Art. LV.—*The Electrical Resistance of the Alloys of Ferro-Manganese and Copper;* (From determinations made by Mr. B. H. Blood); by Edward L. Nichols.

[Contributions from the Physical Laboratory of Cornell University, No. 6.]

In the selection of a material for standards of electrical resistance, the influence of temperature upon the conductivity of the wire to be used in their construction is a factor of prime importance. Since the report of the British Association Committee (1867) on electrical standards, no great progress has been made in this matter. The manufacturers of German silver and of similar alloys have, it is true, succeeded in reducing considerably the temperature-coefficients of their metals; so that it is now possible to obtain wires the resistance of which changes less than two hundredths of one per cent per degree Centigrade. Such a variation is, however, by no means negligible in operations of precision; and the coefficient of different wires, even when made from the same metal, vary greatly. In a single resistance box, as has been shown by Professor Anthony, one may have coils which are well adjusted at some one temperature but to which, no single temperature-correction will apply.* On this and on many other accounts, the discovery of an alloy, the resistance of which is unaffected by temperature is a matter of some importance.

In 1888 patents were granted by the United States government, for two new alloys to be used in the construction of resistance coils.† The properties claimed for these alloys were so remarkable—complete freedom from change of resistance upon heating in the one case and a decrease of resistance with rise of temperature, in the other—that in the absence of more complete data concerning them than are contained in the patent office specifications, it seemed to me a matter of some importance to subject them to a detailed experimental investigation.

The necessary experiments were undertaken at my suggestion by Mr. B. H. Blood, and it is upon his results that the following statements are based.‡

* W. A. Anthony: On the Differing Temperature Coefficients of the Different Coils of a fine Rheostat. Transactions of the American Institute of Electrical Engineers, vol. iv, p. 137.

† See Edward Weston, U. S. patents, Nos. 381,304 and 381,305; Specifications and Drawings of Patents, April 17, 1888, p. 1507. Also Official Gazette of the U. S. Patent Office, vol. xliv, p. 339.

‡ B. H. Blood: Temperature Coefficients of Ferro-manganese-Copper Alloys, Thesis (in MS.); Library of Cornell University, 1889.

The materials used in Mr. Blood's investigation were the pure copper of commerce and "ferro-manganese" containing seventy-nine per cent of manganese. These were fused together in a small carbon crucible, the sides of which were lined with porcelain. The mixture was placed in the bottom of the crucible in contact with the carbon, which was connected with the positive pole of a storage battery. A carbon pencil, connected with the other pole of the battery, was then brought into electrical contact with the charge from above, and quickly withdrawn to a distance of a few millimeters. Under the action of the arc thus formed, a charge weighing three or four grams was completely fused in about thirty seconds, without any considerable oxidation of the metals. The irregular ingot thus formed was afterward rendered more nearly homogeneous by being re-melted in the voltaic arc, for which purpose it was removed from the crucible and placed upon a metal plate. The globule of metal thus obtained was rolled into a thin strip, from which was cut a piece fifteen centimeters long and of such width as to give a resistance of about eight-tenths of an ohm.

The method of measurement employed was as follows: The strip of alloy to be tested was connected in series with a comparison standard, the resistance of the two being approximately equal. These, together with a third resistance of about one hundred and fifty ohms, formed the outer closed circuit of a single gravity cell. "Potential wires" from the terminals of the strip of alloy and of the standard, were joined to a switch of such construction that a mirror galvanometer could be connected in shunt with either. The galvanometer had a resistance of two thousand ohms. A comparison of deflections when the galvanometer was shunted around the resistance standard, and around the test piece, afforded data for the calculation of the resistance of the latter.

This method is exceedingly sensitive, and when properly conducted, it is capable of a high degree of accuracy. In the experiments under consideration, a check upon errors arising from fluctuations in the amount of current traversing the test piece and from changes in the constant of the galvanometer, was obtained by ever repeated reference to the indications of the latter when connected with the terminals of the standard.

In order to relieve the observer of the necessity of maintaining the reference standard at a constant temperature, or of applying temperature-corrections to the results obtained, a compensated carbon standard, of the type recently described by the writer, was constructed.* The resistance of this stand-

* On Compensated Resistance Standards; Transactions of the American Institute of Electrical Engineers, vol. v, No. 10, 1888.

ard was 0·770 ohms; and its temperature-coefficient was about ·000010 per degree Centigrade.

The test piece, enclosed in a U-shaped tube of glass, was placed in an oil bath and alternately heated to 100° C. and cooled to 20°. The reference standard was kept at the room temperature. Its changes of resistance were regarded as negligible.

