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Singularity in Pure Zinc at High Temperatures*

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Synopsis

Precise measurements of the temperature dependence of the electrical resistance of pure zinc were made without any imaginable disturbance, and no anomaly was found in the range from room temperature to the melting point. The study of quenching effect on the specific gravity showed, contrary to the result by Bingham, also no anomalous change. It was concluded that pure zinc had no singularity at high temperatures.

I. Introduction

One(1) of the present authors carried out accurate measurements of the electrical resistance of pure polycrystalline zinc, and found two anomalous changes respectively either at 170 or at 200 and at 320°C. They were in good agreement with those reported by many workers. A careful examination, however, led to the following conclusion: The anomaly at 170 or at 200°C is related to the eutectic phenomena of the "alloy" of zinc and the solder used in the electrical connection which is formed locally at the ends of the specimen during annealing. The temperature at which the anomaly appears depends on the kind of the solder used. On the other hand, the anomaly at 320°C, very small but appreciable, is due probably to the original impurities, mainly Pb, in the specimen. In both cases, therefore, the origin of anomaly lies in the "impurity" in the specimen. From this point of view, all other results(2-11) concerning this problem will be explicable in the same way as the above. These experimental results are illustratively in Fig. 1: they are the resistance-temperature curves, the ordinate scale being arbitrary. In Figs. 1 (a) and 1 (b), the arrows indicate the anomalous changes, in other words, the so-called transformation points observed by the respective workers. Fig. 1 (b) shows the $\Delta\sigma$-curves corresponding to curves 4, 8

* The 816th report of the Research Institute for Iron, Steel and Other Metals.

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(4) M. Werner, Z. anorg. Chem., **83** (1913), 275.
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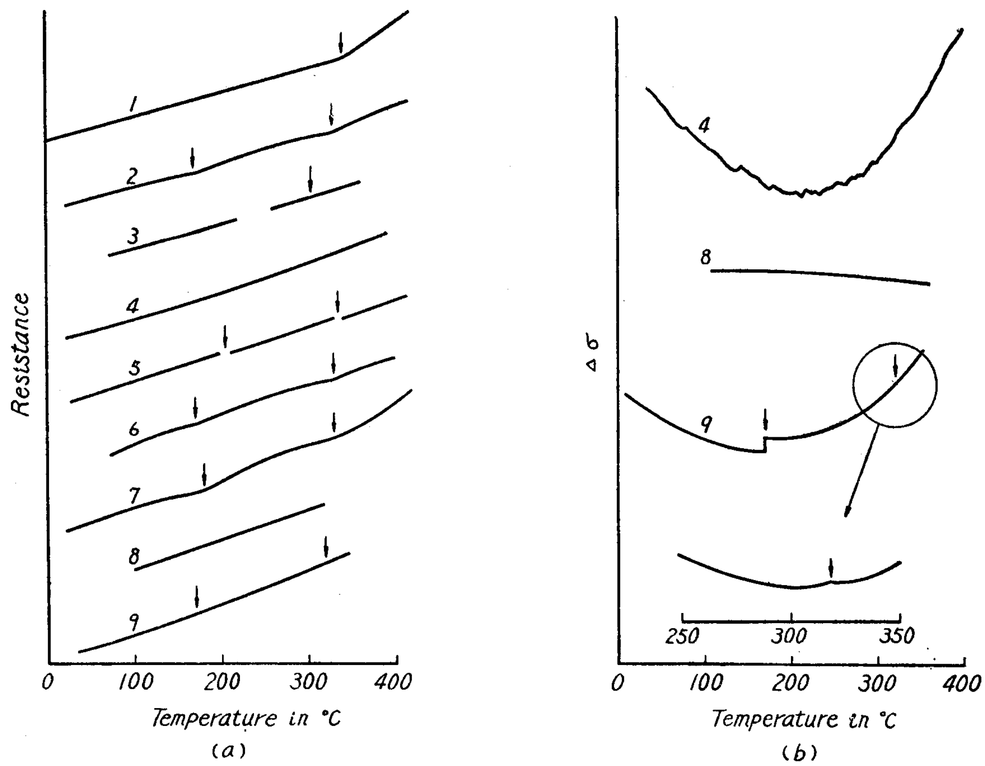

Fig. 1. Temperature dependence of resistance of zinc, obtained by various workers. (a) Resistance-temperature curves. (b) $\Delta\sigma$-curves corresponding to curves 4, 8 and 9 in (a). 1-Le Chatelier, 2-Benedicks, 3-Werner, 4-Benedicks and Arpi, 5-Bingham, 6-Schulze(8), 7-Pietenpol and Miley, 8-Schulze(11), 9-Satô and Suzuoka(1).

and 9 in Fig. 1(a) after the original papers, where $\Delta\sigma$ is the deviation of the observed resitance from a linear course; such a curve has often been adopted to magnify the behavior of an experimental curve (cf. reference 1).

