alkyl nitrite as compared to the alkoxyl radical. This factor is apparently offset by the much lower activation energy of (6). Step (6) is probably accompanied by the reaction suggested by Rice and Rodowskas

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O \qquad (7)$$

Since (6) is bimolecular and (7) is unimolecular, it will be seen that lower pressures will favor (7) and the yield of ethyl alcohol and acetaldehyde as compared to formaldehyde would depend on the pressure and temperature. Since as mentioned earlier the infrared spectrum of the products in expt. 11 indicates that little acetaldehyde was formed, it appears that at these pressures and at this temperature (7) predominates over (6). In the other extreme, the pyrolysis of 2-octyl nitrite in the liquid phase, the high yield of alcohol and ketone is consistent with the relatively high concentration of alkoxyl radicals.

Rice and Rodowskas have written as a further reaction of the methyl radical

$$CH_3\cdot + CH_3CH_2ONO \longrightarrow CH_4 + CH_3\underset{\cdot}{\overset{H}{C}}ONO \qquad (8)$$

Since in expt. 11 and 12 there was no induced decomposition of the ethyl nitrite, it appears that here the true fate of the methyl radicals is

$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (9)$$

This result is similar to one found by Rebbert and Laidler in the diethyl peroxide decomposition. Despite the presence of a large excess of toluene the major product was ethane and only small amounts were found of methane and dibenzyl, products of

$$CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2\cdot$$
$$2C_6H_5CH_2\cdot \longrightarrow C_6H_5CH_2CH_2C_6H_3$$

The presence of carbon monoxide in the products can be explained here, as it was in the case of diethyl peroxide,[3,4] on the basis of a radical-induced decomposition of the aldehydes.

It thus appears that a satisfactory picture of the alkyl nitrite decomposition is represented by equations (1), (6), (7) and (9) with the sequence (1), (6) predominating at higher pressures and (1), (7), (9) taking over at lower pressures.

In other reactions where ethoxyl radicals are involved, *e.g.*, the decompositions of diethyl peroxide and ethyl nitrate[6,8] the tendency has been to write mechanisms involving steps like step (2). It seems quite likely that ethyl nitrate and diethyl peroxide are not particularly good chain breakers and that steps like step (6) and (7) are more important.

NOTE ADDED IN PROOF.—Style and Mortlock[9] have recently reported the formation of ethyl nitrite from diethyl peroxide–nitric oxide mixtures at room temperature. To check this apparent discrepancy with the results reported here, two bulbs were filled with mixtures similar to that of experiment 8, Table I. Both bulbs were kept at room temperature in the dark for a week. Examination of the contents of one at that time showed only the original components present and no ethyl nitrite. The other was then heated for six minutes at 181° and gave the same results as reported for experiment 8. In a private communication, Dr. Style suggests that the formation of ethyl nitrite in his and Mortlock's work may be due to catalysis by quite special surfaces. He also suggests the possibility of a photochemical reaction in a part of the apparatus which was exposed.

Acknowledgment.—The author would like to take this opportunity to express his thanks to Mr. Archie E. Davis for his valuable assistance in carrying out out these experiments, to Dr. Robert M. Talley and Mrs. Marion B. Glickman, of the Physics Research Department, for making available a Perkin-Elmer Model 21 Infrared Spectrometer, and to Mr. Thurman E. Spriggs of the same department for carrying out the mass spectrographic analysis of the diethyl peroxide.

(8) L. Phillips, *Nature*, **165**, 564 (1950)

(9) D. W. G. Style and H. N. Mortlock, *ibid.*, **170**, 706 (1953).

SILVER SPRING, MD.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Ferromagnetic Alloys in the System Copper–Manganese–Indium

BY ROBERT R. GRINSTEAD AND DON M. YOST

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An investigation of the copper-rich portion of the ternary ferromagnetic alloy system copper–manganese–indium has been made using thermal, microscopic and magnetic methods. Approximate limits of the α- and β-phases have been determined, and appear to be extensions of the corresponding α- and β-phases in the copper–indium system. The single-phase β region does not include the point Cu_2MnIn. Ferromagnetic Curie temperatures were obtained for the alloys as prepared, after quenching from solidus temperatures and after subsequent aging at 100°. For freshly quenched alloys the highest Curie temperatures, between 250 and 300°, were found in the vicinity of the Cu_2MnIn composition. Aging any of the alloys at 100° generally increased the Curie temperature, probably because of ordering of the structure.

The existence of ferromagnetism in the ternary alloy system copper–manganese–indium has been previously reported by several workers.[1-4] Ferromagnetic alloys composed of copper and manganese, with Al or Sn as the third metal, have been known for some time,[5] and it is found in each case that these properties are associated with a phase possessing an ordered body-centered cubic lattice.[6,7] It is also found that the largest value of magnetic

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(1) S. Valentiner, *Naturwissenschaften*, **4**, 123 (1947).

(2) F. A. Hames and D. S. Eppelsheimer, *Nature*, **162**, 968 (1948).