The application of the method just described, to a number of ferro-manganese-copper alloys, brought to light a remarkable and very troublesome property of this class of metals. It was found that they decreased in resistance each time that they were subjected to a change of temperature, even through the small range made use of in the attempt to determine their temperature-coefficients. The character of these changes can best be illustrated by quoting a series of measurements to which one of the alloys was subjected. An alloy containing 80·82 per cent of copper and 19·12 per cent of ferro-manganese, had been hard drawn in the process of obtaining a strip suitable for measurement. Its specific resistance at 20°, referred to pure copper as unity, was 30·38. It was repeatedly heated to 100° and cooled to 20° with the following result:

TABLE I.

Effect of repeated heating and cooling upon the resistance of Alloy No. 6, (*hard drawn*).

Observation.	Temperature.	Specific resistance.	Relative resistance.
1	20°	30·380	1·0000
2	100	30·186	·99331
3	20	30 163	·99287
4	100	30·151	·99255
5	20	30·138	·99202
6	100	30·121	·99180
7	20	30·118	·99134
8	100	30·118	·99134
9	20	30·105	·99093
10	100	30.099	·99072
11	20	30·092	·99051
12	100	30·104	·99092
13	20	30·079	·99007
14	100	30·104	·99092
15	20	30 072	·98985

We have, in the case of this alloy, a substance which increases in conductivity each time it is heated and cooled through the small range of 80°, the change in resistance diminishing in amount with each operation, but still perceptible at the end of the seventh cycle. At the same time a positive temperature-coefficient is being developed, which continues to increase as the heating and cooling process is repeated.

After being heated to 100° seven times, with the result shown in Table I, the alloy was raised to a red heat. Its temperature-coefficient was then redetermined with the result shown in the following table:

TABLE II.

Resistance and temperature coefficient of Alloy No. 8, (*after annealing at a red heat*).

Temperature.	Specific resistance. (At 20°)	Specific resistance. (At 100°)	Coefficient.
20°	28·478	------	--------
100	------	28·610	+·000052
20	28·446	------	--------
100	------	28·597	--------
20	28·440	------	+·000052

The effect of repeated annealing upon the resistance and coefficient of these alloys, is still more strikingly exhibited in the behavior of a specimen containing a larger proportion of ferro-manganese. The alloy in question consisted of 70·65 parts of copper and 29·35 parts of ferro-maganese. After being brought into a condition of stability, such that further heating and cooling through a range of eighty degrees had but little permanent effect upon its conductivity, it still showed, when hard drawn, an appreciable negative coefficient. It was then annealed three times at a red heat; specific resistance and coefficient being determined for the range 20° to 100°, after each annealing. The results are given in Table III.

TABLE III.

Effect of repeated annealing upon Alloy No. 11.

Condition.	Specific resistance. 20°	100°	20°	Coefficient.
Rather hard	46·10	45·99	46·09	—·000024
Once annealed	45·10	45·18	45·09	+·000021
Twice annealed	44·07	44·33	44·06	+·000068
Thrice annealed	42·76	43·58	42·74	+·000192

This metal possessed very nearly indeed the composition for which, in the patent specifications already referred to, the remarkable property of decreasing resistance with rise of temperature was claimed; which claim is substantiated, so far as the hard-drawn alloy is concerned. It will be seen that the coefficient depends upon the temper of the metal, and that it would probably be an easy matter to bring the latter into such a state that the change of resistance, which is, in all conditions of the alloy, very much smaller than in any other of which we have definite data, would be too small to be detected.

It appears, moreover, that the conductivity of this alloy was increased about 2 per cent by each successive annealing at a red heat, and that even after being thus annealed three times, it was subject to a further slight but measurable increase of conductivity, amounting to at least ·02 per cent, when subsequently heated to 100° and cooled to 20°.

The influence of temper upon the temperature-coefficient of a number of similar alloys was investigated by the method just described. The alloys showed, when hard rolled, a coefficient very near to zero, sometimes positive, sometimes negative. After annealing at 300° to 400° a well defined negative coefficient, after annealing at a red heat, a still larger positive coefficient, was developed. It was found that the positive coefficient produced by annealing, could be reduced again by rolling the alloy. Table IV shows the character of the results obtained. They were verified in every essential detail by frequent repetitions.

TABLE IV.

Influence of alternate annealing and hardening upon the temperature-coefficient.

Alloy No. 7. (Copper, 80·40%, Ferro-manganese, 19·60%).

