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The constitution of Cu-Ni-Mg alloys

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The location of the monovariant eutectic trough extending from the binary eutectic Cu-Cu_2Mg into the Cu-Mg-Ni ternary alloy system has been established for alloys containing up to 25 at.% Ni. Liquidus and solidus temperatures along this eutectic trough were determined by thermal analysis. Microscopic and electron microprobe analyses confirm the existence of a peritectic reaction in the Cu_2Mg-Ni_2Mg quasibinary system and establish its participation in the ternary system. The foregoing, together with data from earlier literature, allow the equilibrium phase relationships for the entire Cu-Mg-Ni ternary system to be estimated.

1. Introduction

Many binary eutectics have been unidirectionally solidified to obtain structures with composite mechanical behaviour. More recently, ternary components have been added to binary eutectic alloys to modify the volume fractions and mechanical properties of the different phases in the microstructure. To study the effect of ternary additions one would like to work with systems in which the eutectic microstructure is retained over large ranges of ternary additions. This should occur in systems like copper-magnesium where it appears that the addition of nickel leads to a monovariant eutectic trough which connects the binary Cu_2Mg and Ni_2Mg eutectics. Therefore this phase diagram investigation of the copper-rich corner of the Cu-Mg-Ni ternary alloy system was undertaken to aid the interpretation of solidification microstructures of monovariant Cu-Cu_2Mg eutectic alloys. The alloy compositions and corresponding liquidus and solidus temperatures along the eutectic trough from the Cu-Cu_2Mg binary eutectic up to alloys containing 25 at. % Ni were of primary concern.

Available literature concerning this system is contradictory. From their liquidus surface determination, Mikheeva and Babayan [1] postulate a continuous monovariant eutectic trough extending between the Ni-Ni_2Mg and Cu-Cu_2Mg binary eutectics and predict a corresponding complete series of solid solutions in the Cu_2Mg-Ni_2Mg quasibinary system. Koster [2] also found the monovariant eutectic trough to be continuous across the system. X-ray data by Lieser and Witte [3] however, show that the crystal structures of Cu_2Mg and Ni_2Mg are not isotypic, making the formation of a complete series of solid solutions impossible. Cu_2Mg has a face-centred cubic crystal structure of the type C16 while Ni_2Mg is hexagonal with a C36 type crystal structure. In addition, the investigation by Lieser and Witte indicated a peritectic reaction in the Cu_2Mg-Ni_2Mg system. Also, the composition of the binary eutectic between Cu and Cu_2Mg as reported by Mikheeva and Babayan is at variance with that reported by Hansen [4].

2. Experimental procedure and results

Materials used in this investigation had the following purity: Cu-99.95, Mg-99.99, Ni-99.95.

2.1. Thermal analysis

175 g ingots were induction melted under flux in a well insulated graphite crucible. The melts were held at approximately 1000°C for 10 to 15 min and then cooled at rates of approximately 2°C/min. A continuous recording of temperature versus time was made from the output of a graphite sheathed thermocouple located near the centre of the ingot. Each thermocouple was calibrated by taking a cooling curve from a Cu-Cu_2Mg binary eutectic ingot.

Because the alloy compositions along the eutectic trough were not well established, the ingots for thermal analysis were prepared to be magnesium rich with respect to the eutectic

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compositions determined by Mikheeva and Babayan [1]. The cooling curves from each of these ingots therefore exhibited an inflection point due to primary solidification of Cu_2Mg as well as an inflection point at the temperature at which the melt became doubly saturated in α and Cu_2Mg. Alloy compositions along the eutectic trough were determined by adding known weights of copper to each ingot until only one liquidus inflection point was observed. Analysis for nickel by atomic absorption spectroscopy was performed on the ingots and in every case there was close agreement with the prepared compositions (Table I).