The singularity found by Le Chatelier(2), Benedicks(3) and Werner(4) would have been due undoubtedly to impurities. The observation by Benedicks and Arpi(5) with pure zinc was not sufficient in accuracy as seen from its $\Delta\sigma$-curve, and against their conclusion the effect of the solder used may be pointed out. Bingham(7) did not use so pure a sample, and perhaps so with Schulze(8). Pietenpol and Miley(10) determined, with high accuracy, the resistivity of highly pure zinc, but as Wood's metal was used in the connection and, accordingly, the sample was considerably contaminated by it as shown later. The experiment of Schulze(11) was the first that satisfied both the two conditions of the highest purity and the connection without soldering, and hence his conclusion might not have been erroneous except that no attention was paid to the influence of soldering, and his measurement was so inadequate that the temperature curve became upward convex, owing probably to the large thermal force.

Besides the resistance, other physical properties of zinc were examined at high temperetures by many workers. As to thermal analysis, Mönckemyer(12) reported

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a transformation at 321°C, but Żemcżużnyj(13), Bornemann(14), Arnemann(15), Bingham(7), and Eastman, Williams and Young(16) could not observe it, whereas Jenkins(17) showed three allotropies. As to specific gravity, Cohen and Helderman(18) inferred a modification at high temperatures, which Bingham observed at 170°C and Losana(19) at 174 and 323°C. As to thermoelectromotive force, Werner observed an anomalous change at 300°C and similarly Lastschenko, Buikov and Efremov(20) at 310°C, while Bingham observed none. As to micro-structure, Petrenko(21) reported two transformations respectively at 175 and 300°C. As to pressure measurement, Jänecke(22) obtained a transition point between 104 and 120°C. As to electrode potential, Bingham found two anomalous changes respestively at 180 and 310°C and Stockdale(23) at 315°C. As to hardness, Bingham found transformations at 160 and 330°C, while Shishokin(24) at 180°C, and Molnar(25) at 200°C. As to specific heat, Lastschenko(26) observed a bend at 345°C but Behreus and Drucker(27), and Eastman, Williams and Young found no such singularity. Poppema and Jaeger(28), though observed it at about 170 and 335°C, ascribed the phenomenon to impurities in the specimen. Finally, as to thermal expansion, including measurements by X-ray method, all the results(29-34) were negative.

In surveying these reults, it will be seen that such a character of zinc is hardly questionable from the biginning. In spite of it, the controversy lasted for a long time until a series of X-ray study resulted in the tendency towards negative evidences. For this reason, it may be said that the study of resistance is the most useful method for this problem, because it has the highest degree of accuracy and the highest degree of probability to show the singularity.

It is, therefore, still essential that the discussion of the problem should be accompanied by a study of resistance. As already mentioned, a recent work(1)

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(16) E. P. Eastman, A. H. Williams and T. F. Young, J. Amr. Chem. Soc., **46** (1924), 1178.
(17) C. H. M. Jenkins, J. Inst. Metals, **36** (1926), 63.
(18) E. Cohen and W. D. Helderman, Verslag Acad. Wetenschappen, **22** (1913), 532, 1301.
(19) C. Losana, Gazz. chim. ital., **53** (1923), 539.
(20) P. N. Lastschenko, S. F. Buikov and S. U. Efremov J. Russ. Phys. Chem. Soc., **48** (1916), 279.
(21) G. I. Petrenko, J. Russ. Phys. Chem. Soc., **46** (1914), 176; Z. anorg. Chem., **162** (1927), 251; ibid., **167** (1927), 411.
(22) E. Jänecke, Z. phys. Chem., **90** (1915), 313.
(23) D. Stockdale, J. Chem. Soc., **127** (1925), 2951.
(24) V. P. Shishokin, Zhur. Prikladnoi Khim., **2** (1929), 675.
(25) A. Molnar, Compt. rend., **190** (1930), 1423.
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(28) T. J. Poppema and F. M. Jaeger, Proc. Roy. Acad. Amsterdam, **38** (1935), 38.
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(33) E. A. Owen and J. Iball, Phil. Mag., **16** (1933), 479.
(34) E. A. Owen and E.L. Yates, Phil. Mag., **17** (1934), 113.

remarked that the solder used influenced the resistance of zinc at high temperatures and that the previous results were also explainable from this point of view. To confirm it further, in the present study the resistance of zinc was measured without such an effect, and the true electrical behavior was observed at high temperatures. Furthermore, a study was made, of the quenching effect on the specific gravity of zinc similar to that by Bingham, for it is one of the most effective tests for the problem in question.