(3) B. R. Coles, W. Hume-Rothery and H. P. Myers, *Proc. Roy. Soc.* (*London*), **A196**, 125 (1949).

(4) R. R. Grinstead and D. M. Yost, *Phys. Rev.*, **75**, 984 (1949).

(5) Fr. Heusler, W. Stark and E. Haupt, *Verh. deuts. phys. Ges.*, **5**, 219 (1903).

(6) A. J. Bradley and J. W. Rogers, *Proc. Roy. Soc.* (*London*), **144**, 340 (1934).

(7) L. A. Carapella and R. Hultgren, Metals Technology, T. P. 1405 (Oct. 1941).

moment per atom is possessed by the alloy with composition Cu_2MnAl[8] or Cu_2MnSn,[7] where the atomic ratios are such as to permit complete ordering of the structure.

In the case of the Cu–Mn–In alloys the same situation appears to exist. Most of the work reported thus far has concerned only the alloys containing the metals in the approximate ratios Cu: Mn: In = 2:1:1, but it has been shown that these alloys, which exhibit magnetic properties, also have an ordered body-centered cubic structure.[1,3,9]

In the present paper are described the results of thermal and magnetic studies which were undertaken for the purpose of obtaining information about the rest of the Cu–Mn–In system. In view of the above mentioned relation between magnetism and structure it was decided at the start of this work that a study of this system would be most profitably begun with an investigation of the phase equilibria involved. Consequently, the work reported here deals mainly with liquid–solid equilibria and the equilibrium regions of phases in the copper-rich portion of the ternary equilibrium diagram.

Nearly 50 alloy specimens were prepared and cooling curves of them were recorded in the region of liquid–solid equilibrium. Most of the alloys were subsequently annealed at temperatures just below the solidus, quenched and examined under the microscope in order to obtain additional information about the equilibria at these temperatures. As a simple means of observing and indicating the existence of magnetism ferromagnetic Curie points of the alloys were determined, both before and after the heat treatment.

Apparatus, Materials and Procedure

Thermal Measurements.—Metallic indium of 99.97% purity was obtained from A. D. Mackay and Co. of New York and from the Indium Corporation of America. Manganese of purity greater than 99.9% was obtained from the U. S. Bureau of Mines, and copper wire was obtained from the Malin Wire Company. Purity of all three metals was checked by chemical analysis and found to be at least 99.9% in all cases.

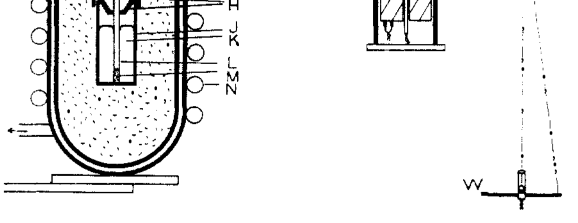

Fig. 1.—Left, vertical cross-section of induction melting and cooling curve system; right, plan view of Curie temperature apparatus.

All alloy specimens were prepared by melting 50-g. charges of the metals under argon in an induction furnace, using a Westinghouse 10 KW R.F. generator as a source of power. The furnace, shown in Fig. 1, was similar to that described by Van Dusen and Dahl.[10] The furnace was enclosed in a 60 mm. Pyrex tube E, to which a Pyrex plate A was fixed with wax. A side-arm provided connection to vacuum and argon sources. Power was applied through a coil of $^3/_8$ inch copper tubing N, through which was circulated cooling water. An inner Pyrex tube F held the crucible J, alloy K and thermowell L, which were surrounded with zirconia packing G. Alundum extraction thimbles were used as crucibles, and, except for small losses due to porosity of the walls, proved to be quite satisfactory. The thermocouple protective tubing was of an alumina–silica composition, and was closed off at one end by magnesia packing M. Two alundum forms H served to retain the thermowell in a vertical position. A refractory tube D served as a packing retainer. Three mica "doughnuts" B and two Pyrex spacers C served as radiation and convection shields, to reduce heat losses.

Temperatures were measured with chromel–alumel thermocouples which had been calibrated with a Pt to Pt-Rh couple. The latter had been calibrated at the freezing points of zinc, lead and antimony. At first thermal e.m.f.'s were measured with a Leeds and Northrup type K potentiometer; later a Brown recording potentiometer was obtained, with which cooling curves were drawn automatically. Temperatures thus obtained and recorded were considered accurate to ±3°.

Two meltings were used to prepare an alloy. After the first melting the alloy was removed from the furnace, ground up and remelted. Chemical analyses of the top and bottom of each alloy were subsequently made, the alloy being accepted as homogeneous if the two analyses agreed to about 0.5% of the total weight.

After the second melting the induction generator power was reduced and the sample was allowed to cool at the rate of about 10° per minute while time and thermal e.m.f. readings were taken. Observations were continued through the region of solidification.

