DEVIATIONS FROM MATTHIESSEN'S RULE FOR COLD-DRAWN WIRES

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Summary

An A.C. bridge method of high accuracy has been developed to measure deviations from Matthiessen's rule. Deviations have been shown to exist in cold-drawn wires of copper, aluminium, bronze, and 80/20 brass.

I. Introduction

In a recent investigation (Boas and Nicholas 1953) it was found that the slope $\Delta\rho/\Delta T$ of the resistivity *v.* temperature curves of cold-drawn wires was smaller by a few per cent. than that of annealed wires in the cases of 75/25 brass and an aluminium bronze. However, for six other metals and alloys the difference in slope was within the limits of experimental accuracy. The purpose of the present work was to check the previous results for brass and aluminium bronze and to find out whether pure metals observe Matthiessen's rule strictly, or also show a change in $\Delta\rho/\Delta T$ on cold-drawing.

Boas and Nicholas measured the resistances of their wires using a Kelvin double bridge, the wires being immersed one at a time and individually measured in melting ice and liquid oxygen. In the present experiments an A.C. bridge method was used which offers the advantage of high sensitivity and elimination of errors due to thermo-e.m.f.'s. The high sensitivity available enabled the use of small measuring currents, thus avoiding errors due to temperature rise in the wires being measured. Moreover, both wires were immersed together in the same bath ensuring that their temperature was almost the same and were measured almost simultaneously so that errors in the measurement of the temperature of the bath are not critical.

II. Experimental

(*a*) *Preparation of Specimens*

The materials used (conductivity copper, 80/20 brass, and an aluminium bronze) and their compositions were the same as those used in the previous experiments. They were originally in the form of factory annealed wires of approximately 4 mm diameter and were given the following heat treatment prior to drawing. The copper wires were annealed *in vacuo* at 600 °C for 1 hr. The 80/20 brass wire was sealed in coal gas at atmospheric pressure, the aluminium bronze specimens were sealed in coal gas at approximately 1 mm Hg ; they

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were annealed at 600 °C for 1 hr. The wires were then drawn on a power draw bench at room temperature. The drawing speed was maintained as constant as possible at about 4½ ft/min. A specimen was taken from each wire, one-half of which was left in the cold-drawn condition and placed in a refrigerator, while the other half was annealed under the same conditions as those given for the primary material.

It was found that the diameter of a wire could increase from beginning to end by more than 1 per cent. if only short lengths (2 or 3 ft) were drawn. Since most of the change occurred in the first 8 ft of the wire no specimens were taken from the first 12 ft of wire to pass through the die. The cause of these diameter variations is not completely understood. It seems likely that heating of the die and the consequent changes in the properties of the lubricant used could account for most of the diameter variation. Along the specimen length (approximately 60 cm) the diameter variation was less than 3×10^{-5} in.

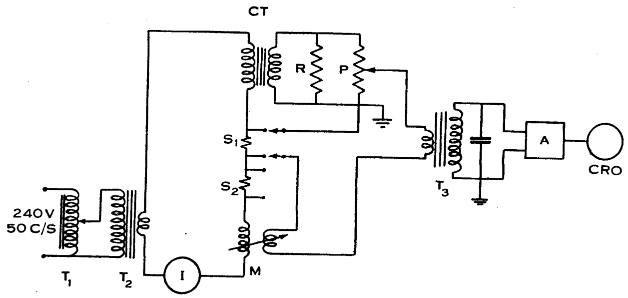

Fig. 1.—A.C. bridge circuit for resistance measurements.

(b) *Apparatus*

The resistance measurements were made by an A.C. bridge method similar to that used by Broom and Clothier (1952). The circuit is shown in Figure 1. Current at 50 c/s is supplied from the variable auto-transformer T_1 and isolating transformer T_2, to the specimens S_1 and S_2 and also to the primaries of the current transformer *CT* and variable mutual inductor M. The secondary current of *CT* flows through a low value four-terminal resistor R, the potential terminals of which are connected to a Thomson-Varley potential divider P. The settings of P and M are adjusted until the detector indicates balance. The balance detector comprises a tuned step-up transformer T_3, tuned amplifier A and cathode-ray oscillograph *CRO*.

