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A contribution to the ternary copper–magnesium–nickel phase diagram*

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Abstract

The ternary Cu–Mg–Ni phase diagram has been studied by differential thermal analyses, X-ray powder diffraction and isopiestic vapour pressure measurements. Three different isopleths with constant x_{Cu}/x_{Ni} ratios of 2.0, 1.0 and 0.5, and one with a constant magnesium content of 71 at.% were constructed from these measurements. Together with literature information it was possible to define the four invariant four-phase equilibria in the system with respect to the temperature and compositions of the participating phases, and to derive the monovariant reaction lines on the liquidus surface. Furthermore, it was confirmed that Mg_2Ni dissolves up to about 25 at.% Cu at 450°C.

Keywords: Phase diagrams; Light alloys; Solid solutions; Copper

1. Introduction

In a recent investigation of the thermodynamic properties of ternary Cu–Mg–Ni alloys using an isopiestic vapour pressure method [1] it was discovered that the experimental data points were not in full agreement with the shape of the liquidus surface as described in the compilation by Chang et al. [2]. For the three investigated isopleths (with $x_{Cu}/x_{Ni} = 2.0$, 1.0, 0.5) the kinks in the isopiestic equilibrium curves (sample temperature vs. sample composition) indicated a liquidus surface which was shifted to lower magnesium contents in the composition range between about 40 and 70 at.% Mg. This may not be surprising since the liquidus surface in Ref. [2] was based mainly on the results of thermal analyses by Mikheeva and Babayan [3], who had employed open corundum crucibles both for the preparation of the alloys and the measurements themselves. Owing to the chemical reaction of magnesium with Al_2O_3 at elevated temperatures and owing to possible losses of magnesium by evaporation, systematic errors are likely to be expected in their data, especially in the magnesium-rich part of the system.

Another open question which had not been fully resolved up to now was the extent of the mutual solid solubility between the binary intermetallic compounds in the Cu–Mg and Mg–Ni systems, where contradictory results can be found in the literature [4–8]. Thus Lieser and Witte [5] reported that the two Laves phases Cu_2Mg (f.c.c.; space group *Fd*3*m*) and $MgNi_2$ (hexagonal; space group *P*6$_3$/*mmc*) formed a pseudobinary system of the peritectic type with solid solubilities reaching nickel and copper contents of up to 30 at.%. Fehrenbach et al. [6], however, concluded that there was "...considerably less solubility of copper in $MgNi_2$ than reported by Lieser and Witte". Furthermore, an isothermal section at 475°C was given in Ref. [6], in which the other two binary phases $CuMg_2$ (orthorhombic; space group *Fddd*) and Mg_2Ni (hexagonal; space group *P*6$_2$22) did not exhibit any appreciable mutual solid solubility. Several years later Karonik et al. [7] investigated the magnesium-rich part of the ternary system and found a very large solubility of Cu in Mg_2Ni at 400°C, whereas the solubility of Ni in $CuMg_2$ was less than 2 at.%.

All these prompted us to start a new investigation of the ternary Cu–Mg–Ni phase diagram, using well equilibrated samples which were available from the thermodynamic study. These samples were employed in a series of differential thermal analysis (DTA)

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* Dedicated to Prof. Dr O.F. Olaj on the occasion of his 60th birthday.

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measurements along the same three isopleths that had also been studied by vapour pressure measurements (see above). In addition, a number of samples were prepared with a constant magnesium content of 71 at.% in order to establish the extent of the solid solutions based on $CuMg_2$ and Mg_2Ni; they were used both for thermal analyses and X-ray measurements. This particular composition of 71 at.% Mg was selected for practical purposes, i.e. to be able to construct an isopleth without major interference by the phase equilibria emanating from the binary peritectic reaction in the Mg–Ni system, originally given at 760°C and 71 at.% Mg by Nayeb-Hashemi and Clark [9].

2. Experimental procedure

2.1. Sample preparation

As already discussed, all samples along the three isopleths with constant x_{Cu}/x_{Ni} ratios of 2.0, 1.0 and 0.5 were taken from the isopiestic vapour pressure measurements [1]; their compositions are listed in Table 1. Details about starting materials and experimental procedures can be found in Ref. [1].

