

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ST. LOUIS UNIVERSITY]

AN X-RAY STUDY OF THE CONSTITUTION OF SOME
COPPER-NICKEL-ALUMINUM-MANGANESE ALLOYS¹

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Previous work^{1a} has shown that certain copper-nickel-aluminum-manganese alloys composed of 1% Mn, 2-6% Al and having a nickel-copper ratio of 1.5-2.5 possess some very valuable properties. Some of these alloys will effectively resist corrosion by strong nitric acid for long periods of time, have tensile strengths of from 60,000 to 100,000 pounds per square inch and can be machined very easily. The manganese appears to have a very important influence on the tensile strength, the alloys containing 1% of manganese having approximately double the tensile strength of those without it.

A comparison has also been made between the properties of these alloys when chill-cast, sand-cast and annealed and the equilibrium diagram studied by means of cooling curves, photomicrographs and density changes.² It has been shown that these alloys are for the most part composed of one kind of solid solution but a second constituent was indicated which could not be positively identified by means of photomicrographs. In view of this fact an x-ray study has been made of the part of the system copper-nickel-aluminum-manganese having the composition indicated above.

Methods and Apparatus.—The apparatus was constructed according to suggestions of Wyckoff³ and Bain.⁴ The sample was reduced to a 200-mesh powder and rotated at the center of an arc of approximately 10 cm. radius inside of which the x-ray film was placed. The film holder was arranged so that the first few lines of the pattern were obtained on each side of the zero. The film holder was standardized by using sodium chloride as a standard, the salt being mixed with the sample in order to avoid errors due to differences in densities. The tube, which had a molybdenum target, was operated continuously at 35 kv. and 10 ma. and the x-rays were filtered through zirconia. The rays used were the MoK α doublet.

Table I shows data for check runs for salt and for one of the alloys where *L* stands for the film distances in millimeters from the zero beam to the

¹ Read before the physical and inorganic section of the Atlanta Meeting of the American Chemical Society.

^{1a} L. J. Wood and S. W. Parr, Preprint of the American Institute of Chemical Engineers, December 2, 1925.

² L. J. Wood, *J. Phys. Chem.*, **31**, 1693-1703 (1927).

³ Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, 1924.

⁴ Bain, *Chem. Met.*, **25**, 657-663 (1921).

middle of the lines indicated.⁵ By taking 5.628 Å. for the cube edge of sodium chloride and 0.710 Å. for the average wave length of the MoK α doublet and substituting into the formula $n\lambda = 2d \sin \theta$ and setting θ proportional to L , we get $\theta = 0.2949L$ for this particular film holder when using the MoK α doublet.

TABLE I
COMPARISON OF DATA FROM DUPLICATE RUNS
Equations: $L =$ Distance from zero to middle of line in mm.

Material	Indices (<i>hkl</i>)	L 1st run	L 2d run	L Av.
Rock salt	200	24.55	24.6	24.58
	220	34.95	34.8	34.88
	222	42.75	42.8	42.78
	400	49.75	49.6	49.68
	420	55.55	55.7	55.63
Alloy 104	111	34.15	34.21	34.18

TABLE II
COMPARISON OF OBSERVED DATA FOR ROCK SALT WITH CALCULATED VALUES
Equations: $\lambda(h^2 + k^2 + l^2)^{1/2}/2a = \sin \theta$; $\theta = 0.2949L$

Indices (<i>hkl</i>)	$\sin \theta$	L (calcd.)	L (obs.)
200	0.12613	...	24.58
220	.17833	34.84	34.88
222	.21853	42.80	42.78
400	.25235	49.56	49.68
420	.28213	55.58	55.63

The data given in Table II show that the sample was located at the center of a perfect arc within the limit of measurement, which from Table I appears to be somewhat less than 0.1 mm. along the film which corresponds to an arc of about 1'30" or about ≈ 0.005 Å. in terms of interplanar distances.

Results.—The alloys examined had the composition indicated in Table VI and were all annealed as previously described. Table III shows the data obtained in the case of one of the alloys. The observed data are compared with values calculated for a face-centered cube and are seen to check within the limit of error in measurement. The sum of the squares of the *hkl* indices of the planes which give lines in the case of a face-centered cube (pure metal) are 3, 4, 8, 11, 12, 16, 19, 20, 24, etc. The number and arrangement of the lines obtained for this alloy are in perfect agreement with the assumption of a face-centered cube.

Table IV shows the results of some intensity measurements made by means of a differential photo-electric photometer built according to a description by Richtmyer. (The author's sincere thanks are hereby expressed to Dr. F. E. Poindexter of the Physics Department of St. Louis

⁵ Clark's nomenclature has been adopted, "Applied X-Rays," McGraw-Hill Book Co., Inc., New York, 1927.