TABLE I Ingot compositions and liquidus and solidus arrest temperatures

Ingot composition (at. %)				Thermal arrests (°C)	
Cu	Mg	Ni	Ni*	Liquidus (average)	Solidus
75.97	21.68	2.35	2.36	736.7	728
73.59	21.65	4.76	4.92	758.8	743.5
71.82	20.92	7.26	7.23	775.7	750
69.82	20.85	9.33	9.56	786	756
67.93	20.56	11.51	11.57	794	767.5
63.29	20.28	16.43	16.16	818	781.5
63.33	18.87	17.8	18.0	829	794.5
58.86	19.61	21.53	21.28	840.6	808.5
57.79	18.99	23.22	23.36	844.9	807.5
56.18	18.84	24.98	not analysed	848	809

*Determined by atomic absorption spectroscopy.

Once the alloy composition was determined to be on the eutectic trough, several additional heating and cooling curves were recorded. The solidus inflections observed in these heating and cooling curves were not well defined due to the solidification segregation occurring even at cooling rates of 2°C/min. To overcome this effect, the solid ingots were homogenized under argon for 70 h at 700°C, after which a heating curve was recorded. The only solidus data appearing in Table I is from the heating curve after the homogenization treatment. In all cases homogenization sharpened the solidus inflection in the heating curves.

After the final cooling curve was obtained, each ingot was quenched from just below the solidus temperature.

2.2. X-ray analysis

X-ray diffractometer specimens of size $1 \times \frac{1}{2} \times \frac{1}{8}$ in. were cut from the centre plane of the ingots, ground flat, annealed for 20 min at 350°C and electrolytically polished. Diffractometer traces were obtained, using CuKα radiation with a Ni filter, over 2θ angles from 20° to 95°. The diffraction peaks observed were matched to diffracting planes in Cu, Cu_2Mg and Ni_2Mg through the ASTM Index to the Powder Diffraction File and lattice parameters were calculated from each peak.The matching of peaks to the diffracting planes in Cu and Cu_2Mg as the nickel content varied was made easier by starting with a "pure" Cu-Cu_2Mg eutectic specimen and following the 2θ angles with increasing nickel concentration. Averaged lattice parameters of the Cu-Ni solid solution (hereinafter termed α) and Cu_2Mg are shown in Table II. Measured lattice parameters for the Ni_2Mg phase are also included.

TABLE II Lattice parameters of the phases occurring along the monovariant eutectic trough

Bulk alloy composition at. % Ni	α-phase a(Å)	Cu_2Mg phase		Ni_2Mg phase	
		a(Å)	Ni content* at. %	a(Å)	c(Å)
0	3.634	7.029	0	—	—
2.36	3.662	6.999	7.8	—	—
4.92	3.655	6.995	9.0	—	—
7.23	3.650	6.986	11.8	—	—
9.56	3.648	6.979	13.9	—	—
11.57	3.645	6.966	16.4	—	—
16.16	3.638	6.954	20.0	4.92	15.79
18.0	3.635	6.958	19.3	4.93	15.98
21.28	3.632	6.950	21.1	4.90	15.84
23.36	3.631	6.933	25.4	4.91	15.68

*From data by Pearson [8].

2.3. Microscopic examination

Microscopic examination of the slowly cooled samples showed considerable segregation due to solidification (Fig. 1). Therefore, these slowly cooled samples were homogenized for 70 h at 700°C. Precipitation of Cu_2Mg in α was observed after homogenization in all samples but was most evident in samples containing more than 7 at. % Ni.