Samples for the section with a constant magnesium content of 71 at.% were prepared separately; their compositions were: 0.0, 6.0, 9.5, 10.2, 14.5 (two samples), 19.3, 23.0, 28.3 and 29.0 at.% Cu. Starting materials were nickel foil (0.125 mm thickness; 99.99%; Advent, Halesworth, England), copper wire (1 mm diameter; 99.98 + %; Goodfellow, Cambridge, England), and magnesium rods (15 mm diameter; 99.95%; Johnson & Matthey, London, England). Appropriate amounts of the pure elements were weighed into crucibles made from pure iron (99.5%; Goodfellow) which held an inner container fabricated from graphite (quality E506; Ringsdorff, Vienna, Austria) to prevent any reaction between iron and nickel.

The loaded crucibles were evacuated down to about 10^{-2} Pa through a thin-walled evacuation tube and flushed several times with purified argon. The evacuation tube was crimped under vacuum and closed by welding. (Argon arc welding was used for all the necessary metal connections and for the sealing of the iron crucibles.) To prevent oxidation, each iron crucible was additionally sealed under vacuum in an outer quartz container. The samples were heated at 800°C for several days and furnace cooled. Their compositions were checked by chemical analysis.

Table 1
Composition of samples investigated by DTA with constant x_{Cu}/x_{Ni} ratios; values are in at.% Mg

$x_{Cu}/x_{Ni} = 2.0$	$x_{Cu}/x_{Ni} = 1.0$	$x_{Cu}/x_{Ni} = 0.5$
20.2	33.0	15.4
27.7	34.3	27.7
36.1	35.8	36.7
48.7	42.4	42.2
54.2	49.3	51.3
60.7	54.5	61.0
66.2	59.2	65.6
70.8	66.8	69.7
86.7	73.7	75.6
	81.5	

2.2. DTA measurements

Due to the reactivity of magnesium and its high vapour pressure, it was not possible to use the usual DTA crucibles made from quartz or alumina. Special DTA containers had to be devised, which were machined from pure iron, and additional graphite inserts were used to prevent the attack of liquid alloys containing different amounts of nickel on the iron. The design of such a crucible is shown in Fig. 1. In order to avoid any significant reaction between iron and carbon which might lead to the destruction of the crucibles, the DTA measurements were restricted to temperatures below 1060°C, i.e. well below the eutectic between γ-Fe and Fe_3C at 1148°C [10]. Neverthe-

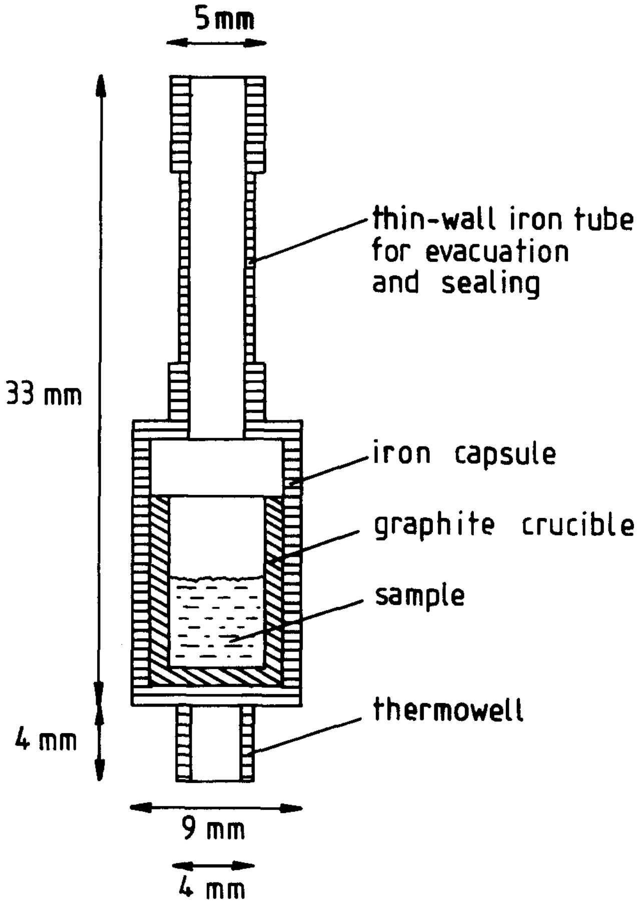

Fig. 1. Iron crucible for DTA measurements; after pinching and welding the total length is approx. 25 mm.