II. Electrical resistance at high temperatures

The experimental apparatus and procedure were the same as in the previous case, except the following improvement: Two potentiometers were used, one (Yokogawa's P-7 for low voltage) for measuring the resistance and the other (Yokogawa's P-1) for measuring the temperature, because if these two kinds of quantities were alternately measured only with one potentiometer, the maximum error arising from the contact resistance of the dial switches would be of about 1.5 micro-volts, namely, 0.03 per cent of observed values.

Specimens were also the same wires as those in the previous case, that is, 1 mm in diameter and 99.992 per cent in purity.

Now, in order to avoid any intrusive disturbance, the same zinc wires as the specimen instead of the electrical leads of copper, were welded by fusing to the specimen as shown in Fig. 2. In this way, such an effect as that due to the solder could be removed at any heat treatment, and moreover, no foreign metal could cause the thermal force at the junctions. This electrical circuit, however, has the following defect: Zinc grains, when annealed, can easily grow up and the wires become strongly heterogeneous with respect to thermoelectricitiy. For the specimen, however, it is a matter of no importance so long as it lies in a uniform temperture range, wherers for the potential leads this gives a thermal force because these wires form a thermo-couple. The thermal force increases as the tempreature of the furnace rises, reaching several tens of microvolts at 400°C, which is detectable by the reversal method.

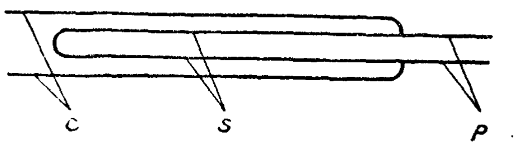

Fig. 2. Electrical connection of specimen. S, specimen; c, current leads; p, potential leads. These are respectively insulated by inserting into fine quartz tubes which are not drawn in the figure.

The result of a preliminary measurment of the resistance of pure zinc annealed at 210°C for 4 hours is shown by $\Delta\sigma$-curve 1 in Fig. 3. In this case, the reversal method could not be carried out because the reading had to be taken every minute, so that the large thermal force could not be corrected, and accordingly, the curve shows the temperature dependence merely with relative accuracy. From the $\Delta\sigma$-curve it will be seen that there is no singulularity whatever in pure zinc, the resistance increasing very smoothly from room temperatur to 417°C immediately below the melting point.