In samples containing more than 16 at. % Ni, small amounts of a third phase were present (Fig. 2). This phase always had a dendritic morphology and was identified by electron microprobe analysis and X-ray diffraction to be Ni_2Mg. Additional alloys containing 35 at. % Ni,

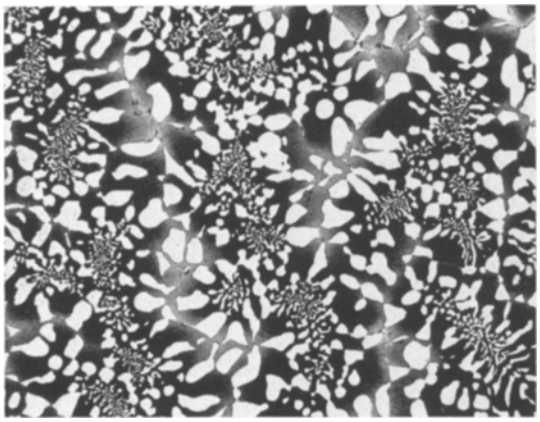

Figure 1 10 at. % Ni alloy slowly cooled ($\times$ 60). α appears white, Cu_2Mg is the grey-black phase.

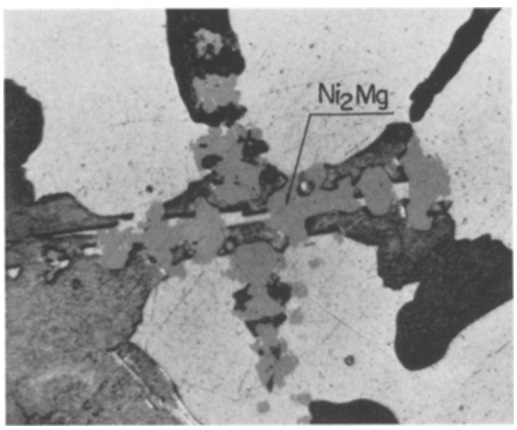

Figure 2 Typical dendritic morphology of Ni_2Mg in the 25 at. % Ni alloy ($\times$ 380).

48 Cu, 17 Mg and 46 at. % Ni, 39 Cu, 15 Mg and homogenized at 800° C for 70 h also consisted of three phases: α, Cu_2Mg and Ni_2Mg. The results of microprobe analysis on the Ni_2Mg phase in homogenized alloys indicated a copper content of between 3 and 7 at. % and a nickel concentration of 63 at. %.

Microscopic examination also revealed that slowly cooled Cu-Cu_2Mg binary eutectic alloys of the composition reported in [4] consisted solely of the eutectic microstructure.

3. Discussion of results

3.1. The Cu-Cu_2Mg-Ni_2Mg-Ni region

Because the quasibinary system Cu_2Mg-Ni_2Mg divides the Cu-Ni-Mg ternary system into two partial systems [1], phase relationships in the section shown in Fig. 3 may be considered independently. Fig. 3 includes the relevant binary [4] and quasi binary [3] phase equilibrium relationships. The data points locating the position of the monovariant eutectic trough running from the Cu-Cu_2Mg eutectic are also shown in this figure.

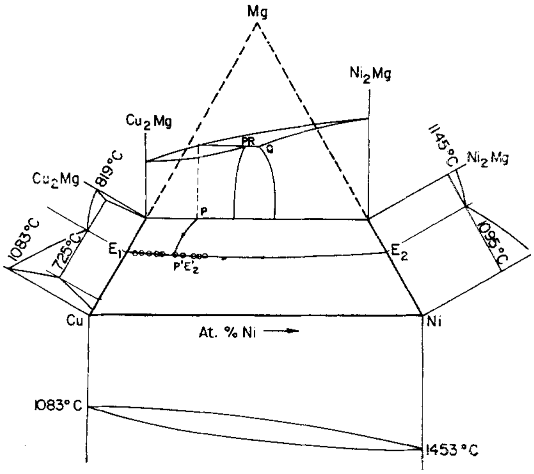

Figure 3 Lower half of Mg-Cu-Ni system.

It is a well established principle [5-7] that the liquidus points of eutectic and peritectic reactions in participating binary systems must move into the ternary system. This gives rise to a network of troughs or breaks on the ternary liquidus surface.

