

FACTORS AFFECTING THE ELECTROMOTIVE FORCE OF BINARY SOLID ALLOYS

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The great advance in the knowledge of the metallic alloys which has been made in recent years through the application of thermal analysis and micrography has given, in the equilibrium diagrams, a rational basis for the investigation of the properties of these substances, and there appears to be no important property which has remained wholly unstudied.

In nearly every instance certain relations have been found between the property in question and the metallographic structure of the alloy, so that the observation of each property constitutes in principle a method which might be expected to correct and amplify the thermal and micrographic results with regard to constitution. Hence it is at first thought surprising that this expectation can scarcely yet be said to have been fulfilled by even the best-studied of these properties, as is shown by the preference very generally given to the thermal, and particularly the micrographic evidence, where these conflict with the indications of electrical conductivity, electromotive force, thermoelectromotive force, hardness, etc., etc.

The reasons for this state of affairs are, however, not obscure. For in order to obtain accurate values for the measure of any property as a function of composition and structure it is necessary that these be both uniform and accurately known throughout the region observed, while it is notoriously difficult to obtain even apparent uniformity throughout a sample of sufficient size to permit the observation of most of the properties under consideration. Thus the electrical resistance observed for an alloy of such and such composition is in reality a value integrated over a region of considerable size, within which composition and struc-

ture vary, and does not correctly represent the resistance of the alloy in question. This involves an error which robs the method of much of the value which it would otherwise have for determining, for example, the limits of a region of solid solutions.

Since it is impracticable to avoid this source of error by observing conditions at a geometrical point in the alloy, the methods which may be expected to give the most accurate information are those in which the observations can be confined to a small area in a single plane, the more so since the causes chiefly responsible for differences of composition, at least in the case of alloys cooled in the crucible, operate in the vertical direction, so that horizontal sections may be obtained of a relatively high degree of uniformity. This advantage of permitting the observation of conditions in a small plane area is possessed by micrography, and undoubtedly is in a measure accountable for the exceptional value of this method of metallographical investigation. It appears to lend particular promise, as an additional method for the study of the solid alloys, to the observation of their electromotive force against electrolytes, and we have been led in consequence to undertake a somewhat detailed study of the factors affecting the potential of a binary solid alloy. In the present paper are given the introductory discussion and methods, with the results of some preliminary experiments.

The general dependence of potential on composition and structure has already formed the subject of numerous investigations for which reference may be made to the bibliographies available.¹ We may therefore confine ourselves to noting some respects in which further development appears to be needed.

In the first place, it would seem to be worth while to devote more attention than has usually been given to obtaining alloys free from oxides. To this end we have melted our samples only under borax, and have avoided casting.

¹ The fullest is probably that given by W. Broniewski: *Thèse*, Paris, pp. 138-9 (1911).

The attainment of uniform composition, in order that the electrode surface determining the potential may have, as nearly as possible, the same proportions of the components as are shown by analysis, is a consideration equally important, and has led us to prolong the time during which the alloy was maintained in a state of fusion, with frequent stirring, as well as the duration of annealing. As a control, the entire electrode surface of each test-piece has been subjected to microscopic examination. These precautions, together with the manner of selecting the test-piece, explained elsewhere, give specimens of brass which may reasonably be regarded as exceptionally uniform.

In the next place, the prevailing theory of solid alloy potentials, developed by Nernst¹ and Reinders,² is still in need of adequate experimental confirmation.³ And if the validity of the theory be assumed, certain details of its application in the conduct of measurements remain yet to be worked out. In particular, a method is needed of ascertaining the composition of the equilibrium electrolyte which corresponds to each composition of the alloy. Lacking this knowledge, it has been the usual practice to allow the alloy and an electrolyte of composition not greatly removed from that of equilibrium to interact, the value at which the potential became approximately constant being taken as that of the alloy. This method is known to give inaccurate results because of the change produced in the surface of the electrode, in consequence of which the final potential is in reality that of an alloy of somewhat altered composition. The true potential corresponding to the composition of the alloy at the time of immersion, and hence of analysis, would be obtained only in case the electrolyte possessed, to begin with, the equilibrium composition. It may be noted that experience has

¹ Nernst: *Zeit. phys. Chem.*, **22**, 539 (1897).

