THE THERMOELECTROMOTIVE FORCE OF COPPER-MANGANESE ALLOYS.

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Synopsis.

Thermoelectromotive Force of Alloys of Copper with 5 to 23 Per Cent. Manganese for the Range 0° to 100° C.—The alloys were prepared from electrolytic copper and thermite manganese but contained as impurity about one fiftieth as much iron as manganese. The alloys were cast and then drawn to fine wires. After they had been annealed at 200° C. for 8 hours, the thermoelectromotive forces against fine pure copper wire were determined for various temperatures of the hot junction up to 100° C. The curves, as usual, correspond to the equation $E = \alpha t + \beta t^2$. For $t = 100°$ C., E is positive for all the alloys, especially if allowance is made for the effect of the iron content, though practically zero for alloys with less than 10 per cent. Mn. The alloys as cast and as drawn were more positive than after annealing. However, E showed negative values for the lower manganese alloys and for the lower temperatures, especially when the iron content was increased. In fact, though α is probably positive for all pure Cu-Mn alloys, *the effect of small percentages of iron*, carefully studied to 2 per cent. with a series of 30 alloys, was found to be to decrease α so that for 13 per cent. Mn and more than 0.50 per cent. Fe and for less than 11 per cent. Mn and more than 0.20 per cent. Fe, α is negative. On the other hand β is always positive but tends to decrease as the percentage of Mn is increased. Two alloys indicated that the *effect of 2 per cent. nickel* is to decrease α nearly as much as an equal amount of iron. *The effect of aluminum* seems to be the reverse but the five alloys tested did not give consistent results. *Ordinary manganese* contains just enough iron as impurity to make its E slightly negative at ordinary temperatures but adding 1 per cent. more iron, as suggested by Hunter and Bacon, would lower it too much.

Discussion of Electron Theory of Thermoelectromotive Force.—The electron theory does not account for the fact that E is positive rather than negative for Cu-Mn alloys against Cu, and that while Fe itself is positive against Cu its effect on E for these alloys is negative. It is suggested that the effect of atomic and molecular forces on the free electrons will have to be taken into account.

A KNOWLEDGE of the thermoelectromotive force of copper-manganese alloys and the way in which it is influenced by admixtures of other elements such as iron, nickel and aluminum is important because one or more of these alloys is widely used as standards for resistance. The data on this point being insufficient and somewhat contradictory, it was decided to study carefully the thermoelectromotive force of a large number of copper-manganese alloys.

In preparing the sample throughout this investigation electrolytic copper and thermit manganese were used and the metals were alloyed in Tammann tube furnaces. To protect from oxidation the necessary quantity of barium chloride was first melted in the furnaces and the metals to be alloyed were charged in convenient order into them. Then the melted alloys were poured into porcelain tube crucibles which had been preheated to about 500° C. and the ingots were slowly cooled. An ingot about 10 cms. long and 1.8 cms. thick thus obtained, was annealed at 800° C. for 30 min. and then drawn into a wire the diameter of which was about 5 mm. This wire was drawn cold in the usual manner. The diameter of the wire was reduced two numbers (B. & S.) with one drawing to gauge number 13 and after that was reduced only one number at each drawing. Until the diameter of the wire reached its final value, it was annealed several times for 8 hrs. in an oil bath at 200° C. All the specimens used for this investigation were in the form of wire (B. & S.).

After the specimen had been once more annealed at 200° C. for 8 hrs. in the oil bath, its mean thermoelectromotive force between 0° and 100° C. was measured against pure, fine copper wire. The hot junction of the thermoelement, consisting of the specimen and the pure copper wire, was kept in a hypsometer and the cold junction in an ice bath. Of course, the usual expression "mean thermoelectromotive force over a certain range of temperature" has no meaning for a thermoelement for which the thermoelectromotive force varies with the temperature so as to have a minimum or a maximum within the range. Some samples of copper-manganese alloys correspond to this case. For simplicity, however, the mean thermoelectromotive force was measured at first as usual. For the measurement of the thermoelectromotive force a Rap potentiometer made by Siemens and Halske and a d'Arsonval galvanometer made by Leeds and Northrup were used.