Upon completion of the cooling runs the specimens were cooled to room temperature in about 2 hours, crushed as finely as possible and annealed under argon in an electric furnace for at least 24 hours. The annealing temperature varied from sample to sample and was below and close to the solidus temperature of the particular alloy under treatment. By examining under the microscope alloys which had been annealed for varying lengths of time it was determined that in 24 hours at temperatures of 500 to 700° equilibrium with respect to structural rearrangement had been reached. Control of annealing temperatures to ±2° was accomplished with a chromel–alumel thermocouple in conjunction with the Brown potentiometer. At the end of the annealing period the alloys were quenched by allowing them to drop directly from the furnace into cold water. Due to the small particle size quenching was extremely rapid. Larger pieces of the quenched alloy were mounted in lucite, polished, etched and examined under a microscope. Photomicrographs of most of the specimens were made. In connection with the magnetic measurements the quenched alloys were further heat-treated by aging them in an oven at 100° for periods of 200 to 300 hours.

Magnetic Measurements.—Ferromagnetic Curie points of the specimens were determined in an apparatus, a plan view of which is shown in Fig. 1. The method was essentially that of Ewing,[11] in which a magnetometer needle was used to indicate the strength of the magnetic induction in the sample. The specimen S and a thermocouple T were placed within a copper tube R, on which was wound a heating element. The furnace was surrounded by magnesia insulation Q and placed inside the magnetizing solenoid P. A second solenoid U was placed opposite the first, so that at the magnetometer V the fields due to the two coils just cancelled each other.

By placing the specimen on an east–west line, so that the

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[8] O. Heusler, *Ann. d. Physik*, **19**, 155 (1934).

[9] F. A. Hames and D. S. Eppelsheimer, *J. Metals*, **185**, 495 (1949).

[10] M. S. Van Dusen and A. I. Dahl, *Bur. Stds. J. Research*, **39**, 291 (1947).

[11] J. A. Ewing, "Magnetic Induction in Iron and Other Metals," the Electrician Publishing Co., London.

direction of its field at the magnetometer was at right angles to the earth's field, the deflection of the light beam on the scale W was directly proportional to the intensity of magnetization of the specimen.

By heating the alloy in a constant magnetic field, meanwhile recording temperature and needle deflection, curves similar to the one shown in Fig. 2 were obtained. The Curie temperature was taken as that temperature where a linear extrapolation from the point of maximum slope crossed the horizontal null line. A normal temperature-deflection curve is shown in Fig. 2A. Curve B represents an alloy with two Curie points, due to the presence of two different magnetic phases. In the cases where a Curie point below room temperature is indicated the alloy was immersed in liquid air and its subsequent effect on the magnetometer needle noted qualitatively. Curie point determinations were carried out for alloys in the as-prepared state, after the high-temperature anneal and quench, and after aging at 100°.

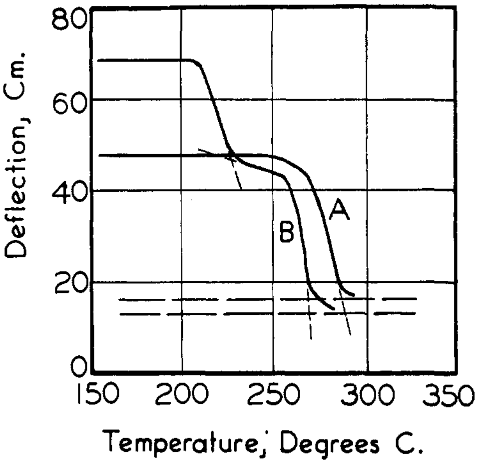

Fig. 2.—Typical temperature–magnetometer deflection curves; curve A, alloy A49, annealed at 507° 22 hours, quenched and reannealed at 100° 14 days; curve B, alloy A24, as prepared.

Chemical Analyses.—All samples were chemically analyzed to ensure homogeneity and to determine their exact composition. In most cases only copper and manganese were determined directly, the indium content being obtained by difference. Indium analyses were made in only a few cases as a check.

The sample was dissolved in 16 N HNO_3, and $KClO_3$ was added to precipitate the Mn as MnO_2. After filtering, Mn was determined by titrating the MnO_2 precipitate iodometrically.[12] When indium was to be determined the filtrate was neutralized with NH_3 and the indium hydroxide precipitate filtered off, ignited and weighed as In_2O_3. When the indium analysis was omitted the filtrate from the MnO_2 precipitation was partially neutralized and the copper titrated iodometrically. The compositions thus determined are believed accurate to ±0.5%.

Results and Discussion

Thermal and Metallographic Results.—Cooling curves of two representative alloys are shown in Fig. 3. Under the microscope A 40 appeared to be a single phase alloy after quenching. This conclusion was confirmed by the appearance on the curve of an arrest at the liquidus temperature and a break or end-point at the solidus temperature. In the case of A 17, which was a two-phase alloy in the solid state, two arrests occur on the cooling curve, corresponding to the successive appearance of two solid phases. An end-point indicates the temperature at which the liquid phase disappeared on cooling, leaving a solid two-phase alloy. It can be seen from an inspection of the cooling curves that selection of the temperature corresponding to an arrest was a relatively simple matter. End-point temperatures may be in error by several degrees C., however, since the location of the point of inflection corresponding to resumption of the original cooling rate was usually somewhat in doubt.