² Reinders: *Ibid.*, **42**, 225 (1903).

³ See comments of Tammann: *Lehrbuch der Metallographie*, Leipzig, pp. 338-9 (1914).

led Broniewski,¹ and apparently also Puschin,² to views not altogether in accord with this conception.

Finally, there have accumulated, since the earlier studies of solid alloy potentials, various considerations which raise questions as to the reproducibility of the potential, and the possible influences of heat treatment and surface treatment of the alloy. Here it will be enough to mention the dynamic conception of allotropy developed by Smits³ since 1910, the work of Cohen⁴ on the metastability of the metals, including copper and zinc, Beilby's observations, extended by Rosenhain,⁵ regarding the nature of polished surfaces and the possible existence of amorphous metal, and certain experiments upon the variability of the electrode potentials of pure metals.⁶

The factors affecting the electromotive force of a binary solid alloy, which are particularly in need of investigation, may therefore be said to be (a) the effect of heat treatment and surface treatment of the alloy, and (b) the composition of the electrolyte.

Among the most necessary precautions, other than those already indicated, must be reckoned exclusion of air, which is well known to exert a disturbing influence, and the avoidance of changes of concentration in the electrolyte. In the latter connection it is necessary to guard against evaporation, and against local changes due to convection currents or to relative motion of electrode and electrolyte.

Convection currents are not likely to be troublesome in an electrode vessel such as that which we have employed, in which the electrode chamber proper is surrounded by a second vessel with which it connects only through a small

¹ W. Broniewski: *Loc. cit.* and *Ann. Chim. Phys.*, (8) **25**, 1 (1912).

² N. Puschin: *Jour. Russ. Phys. Chem. Soc.*, **39** (1907); through *Zeit. anorg. Chem.*, **56**, 1 (1908).

³ See especially *Zeit. phys. Chem.*, **88**, 743 (1914).

⁴ E. Cohen: *Zeit. phys. Chem.*, **1913**, et seq.

⁵ Reviewed by W. Rosenhain: *Internat. Zeit. Metallog.*, **5**, 65 (1914).

⁶ G. N. Lewis and W. N. Lacey: *Jour. Am. Chem. Soc.*, **36**, 804 (1914); F. H. Getman: *Trans. Am. Electrochem. Soc.*, **26**, 67 (1914).

opening, especially where the temperature throughout is highly uniform.

As regards the influence of electrode motion, we have observed that, whenever in the midst of a set of readings showing a progressively changing potential, the cell is shaken, the E. M. F. drops back to a value shown some time before, and then gradually recovers, if the system is left undisturbed. It may therefore be supposed that the effect is due to the access to the electrode of fresh electrolyte not yet greatly altered in composition by interaction with the alloy.¹ It is evident that for the present purposes the altered layer of electrolyte in immediate contact with the electrode should not be removed, and that means intended to maintain uniformity in the composition of the liquid, such as stirring, are altogether inadvisable. The method of Kistiakowski, with rotating electrode, would increase the very changes in the alloy which it is here sought to minimize, and should only be employed when these are to be studied separately. We have therefore endeavored to keep the electrolyte as still as possible, even stopping the flow of nitrogen through the apparatus before beginning our observations.

In preparing the alloys Kahlbaum's "Kupfer, elektrolytisch, geraspelt," and "Zink I, geraspelt" were employed. Borax was melted in a 10 gram Battersea fire-clay crucible, which was heated in a Nichrome-wound furnace, and the metals were alternately stirred under in small portions until the calculated quantities had been added. Although rapidly attacked by the flux, stirrers of porcelain were used, as it was thought desirable to avoid the employment of carbon. This procedure is attended by a considerable loss of zinc, amounting to some twenty percent in the case of an alloy which finally contained 64 grams of zinc and 115 grams of copper, but it makes possible the preparation of brasses of

¹ Compare W. Kistiakowski: *Zeit. Elektrochemie*, **14**, 113 (1908); Nernst *Festschrift*, 215 (1912); St. Procopiu: *Annales de Jassy*, **7**, 224 (1912), through *Fort. der Phys.*, **68**, I, 369 (1912); F. Giraud: *Comptes rendus*, **157**, 586 (1914).

fairly high copper content with a simple furnace not capable of melting pure copper, and yields an alloy free from oxides.