The specimen resistance is given in terms of the ratio of *CT*, the value of R, and the setting of P at balance. The value of M is very small and it does not enter significantly into the determination of R. Relative values of specimen resistance are given directly by the relative settings of P. The measuring current in all cases was 0·4 A. Several different values for R were used in the course of the measurements, the value selected being one which ensured adequate reading accuracy on P for the particular specimen pair under test.

Since the resistance of a wire is altered when it is stressed, the comparison of resistivities to the required accuracy is only possible if the wire is not heavily loaded. Moreover, owing to the dimensional changes that occur in the specimen and its support between the upper and lower extremes of temperature used in the test, special precautions must be taken to avoid movement of the contacts relative to the specimen. Therefore, the usual type of specimen holder, in which the wire is held straight in tension and then two knife-edges brought into contact with it, is not satisfactory.

The specimen holder used consisted of a number of " Perspex " plates held parallel by a brass channel. Each plate was drilled with holes, the centres of which were collinear. These holes constrained the specimen wires to lie in a straight line. The knife-edges were supported by the specimen wires themselves ; they were formed from U-shaped loops of 20 gauge piano wire, one end being set in a small " Perspex " block which was grooved to hold the specimen wire. The arrangement is shown in Figure 2. A small manipulator was used to place

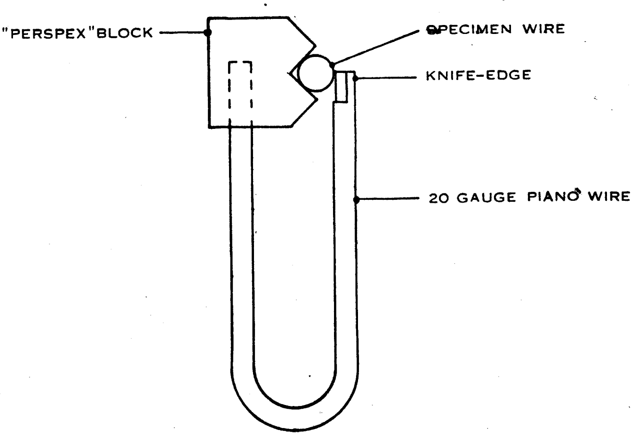

Fig. 2.—Knife-edge assembly.

the knife-edges on the wire so that the least possible bending and surface damage was caused. The separation between the knife-edges, which were about 15 cm apart, was measured with a cathetometer which could be read to 0·001 cm. The wires were connected in series using a bridging piece at one end. The specimen assembly was sufficiently small to fit comfortably into a medium size parallel-sided Dewar flask which served as a constant temperature bath for the measurements at low temperature. The measurements were carried out at room temperature and at liquid oxygen temperature.

The temperature at which the measurements were made was not of prime importance, but it was necessary that the temperatures of the specimen wires be equal to high precision (better than 0·01 °C). To achieve this in the water-bath at room temperature efficient stirring was necessary. Preliminary measurements established that the conductivity of tap water was not high enough to interfere with the electrical measurements. As a precaution, however, distilled water was used. The experiments were performed in a constant temperature room and, since the bath was large and at the same temperature as the surrounding air, temperature drifts were extremely slow.

The low temperature bath was liquid oxygen. It was necessary to leave the specimen assembly in the bath for at least 10 min before measurements were started to ensure temperature equilibrium. In addition, all metal parts of the specimen assembly had to be completely covered by the liquid oxygen, otherwise irregular temperature changes caused variations in the resistance of the wires. Under these conditions the temperature difference between the wires was very small. This was shown by stirring the bath and finding that, with two identical wires in the holder, the ratio of the resistances remained constant. The observed change in resistance of each wire would have been accounted for by a fall in temperature of approximately 0·1 °C.