An absolute measurement was next made by reversal. The size of the specimen

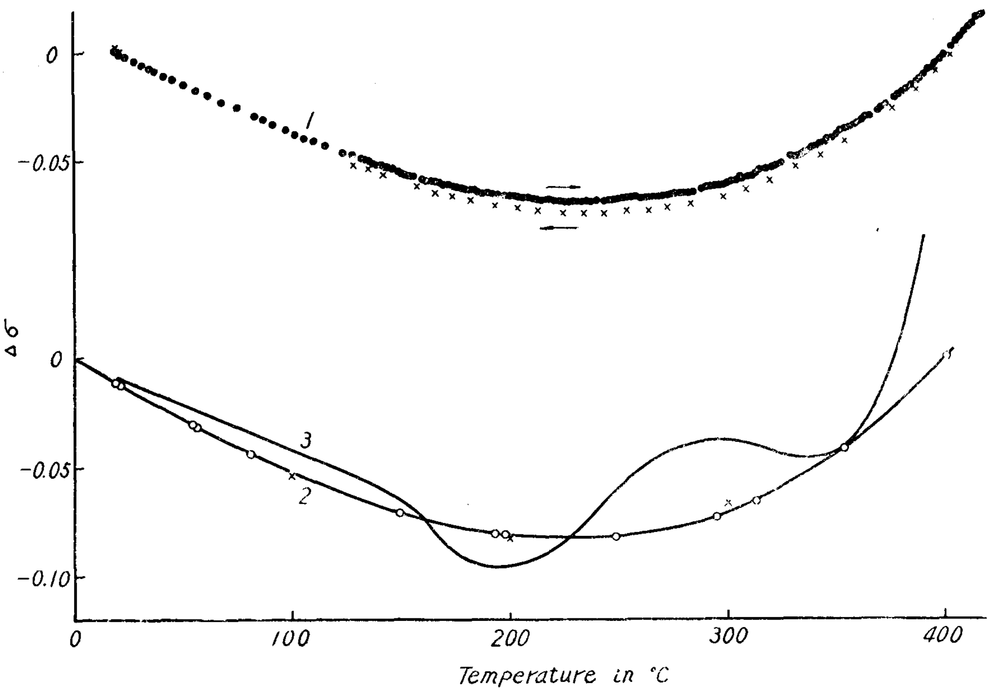

Fig. 3. $\Delta\sigma$-curves of zinc. Curves 1 and 2 are obtained from the present study, and curve 3 is calculated from the data by Pietenpol and Miley. Crosses express Holborn's values.

was 778.8mm in length and 1.005mm in diameter at about 20°C, the mean diameter being obtained from several micrometer readings at thirty-six different positions. It was annealed at 210°C for 4 hours as before. The results are given in Table 1. The numerical values in the second column, $\sigma = r/r_0$, are the ratios of the

Table 1. Resistance ratio and resistivity of pure zinc at high temperatures, the former being compared with Holborn's values.

Temperature t in °C	Resistance ratio $\sigma = r/r_0$	Holborn's σ	Resistivity in micro-ohm-cm
0	1.0000	1.0000	5.463
20	1.0822		5.917
40	1.1647		6.373
60	1.2476		6.833
80	1.3312		7.296
100	1.4158	1.4146	7.766
120	1.5013		8.242
140	1.5880		8.724
160	1.6760		9.215
180	1.7654		9.715
200	1.8564	1.8556	10.224
220	1.9488		10.740
240	2.0428		11.267
260	2.1385		11.804
280	2.2361		12.353
300	2.3360	2.3407	12.915
320	2.4384		13.491
340	2.5434		14.083
360	2.6511		14.691
380	2.7618		15.317
400	2.8756		15.961

resistance at a given temperature to that at 0°C; the resistance values were determined by inter- and extrapolating the observed values, the specific accuracy of which was evaluated to be within 0.01 per cent. Its $\Delta\sigma$-curve is shown by curve 2 in Fig. 3. The resistivity at 20°C was 5.917 micro-ohm-cm, and was in good agreement with 5.916 micro-ohm-cm(35) shown in *Metals Handbook* (1948). From this value of resistivity and the thermal expansion coefficient of zinc, 3.95×10^{-5} per degree(36), the resistivity at any temperature was calculated, and the results are shown in the fourth column of the table. The resistivity of solid zinc at the melting point was estimated to be 16.60 micro-ohm-cm.

The value σ in the temperature ranging from 0 to 400°C accords with the following empirical formula with a deviation less than 0.06 per cent*:

$$\sigma = 1+0.0041167\ t+1.726\times10^{-7}\ t^2+3.1633\times10^{-9}\ t^3$$

From these features it may be concluded that the resistance of pure zinc increases very smoothly with increasing temperature, that is, it was no anomaly in the temperature range from 0°C to the melting point.

For comparison, the $\Delta\sigma$-curve calculated from the data by Pietenpol and Miley(10) will be shown. It may easily be supposed that their extra-pure specimen (99.993 per cent) would strongly be spoiled by the Wood's alloy used in the electrical connection. Curve 3 in Fig. 3 is the result. It will be seen that this curve greatly deviates from the smooth curve 2 of the present result and that melting begins at considerably lower temperature. Zinc used in the present experiment, however, showed no sign of melting up to 417°C. On the other hand, the values given by Holborn(6), who determind chiefly the temperature coefficients of resistance of various metals, agree very well with the present results.

III. Effect of quenching on specific gravity

The study of the state of zinc by specific gravity was first carried out by Cohen and Helderman(8), who deduced from the observation of the change in specific gravity with heat treatment a certain "modification" at temperatures above 100°C, in which zinc was meta-stable and could return only very slowly to the stable state at ordinary temperature. Miss Bingham(7) measured the specific gravity of zinc quenched at various temperatures and found that it jumped sharply by about 1 per cent when the zinc was quenched at 170°C as shown in Fig. 4. Her zinc was 99.97 per cent pure. By a dilatometric method, Losana(19) observed the specific gravity of zinc from −130 to 350°C, and found that it increased at 176°C by 1.02 per cent and decreased at 320°C by 0.42 per cent. From further studies by Le Chatelier-Broniewski's differential method, he concluded that three allotropies existed in zinc, the transformation points being 174 and

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(36) "Zinc and Its Alloys", Bur. Stand. Circ., 395, Nov. 6, 1931.
* Compared with the recent pure zinc of 99.999 per cent, our zinc is rather impure. This deviation of ±0.06 per cent is not a random fluctuation but is of wavy form. This slight deviation is due probably to the impurities, since its form, though small in magnitude, is similar to that of the contaminated specimen used by Pietenpol and Miley.