The results are summarized in Table I. and are also plotted in curve E of Fig. 1. For most of the specimens the quantity was insufficient to allow the small percentage of iron in them to be determined by analysis. But as all specimens were made from the same materials by the same treatment, the content of iron in them may be presumed to be of the same order as in the case of those specimens whose iron content could be determined by quantitative analysis.

From these results it will be seen that the mean thermoelectromotive force of copper-manganese alloys between 0° and 100° C. at least when the manganese content is between 5 and 25 per cent., is certainly positive against copper and that within the same limit of manganese content, the greater the proportion of manganese the greater is the thermoelectromotive force. Our results at this point confirm those of Feussner and Lindeck.[1] It is true that in Table I. there may be seen a few samples

[1] Feussner and Lindeck, Abh. Phys. Tech. Reichsanstalt, 2, 515.

giving negative thermoelectromotive forces which casts a doubt on our conclusion. If Nos. 89, 102, 99 and 91 are considered, it will be noticed that even among samples with nearly the same percentage of manganese

Table I.

Manganese Content and Mean Thermoelectromotive Force.

No. of Specimens.	Cu. (Per Cent.)	Mn. (Per Cent.)	Fe. (Per Cent.)	$E/°$ C. (Micro-V.)	$E'/°$ C. (Micro-V.)
84........	94.37	5.42	——	+ 0.03	+ 0.38
85........	92.74	6.97	0.133	− 0.04	+ 0.45
94........	91.85	8.04	——	− 0.01	+ 0.57
112........	90.29	9.52	——	+ 0.34	+ 1.24
100........	89.31	10.44	0.150	+ 0.02	+ 0.72
88........	89.26	10.45	0.150	+ 0.22	+ 1.04
89........	88.44	11.33	——	+ 0.38	+ 1.25
102........	88.40	11.46	0.170	+ 0.20	+ 1.02
99........	88.18	11.51	——	− 0.03	+ 0.61
91........	88.18	11.62	——	+ 0.12	+ 1.03
97........	87.30	12.40	——	+ 0.52	+ 1.48
101........	86.21	13.58	——	+ 0.50	+ 1.45
103........	86.07	13.65	——	+ 0.54	+ 1.50
90........	85.64	14.24	——	+ 0.65	+ 1.70
93........	83.50	16.29	0.290	+ 0.74	+ 1.85
95........	82.65	17.03	0.330	+ 0.78	+ 1.65
86........	82.11	17.58	——	+ 1.17	+ 2.10
96........	79.56	20.12	——	+ 1.73	+ 2.68
98........	77.05	22.52	——	+ 1.74	+ 2.58

there are very large irregularities in the thermoelectromotive force. According to our experiments a small percentage of such impurities as iron, nickel and chromium can easily cause the lowering of the thermoelectromotive force. Judging from curve E of Fig. 1 drawn through all

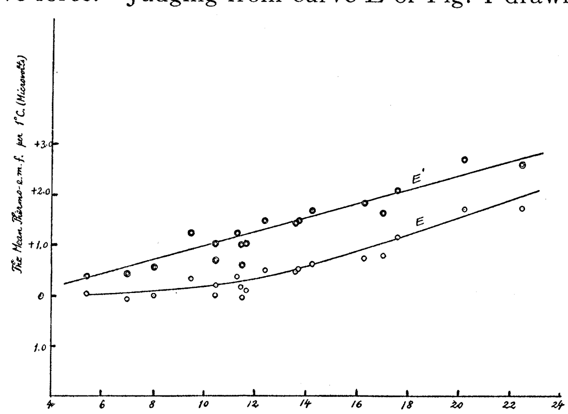

Fig 1.