The alloy, which was in every instance remelted and well stirred to increase its uniformity, formed on cooling a slightly conical block, of nearly equal height and diameter, having a volume of approximately 30 cc. From this block horizontal layers were cut, and these in turn were divided into strips of about $30 \times 3 \times 3$ mm, which constituted the test-pieces.

The particular alloy upon which the measurements reported in this paper were made yielded eight layers, the copper content of which varied from 50.67 percent in the uppermost to 49.54 percent in the bottom one, showing a change from layer to layer of about 0.16 percent. That this decrease was quite regular from top to bottom may be inferred from the fact that the fifth layer, counting from the top, showed an analysis of 50.01 percent copper, as compared with the interpolated 50.03 percent.

The analyses were made on one-half gram samples, the copper being deposited electrolytically from a nitric acid solution.

After grinding and polishing and etching with nitric acid, a microscopic examination showed some lack of uniformity and the test-pieces were accordingly annealed for from ninety-six to one hundred and sixty-seven hours at a temperature of 700° – 750° C. For this purpose they were enclosed in hard glass tubes which were then evacuated with the water pump. After admitting nitrogen the pressure was reduced to 190 mm of mercury, when the tubes were sealed. These tubes were embedded in sand in an electric furnace and, with the exception of a few which gave way, with consequent destruction of the test-pieces, remained gas-tight throughout the annealing, as was shown by the vacuum found upon opening, and by the entire absence of any evidences of oxidation. The outer layers of the glass, perhaps because of the inoculating action of the sand, were devitrified to some depth.

The annealing temperatures were observed with a Siemens and Halske direct-reading galvanometer, and a platinum

platinum-rhodium thermocouple imbedded in the sand in the midst of the tubes containing the test-pieces.

A microscopic examination of the annealed test-pieces, Nos. 1 and 2 below, after polishing and etching with nitric acid, showed large polygons which appeared to have undergone a transformation resulting in an extremely fine-grained structure, which the highest available magnification of 740 diameters was insufficient to resolve clearly. This is the structure to be expected if the β solid solutions undergo at 470° a eutectoid change into $\alpha + \gamma$, in accordance with the views of Carpenter. That there was no appearance of pitting may be regarded as evidence of the absence of oxides.¹

As it was desirable because of the ease with which our results under these conditions might be compared with the requirements of the Nernst-Reinders theory, to employ electrolytes 1-normal in copper and zinc combined, but having different very small concentrations in copper, and as it was further advisable to make the liquid-junction potentials between these solutions and those of the reference electrodes either negligible or constant, it was determined to make all solutions 1-normal in sodium sulphate and 1-normal in copper sulphate and zinc sulphate together. It may be supposed that such hydrolysis as occurs in these solutions is practically constant, and that consequently the ion concentrations are very nearly proportional to the equivalent normal concentrations. The sulphate solutions were adopted only after numerous experiments had convinced us that it was impracticable because of hydrolysis to employ chloride solutions 1-normal in potassium chloride in order to eliminate entirely the liquid-junction potential against a normal calomel electrode.

The electrolytes were prepared from Kahlbaum's Brown Label salts, two stock-solutions being made up of which one was 1.4-normal in zinc sulphate and of like concentration in sodium sulphate, while the other was 1.4-normal in both copper and sodium sulphates. The further steps are best

¹ Cf. Turner: Jour. Inst. Metals, 8, 248 (1912).

explained by giving the procedure used to obtain a solution $1.0 \cdot 10^{-5}$ -normal in copper. For this, 71.43 cc of the zinc stock-solution were measured from a burette graduated to 0.1 cc, into a 100 cc volumetric flask, and to this was added 1.0 cc of a solution obtained by diluting 0.71 cc, or ten drops, of the 1.4-normal copper stock-solution to one liter. On filling the flask to the mark there was thus obtained a solution $1.0 \cdot 10^{-5}$ -normal in copper sulphate, approximately 0.999-normal in zinc sulphate, and 1-normal in sodium sulphate. To make the dilution of the copper stock-solution a simple operation it is evidently necessary only that, for a dropping tube giving a drop of volume v cc, the stock-solution have such a normal concentration, c , that $v \cdot c = 1.0 \cdot 10^{3-x}$, where x is a small integer, and hence 1 drop = $1.0 \cdot 10^{-x}$ equivalents. Since our dropping tube gave, with the copper stock-solution, a drop of 0.071 cc, 1.4-normal stock-solutions were convenient. All measuring flasks, burettes, and pipettes were calibrated for 20° C, from which the room temperature varied by not more than three degrees.