Fig. 4 is a plot of the liquidus and solidus lines determined by thermal analysis along the eutectic trough extending from the Cu-Cu_2Mg eutectic. The experimental scatter in the liquidus temperature determinations are shown in this figure. Since the liquidus temperatures increase as the trough proceeds into the ternary system, the Cu-Cu_2Mg eutectic is established as the composition of lowest freezing temperature in this portion of the ternary phase diagram, ruling out the possibility of a ternary eutectic. This implies that the monovariant eutectic trough extending from E_2 (Fig. 3) and the break in the liquidus surface extending from the quasibinary peritectic point P meet at point $P'E'_2$ from which the monovariant eutectic trough extends to the Cu-Cu_2Mg binary eutectic E_1. At point $P'E_2'$ (at 808°) a four-phase invariant reaction occurs in which liquid reacts with Ni_2Mg to form α + Cu_2Mg. Below this temperature a eutectic trough and associated three-phase (liquid + α + Cu_2Mg) region will move from the intersection point $P'E_2'$ to the Cu-Cu_2Mg binary eutectic, leaving behind a solid

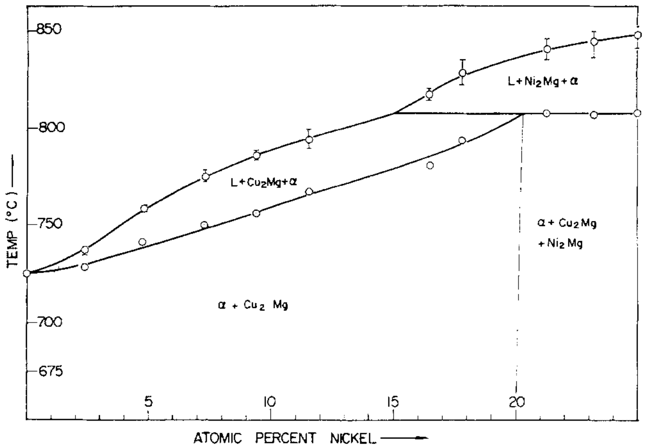

Figure 4 Plot of liquidus and solidus along the eutectic trough up to 25 at. % Ni.