less there were a few instances where the reaction between solid iron and carbon was clearly observed at much lower temperatures, and the austenite eutectoid appeared in the DTA curves at temperatures around 730°C, with increasing intensity on repeated heating and cooling.

Samples for the DTA measurements were crushed, and approx. 150 mg were filled into the iron crucibles, which were evacuated, flushed several times with purified argon, and finally closed by welding. Before running the thermal analyses, all samples were annealed at temperatures between 400 and 500°C for periods of two to six weeks. For this purpose the entire DTA crucible was sealed under vacuum in an outer quartz tube to prevent oxidation.

The thermal analyses were performed on a DTA 404S/3 (Netzsch, Selb, Germany) under a flowing gas atmosphere of 95% Ar and 5% H_2, employing heating and cooling rates of 2 K min^{-1}. An empty iron crucible with graphite insert served as reference. Unfortunately, the mass of the samples was relatively small compared with that of the crucibles themselves (approx. 5 g), which reduced the sensitivity of the measurements considerably. As a result, most thermal effects were rather weak, some of them too weak to be detected at all. Additionally, a number of effects were covered entirely by the peaks due to transformations in the crucible material itself, i.e. the magnetic transition at 770°C and the b.c.c. $\rightleftharpoons$ f.c.c. transformation at 912°C [10].

2.3. X-ray measurements

All samples in the section with a constant Mg content of 71 at.% were investigated by X-ray powder diffraction. They were finely powdered and annealed at 450°C for about three weeks. The phase composition of the samples and the corresponding lattice parameters were determined by a Guinier powder technique (Guinier-Huber camera, 57.3 mm radius) using $\text{Cu}_{K\alpha 1}$ radiation and pure germanium as an internal standard. A lattice parameter $a = 0.5657$ nm was obtained for germanium, which is in good agreement with the literature value of $a = 0.56574$ nm [11].

3. Experimental results

The results of the DTA measurements for the three isopleths with constant ratios x_{Cu}/x_{Ni} are shown in Figs. 2 to 4. Included in these diagrams are also the results for the corresponding compositions of the section with a constant magnesium content of 71 at.%, which are given separately in Fig. 5. The necessary information about the three binary systems was taken