Manganese content and mean thermoelectromotive force per 1° C. between 0° and 100° C. Curve E' for wires as drawn and curve E for wires after annealing.

the experimental points, No. 99 which gives a slight negative value may be considered an abnormal value due to the above cause. But this simple explanation is not sufficient to prove that the thermoelectromotive forces of the samples Nos. 89, 102 and 91 are nearer to the normal value than the thermoelectromotive force of No. 99, because if there are other reasons for raising the thermoelectromotive force of these samples, the opposite may equally well be concluded. For instance it was observed that the cast samples, even when they had been cooled at moderate speed, sometimes gave higher thermoelectromotive forces than those given by the same annealed samples. Curves I. and II. of Fig. 2 represent

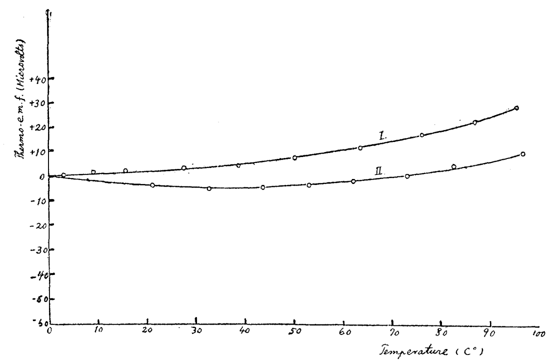

Fig. 2.

Thermoelectromotive forces of a copper-manganese alloy before and after annealing. Curve I. before annealing. Curve II. after annealing.

the thermoelectromotive force of a rod of copper-manganese alloy just cast and the same rod after annealing.

The effect of cold drawing must be taken into consideration as another cause of an increase in thermoelectromotive force. The value of the thermoelectromotive force represented by E' in Table I. and by E' in Fig. 1 are those obtained for samples just drawn, the corresponding values of the thermoelectromotive force for the same samples after annealing being represented by E in the same table and figure. It is, therefore, uncertain which value of the thermoelectromotive force, that of sample No. 99 or that of one of the samples Nos. 89, 102 and 91 is nearer the normal value. But if the state of the samples which gave the value of the thermoelectromotive force represented by curve E can be said to be normal, that is if the effect of the manufacturing process in our laboratory upon the majority of these samples can be said to be normal, then such samples as No. 99 can be considered abnormal. Iron may be considered as one of the causes of this abnormality.

Thermoelectromotive Force per Unit Difference in Temperature.

In the previous section the mean thermoelectromotive force of copper-manganese alloys between 0° and 100° C. was found to be decisively positive against copper. Since the mean thermoelectromotive force is meaningless when the thermoelectromotive force per unit difference in temperature changes its sign between the two given limits of temperature, the variation of the thermoelectromotive force between 0° and 100° C. was studied for small temperature intervals. The hot junctions of the thermoelements were kept in an oil bath instead of in a hypsometer as in the preceding experiment. The oil bath was gradually heated by two incandescent lamps immersed in it and the temperature of the oil was kept uniform by means of a pump. The potentiometer was so adjusted that one division of the end dial just corresponded to one microvolt and a highly sensitive Thomson galvanometer was used for balancing.

The samples as before were in the form of wires and the results of their chemical analyses are shown in Table II. The iron in these samples

Table II.

No. of Specimens.	Cu. (Per Cent.)	Mn. (Per Cent.)	Fe. (Per Cent.)	Ni. (Per Cent.)
184...........	94.318	5.198	0.1416	
185...........	94.833	5.002	0.1416	
186...........	91.541	7.920	0.1770	
187...........	91.541	8.003	0.1947	
188...........	88.196	11.575	0.1947	
189...........	89.182	10.147	0.1947	
190...........	87.103	12.292	0.2655	
191...........	86.842	12.540	0.2832	
192...........	83.774	15.840	0.3009	
193...........	82.996	16.253	0.3186	
195...........	86.337	11.673	0.168	1.830
197...........	85.556	11.424	0.186	2.616

is merely due to the impurity in the manganese. The results of the experiments on these samples have been plotted in Fig. 3. The values of α and β in the formula of the thermoelectromotive force, $E = \alpha t + \beta t^2$, have been calculated and plotted in Figs. 4, 5 and 6.[1] It is seen from these curves that α is negative for samples of lower manganese content and positive for those of higher manganese content, while β is always positive. The relation between α and the percentage of iron for various concentrations of manganese is brought out in Fig. 4 and the relation