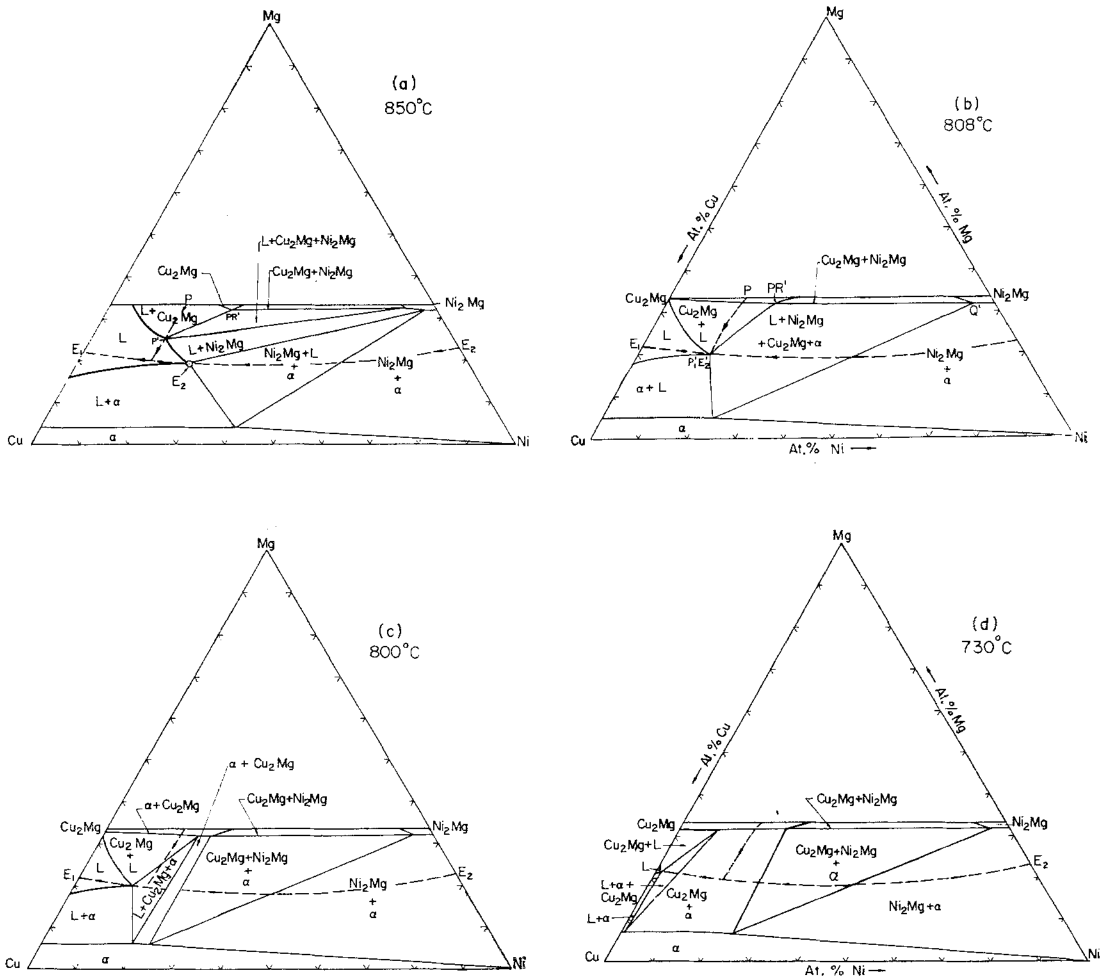

Figure 5 Isothermal sections at (a) 850°C; (b) 808°C; (c) 800°C; (d) 730°C.

phase region of α + Cu_2Mg + Ni_2Mg on the phase diagram. The situation is illustrated by a series of isothermal sections (Fig. 5). In these sections the monovariant eutectic troughs and peritectic break in the liquidus surface are shown projected on each section as dashed lines. Phase boundaries are drawn as far as possible in accordance with the four vertical sections shown in Fig. 4, the liquidus surface as determined by Mikheeva, and experimental data from this study.

The progress of the point of maximum solubility of copper in Cu_2Mg with increasing nickel content is shown in Fig. 6, assuming a constant magnesium concentration. Experimental points on this curve are a combination of X-ray data and thermal analysis data. The nickel content of the Cu_2Mg phase (Table II) was determined by matching the lattice parameter data for this phase in each ingot against a curve of the lattice parameter of Cu_2Mg versus nickel concentration [8].

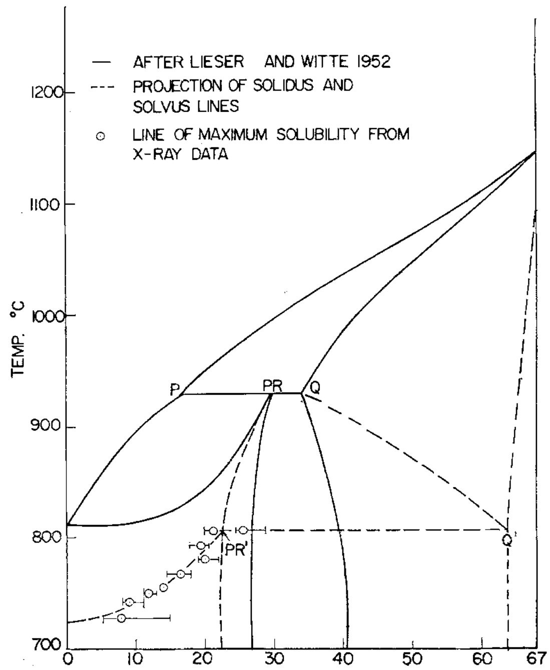

Figure 6 Quasibinary section from Lieser and Witte including data points for maximum copper solubility versus nickel.