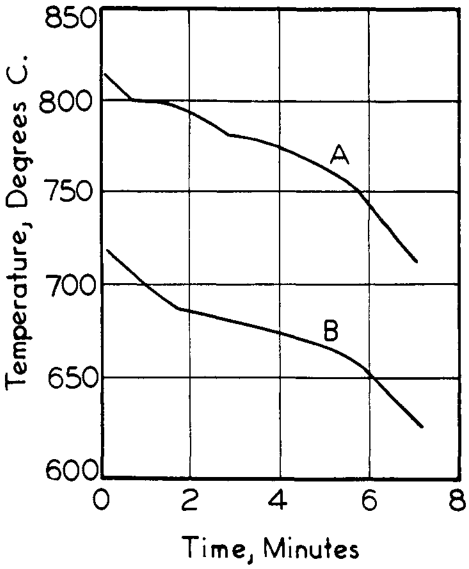

Fig. 3.—Typical cooling curves; curve A, alloy A17; curve B, alloy A40.

In Fig. 4 are shown the alloy compositions which were prepared and studied. Thermal analysis data appear in Table I and liquidus temperatures (column 5 in Table I) have been used to construct contours of the surface of primary crystallization, in Fig. 4. Alloys 60, 63 and 66 have not been included in Fig. 4, since they were investigated only briefly, as possible guides to further research.

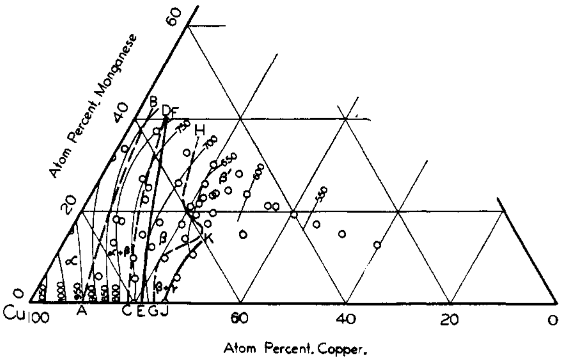

Fig. 4.—Partial phase diagram of the Cu–Mn–In system. Contours of the surface of primary crystallization are shown as light lines with the corresponding temperature in °C. Heavy lines represent projection of phase boundaries on an isothermal plane. Circles indicate alloy compositions prepared and studied.

The regions of existence of the various phases at temperatures slightly below the solidus surface are indicated in Fig. 4 by broken lines. These lines are projections on an isothermal plane of the intersection of the solidus surface with other equilib-

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[12] E. H. Swift, "A System of Chemical Analyses," Prentice-Hall, Inc., New York, N. Y., p. 351.

