ Cu

For the designation of the phases see Figs. 3 and 4; N.A. means not analysed.

maximum overall sensitivity in our case of 5 counts s⁻¹ full scale. Reflections with a peak intensity of no more than 1 count s⁻¹ were reproducibly recorded in this way.

Experimental results

Table 1 gives the types of couples, used for the investigation of the 800 and 870 °C cross sections through the Ti-Ni-Cu phase diagram, together with the developed single-phase layers. In Fig. 2 three of the diffusion paths are mapped in the composition triangle at 870 °C.

The measurement of the various diffusion paths proceeded without difficulty, except for the accurate determination of the Ni and Cu concentrations at the D/E interface and the D/TiCu₂ interface (see Figs. 3 and 4) where very steep concentration gradients develop.

In Tables 2 and 3 the results are given of microprobe analysis and X-ray analysis, respectively, of a number of equilibrated alloys.

In Tables 4 and 5 the diffractograms are given of compounds of composition Ti₄₀Ni_{56.5}Cu_{3.5} and TiNi₂Cu, respectively, using ultralow speed and high sensitivity X-ray diffractometry.

Evaluation of the experimental results

Figures 3 and 4 represent the isothermal cross sections at 800 and 870 °C found by us by a combination of the diffusion couple technique and the analysis of equilibrated alloys.

TABLE 3

Phases present in some alloys homogenised at 870 °C and their structure data according to X-ray diffraction at room temperature

Alloy	Phases	Structure type	Lattice parameters (Å)
Ti ₂₅ Ni ₇₅	TiNi ₃	Hex. A ⁴	a = 5.11; c = 8.32
Ti ₂₅ Ni ₇₃ Cu ₂	TiNi ₃	Hex. A ⁴	a = 5.11; c = 8.33
Ti ₂₅ Ni ₇₁ Cu ₄	TiNi ₃	Hex. A ⁴	a = 5.11; c = 8.34
	A	Hex. A ⁹	a = 5.11; c = 18.85
Ti ₂₅ Ni ₆₉ Cu ₆	A	Hex. A ⁹	a = 5.11; c = 18.85
Ti ₂₅ Ni ₆₇ Cu ₈	A	Hex. A ⁹	a = 5.11; c = 18.85
Ti ₂₅ Ni ₆₅ Cu ₁₀	A	Hex. A ⁹	a = 5.11; c = 18.85
Ti ₂₅ Ni ₄₉ Cu ₂₆	C	Tetr. VNi ₃ -type	a = 5.11; c = 18.85
Ti _{33.5} Ni _{61.5} Cu ₅	TiNi ₃	Hex. A ⁴	a = 3.611; c = 7.459
	TiNi	Hex. A ⁴	^a
	D	Cub. CsCl-type	a = 3.00
Ti _{33.5} Ni _{51.5} Cu ₁₅	D	Tetr. MoSi ₂ -type	a = 3.09; c = 7.99; c/a = 2.584
Ti _{33.5} Ni _{46.5} Cu ₂₀	D	Tetr. MoSi ₂ -type	a = 3.10; c = 7.98; c/a = 2.571
Ti _{33.5} Ni _{36.5} Cu ₃₀	D	Tetr. MoSi ₂ -type	a = 3.11; c = 7.97; c/a = 2.566
Ti _{33.5} Ni _{26.5} Cu ₄₀	D	Tetr. MoSi ₂ -type	a = 3.12; c = 7.965; c/a = 2.556
Ti _{33.5} Ni _{16.5} Cu ₅₀	D	Tetr. MoSi ₂ -type	a = 3.13; c = 7.97; c/a = 2.546
Ti _{33.5} Ni _{11.5} Cu ₅₅	D	Tetr. MoSi ₂ -type	a = 3.14; c = 8.00; c/a = 2.546
	TiCu ₂	Tetr. MoSi ₂ -type	a = 3.145; c ^a
Ti _{33.5} Ni _{6.5} Cu ₆₀	D	Orthorhomb. VAu ₂ -type	a = 4.44; b = 8.00; c = 4.47
	TiCu ₂	Tetr. MoSi ₂ -type	a = 3.145; c ^a
	Ti ₂ Cu ₃	Orthorhomb. VAu ₂ -type	a = 4.42; b = 8.00; c = 4.51
Ti _{33.5} Cu _{66.5}	TiCu ₂	Tetr. Ti ₂ Cu ₃ -type	^a
	Ti ₂ Cu ₃	Orthorhomb. VAu ₂ -type	a = 4.40; b = 8.00; c = 4.51
	B	Tetr. Ti ₂ Cu ₃ -type	^a
Ti ₄₀ Ni _{56.5} Cu _{3.5} ^b	Ti ₂ Cu ₃	Tetr. cell, related to Ti ₂ Cu ₃	a = 4.403; c = 13.525
Ti ₄₀ Cu ₆₀ ^b	Ti ₂ Cu ₃	Tetr. Ti ₂ Cu ₃ -type	a = 3.140; c = 14.014