[1] Computed from the curves for $t = 40°$ and $t = 80°$ C.

between β and the concentration of iron in Fig. 5. The variation of α with the concentration of manganese for different percentages of iron in the alloy has been represented in Fig. 6.

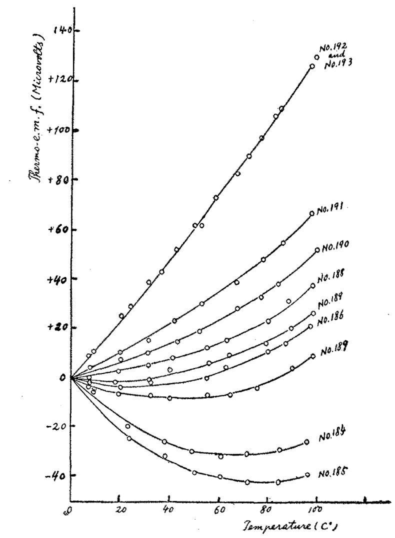

Fig. 3.
Manganese content and the temperature variation of the thermoelectromotive force as a function of the temperature of the hot junction.

In our opinion the difference between the curves in Fig. 3 is due to the fact that the effect of iron on the thermoelectromotive force varies widely with the proportions of copper and manganese. The samples Nos.

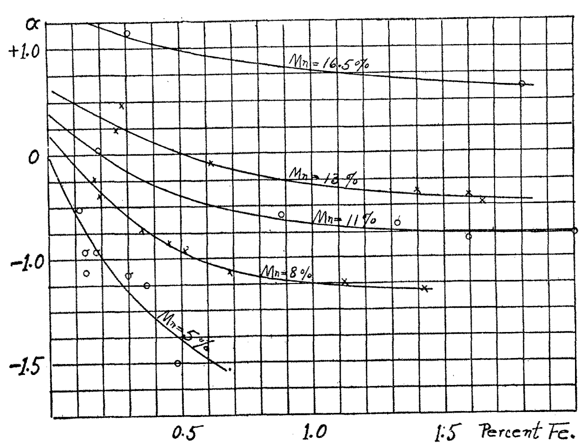

Fig. 4.
The variation of α in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of iron.

184 and 185 show exceptional negative thermoelectromotive forces and these results seem inconsistent with those obtained for sample No. 84 in Table I. Perhaps this discrepancy may also be attributed to the difference in the quantity of iron as an impurity. Though the above

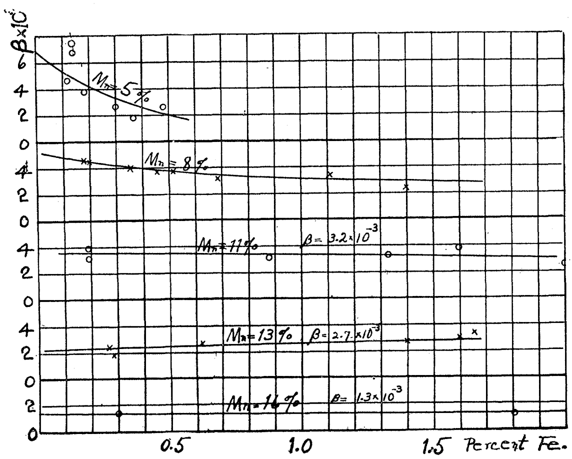

Fig. 5.