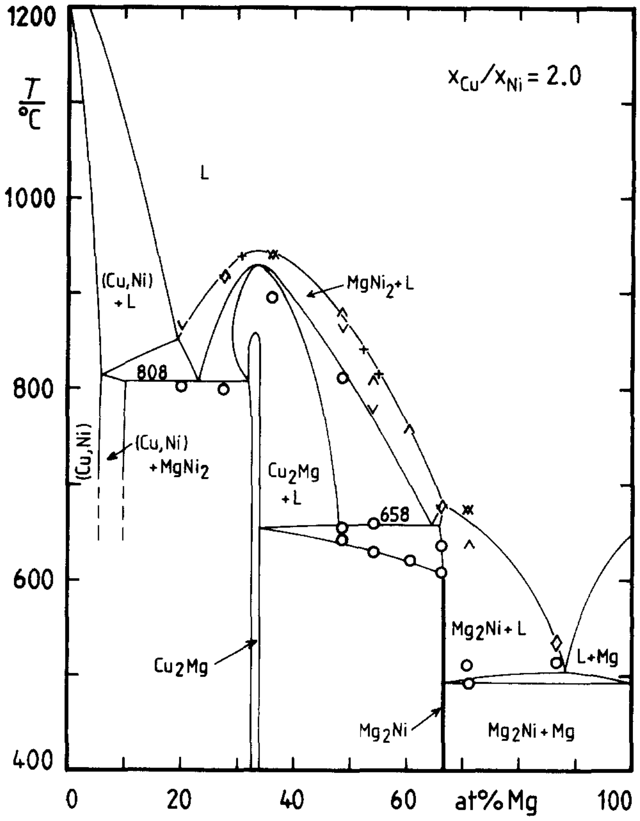

Fig. 2. Isopleth at constant ratio $x_{Cu}/x_{Ni} = 2.0$; ∧, ∨: liquidus on heating or cooling, resp.; ○: other thermal effects; +: phase boundary from isopiestic measurements [1].

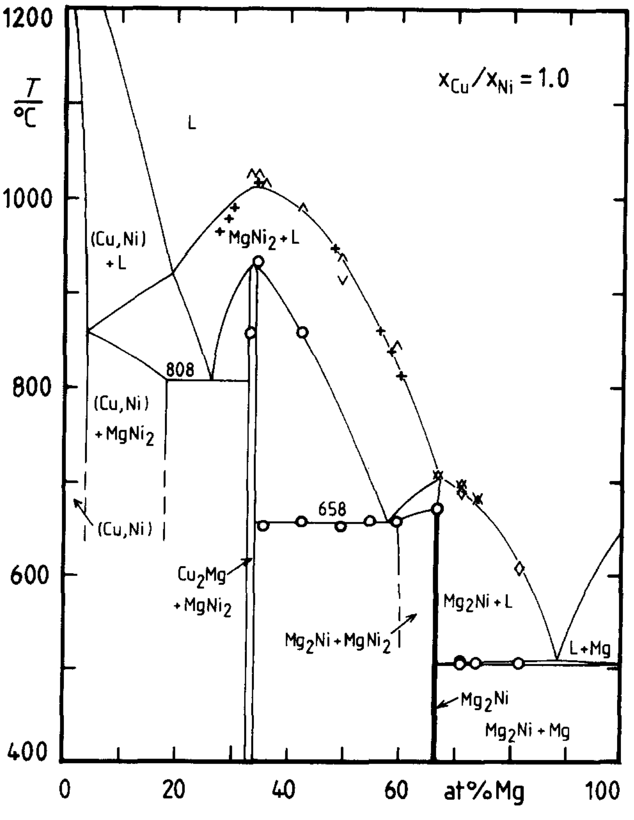

Fig. 3. Isopleth at constant ratio $x_{Cu}/x_{Ni} = 1.0$; symbols as in Fig. 2.

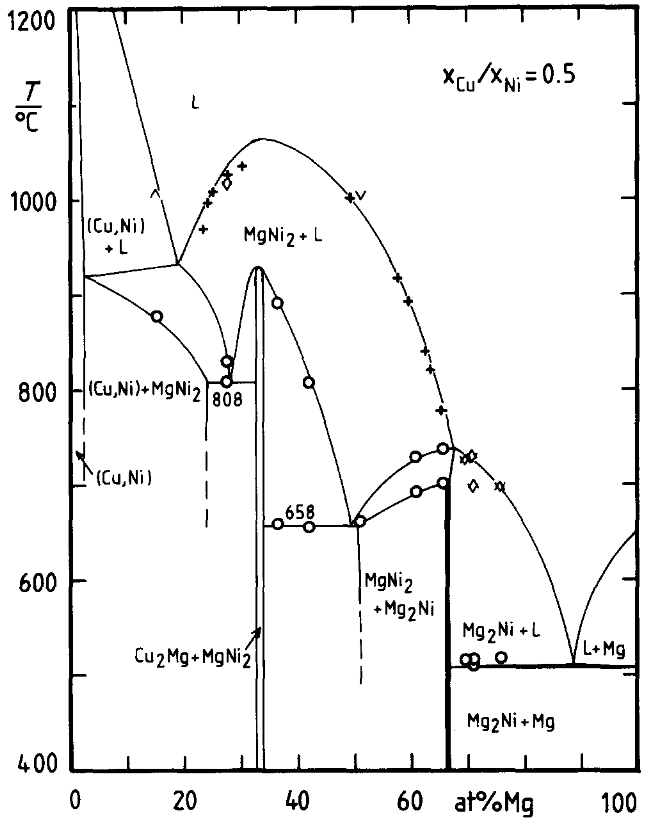

Fig. 4. Isopleth at constant ratio $x_{Cu}/x_{Ni} = 0.5$; symbols as in Fig. 2.