TABLE I

THERMAL, MAGNETIC AND CHEMICAL DATA FOR ALLOY SPECIMENS

Alloy No.	Composition Atom per cent.			Thermal analysis data, °C. Arrests				Annealing		Aging at 100° hr.	Curie temperatures, °C.		
	Cu	Mn	In	1st	2nd	3rd	End-points	Temp., °C.	No. phases after quench		As prepared	Quenched	Aged
4	57.4	21.5	21.1					530	2				
9	84.6	15.4		980			928						
10	68.3	31.7		890			866						
11	65.5	33.1	1.4	870			848				279		
15	65.0	24.9	10.1	745	735		708	693	1	380	269	None	<R.T.[d]
17	57.1	37.2	5.6	801	783		748	704	2	150	277	<R.T.	144
19	59.0	25.9	15.1	700			646	628	1	290	246	135	151
20	53.9	25.9	20.2	649	625		609	582	2	290	208	181	198
21	52.1	24.0	23.9	616			565	556	2	290	265	261	262[b]
22	47.0	23.7	29.3	600			511	505	2	240	276	255	272
23	43.0	21.0	36.0	572			509				280		
24	40.1	19.1	40.8	553			509				223		
											268		
25	37.0	17.0	46.0	547			512						
26	33.4	15.1	51.5	532			501						
27	27.6	12.9	59.5	521			501						
29	80.1		19.9	719	705		685						
32	84.0	5.9	10.1	865	686		678						
33	77.2	13.4	9.4	826	695		682	653	2	250	228	>R.T.	>R.T.
36	73.4	17.8	8.8	797	704		680	653	2	170	244	R.T.	R.T.
38	77.5	5.1	17.4	752	711		693	679	1	360	[a]	None	<R.T.
39	69.6	5.2	25.2	663			632	633	2	260	206	None	None
40	71.0	12.0	17.0	687			656	633	1	330	203	None	<R.T.
41	65.9	18.0	16.1	679			642	592	1	350	133	205	212
											224		
42	57.6	17.2	25.2	621			599	582	2	260	270	<R.T.	<R.T.
43	64.0	10.7	25.3	650			636	612	2	200	[c]	None	None
44	52.0	14.9	33.1	590	510						280		
45	64.1	27.5	8.4	750	729		703	670	2	330	279	None	115
46	74.6	17.9	7.5	797	692		682						
47	53.6	32.8	13.6	717			660	653	1	290	244	171	177
48	50.0	30.0	20.0	660	637		619		1	330	261	233	232
49	45.4	28.0	26.0	608			513	507	2	340	294	285	288
50	44.4	21.0	34.6	578			518	507	2	340		258	272
51	66.9	22.3	10.8	727	710		686	673	1	250	269	<R.T.	117
52	59.0	19.0	22.0	640	619		611	587	2	336	79	169	203
											225		
53	70.7	15.8	13.5	725	700		677	663	1	350	324	<R.T.	101
54	73.7		26.3	661									
55	53.0	23.6	23.4	617			579	566	2	260	266	244	260
56	75.3	9.6	15.1	738	691		670	653	1	250	190	None	250
57	55.6	22.8	21.6	626	623		612	602	2	260	230	198	210
58	50.2	24.2	25.6	607			577	561	2	200	268	253	264
59	59.0	20.8	20.2	661	652	633	630	602	2	260	90	172	183
											227		
60	35.6	44.9	19.5	626			605				286		
61	69.9	9.3	20.8	674	656		653	633	2	250	66	None	<R.T.
											202		
62	62.7	17.2	20.1	661	647		641 1	633	1	240	110	R.T.	122
											212		
63	14.3	65.0	20.0	1020	955	917					293		
64	63.6	13.7	22.6	651			638	612	1	220	65	None	None
65	55.6	19.2	25.2	636	611		609	592	2	190	265	132	247
66	18.0	32.2	49.8	705	520		517				283		

[a] Alloy was magnetic, but too weak to give measurable indication in apparatus. [b] After further annealing at 350° for days, this alloy had a Curie temperature at 266°. [c] Alloy was magnetic, but insufficient sample prevented Curie temperaure determination. [d] R.T. denotes room temperature.

ium surfaces. Choice of α-, β- and γ- as phase esignations has been made because these areas ppear to be extensions of the α-, β- and γ-phases of the copper-indium binary system.[13] The sym-

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(13) F. Weibke and W. Eggers, *Z. anorg. allgem. Chem.*, **220**, 273 (1934).

bol β' is used to designate the area where a superlattice or ordered structure is believed to exist. On this basis the structure to be expected for each of the phases would be: α, face-centered cubic; β, body-centered cubic; γ, the "γ-brass" type of structure; and β' an ordered body-centered cubic structure.

To the left of the dotted line AB the α-phase is present. Between the two dotted lines AB and CD the α- and β-phases coexist in the solid state. That this is so was determined from the fact that alloys represented by compositions between these lines contained two phases upon quenching from a temperature near the solidus. In addition, two arrests appeared on cooling curves of these alloys, indicating the temperatures at which the two solid phases first appeared. The liquid–solid equilibrium here can be thought of as an extension into the three-component system of the peritectic reaction relating the α- and β-phases in the binary copper–indium diagram. In the latter system the reaction

$$\beta \longrightarrow \alpha + \text{liquid}$$

occurs as the temperature is raised. The binary peritectic temperature is fixed and is represented by a horizontal line on a temperature–composition diagram. The addition of a third component, manganese, bestows an extra degree of freedom upon the system, and the horizontal peritectic line now becomes a surface in the three-component system. This surface is not horizontal, however, since by virtue of the extra degree of freedom three phases may coexist over a range of temperatures. The existence of this type of relationship may be inferred from the data in Table I. Cooling curves of alloys 29, 38, 56, 53, 51 and 15 contained two arrests, signifying the successive appearances of two solid phases, yet all specimens contained but a single phase upon quenching from a high temperature. In other words, one of the two phases originally present during solidification subsequently disappeared. The phase remaining was observed to be the β-phase, which, for compositions to the right of the line EF, is stable up to the melting point.

The line EF represents the intersection of the liquidus surfaces overlying the α- and β-regions. From melts with compositions lying to the right of this line the β-phase crystallizes alone, and cooling curves similar to that in Fig. 3B are observed. From melts with compositions lying to the left of EF the α-crystal appears first, but part or all of it subsequently undergoes the reaction

$$\alpha + \text{liq.} \longrightarrow \beta$$

when the underlying equilibrium region is that of the pure β- or of the $\alpha + \beta$-phases. In Fig. 5 the appearances of the α- and β-phases are shown by photomicrographs of two alloys. A 51 consists of the pure β-phase, the grain contrast of which is brought out by the persulfate etch. A 36 contains a matrix of the β-crystal, in which can be seen the lighter α-phase.