323°C. The zinc used was inferior to that in Bingham's case, containing not small amounts of Pb, Sn and Fe.

The reason for taking the specific gravity as an effective means in the present study was that this property of zinc was the only one which could give a positive and distinct evidence without exception. Although the above mentioned studies were not so sufficient with respect to both accuracy and purity of specimen, the evidence was distinct. Hence, if it was true, it would, of course, be detectable by an observation with a higher accurancy and a purer specimen; on the contrary, if it could not be observed even with the highest accuracy possible, the impurity in the specimen would be taken to give rise to the phenomenon in question. As in the case of Bingham, so in the present study the quenching effect on the spesific gravity was examined with the purest zinc.

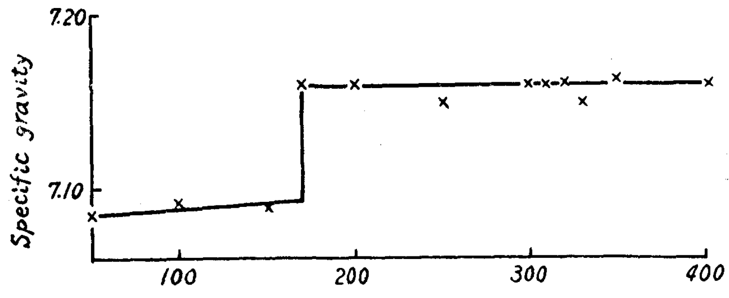

Fig. 4. Quenching effect on specific gravity of zinc odtained by Bingham.

The experiment was carried out by the usual method of chemical balance. The specimen was cubic, about 47 grams in weight, which was prepared by pressing a cast cubic ingot under the pressure of 2 tons per cm^2. It was primarily annealed at 310°C for 30 hours and slowly cooled to room temperature, taking 20 hours. This specimen was quenched in water after annealing for 30 minutes at various temperatures and the specific gravity was measured at 25°C. The difficulty of keeping the specimen at this temperature was presumably responsible for the experimental error of 0.003 per cent in the present measurements.

Observations were made on the specimen quenched at temperature ranging from 25 to 370°C. As seen from the results given in Table 2, it was surprising that no quenching effect was observable and that the specific gravity was invariable within the experimental error. It follows, therefore, that pure zinc has no such anomaly as found by Bingham. The results by Bingham and by Losana were obviously affected by impurities, while that by Cohen and Helderman was too primitive to discuss.

Table 2. Specific gravity of quenched zinc (at 25°C).

Quenching temperature in °C	Specific gravity
25	7.1319
50	7.1317
100	7.1318
152	7.1318
161	7.1319
171	7.1318
176	7.1318
200	7.1317
210	7.1316
252	7.1320
300	7.1319
318	7.1317
324	7.1319
369	7.1313

The specific gravity at 20°C calculated from the thermal expansion coefficent already stated is 7.1360, while according to *Metals Handbook* (1948), it is 7.133[36].

IV. Discussion

There is no doubt that the anomalous changes in the electrical resistance of zinc at high temperatures is due to impurities in the sample. They may be either the original impurities or the contamination by the solder, or the both. The solder, in paticular, will play an important *rôle*, since the principal elements of common solders, Cd, Pb, and Sn, are liable to be dissolved in zinc and will behave themselves like original impurities. The superposition of these two effects will frequently pretend the singularity. As for the specific gravity, it is interesting that the effect of quenching was not observable, which may be said to be the verification for the non-existence of singularty in zinc.

All the other results may also be interpreted by the impurities in zinc. In these cases, however, a complete analysis is not always easy, for in many cases the kinds and amounts of impurities are uncertain, and the phase diagrams of zinc and impurities in it are known only insufficiently and inaccuarately. Though such are the circumstances, it may safely be concluded that pure zinc has no anomaly in the range from room temperature to the melting point, and that the apparent anomalous changes obtained by previous workers are due to the impurities in zinc.

Acknowledgement

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