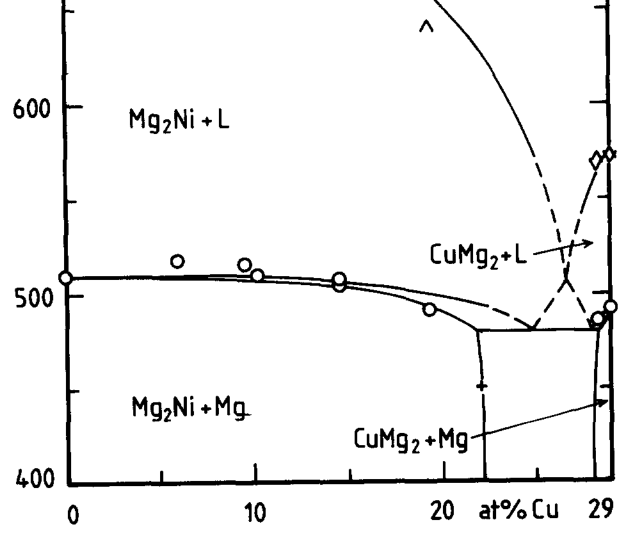

Fig. 5. Isopleth at constant magnesium content of 71 at.%; ∧, ∨: liquidus on heating or cooling, resp.; O: other thermal effects; +: phase boundary from X-ray measurements.

from the literature [9,10,12], including a recent evaluation of the binary Mg–Ni system by Jacobs [13].

The temperatures are estimated to be accurate within ±3°C; however, in some instances, where the thermal effects were rather weak (some of the liquidus effects) the uncertainty may be somewhat larger. The compositions of the isopiestic samples should be accurate within ±0.2 at.% [1], and those of the samples which were prepared separately within approx. ±1 at.%.

As already discussed in Section 1, valuable information on the phase diagram can be obtained from isopiestic vapour pressure measurements, where kinks in the so-called equilibrium curves are usually associated with phase boundaries. Table 2 gives a list of the corresponding data on the liquidus surface, which were obtained in the study by Gnanasekaran and Ipser [1]; the data points are also included in Figs. 2–4.

All diagrams (Figs. 2–5) were constructed in such a way that they are consistent with each other and also with the known phase diagrams of the limiting binary systems. In particular, it was checked whether the shown liquidus lines of the different isopleths would result in reasonable and consistent slopes for the ternary liquidus surface, and whether the troughs associated with three-phase equilibria would appear as smooth lines without any kinks in between the four-phase equilibria existing in the ternary Cu–Mg–Ni system. Fig. 6 shows a projection of these monovariant reaction lines in the Gibbs triangle. In addition it was ensured that all three-phase fields shown in Figs. 2–5 yield triangles with straight edges when plotted in an isothermal section. In all parts where our own results did not yield enough information, the diagrams were drawn so as to comply with previous literature results, especially from Refs. [2,6,7].

Fig. 7 shows the variation of the lattice parameters of the Mg_2Ni-phase with increasing copper content in

Table 2
Data points for the liquidus surface from isopiestic vapour pressure measurements [1]

$x_{Cu}/x_{Ni} = 2.0$		$x_{Cu}/x_{Ni} = 1.0$		$x_{Cu}/x_{Ni} = 0.5$	
T (°C)	at.% Mg	T (°C)	at.% Mg	T (°C)	at.% Mg
939	30.9	1017	34.2	1036	30.6
		991	30.0	1027	28.3
		979	28.8	1009	25.7
		964	27.5	997	24.5
				970	23.7
842	52.5	947	48.4	1002	49.4
817	55.2	861	56.5	917	57.9
		838	58.3	892	59.8
		814	60.0	840	62.8
				820	63.8
				778	65.7