^a Lattice parameters not measurable accurately because of coinciding diffraction lines.^b Homogenised at 800 °C.For the designation of the phases see Figs. 3 and 4; for the structure types and their relations see Pfeifer *et al.* [15].

TABLE 4

Diffraction pattern of $\text{Ti}_{40}\text{Ni}_{56.5}\text{Cu}_{3.5}$ (phase B); Cu K_{α} radiation; d_m , measured interplanar spacing; d_{calc} , calculated spacing using a tetragonal cell with $a = 4.4028$ and $c = 13.525$ Å

d_m	d_{calc}	hkl	I	d_m	d_{calc}	hkl	I
6.76	6.76	002	3	1.2367	1.2405	1.1.10	11
4.191	4.187	101	1		1.2379	315	
3.391	3.381	004	<1	1.2309 ^b	1.2299	306	3
3.028	3.034	111	3		1.2296	0.0.11	
2.562	2.562	113	<1	1.1524	1.1524	2.0.10	6
2.306	2.305	105	3	1.1142	1.1148	2.1.10	1
2.256 ^a	2.254	006	1		1.1130	325	
2.202	2.201	200	90	1.1012	1.1007	400	2
2.095	2.093	202	1	1.0918 ^b	1.0919	1.0.12	1
2.011 ^b	2.042	115	100	1.0684	1.0693	403	1
1.9693	1.9690	210	3		1.0678	410	
1.7024	1.7074	205	<1	1.0201	1.0210	2.2.10	3
	1.7015	214			1.0195	405	
1.6415	1.6417	117	2	0.9842	0.9845	420	2
1.5728	1.5750	206	<1	0.9669	0.9689	335	2
1.5540	1.5566	220	9		0.9661	0.0.14	
1.4598	1.4590	301	<1	0.8659	0.8661	1.1.15	3
1.3538	1.3534	119	6		0.8650	2.2.13	
	1.3525	0.0.10		0.8546	0.8565	512	1
	1.3492	225			0.8539	339	
1.2917	1.2929	1.0.10	2		0.8537	4.0.10	
	1.2900	305					

^a Coinciding with K_{β} peak from (115) reflection.

^b Coinciding with lines of TiNiCu, present in small amounts.

At first, let us compare our results at 800 °C with those of Pfeifer *et al.* (Figs. 3 and 1). The most conspicuous difference is the much larger homogeneity region of the TiNi phase found by us: much more Cu is soluble in this phase than Pfeifer *et al.* assume.