TABLE III

ALLOY 127. COMPARISON OF OBSERVED FILM DISTANCES WITH CALCULATED DISTANCES FOR A FACE-CENTERED CUBE

Equations:^a $\lambda(h^2 + k^2 + l^2)^{1/2}/2a = \sin \theta$; $\theta = 0.2949L$

Indices (<i>hkl</i>)	Sin θ	<i>L</i> (calculated)	<i>L</i> (observed)
111	0.17320 ^b	..	33.8 mm.
200	.20000	39.1	39.2
220	.28280	55.7	55.9
311	.33166	65.7	65.8
222	.34641	68.7	68.6
400	.40000	79.9	^c
331	.43589	87.6	87.7
420	.44721	90.1	90.2
422	.48990	99.4	99.3

^a $a = 3.555 \text{ \AA}$. calculated from $L = 33.8$ millimeters. ^b Calculated from $L = 33.8$.
^c Very faint line. Could not measure accurately.

TABLE IV

PHOTOMETRIC DATA

Alloy	111	Relative densities of lines (Obs.)			Density ratios	
		200	220	311	111/220	111/311
132	10	8.2	4.5	4.2	2.2	2.4
127	10	6.4	4.8	3.5	2.1	2.8
100	10	6.6	4.6	^a	2.2	^a
Calcd.	10	5.4	4.7	6.5	2.1	1.5

^a Light film.

University for the use of this apparatus.) A comparison of observed values with values calculated on the assumption of a face-centered cube shows very close agreement.

Table V shows the experimental data obtained for the alloys examined when a stands for the unit cube edge and A stands for the average atomic weight. The calculated values of a were obtained by means of the third equation given in the heading of the table. The values of A used in these calculations were obtained by means of the last equation given in the same heading, which assumes a substitutional solid solution. The values of a observed from the different planes vary among themselves slightly, which is not surprising in view of the fact that we are dealing with a solid solution and hence the distribution of a given kind of atom in the various sets of parallel planes may vary. Also, the calculated values for a are in some cases appreciably larger than the observed values, a possible explanation for which will be offered below.

The observed values of a obtained from the 111 planes are considered most reliable, for in these cases the values of L were obtained by measuring the film distance between corresponding lines on the two sides of the zero beam and dividing the distance by two. The values of L for the other sets of planes were obtained by measuring from the 111 lines and adding to the

TABLE V
COMPARISON OF EXPERIMENTALLY DETERMINED VALUES OF a WITH THE CALCULATED VALUES

Equations: $\Theta = 0.2949L$; $\lambda(h^2 + k^2 + l^2)^{1/2}/2 \sin \Theta = a$ (Exp.)
 $(4 \cdot A \cdot 1.65/\text{Density})^{1/2} = a(\text{calcd.})$; $A = \frac{100}{\frac{\% \text{ Cu}}{65.57} + \frac{\% \text{ Ni}}{58.68} + \frac{\% \text{ Al}}{27} + \frac{\% \text{ Mn}}{54.93}}$

Alloy	L in mm. 111	L in mm. 220	L in mm. 311	a 111	a 220	a 311	a (calcd.)
104	34.2	56.3	66.2	3.510	3.515	3.525	3.560
105	34.2	55.8	66.1	3.515	3.550	3.530	3.565
106	34.2	56.0	66.5	3.510	3.530	3.505	3.565
108	34.0	56.0	66.0	3.530	3.530	3.535	3.560
109	34.0	56.1	66.4	3.535	3.530	3.515	3.605
113	33.9	56.0	66.5	3.540	3.530	3.510	3.560
127	33.8	55.9	65.8	3.555	3.540	3.545	3.560
132	33.9	55.8	65.9	3.545	3.540	3.540	3.570
133	34.1	56.6	67.0	3.520	3.495	3.485	3.565
134	34.2	56.3	66.4	3.515	3.515	3.515	3.560
137	34.1	56.6	66.1	3.525	3.500	3.530	3.570
138	33.7	55.4	65.5	3.570	3.570	3.560	3.580
140	33.8	^a	^a	3.555			3.570

^a Light film.

L value for the 111 planes. The absolute error in measuring the values for L for the 111 planes is thus seen to be one-half that for the other planes.

The observed values for a obtained from the 111 planes are shown in Table VI. The values for a are compared with the nickel-copper ratio for

TABLE VI
COMPARISON OF OBSERVED VALUES OF a WITH CALCULATED VALUES

No.	Mn, %	Al, %	Ni/Cu	a (obs.)	a (calcd.)
133	1	2	1.94	3.520	3.565
134	1	2	2.03	3.515	3.560
104	1	2	2.23	3.510	3.560
113	1	2	2.34	3.540	3.560
140	1	3	1.51	3.555	3.570
108	1	3	2.31	3.530	3.560
132	1	4	1.88	3.545	3.570
137	1	4	2.00	3.525	3.570
127	1	4	2.06	3.555	3.560
106	1	4	2.28	3.510	3.560
138	1	6	1.82	3.570	3.580
105	1	6	2.23	3.515	3.565

a constant aluminum content. The cube edge generally increases with rising aluminum content and falls with rising nickel-copper ratio, which in each case is what would be expected if the alloys are solid solution of one kind. In two or three cases the observed values almost reach the calculated values while the others are lower. These facts can be explained if it

is assumed that in the case of most of the alloys not all of the aluminum is held in what has been called the α -solid solution. On a few films a few "Extra Lines," *i. e.*, lines not belonging to the α -solid solution pattern, were found. The locations of these lines are given in Table VII.