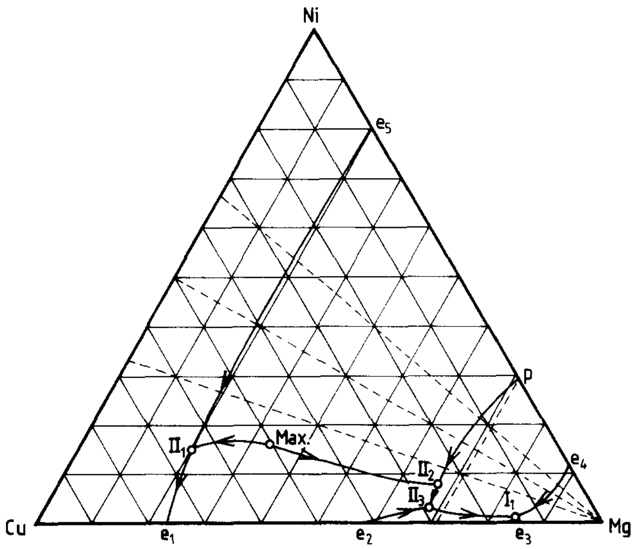

Fig. 6. Invariant four-phase equilibria and monovariant reaction lines in the liquidus surface of the ternary Cu–Mg–Ni system (the grid is in at.%); e_i, p: binary eutectic or peritectic, resp.; I_i, II_i: class I or class II four phase equilibrium, resp.; the dashed lines show the investigated sections.

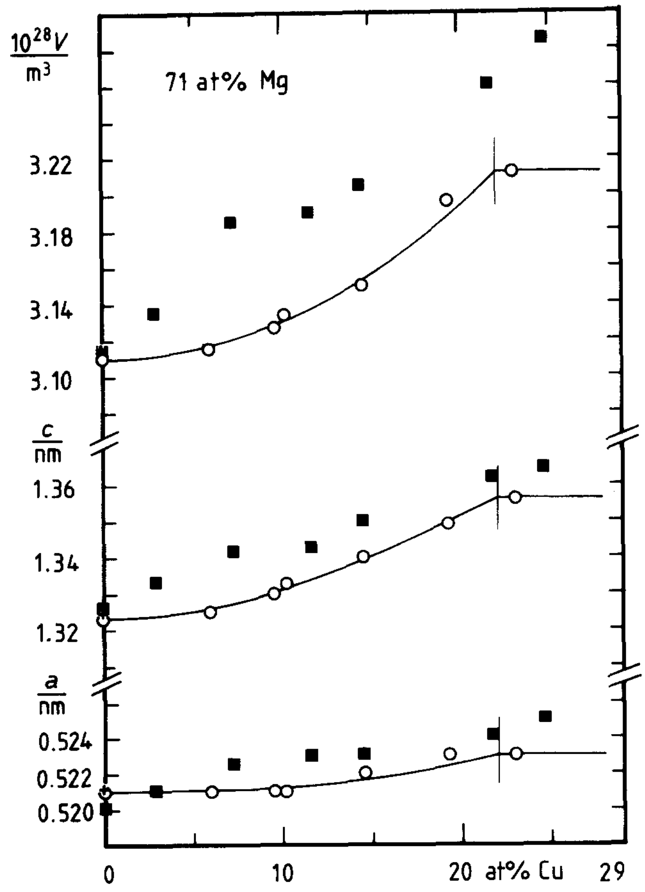

Fig. 7. Lattice parameters of the solid solution of Cu in Mg_2Ni for the section with 71 at.% Mg; ○: this study; ■: Darnaudery et al. [8] (the compositions were converted from 66.7 at.% Mg to 71 at.% Mg assuming an unchanged x_{Cu}/x_{Ni} ratio); +: value for pure Mg_2Ni according to Buschow [16].