The half-cell in which the test-piece was placed as electrode for observation of its potential, consisted of a narrow-necked glass cylinder 14 cm in height and 4 cm in diameter, within which was supported an inner vessel, or bell, about 1.2 cm in diameter containing the brass. The outer vessel stood upon a leaden disc, to which it was clamped to prevent floating in the thermostat. The inner bell, which was closed at the bottom by a one-holed rubber stopper secured with platinum wire, narrowed above to a 5 mm tube, or neck, which passed up through the large rubber stopper at the mouth of the outer vessel, and ended just above. Through this neck of the bell entered a narrower, rather closely-fitting tube, the draw-tube, which was sealed at the lower end, and had a small orifice in the side at a point about 1 cm higher up. Both this draw tube and a third tube of similar size, the inlet tube, which passed through the large stopper and ended open near the bottom of the annular space between inner and outer vessels, were connected by black rubber tubing to the forked

outlet of the wash bottle through which nitrogen was introduced. The large stopper which closed the outer and supported the inner vessel, admitted also a siphon, which served as salt-bridge to the intermediate vessel, and a small gas-exit tube with a bubble trap to prevent entrance of air.

The test-piece was secured with a drop of marine glue against the inner surface of the bell, and a fine copper wire, firmly wound about the upper end of the test-piece, passed between the neck of the bell and the draw-tube, and thence out to the potentiometer. A short piece of rubber tubing surrounding the draw-tube just above the neck of the bell, could be slipped down to close the opening between the two, and prevent ingress of air after the bell had been filled with nitrogen.

The electrolyte having been placed in the outer vessel, the large stopper bearing the bell, inlet tube, siphon and bubbler was inserted, the draw tube being at this time thrust down into the hole in the small rubber stopper at the bottom of the bell, and so preventing the entrance of electrolyte into the latter, and its access to the brass.

Nitrogen was now admitted, and entered the bell through the orifice in the draw-tube, its passage into the outer vessel through the inlet tube being prevented by the hydrostatic pressure of the electrolyte beneath which the latter ended. When the bell had been filled with nitrogen it was closed from the air by pushing down the short piece of rubber tubing already mentioned, and the draw-tube was thrust down until the orifice near its lower end came within the hole in the small stopper at the bottom of the bell, thus preventing the further passage of nitrogen through the bell, and compelling the gas to make its way through the inlet tube into the outer vessel, and thence out through the bubbler. After the outer vessel also had been filled with nitrogen, the draw-tube was raised until clear of the small stopper, through the hole in which the electrolyte then entered the bell and came in contact with the test-piece.

This type of cell permitted the brass to attain the tem-

perature of the electrolyte before actually coming in contact with it, so that the initial readings were little affected by errors due to differences of temperature.

The nitrogen employed was commercial tank nitrogen, passed through alkaline pyrogallol, and then through a portion of the electrolyte contained in a wash bottle which stood in the thermostat. An appreciable change in the composition of the electrolyte in the cell during the twenty minutes for which the gas flowed was thus avoided, while the fact that at the end of an experiment the part of the brass which had been at the contact of the electrolyte and the gas phase showed none of the corrosion observable when a similar experiment was made in air, indicated that the influence of any residual oxygen in the gas must have been extremely small.

Circuit with the reference-electrode was made through the siphon which contained the cell-electrolyte and thence through an intermediate vessel containing 1-normal potassium chloride, when a normal calomel electrode was in use, and 2-normal sulphuric acid, when the electrode employed was mercurous sulphate with the same 2-normal acid. The reference electrodes were carefully checked against each other and against a hydrogen electrode.