The homogeneous β-region extends to the line GH where a second two-phase region appears. At low manganese concentrations the phase in equilibrium with β is presumably an extension of the binary Cu–In γ-phase. In Fig. 4 the line JK indicates the probable direction of the eutectic trough between the two phases.

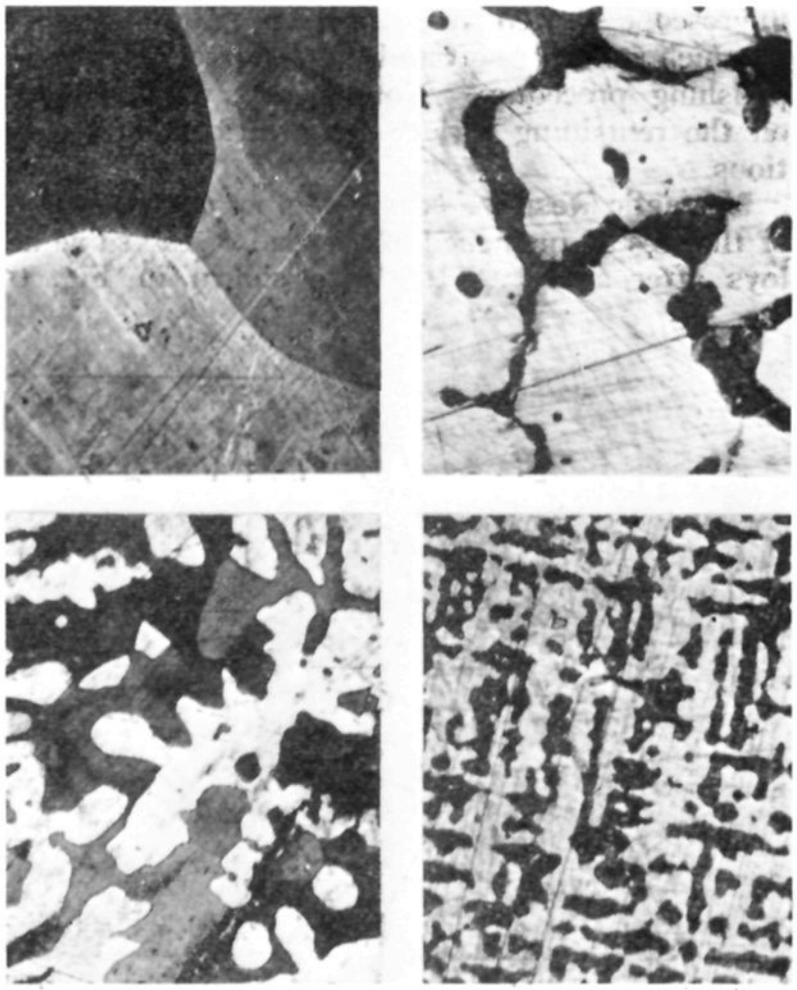

Fig. 5.—Photomicrographs of quenched alloys; × 50, $(NH_4)_2S_2O_8$ etch; upper left A 51, upper right A 58, lower left A 36, lower right A 57.

It has been reported that alloys of composition approximating the ratio Cu_2MnIn are homogeneous and contain an ordered structure,[9,11] designated usually as β'. Thus in the region of about 25% Mn the two phases in equilibrium to the right of GH must be β and β'. Nearly all the alloys in this region contained two phases after quenching, although alloy 48 contained a single phase and alloys 21 and 58 contained only a small portion of a second phase. A 48 also showed two arrests on its cooling curve, indicating that perhaps the equilibrium here resembles the $\alpha + \beta$-equilibrium. However, with the small number of alloys prepared in this region, it was not possible to locate the boundaries of the β'-phase.

Photomicrographs of two representative alloys are shown in Fig. 5. A 57 is in the two phase region and contains both β (dark) and β' (light). A 58 has the composition $Cu_{2.00}Mn_{0.98}In_{1.02}$ and was the alloy most closely approximating the composition Cu_2MnIn. This alloy, when quenched and examined, contained cracks and holes, and it was therefore difficult to determine whether it was homogeneous or whether a small amount of a second phase was present. The single phase alloys prepared by other workers were of slightly different composition and corresponded, respectively, to the ratios $Cu_{2.00}Mn_{0.95}In_{0.93}$[3] and $Cu_{2.00}Mn_{0.95}In_{1.00}$.[9]

Beginning with the alloys 22 and 49, the specimens became increasingly softer with increasing indium content. Their appearance under the microscope showed the presence of two phases, one of which was very soft and was removed during the polishing procedure. No contrast was obtained on the remaining surface with various etch solutions.

Magnetic Results.—Curie temperature contours of the freshly-quenched alloys and of the same alloys after aging at 100° are shown in Fig. 6. The corresponding data are contained in Table I. It will be noticed that alloys which lie to the right of GH, and thus probably contain the β'-phase as a constituent, are magnetic even when quenched from near their melting points, and their Curie temperatures do not change appreciably with the succeeding ageing at 100°. Alloys in the β-region were much more weakly magnetic and exhibited definite increases in Curie temperature after aging at 100°.