the section with 71 at.% Mg. Values of the parameters a and c are estimated to be accurate within ±0.001 nm. It can be seen from Fig. 5 that a two-phase field ($Mg_2Ni + Mg$) extends from the binary Mg–Ni system into the ternary diagram; thus all values in Fig. 7 refer to the Mg_2Ni-phase saturated with magnesium. The sample with 23.0 at.% Cu showed the first signs of the $CuMg_2$-phase, corresponding to the three-phase field ($CuMg_2 + Mg_2Ni + Mg$). From this it can be concluded that the boundary between two-phase and three-phase fields is at about 22 at.% Cu (see Fig. 7). Extrapolating this phase boundary to 66.7 at.% Mg with the assumption that Mg does not dissolve any Cu or Ni (cf. Karonik et al. [7]), one obtains the limit of the solid solution of Cu in Mg_2Ni at approx. 25 at.% for a temperature of 450°C.

In the sample with 28.3 at.% Cu and 71 at.% Mg no signs of the Mg_2Ni-phase could be detected. The lattice parameters of the orthorhombic $CuMg_2$-phase were determined as $a = 0.9052$ nm, $b = 1.8216$ nm and $c = 0.5296$ nm, in good agreement with the values given by Runqvist et al. [14]. Our value refers again to $CuMg_2$ saturated with Mg.

4. Discussion

Four invariant reaction equilibria exist in the ternary Cu–Mg–Ni system, and the compositions of the participating liquids are labelled I_1 (class I four-phase equilibrium) and II_1 through II_3 (class II) in Fig. 6. Although the reaction sequence elaborated by Fehrenbach et al. [6] could be confirmed in the present study, some of the compositions of the phases involved in the invariant reactions (as summarized by Chang et al. [2]) had to be shifted.

Starting with the ternary eutectic I_1 at 480°C ($L \rightleftharpoons Mg_2Ni + CuMg_2 + Mg$), it is obvious that the reaction triangle has to be much smaller than given in Ref. [2], owing to the high solubility of copper in the Mg_2Ni-phase. From our results it is estimated that the liquid is in equilibrium with Mg_2Ni containing about 25 at.% Cu, $CuMg_2$ containing about 1 at.% Ni, and practically pure Mg, as listed in Table 3. These data are in good agreement with the results of Karonik et al. [7].

Our value for the solubility of Cu in Mg-saturated Mg_2Ni is somewhat less than that reported by Darnaudery et al. [8], who found approx. 28 at.% at 600°C. Although the width of the ternary Mg_2Ni-phase in terms of magnesium content seems to be rather small (less than 0.5 at.% according to Karonik et al. [7], in accordance with the negligible homogeneity range of the binary Mg_2Ni-phase [15]) it may be possible that strictly stoichiometric Mg_2Ni dissolves somewhat more copper. This may also be an explana-

Table 3
Approximate composition of the phases participating in four-phase equilibria

Reaction type	T (°C)	Phase	Composition		
			at.% Cu	at.% Mg	at.% Ni
I_1	480	L[a]	15	84	1
		Mg	0	100	0
		Mg_2Ni	25	67	8
		$CuMg_2$	32	67	1
II_1	808	L	65	20	15
		Cu_2Mg	45	32	23
		$MgNi_2$	5	32	63
		(Cu, Ni)	72	5	23
II_2	658	L	25	67	8
		$MgNi_2$	5	34	61
		Mg_2Ni	21	67	12
		Cu_2Mg	41	34	25
II_3	540	L	29	68	3
		Cu_2Mg[a]	65	35[b]	0
		Mg_2Ni	25	67	8
		$CuMg_2$	32	67	1

[a] Value taken from Chang et al. [2].
[b] Homogeneity limit of binary Cu_2Mg at 540°C according to Bagnoud and Feschotte [15].

tion for the noticeable deviation of our lattice parameter values from those reported by Darnaudery et al. [8] (cf. Fig. 7). Since our lattice constants of pure binary Mg_2Ni are in excellent agreement with values given by Buschow [16], it may be speculated that the width of this Mg_2Ni-phase increases somewhat with the dissolution of copper. Additionally, one has to consider the different annealing temperatures of 450°C (present study) and 600°C [8], which might be an additional reason for the difference in the lattice parameter values.