As a check, the resistances were frequently remeasured at room temperature after the specimens had been in the liquid air bath, and then again in the low temperature bath. After correcting for temperature changes in the room temperature bath it was found that the resistance of the wires, after immersion in liquid oxygen, changed by less than 0·02 per cent.

On removing the specimen assembly from the room temperature bath, prior to immersion into liquid oxygen, it was passed through two successive alcohol baths and then dried in an air stream. It was necessary to ensure that no water was left under the knife edges, since the presence of ice can cause trouble by lifting the knife-edges out of contact with the wire. For the same reason it was found necessary to avoid icing of the contacts in transferring the specimen assembly from the liquid oxygen bath to the water-bath. Failure to observe this precaution caused large changes in the measured resistance of the wires, due, it is believed, to displacement of the contacts. In order to avoid temperature changes in the room temperature bath, the specimen assembly was brought nearly to the correct temperature in an intermediate water-bath before placing it in the room temperature bath for measurement.

After the completion of the electrical tests the portion of the specimen between the potential points was cut out and its ends were squared. It was weighed and its length was measured whilst held straight in a glass capillary tube.

III. Results

The experimental results are summarized in Table 1, which also gives the results of Boas and Nicholas for comparison. The deviations from Matthiessen's rule found in the present work lie within the rather large limits of error of the previous experiments. Further, such deviations have now been shown to exist in copper. The specimens investigated all showed " negative " deviations from Matthiessen's rule, that is, $(\Delta\rho/\Delta T)_D$ is less than $(\Delta\rho/\Delta T)_A$. Absolute values of the resistivity can be calculated only if the cross sections of the wires are known. In uniform wires of small diameter the most accurate method of determining cross section is to measure the mass and length of the wires. This method requires a knowledge of the density. As this information is not available to the necessary precision, the products of the resistivity and the density are tabulated. In the determination of relative resistivity it is assumed that the densities of the deformed and annealed wires forming a specimen pair are the same.

TABLE 1

SUMMARY OF RESULTS

1	2	3	4	5*	6*	7	8
						$\left[\frac{(\Delta\rho/\Delta T)_D}{(\Delta\rho/\Delta T)_A}-1\right]\times 100$	
Metal	State	Diameter (in.)	Logarithmic Strain	$(\rho\times d)\times10^{-5}$ at Room Temp.	$(\rho\times d)\times10^{-5}$ at Liquid Oxygen Temp.	Present Work	Boas and Nicholas
80/20 Brass	Deformed	0·0359	3·19	5·632	4·101	−0·02±0·04	
	Annealed	,,	,,	4·721	3·190		
	Deformed	,,	,,	5·631	4·100	−0·06±0·04	−0·06±0·66
	Annealed	,,	,,	4·721	3·189		
Aluminium bronze	Deformed	0·0159	4·97	11·275	9·806	−2·2 ±0·04	
	Annealed	,,	,,	8·639	7·137		
	Deformed	0·0285	3·81	11·238	9·766	−1·7 ±0·04	
	Annealed	,,	,,	8·654	7·156		−1·98±1·69
	Deformed	,,	,,	11·238	9·755	−1·9 ±0·04	
	Annealed	,,	,,	8·654	7·142		
	Deformed	0·0403	3·11	11·153	9·677	−1·7 ±0·04	
	Annealed	,,	,,	8·607	7·104		
Copper	Deformed	0·0179	3·93	1·5559	0·3096	−0·29±0·04	
	Annealed	,,	,,	1·5107	0·2608		
	Deformed	0·0201	3·70	1·5543	0·3076	−0·29±0·04	
	Annealed	,,	,,	1·5112	0·2607		
	Deformed	0·0253	3·24	1·5472	0·3052	−0·19±0·04	0·02±0·30
	Annealed	,,	,,	1·5046	0·2602		
	Deformed	0·032	2·77	1·5428	0·3033	−0·22±0·04	
	Annealed	,,	,,	1·5019	0·2595		
	Deformed	0·0403	2·31	1·5436	0·3009	−0·12±0·04	
	Annealed	,,	,,	1·5038	0·2597		

* The values for the product of the resistivity and the density, $\rho\times d$, given in columns 5 and 6 have been rounded off after calculating column 7.