Each experimentally determined composition of Cu_2Mg is plotted at its solidus temperature and is projected onto the Cu_2Mg-Ni_2Mg quasibinary plane in Fig. 6. These experimental points must be viewed as approximations because of the large scatter with respect to nickel concentrations and the uncertainty of the exact copper and magnesium concentrations in the Cu_2Mg phase. The maximum nickel content in the Cu_2Mg phase along the eutectic trough is represented by PR′ (Fig. 5b), and is located in Fig. 6 between two experimentally determined compositions from alloys having the same solidus temperatures. Several factors may contribute to this apparent variation in composition, but we have not experimentally differentiated between these possibilities.

Alloys on the trough containing more nickel than composition P_1' E_2' (Fig. 5b) will form the Ni_2Mg phase during solidification. The maximum copper content in this phase from such alloys is represented by Q′ (Figs. 5b, and 6), and at 808° C this phase should react with the liquid to form Cu_2Mg of composition PR′.

The phase boundaries between Ni_2Mg and the two-phase Cu_2Mg + Ni_2Mg region are also shown as dashed lines, both in Fig. 6 and in the isothermal sections. Both the microprobe data from alloys containing Ni_2Mg and the fact that alloys at 35 and 42 at. % Ni are three phase, indicate considerably less solubility of copper in Ni_2Mg than reported by Lieser and Witte [3]. These phase boundaries are drawn in accordance with experimental data from this study.

All of the experimental data support the foregoing phase equilibrium relationships. Both metallographic and X-ray data showed the presence of Ni_2Mg in alloys along the eutectic trough containing greater than 16 at. % Ni. In view of the dendritic nature (Fig. 2) of this phase, it is undoubtedly formed from the melt. The reason for its existence in alloys, which according to the phase equilibrium relationships discussed above should only have contained α and Cu_2Mg, can be ascribed to the sluggishness of the peritectic reaction. The interaction between the liquid and Ni_2Mg undoubtedly soon results in the coating of Ni_2Mg by α and Cu_2Mg, so that further reaction is limited by solid state diffusion either through these phases or along the interfaces between them. This would explain why the peritectic arrest was not observed on cooling curves for alloys containing between 15 and 20 at. % Ni. The absence of such arrests is explained also by the similarity of the Ni_2Mg and Cu_2Mg phases [3] as well as the continuing presence of a significant amount of α phase which would also tend to minimize the thermal effects.