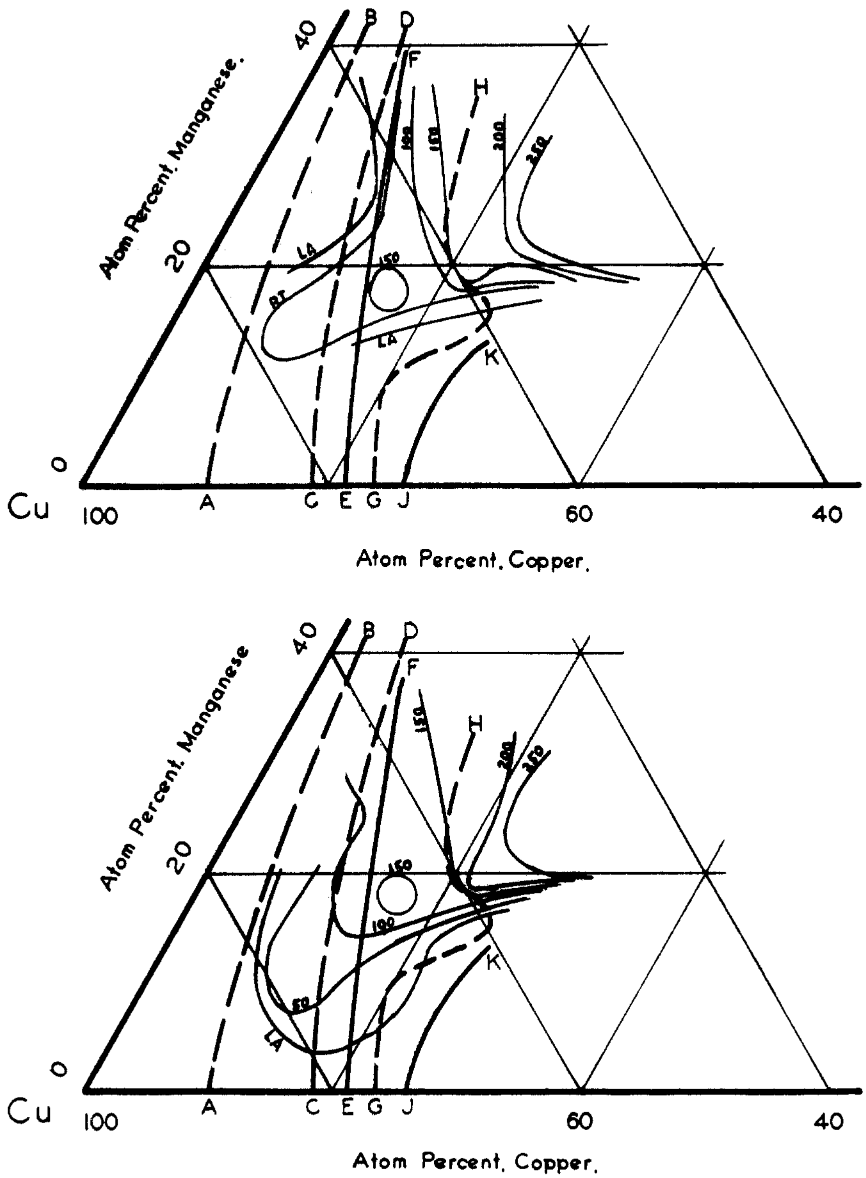

Fig. 6.—Curie temperatures of alloys. Upper diagram, alloys quenched after annealing at temperatures just below solidus; lower diagram, quenched alloys after reannealing at 100°. Temperatures are given in °C.; R.T. refers to room temperature, L.A. to liquid air temperatures. Heavy lines represent projection of phase boundaries on an isothermal plane.

Magnetism in this type of alloy seems to be associated with an ordered structure, and since the β'-phase has been found to be ordered up to the melting point it might be expected that quenching of β'-alloys would have little effect on their magnetic properties. Because of its weaker magnetic properties it would appear that the β-phase is ordered very little at the solidus temperatures, but that some local ordering occurs as a result of aging at a lower temperature.

An abrupt disappearance of the magnetic properties occurs with decrease of Mn content at about 18% Mn and 25% In. This is probably associated with the boundary between the β'- and γ-phases, since alloys containing appreciable amounts of the γ-phase were non-magnetic.

Alloy 41 appears to have an anomalously high value of Curie temperature, which may be the result of a solid state transition. Neither A 41 nor A 62 exhibited simple cooling curves, as would be expected from specimens which consist of a single phase in the solid state. Extra breaks appeared on the curves, possibly indicating a solid state transition, resulting in decomposition of the initially precipitated β-phase.