The variation of α in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of manganese.

conclusion is very probable, further investigation will be necessary as to the thermoelectromotive forces of copper-manganese alloys in which the manganese content is less than about 6 per cent.

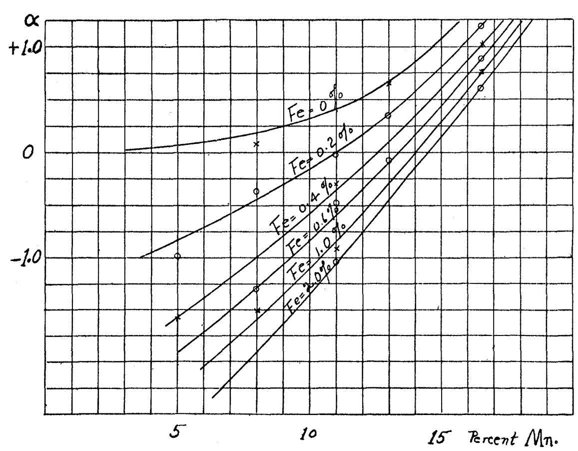

Fig. 6.

The variation of β in the equation, $E = \alpha t + \beta t^2$, as a function of the concentration of iron.

Effect of Nickel, Iron and Aluminum on Thermoelectromotive Forces of Copper-Manganese Alloys.

According to Feussner and Lindeck the positiveness of the sign of the thermoelectromotive force of copper-manganese alloys against copper can be annulled by the addition of a small quantity of nickel. For example, in a sample of about 12 per cent. manganese, about 2 per cent. nickel was suggested for this purpose.

It has already been seen that even though the mean thermoelectromotive force of copper-manganese alloys has a considerable positive value, dE/dt may not always be positive at ordinary temperatures. If attention is directed to the thermoelectromotive force of sample No. 189, it is seen that the mean thermoelectromotive force is about $+0.13$ microvolt per degree Centigrade. But dE/dt for the same sample is negative for any temperature less than about 18° C. and it becomes zero at about 20° C. Thus it will be seen that copper-manganese alloys containing the same order of manganese as that in the ordinary manganin have a very small temperature coefficient of the thermoelectromotive force against copper at ordinary temperatures and that at lower temperature dE/dt becomes negative. If a small percentage of nickel is added to these samples, the thermoelectromotive force has a very large negative value at room temperature. This fact is clearly seen in samples of manganin wire on the market as well as those prepared in our laboratory (Fig. 7).

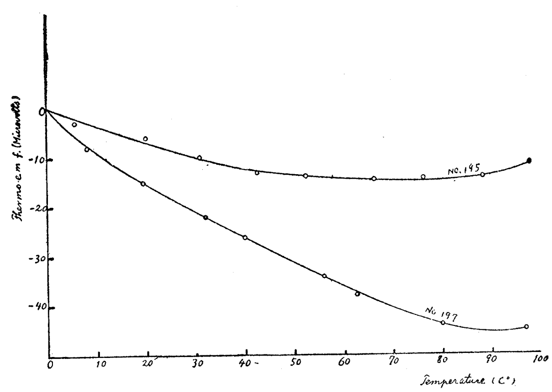

Fig. 7.

The effect of nickel on the thermoelectromotive force of a copper-manganese alloy containing about 11.5 per cent. manganese, as a function of the temperature of the hot junction.

It is thus seen that aside from its influence on the temperature coefficient of the resistance of manganin, the addition of nickel to manganin is not desirable where the manganin is to be used for standard resistances. Hence the idea of Feussner and Lindeck that nickel could be added to manganin to cancel the positiveness of the sign of the thermoelectromotive force, is not satisfactory because the effect is too large.