The temperature of the four-phase equilibrium I_1 (480°C) was taken from the literature [2], since the isopleths shown in Figs. 2-5 did not intersect it. It is not clear why the temperatures of our thermal effects in the composition range between 67 and 90 at.% Mg were several degrees higher than expected. Since the three-phase region ($Mg_2Ni + Mg + L$) starting from the binary eutectic in the Mg-Ni system at 510°C (according to our results) must move down to lower temperatures into the ternary system, finally touching the invariant reaction isotherm at 480°C, the corresponding three-phase fields were constructed in a corresponding way in all figures.

The temperature of the four-phase equilibrium II_3 at 540°C ($L + Cu_2Mg \rightleftharpoons CuMg_2 + Mg_2Ni$) was again taken from the literature [2], since the sections represented in Figs. 2-5 do not touch it. In view of the wide extension of the Mg_2Ni-phase into the ternary system, the corresponding reaction quadrangle must be rather narrow. Since no signs of this invariant reaction was found in the isopleth with $x_{Cu}/x_{Ni} = 2.0$ (cf. Fig. 2), the copper content of Mg_2Ni in equilibrium with $CuMg_2$ at 540°C must be higher than 22 at.%, probably somewhere between 22 and 25 at.%. According to the compilation by Chang et al. [2], the liquid phase is in equilibrium with practically pure binary Cu_2Mg; there are no results from the present study which would allow us to confirm or refute this.

The next four-phase reaction II_2 ($L + MgNi_2 \rightleftharpoons Mg_2Ni + Cu_2Mg$) takes place at 658 ± 3°C, and this temperature was obtained from the present DTA measurements. It agrees well with the value of approx. 650°C given in Ref. [2]. Again as a consequence of the high solubility of copper in Mg_2Ni, the shape of the corresponding reaction quadrangle must be different from that suggested by Chang et al. [2]. The compositions of the participating phases, estimated from the present results, are listed in Table 3. It appears that our data confirm a much lower solubility of Cu in $MgNi_2$ (roughly 5 at.% at temperatures between 658 and 930°C, compared with more than 25 at.% in the pseudo-binary diagram shown by Lieser and Witte [5]), as already previously suspected by Fehrenbach et al. [6].

One of the three-phase regions ($Cu_2Mg + MgNi_2 + L$) involved in the isothermal reaction II_2 extends to higher temperatures and finally degenerates into a single line at 33.3 at.% Mg and 930°C, corresponding to the pseudo-binary peritectic reaction $L + MgNi_2 \rightleftharpoons Cu_2Mg$. (The temperature was taken from Lieser and Witte [5].) With decreasing magnesium content the three-phase region opens up again and finally touches the four-phase equilibrium II_1 at 808°C ($L + MgNi_2 \rightleftharpoons (Cu,Ni) + Cu_2Mg$). All data pertinent to this latter invariant reaction were taken from Fehrenbach et al. [6]. The compositions of the participating phases are again listed in Table 3.

Nothing can be said about the width of the Cu_2Mg and $MgNi_2$-phases extending into the ternary system in terms of magnesium content. According to Bagnoud and Feschotte [15], binary Mg_2Ni has a considerable range of homogeneity of up to 3 at.% depending on temperature, whereas the width of Cu_2Mg never exceeds 1 at.%. In our isopleths, the width of the single-phase field Cu_2Mg (Fig. 2) and of the two-phase field ($Cu_2Mg + MgNi_2$) (Figs. 3 and 4) is given schematically with approx. 2 at.%, i.e. from 32 to 34 at.% Mg, independent of temperature.

Although many details of the ternary Cu-Mg-Ni phase diagram have not been touched by the present investigation and many parts of the diagram are shown in a more or less schematic way, it is still hoped that this contribution increases the knowledge of the ternary Cu-Mg-Ni system. Together with the thermodynamic study by Gnanasekaran and Ipser [1] it should provide a sound basis for the development of any higher order technical light alloys based on the three elements copper, magnesium, and nickel.

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