In the table ρ is the mass resistivity. To convert to volume resistivity thermal expansion must be allowed for. Precise figures are not available, but it is clear that

$$\left[\frac{(\Delta\rho/\Delta T)_D}{(\Delta\rho/\Delta T)_A}-1\right]\times 100$$

is not appreciably altered in the cases of copper and aluminium bronze. For 80/20 brass, however, the deviation will be opposite in sign.

IV. Errors

The known sources of error are as follows.

(i) *Uncertainty in the Length of Specimen between the Potential Knife-edges.*—It was required that the wire be unstrained when resistance measurements were being made. On the other hand, to determine the specimen length accurately with a cathetometer, it was necessary that the wire be straight. In the specimen holder, the wire was held very nearly straight. However, for several of the wires the residual irregularities were sufficient to cause errors of about 2 in 10^4.

(ii) *Uncertainties in Temperature.*—Preliminary measurements established that there could be a temperature difference of about $0 \cdot 1$ °C between the liquid oxygen bath and the specimen wires, whilst the difference in temperature between the wires was considerably less than $0 \cdot 01$ °C. Errors due to temperature measurement or to temperature inequality were, therefore, negligible.

(iii) *Errors in Resistance Measurements.*—The absolute accuracy of resistance measurement was better than 2 in 10^4; the accuracy of intercomparison of any specimen pair was about 3 in 10^5 and the sensitivity of measurement was such that a variation of 1 in 10^5 could easily be detected.

(iv) *Inhomogeneity of Specimens.*—Using a short distance between the potential contacts, resistance measurements were made at various positions along a few of the specimen wires. Variations of unknown origin were found. Although these variations would be important in determining absolute resistivities, their effect in this determination of the deviations from Matthiessen's rule is very small.

(v) The length of the wires was measured to an accuracy of $\pm 0 \cdot 005$ mm in a length of about 15 cm. Their weights were determined to $\pm 0 \cdot 00002$ g; the minimum weight being greater than $0 \cdot 2$ g.

The overall accuracy is sufficient to give

$$\left[\frac{(\Delta\rho/\Delta T)_{\mathrm{D}}}{(\Delta\rho/\Delta T)_{\mathrm{A}}}-1\right]\times 100,$$

the deviation from Matthiessen's rule, to an accuracy of $\pm 0 \cdot 04$.

V. Discussion

The higher accuracy of the present results is due to the improved technique of measurement and to the recognition of the serious variation in diameter occurring in the first few feet of a drawn wire. This fact sets an important limit on the reliability of all previous results and throws doubt on the conclusions drawn from them (Rutter and Reekie 1950).

Two conclusions can be drawn from the present results. Firstly, deviations from Matthiessen's rule have been found with the materials investigated. The lower accuracy of their method and not the absence of the effect prevented Boas and Nicholas finding significant deviations in copper. Secondly, all the deviations are of the same sign, that is,

$$\left[\frac{(\Delta\rho/\Delta T)_{\mathrm{D}}}{(\Delta\rho/\Delta T)_{\mathrm{A}}}-1\right]\times 100$$

is negative in all cases, and this difference increases with the extent of deformation. This is in agreement with the findings of Boas and Nicholas.

In a recent paper Sondheimer (1950) has pointed out that deviations from Matthiessen's rule can be expected at intermediate temperatures. As his calculation holds for monovalent metals only, no comparison of the measured values with his calculation has been made.

Broom (1952) in some experiments on the effect of drawing temperature on the electrical resistance of drawn wires assumed the validity of Matthiessen's rule in the calculation of values of $\Delta\rho/\rho$. The results of the present investigation indicate that this assumption was justified to the accuracy given in his results.

VI. References

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