When manganin was first made by Feussner and Lindeck the iron content was perhaps nothing but impurity which came from the manganese. But it has been proposed by Hunter and Bacon that about one per cent. of iron should be added to manganin to improve the temperature coefficient of the resistance. Although there will be difference of opinion about this suggestion, it is important to investigate the effect of the presence of iron on the thermoelectromotive force of copper-manganese alloys, because iron is always present as an impurity in manganese. One example of the results of our experiments in this connection is given in Fig. 8. The results of the chemical analyses of these samples are contained in Tables II. and III.

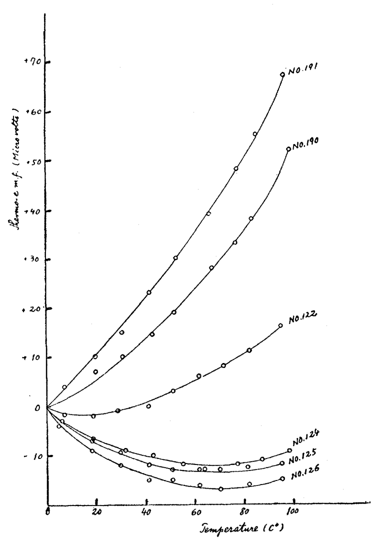

Fig. 8.

The effect of iron on the thermoelectromotive force of a copper-manganese alloy containing about 13 per cent. manganese as a function of the temperature of the hot junction.

Manganese Content and Mean Thermoelectromotive Force.

TABLE III.

Approx. Per Cent. Manganese.	No. of Specimen.	Copper, Per Cent.	Manganese, Per Cent.	Iron, Per Cent.
13............	122	85.573	13.430	0.6195
	124	85.330	12.877	1.3983
	125	85.073	13.117	1.5930
	126	85.330	12.877	1.6544

From these results it must be concluded that a small percentage of iron can cause a considerable lowering of the thermoelectromotive force of copper-manganese alloys and that its effect is of the order of that of nickel or sometimes rather greater than that of nickel. As already pointed out the presence of iron as an impurity in manganin is sufficient to lower the thermoelectromotive force of copper-manganese alloys and that the intentional addition of nickel is unnecessary. Furthermore, Hunter and Bacon's proposal to add about one per cent. of iron, is not desirable for the purpose of minimizing the thermoelectromotive force of copper-manganese alloys, because one per cent. of iron is far too much.

Recently in discussing a paper by Bash, Weimer has stated that an alloy of 84.2 per cent. copper, 11.5 per cent. manganese and 4.2 per cent. aluminum is an ideal material for resistance standards. He points out as the valuable properties of this alloy that its thermoelectromotive force against copper is about one tenth of that of manganin and that the constancy of its resistance seems to be quite good, while its mechanical properties are considerably better than those of manganin. According to our experiments aluminum affects copper-manganese alloys so as to make the thermoelectromotive force slightly more positive. Thus if aluminum is added there will be no need of any precaution against an excessive lowering of the thermoelectromotive force as in the case of the addition of nickel. The aluminum will make it less probable that the iron as an impurity will produce a large thermoelectromotive force. In this respect it is safer to add aluminum than to add nickel. But in our opinion the intentional addition of aluminum will also be unnecessary for the purpose of minimizing the thermoelectromotive force. Samples of this new alloy having various percentages of aluminum were prepared in our laboratory and their thermoelectromotive forces measured. But as our samples seem not to be homogeneous, a more detailed study of these alloys will be left for a later investigation.

Relation of Results to Electron Theory of Thermoelectromotive Forces.

Certain solid solutions have negative thermoelectromotive forces against their solvent metals, while other solid solutions have positive thermoelectromotive forces. Any theory of thermoelectromotive force which makes it necessary for the thermoelectromotive force of solid solutions against their solvent metals to have one sign in all cases, is unable to explain such experimental facts as were obtained in this investigation. The present electron theory which can not in its present form account for such a reversal of sign, does not therefore offer a satisfactory explanation of these results. To make it possible for the electron theory to explain such results, it will be necessary to consider that atomic forces greatly affect the energy of free electrons and therefore the thermo-electromotive forces.

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