VALIDITY OF MATTHIESSEN'S RULE FOR COLD-WORKED WIRES

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Summary

Matthiessen's rule has been tested by determining the slopes of the electrical resistivity-temperature curves for wires of eight common metals and alloys in various states of deformation by wire-drawing. The results show that the slope is independent of deformation, i.e. the rule is true, to within $0 \cdot 5$ per cent. for nickel, copper (two purities), iron, and 80/20 brass, and to within 1 per cent. for aluminium. However, for 75/25 brass and an aluminium bronze, deformations corresponding to logarithmic strains of $2 \cdot 3$ decrease the slopes by 1 and 3 per cent. respectively. As an explanation of this behaviour, it is suggested that deformation causes an increase in the characteristic temperature.

I. Introduction

Matthiessen's rule states that, for a metal or alloy, the product of the electrical resistivity and its temperature coefficient is not affected by either deformation or the addition of small concentrations of solute atoms. Whereas the effect of alloying has been investigated extensively, that of deformation has not attracted much attention. During recent work in this laboratory (Broom 1952) on the resistivity of cold-drawn wires, some results were found which suggested deviations from the rule. The most recent systematic work on the validity of the rule for a metal in various states of deformation is that by Geiss and van Liempt (1925, 1927) who found that, for tungsten, molybdenum, platinum, and nickel, deformation produced variations in the product of up to 2 per cent. They give no indication of their experimental error but conclude that the rule is true. As the rule implies the possibility of separating the resistivity of a metal into a part dependent only on temperature and a part dependent only on deformation, it is of interest to know how closely it is obeyed. Therefore, an investigation has been carried out to test its validity for wires of eight common metals and alloys, the accuracy aimed at being $0 \cdot 5$ per cent.

Since, by definition, the temperature coefficient of resistivity, α, is given by

$$\alpha = \frac{1}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}T},$$

where ρ is the resistivity and T the absolute temperature, Matthiessen's rule can be formulated as either $\alpha\rho$=constant or $\mathrm{d}\rho/\mathrm{d}T$=constant. In this investigation the rule was tested by considering the variation of $\mathrm{d}\rho/\mathrm{d}T$ with deformation.

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II. Experimental

(a) *Preparation of Specimens*

The materials used and their compositions are given in Table 1.

Table 1

COMPOSITIONS OF MATERIALS USED

Nickel	0·03% C; 0·01% Co; 0·12% Mg; <0·05% Mn, Cr, Cu
Spectrographic copper	0·0003% Ag, Ni; <0·0004% Pb
Conductivity copper ..	<0·01% Ag, Cd, Pb, Si; ⩽0·01% Mg, Fe
Spectrographic iron ..	0·002% Cu; 0·005% Ni
Spectrographic aluminium	0·002% Mg; <0·001% Si; <0·0005% Fe, Cu
80/20 Brass	20·21% Zn; 0·02% Fe; 0·01% Pb, Sn
75/25 Brass	25·35% Zn; 0·1% Fe; 0·05% Sn; <0·01% Pb; ⩽0·01% Mn
Aluminium bronze ..	5·67% Al; 0·28% Zn; 0·1% Fe

These were originally in the form of annealed wires of approximately 4 mm. diameter and were then drawn at room temperature to a final diameter of approximately 1 mm. Each time the wire was passed through a die, a length was cut off and annealed for 2 hr. at 600 °C. (400 °C. for aluminium) before the original wire and the cut-off pieces were deformed further. In this way, 11 specimens of each material were obtained, all of similar dimensions (30 cm. long and 1 mm. diameter) but each having been deformed by a different amount since the last annealing. The deformations corresponded to logarithmic strains spread evenly over the range 0–2·3. The similarity in specimen sizes meant that, for each material, all measurements of the same quantity and the corresponding experimental errors were of the same magnitude.