The cell, and the wash bottle designed to saturate nitrogen with the vapor of the electrolyte, were kept, during the observations, in a thermostat containing thirty gallons of kerosene, which was electrically heated and electromagnetically controlled. The temperature was shown by a Beckmann thermometer divided to 0.01°C which had been compared with a certificated standard instrument, and no variation from 25°C could be detected, during or immediately before any set of measurements, which was as great as 0.003°C .

The measurements of E. M. F. were made by means of a Leeds and Northrup potentiometer, using a Broca galvanometer by the Cambridge Scientific Instrument Company as zero instrument. A saturated cadmium cell was employed as standard, which the courtesy of Professor G. A. Hulett allowed us to check against his reference battery of similar cells.

Only in the case of the measurements recorded in Tables 1 and 2 was a less sensitive method employed. For these the E. M. F. was observed by means of a modified compensation apparatus, which permitted the voltage to be read directly on a millivoltmeter to within about three millivolts, a capillary electrometer of closed form being used as a zero instrument. When apparent constancy of the potential was shown by this apparatus, the final potential was measured with the potentiometer. For all later measurements the potentiometer was used throughout.

The twenty minutes or more required for the displacement of air from the cell having already permitted the equalization of temperature, the potential was read as soon as possible after the admission of the electrolyte, observations being taken twice in the first ten minutes and thereafter at ten minute intervals.

The first experiments relate to the constancy of the potential when the surface is untreated, and to the effect of changes of composition in the electrode surface, produced by the action of the electrolyte.

Test-piece No. 1 came from the middle of the sixth layer of eight, numbering from the top, and may be considered to have had before annealing the composition 49.9 ± 0.1 percent copper. After annealing for 96 hours, and polishing, it was employed for the four series of observations, the results of which are given in Table 1. At the head of each double column is shown the composition of the electrolyte, expressed in terms of the normal concentration in copper. Time is given in minutes from the first reading, and E. M. F. in volts.

In these experiments the surface was not renewed between withdrawal from one electrolyte and immersion in the next, but was merely well washed and dried, and air instead of nitrogen formed the atmosphere above the electrolyte. As was the case also with the measurements immediately following, upon test-piece No. 2, readings were discontinued when a potential constant to within three millivolts had been reached, this being the sensibility of the milli-

voltmeter. The last reading only was taken with the potentiometer. The bi-normal sulphate electrode was employed in the hope that it would have certain advantages for the special purpose in view, but was abandoned after the first experiments.

TABLE I

Reference Electrode: $\text{Hg}/\text{Hg}_2\text{SO}_4$, 2-n H_2SO_4

Atmosphere in cell: Air

Test-piece: No. 1; copper 49.9 percent

Annealed: Ninety-six hours at 700° - 750° C

Electrolyte 1.10^{-5} Cu		Electrolyte 1.10^{-6} Cu		Electrolyte 6.10^{-6} Cu		Electrolyte 4.10^{-6} Cu	
Time	E. M. F.	Time	E. M. F.	Time	E. M. F.	Time	E. M. F.
00	0.48	00	0.46	00	0.507	00	0.48 ₂
11	0.47 ₁	13	0.46 ₅	10	0.48	10	0.47 ₉
23	0.47 ₁	40	0.47	22	0.47 ₄	21	0.47 ₄
44	0.47 ₁	55	0.47	36	0.47 ₂	30	0.47 ₄
67	0.47 ₁	90	0.4699	48	0.47	53	0.4745
150	0.4700			58	0.46 ₉		
				69	0.4702		

From these measurements it would appear that a highly uniform, well annealed brass, the surface of which is subjected to no mechanical treatment from one experiment to the next, may give a potential reproducible to within a few millivolts, in spite of slight differences in the copper content of the electrolyte. Such a conclusion would indicate that changes in the composition of the electrode surface play a greater rôle than do changes in the composition of the electrolyte in the attainment of equilibrium between the two. This might indeed be inferred from the fact that changes in the solid phase are doubtless confined to a very thin surface layer, while the ease of diffusion in the liquid distributes the loss or gain of metal through a relatively large volume.