Curie temperatures of the alloys were also determined before the anneal and quench treatment. After preparation they had been allowed to cool to room temperature in about two hours, and in many cases, as determined under the microscope, the high temperature phase had decomposed. These results, recorded in Table I, reveal a much smaller variation of Curie temperature with composition than in the quenched alloys. In addition, all ternary alloys prepared, except A 32 in the extreme copper-rich section, were observed to be magnetic. However, the extent to which magnetism was exhibited, as determined qualitatively with a small Alnico magnet, varied greatly, being strongest near the compound Cu_2MnIn, and barely noticeable near the binary edges of the diagram.

Valentiner[1] has reported the fact that alloys containing copper and manganese in the atomic proportions 2:1 and varying amounts of indium have about the same Curie temperatures. He ascribed the magnetism to the presence of the superlattice, even at low indium concentrations. This would seem to be a plausible explanation, although it appears that the superlattice is stable at high temperatures only in the immediate vicinity of the composition Cu_2MnIn. Elsewhere the β-phase may break down into α and β' at lower temperatures. Complete ordering of the β-phase cannot occur, since there is always an excess of copper atoms in its lattice. Should it decompose, however, a certain quantity of the β'-phase can be formed, with the excess copper going into a second constituent, probably the copper-rich α-phase. The Curie temperature of this alloy would then be a high value corresponding to the β'-phase. Should incomplete conversion of the β into α and β' occur it would be possible to observe two Curie temperatures for a single alloy, a lower one for the β-phase and a higher one for the β'-species. It will be noted that this is the case for several alloys, although no attempt was made to identify the phases present.

On the basis of the above results it appears that a situation exists here which is somewhat similar to that existing in the Cu–Mn–Sn and Cu–Mn–Al systems. A β-phase region has been located which is believed to consist of an unordered body-centered cubic lattice, since it is the extension of the binary Cu–In β-phase. This phase does not include the point Cu_2MnIn. However, as pointed out previously, the composition Cu_2MnIn also has a body-centered cubic structure, although it is an ordered phase and appears to be distinguishable from the β under the microscope. Since both of these phases exhibited ferromagnetism, this phenomenon definitely appears to be associated with the body-centered structure, as is the case in the Cu–Mn–Al and Cu–Mn–Sn systems.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, HOUSTON REFINERY, SHELL OIL COMPANY, INC., AND APPLIED PHYSICS LABORATORY, THE JOHNS HOPKINS UNIVERSITY]

The Decomposition of *n*-Butane in the Presence of Oxygen

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The reaction of butane and oxygen at low oxygen concentrations has been studied in the temperature range 486 to 526°. Complete analysis of the reaction product was accomplished by the method of multiple isothermal distillation supplemented by chemical and spectroscopic tests. The effects of variations of concentration of oxygen from zero to 35 volume per cent. of variation of reaction time, and of Pyrex and KCl coated surfaces were observed under static and flow conditions. An important result of the study was the observation that the initial reaction product at low oxygen concentrations consists primarily of butene and water, indicating that oxygen acts primarily as a dehydrogenating agent under these conditions. Oxygen is shown to have a pronounced accelerating effect on the thermal cracking of butane; 0.5% of oxygen producing a hundred-fold increase in the rate of decomposition of butane. At oxygen concentrations below about 8%, the reaction products within the limits of sensitivity of the analysis consist only of hydrocarbons and water. The rate of reaction was found to be approximately proportional to the square root of the oxygen concentration and to the three-halves power of the butane concentration. The apparent activation energy of the reaction was found to be 21 kcal./mole.

Introduction

The acceleration of the decomposition of hydrocarbons by low concentrations of oxygen has been referred to in the literature by various workers,[2,3] and the reaction was investigated manometrically by Rice and Polly and Bell, Folkins and Thacker.[4] The influence of concentrations of oxygen in the range typical of combustion (production of appreciable concentrations of CO and CO_2) was investigated by Pease.[5]

As part of a broader study of hydrocarbon decompositions in these laboratories, the influence of oxygen on *n*-butane decomposition in the range of oxygen concentrations below 25% was investigated. None of the above authors had published detailed analyses of the reaction products obtained in their work, nor studied the reaction over a wide range of oxygen concentration.

The experimental work reported here was done in 1942. The investigation was interrupted by the war, and subsequent activities by the authors have prevented completion of the paper although the general results of the work were presented at the American Chemical Society Meeting at Chicago in 1948, and at the Symposium on Combustion held at the University of Wisconsin in 1948.

Experimental

Both static and flow experiments were carried out. The former gave information on the influence of oxygen on the

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(1) (a) Shell Oil Company, Inc.; (b) The Johns Hopkins University, Applied Physics Laboratory.

(2) F. D. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 278 (1938).

(3) See also L. S. Echols and R. N. Pease, THIS JOURNAL, **61**, 208 (1939).

(4) F. D. Rice and O. L. Polly, *Trans. Faraday Soc.*, **35**, 850 (1939); R. T. Bell, H. O. Folkins and C. M. Thacker, U. S. Patent 2,397,638 (April 2, 1946).

(5) R. N. Pease, THIS JOURNAL, **51**, 1853 (1929).