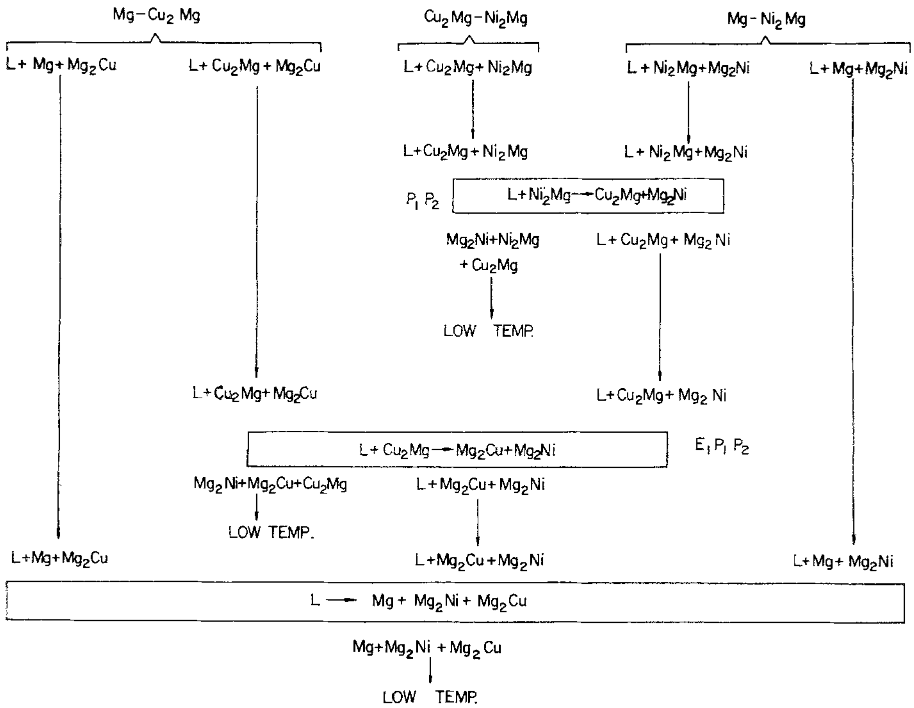

Figure 7 Sequence of reactions in the Mg-Cu_2Mg – Ni_2Mg system.

3.2. The Cu_2Mg-Mg-Ni_2Mg region

Consideration of the remainder of the ternary diagram, keeping in mind the existence of a peritectic in the Cu_2Mg-Ni_2Mg quasibinary system, must lead to a different interpretation of the liquidus surface data by Mikheeva and Babayan and of that by Koster. Using data from the relevant binary [4] and quasibinary [3] systems, and assuming that no ternary compounds are formed, a probable sequence of reactions can be established as shown in Fig. 7. This involves two four-phase invariant reaction planes and one ternary eutectic reaction plane. The network of monovariant reaction lines on the liquidus surface shown in Fig. 8 is drawn to be consistent with the liquidus surface data by Mikheeva and Babayan. Fig. 9 illustrates the resulting phase equilibrium relationships at a temperature just below that of the ternary eutectic (480° C) [1]. The postulated interactions between the monovariant eutectic systems L + Cu_2Mg + Mg_2Cu and L + Cu_2Mg + Mg_2Ni, and the monovariant system L + Mg_2Ni + $MgNi_2$ originating at the peritectic point near Mg_2Ni, result in the formation of two three-phase fields as shown. One reason for these regions not being observed in previous studies is the apparent difficulty in distinguishing between Mg_2Cu and Mg_2Ni [2]. The ternary eutectic and corresponding three-phase field, Mg + Mg_2Ni + Mg_2Cu, would coincide with that determined in [1].

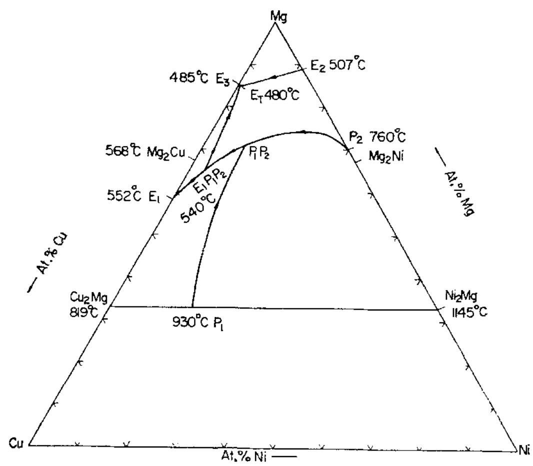

Figure 8 Liquidus surface in the Mg-Cu_2-Mg – Ni_2Mg system.

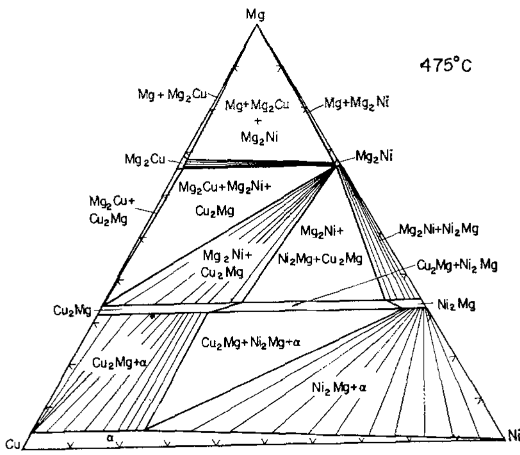

Figure 9 Isothermal section of Mg-Cu-Ni system at 475 °C.

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