Besides emphasizing the necessity of employing the equilibrium electrolyte, if the potential of a surface of known composition is to be obtained with accuracy, the experiments offer evidence of the high uniformity of the alloy, since the

values show in each instance a very gradual steady "drift," the sense of which is determined by the composition of the electrolyte, instead of the highly irregular rise and fall of several centivolts, or even decivolts, observed, for example, by Broniewski¹ with aluminium alloys which had been prepared without special care to secure uniformity.

A similar very gradual variation is shown by test-piece No. 2, which came from the layer below test-piece No. 1 and from the next vertical row, and may be considered to have had before annealing the composition 49.7 ± 0.1 per cent copper. With an electrolyte $6 \cdot 10^{-6}$ -normal in copper the potential against a mercurous sulphate electrode, with an atmosphere of air, fell from 0.48 volt to 0.465 volt in one-half hour; with an electrolyte $4 \cdot 10^{-6}$ -normal in copper from 0.46 volt to 0.45 volt in four hours; and with an electrolyte $2 \cdot 10^{-6}$ -normal in copper from 0.51 volt to 0.478 volt in one and one-half hours.

The next experiments were made to determine the effect of surface treatment on the initial value and variation of the potential. The same two test-pieces as in the foregoing experiments were used and the surface was either polished with rouge on a wheel covered with broad-cloth, or rubbed down with No. FF emery-cloth before each set of readings, so that the change of surface produced by former contact with the electrolyte would not, as in the previous instances, affect the potential. Table 2 shows the variation of potential with change of surface, together with the composition of the electrolyte, the initial potential and the change in thirty minutes. From what has been said it will be understood that the electrolyte designated as 0.0-normal in copper was a 1-normal solution of zinc sulphate, 1-normal also in sodium sulphate.

In these experiments an atmosphere of nitrogen was maintained in the cell, and all observations of E. M. F. were made with the potentiometer. Since the potentials are nega-

¹ Loc. cit.

tive, the minus sign in column four indicates an increase in the values observed, or a rise in potential.

TABLE 2

Reference Electrode: Normal calomel
Atmosphere in cell: Nitrogen
Test-piece: No. 1; copper 49.9 percent
Annealed: Ninety-six hours at 700° – 750° C

Surface	Electrolyte	Initial E. M. F.	Change in 30 minutes
Rouge	0.0 Cu	0.289	—0.065
Emery	0.0 Cu	0.257	—0.048

Test-piece: No. 2; copper 49.7 percent
Annealed: 167 hours at 700° – 750° C

Surface	Electrolyte	Initial E. M. F.	Change in 30 minutes
Emery	$3 \cdot 10^{-6}$ Cu	0.247	+0.087
Emery	0.0 Cu	0.155	+0.006
Rouge	0.0 Cu	0.103	—0.027
Emery	0.0 Cu	0.180	+0.026
Emery	$1 \cdot 10^{-2}$ Cu	0.091	—0.008
Rouge	$1 \cdot 10^{-2}$ Cu	0.096	—0.014

Two sets of observations, from those the results of which have been summarized in Table 2, are given below in full.

TABLE 3

First Expt. of Table 2				Third Expt. of Table 2			
Time	E. M. F.	Time	E. M. F.	Time	E. M. F.	Time	E. M. F.
00	0.289	20	0.350	00	0.247	20	0.168
5	0.320	30	0.354	5	0.230	25	0.164
10	0.338			10	0.198	30	0.160
15	0.345			15	0.180		

These preliminary experiments appeared to establish the possibility of preparing, by the methods described, brasses of such uniformity as to show very gradual progressive changes

of potential, and hence suited to a systematic study of electromotive force. They served also to define clearly the direction which such a study must take.

For from the data of Tables 2 and 3 it is readily apparent that a very marked and as yet undecipherable influence is exerted by surface treatment, producing with a given alloy and electrolyte, "drifts" even the direction of which cannot be foreseen. That these (presumably) mechanical states cannot be obviated by annealing need hardly be said in view of the volatilization of zinc from heated brass,¹ and the consequent alteration of surface composition. If electrode surfaces corresponding to the analysis are to be studied, the exterior of the test-piece must be removed after every annealing, and the influence of sawing, grinding and polishing upon the potential becomes the problem first to be attacked.

Experiments upon these influences are at present in progress.

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¹ Cf. Thorneycroft and Turner: Jour. Inst. Metals, **12**, 214 (1914).