Another important difference is our introduction of a new phase, $\text{Ti}_{40}\text{Ni}_{56.5}\text{Cu}_{3.5}$ (phase B). Wasilewski *et al.* [26] mention a phase Ti_2Ni_3 in the binary Ti-Ni system below 625 °C. This is probably the same phase in view of the positions of the two strongest X-ray diffraction lines given by them. Obviously, this phase is stabilised up to higher temperatures by the presence of Cu. At 870 °C, however, the compound no longer exists. The tetragonal crystal structure is closely related to that of Ti_2Cu_3 , given by Schubert [27] and confirmed by us using ultralow speed and high sensitivity diffractometry. The basic reflections are similar in intensity; the a axis of the Cu-stabilised Ti_2Ni_3 , however, is larger than that of Ti_2Cu_3 by a factor $\sqrt{2}$ (Table 4). The A^{10} -stacking variant proposed by Wasilewski *et al.* was not confirmed by us.

TABLE 5

Diffraction pattern of TiNi₂Cu (phase C); Cu K_α radiation; d_m , measured interplanar spacing; d_{calc} , calculated spacing based on a b.c.t. cell with $a = 3.611$ and $c = 7.459$ Å

d_m	d_{calc}	hkl	I
3.244	3.250	101	2
2.546	2.553	110	<1
2.105	2.107	112	100
2.046	2.048	103	1
1.8648	1.8648	004	4
1.8045	1.8056	200	22
1.6242	1.6251	202	<1
1.5763	1.5778	211	<1
1.3546	1.3543	213	<1
1.2971	1.2972	204	7
1.2760	1.2767	220	3
1.1177	1.1177	116	3
1.0912	1.0919	312	19
1.0535	1.0535	224	9

The same type of structure was found by Gupta *et al.* [28] in Ti-Ni alloys quenched from 670 °C. They suggested a metastable hexagonal close-packed transition phase, with lattice parameters $a = 2.7$ Å and $c = 4.4$ Å. The diffraction pattern found by us does not fit these cell dimensions.

The differences mentioned above affect the positions of the various two- and three-phase fields substantially, of course. As an example, the two-phase fields found by Pfeifer *et al.* between Ti₂Ni and TiCu or TiNiCu are not found by us. A minor difference concerns the homogeneity region of the phase called TiCu₄ by Pfeifer *et al.* We find the phase stable between 21.9 and 22.4 at.% Ti and, following Zwicker [29], prefer to denote this phase as Ti₂Cu₇.

In the 870 °C cross section (Fig. 4) the most conspicuous features are the extension of the phase region E to the binary phase TiCu₂ and the appearance of a new ternary phase C = TiNi₂Cu.

The phase TiCu₂ is not stable in its pure form at 800 °C, but can be stabilised by the substitution of Cu by Ni atoms, thus resembling the stabilisation of Ti₂Ni₃ by Cu atoms. The values of the lattice parameters as a function of concentration in the range Ti₃₃Ni_{67-x}Cu_x ($20 < x < 67$) agree with those mentioned by Pfeifer *et al.* [16].

The TiNi₂Cu phase found by us has the VNi₃ type of structure (Table 5). The X-ray diffraction measurements on a homogenised alloy of this composition were impeded by the rather broad diffraction peaks. A much better result was obtained by the X-ray investigation of a diffusion layer of this composition, found in the couple TiNiCu-Ni₄Cu₆ (Table 1, no. 19) annealed for 235 h at 870 °C.

Both Pfeifer *et al.* [16] and van Vught [30] mention a phase of this structure. Pfeifer *et al.* found it in as-cast alloys of composition $\text{Ti}_{25}\text{Ni}_{51}\text{Cu}_{24}$, van Vught in as-cast alloys of composition TiNiCu_2 .

The TiCu_3 type of structure, found in an ultrarapidly cooled melt of composition TiNi_2Cu by van Vught and in an alloy $\text{Ti}_{25}\text{Ni}_{43}\text{Cu}_{32}$ annealed at 930 °C by Pfeifer *et al.*, has not been found by us and is therefore not stable at 800 and 870 °C.

Acknowledgment

We wish to thank Ir. J. W. G. Hegger for performing a number of measurements taken at 800 °C, and F. C. Krüger and H. de Jonge Baas for carrying out the X-ray diffraction measurements.

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