TABLE VII
COMPARISON OF OBSERVED FILM DISTANCES FOR LINES NOT BELONGING TO THE FACE-CENTERED PATTERN OF THE α -SOLID SOLUTION WITH CALCULATED FILM DISTANCES FOR SOME POSSIBLE LINES

Form ^a	Al F.C.	Film distances (calculated)			Al Cu 104	Film distances (observed)			
		Mn 56 atoms	Mn 20 atoms	Al Ni B. C.		106	113	100	127 un-annealed
a	4.043	8.89	6.289	2.82	8.674				
	(111)				(321)				
	29.67				29.63				29.95
	(200)	(330)	(221)	(110)					
	34.31	33.08	33.06	34.81					
		(332)	(310)						
		36.61	34.86						
		(510)	(311)						
		39.84	36.59						
					(521)				
					43.93	44.76		43	43.65
	(220)			(200)(611)(532)					
	48.76			49.45	49.55	50.8	51.0		49.55

^a All of these are taken as some form of cubic lattice.

Equilibrium Diagram.—Both the photomicrographs and x-ray patterns show conclusively that these alloys are in the main α -solid solution. According to Austin and Murphy,⁶ alloys of copper and nickel with up to about 10% of aluminum should form the α -solid solution at temperatures just below the solidus. With alloys higher in aluminum these authors indicated the formation of a eutectic constituted of α - and β -solid solutions, the β -solid solution resulting from a solution of NiAl and Cu₃Al in each other. Evidence presented by Guillet⁷ and the present author indicates that aluminum is less soluble in copper and nickel at lower temperatures, especially when the percentage of copper is lowered. Jette, Phragmen and Westgren⁸ did not find evidence for Cu₃Al in copper-aluminum alloys. These authors found aluminum dissolving in copper up to 8% and also evidence for a γ' -phase, the cube edge of which varied from 8.704 to 8.652 Å. for alloys with 16–25% aluminum.

Discussion.—The results shown in Table V seem to indicate that in the case of most of the alloys not all of the aluminum was held in the solid solution. The physical properties of these alloys, photomicrographs and

⁶ Austin and Murphy, *J. Inst. Met.*, 29, 327 (1923).

⁷ Guillet, *Compt. rend.*, 158, 704 (1914).

⁸ Jette, Phragmen and Westgren, *J. Inst. Met.*, 31, 193 (1924).

the "Extra Lines" listed in Table VII indicate a second phase of some sort. It might be expected that this second phase would be a solid solution, the composition of which is not known at the present time. The "Extra Lines" occur on the films at about the correct positions for a solid solution having a cube edge of 8.674 Å. (see Table VII), which is intermediate between the high and low values given by Westgren for the γ' -phase in copper-aluminum alloys. It might not be unreasonable to expect a similar γ' -phase in nickel-copper-aluminum alloys, since nickel and copper are known to form a continuous series of solid solutions. However, the "Extra Lines" could be almost equally well explained as being derived from solid solutions having, respectively, cube edges of 4.54, 6.42 or 7.51 Å. Which of these, if any, is correct will have to be determined by further work.

Some preliminary results indicate that the cube edges for the unannealed alloys are larger than the values given in Table V for the annealed alloys, indicating more aluminum held in the α -solid solution in the sand-cast (unannealed) condition than in the annealed condition. This is in agreement with the results obtained from the photomicrographs but is in apparent disagreement with the x-ray evidence for alloy number 127 in which case "Extra Lines" (evidence for a second phase) were found for the unannealed alloy but none for the annealed.

The x-ray study of this alloy system is being continued in order to define more clearly, if possible, the nature and constitution of the second phase, evidence for which has been given. It is also proposed to study some chill-cast alloys of these same compositions, in order to determine whether or not more aluminum is held in solid solution when the alloy is cooled rapidly.

The present study has not thrown any new light on the important influence of the 1% of manganese on the physical properties of these alloys.

Summary

An x-ray study has been made of the constitution of some copper-nickel-aluminum-manganese alloys. Previous work has already indicated that these alloys are in the main α -solid solutions. The present x-ray examination confirms this former finding. Some evidence for a second constituent is presented but complete identification has not yet been made.

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