Condition of the alloy.	Coefficient (20°—100°).
Hard	+·000022
Partially annealed	—·000032
Thoroughly annealed	+·000066
Re-rolled (hard)	+·000021
Again annealed	+·000045

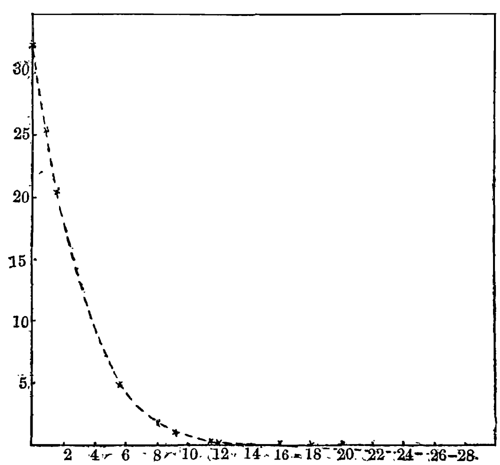
To determine the relation of the composition of these alloys to their temperature-coefficients, Mr. Blood tested twelve specimens, in which the amount of copper ranged from 70 per cent to 99·5 per cent, and also the copper itself from which the alloys were made. The percentage of copper present in each test-piece was determined to within one hundredth of one per cent, by the method of electro-deposition. The results of these determinations are incorporated in Table V.

TABLE V.

Percentage of copper.	Percentage of Ferro-manganese.	Sp. resistance (copper=1·00)	Temperature-coefficient, (20°-100°).		
			Alloy hard.	Alloy semi-annealed.	Alloy annealed.
100·00	0·00	1·00	·003202	------	------
99·58	0·42	1·07	·002579	------	------
99·26	0·74	1·19	·002167	------	------
91·88	8·12	11·28	·000138	------	·000184
91·03	8·97	11·74	·000120	------	------
88·97	11·03	14·07	·000065	------	-----
86·98	13·02	20·40	·000016	—·000021	·000080
83·72	16·28	----	·000010	------	·000023
80·88	19·12	30·38	·000012	------	·000046
80·40	19·60	27·50	·000022	—·000032	·000066
77·80	22·20	----	------	------	·000053
77·20	22·80	35·90	—·000012	------	·000010
70·65	29·35	45·10	—·000024	------	·000021

It was found that specimens containing less than eighty per cent of copper could not be worked without frequent partial annealing. Two such specimens were tested, after rolling and again after subsequent annealing. They showed a negative coefficient after rolling, which may have been due to the previous heating, undergone in the process of working them into the necessary form; but since they were as nearly in the condition of the hard-rolled alloys as it was possible to make them, they have been classified in the table among the hard metals.

The coefficients of the hard-rolled alloys, including those above mentioned, have been used in the construction of the accompanying curve, (figure 1). Abscissæ are percentages of ferro-manganese present in the respective specimens; ordinates are the changes of resistance for 100° C. It will be seen that the coefficient of the unalloyed copper falls considerably below Matthiesen's standard, and that the addition of small quantities of ferro-manganese produces a further very rapid



decrease. With ten per cent of ferro-manganese, the change of resistance is less than one per cent for one hundred degrees. Alloys containing from fifteen to twenty per cent of ferro-manganese possess exceedingly small coefficients, the curve crossing the base line at the point corresponding to eighteen per cent. The curve is intended to represent the variations of alloys which are of the same temper, but it is not possible to determine in how far it does so. Indeed for the entire range from fifteen per cent to thirty per cent the coefficient may be given any value between +·00002 and −·00002, by varying the temper of the metal. A positive coefficient could be obtained, however, in alloys containing more than twenty per cent of ferro-manganese, only by thoroughly annealing the specimen; whereas in metals containing a larger proportion of copper, either hardening or complete annealing developed a positive coefficient.

The marked influence of temper upon the conductivity of these alloys, renders it difficult to determine the precise law of the change in specific resistance with the composition. It appears, however, from the results presented in Table V, that the resistance increases nearly in direct proportion to the percentage of ferro-manganese.

Mr. Blood's investigation also included two alloys which contained nickel as well as ferro-manganese. The methods of preparation and measurement were identical with those which have already been described. The results, which are given in Table VI, show exceedingly small negative coefficients in the case of the hardened alloy. Annealing rendered the coefficient of the alloy containing the smaller percentage of nickel positive, and reduced the size of the coefficient of the other specimen.

TABLE VI.

Composition of the alloy.			Temperature coefficients.	
Copper.	Ferro-manganese.	Nickel.	Alloy (hard).	Alloy (annealed).
78·28%	14·07%	7·65%	—·000011	+·000007
52·51%	31·27%	16·22%	—·000039	—·000032

The experiments described in this paper, show that the alloys of ferro-manganese and copper, so far as their electrical behavior is concerned, must be considered as a distinct class. Up to the time of Mr. Weston's discovery of their properties, increase of conductivity with rise of temperature was supposed to be confined to electrolytes, and to the single solid conductor, carbon. Recent investigations have added sulphur to the list, and it is evident that this set of alloys, at least, belongs there also. It is not improbable that the further study of alloys containing metals of the iron group, will lead to the discovery of other combinations, possessing the same interesting and important characteristic.