(b) *Measurements*

Using a Kelvin double bridge, the resistance of a standard length of each specimen was measured in a bath of melting ice (0 °C.) and in one of liquid oxygen (−183 °C.), all measurements being repeated two or three times. The weights and lengths of the specimens were then measured and, from these, relative values of the mean cross-sectional areas for all specimens of the one material were calculated. Finally, the specimens were annealed (as above) and the resistance measurements repeated on the annealed wires. A few check experiments showed that the changes in length and weight which occurred on annealing were negligible and it was assumed that the density remained constant, so that the geometry of the specimen was taken to be unaltered on annealing.

The temperature of the ice-bath was measured to within 0·1 °C. with a calibrated mercury-in-glass thermometer graduated to this accuracy. When resistance measurements were made the temperature of this bath was usually between +0·5 and −0·5 °C. The temperature of the liquid oxygen bath was measured at intervals with a pentane-in-glass thermometer and the reading of the thermometer was always within ±0·1 °C. of −183·2 °C. A continuous check on the constancy was maintained by means of a thermocouple. The calibration of the thermometer was not checked because any error in its reading would have affected only the absolute values of $d\rho/dT$ and not the relative ones, since the variations in temperature of the baths were small compared with the total temperature difference.

III. Results

The actual results are expressed in terms of $\Delta\rho/\Delta T$, where Δ denotes the change in value between measurements made in the two baths. The subscripts D and A will be used to denote deformed and annealed values respectively.

Table 2

SUMMARY OF RESULTS

1	2	3	4	5	6	7
Metal	$\Delta\rho/\Delta T$ (Normalized Values)		Maximum Deviations of $(\Delta\rho/\Delta T)_D$ from Mean of Annealed Values		$\left(\frac{(\Delta R/\Delta T)_D}{(\Delta R/\Delta T)_A}-1\right)\times 100$	Increase in ρ 0°C. after Logarithmic Strain of 2·3 (%)
	Annealed	Deformed	+ve	—ve		
Nickel	$100\pm0\cdot25$	$100\cdot11\pm0\cdot22$	0·45	0·23	$0\cdot16\pm0\cdot13$	6
Spectrographic copper ..	$100\pm0\cdot18$	$100\cdot01\pm0\cdot15$	0·29	0·26	$-0\cdot06\pm0\cdot26$	3
Conductivity copper ..	$100\pm0\cdot24$	$99\cdot99\pm0\cdot15$	0·12	0·34	$0\cdot02\pm0\cdot30$	3
Spectrographic iron ..	$100\pm0\cdot19$	$100\cdot09\pm0\cdot22$	0·36	0·34	$-0\cdot03\pm0\cdot42$	1
Spectrographic aluminium ..	$100\pm0\cdot38$	$99\cdot92\pm0\cdot54$	0·98	0·74	$0\cdot00\pm0\cdot50$	0·5
80/20 Brass ..	$100\pm0\cdot24$	$100\cdot10\pm0\cdot15$	0·38	0·13	$-0\cdot06\pm0\cdot66$	20
75/25 Brass ..	$100\pm0\cdot30$	$99\cdot47\pm0\cdot50$	0·10	1·00	$-0\cdot35\pm0\cdot43$	25
Aluminium bronze ..	$100\pm0\cdot32$	$98\cdot01\pm1\cdot46$	—	3·88	$-1\cdot98\pm1\cdot69$	28

Absolute values of $\Delta\rho/\Delta T$ would have involved knowledge of the densities of the specimens and of the distance between the potential knife-edges in the resistance bridge as well as an accurate calibration of the low temperature thermometer. Therefore, only relative values are given in the results shown in Table 2, a normalizing factor having been applied to make the mean value of $(\Delta\rho/\Delta T)_A$ equal to 100 in each case. This procedure facilitates comparison of the standard deviations.

In Table 2 the second column also gives the standard deviation of $(\Delta\rho/\Delta T)_A$, the third gives the mean and standard deviation of $(\Delta\rho/\Delta T)_D$, while the fourth and fifth give the maximum deviation of $(\Delta\rho/\Delta T)_D$ from the normalized mean of $(\Delta\rho/\Delta T)_A$. It should be noted that the values in the third column are meaningless if Matthiessen's rule is not true, i.e. if $\Delta\rho/\Delta T$ does vary with deformation, since the individual results from which they are derived refer to different amounts of deformation (logarithmic strains between $0\cdot2$ and $2\cdot3$). However, if the rule is true, then they have a meaning and should agree with the values in the second column.

For the first six metals there is close agreement between the values in the second and third columns and, furthermore, the range of values of $(\Delta\rho/\Delta T)_D$ is only of the magnitude to be expected from the experimental errors, so that it can be concluded that Matthiessen's rule is true within an accuracy of $0\cdot5$ per cent. for nickel, copper (two purities), iron, and 80/20 brass, and within 1 per cent. for aluminium.* However, for the 75/25 brass and the aluminium bronze the mean values of $(\Delta\rho/\Delta T)_D$ are below 100, the standard deviations are large and the maximum deviations are large and asymmetric. In Figure 1, the values of

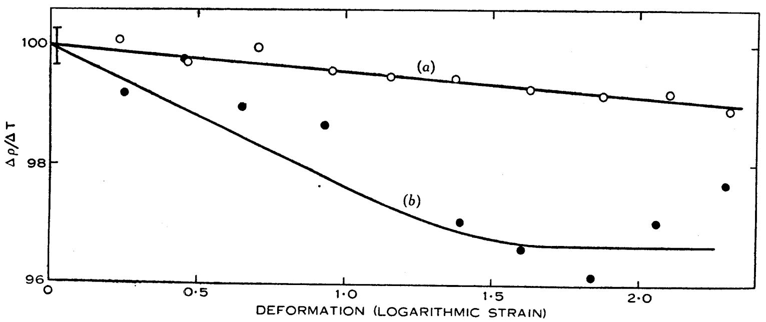

Fig. 1.—Variation of $\Delta\rho/\Delta T$ with deformation for (*a*) 75/25 brass and (*b*) aluminium bronze. The vertical bar at the left-hand side shows the standard deviation of the values of $(\Delta\rho/\Delta T)_A$.

$(\Delta\rho/\Delta T)_D$ are plotted against deformation for these two metals and it can be seen that $(\Delta\rho/\Delta T)_D$ decreases as the deformation increases. Therefore, it can be said that these two metals show negative deviations from Matthiessen's rule, the magnitude of the deviations after a logarithmic strain of $2\cdot3$ being approximately 1 per cent. for the brass and 3 per cent. for the aluminium bronze.

Since the geometry of any particular specimen is constant, we have the relation

$$\frac{(\Delta\rho/\Delta T)_D}{(\Delta\rho/\Delta T)_A}=\frac{(\Delta R/\Delta T)_D}{(\Delta R/\Delta T)_A},$$

where R denotes the resistance. This provides an alternative method of testing the rule and one which does not involve the measurements of length and weight. The test is whether these ratios are unity for all degrees of deformation or whether there is a significant deviation from this value. Table 2 gives the mean and

* The larger experimental variation for aluminium was probably due to the softness of this material causing difficulties in fixing the wires in the resistance bridge so that they were straight and unstrained while still maintaining good electrical contacts with the potential knife-edges in both the ice and the liquid oxygen baths.

standard deviation of the differences between these ratios and unity, but the same restrictions on interpretation apply here as applied for the values of $(\Delta\rho/\Delta T)_D$. It can be seen that there is complete agreement between the two methods of analysing the results.

Table 2 also gives values for the percentage increase, due to deformation, in the resistivity at 0 °C. Comparison shows that the only materials which do not follow Matthiessen's rule are alloys which have a large increase in resistivity on deformation, but the converse is not true as the 80/20 brass shows a large increase in resistivity and still follows the rule.

IV. Discussion

The main source of errors in resistivity measurements on wires is the determination of the mean cross-sectional area. The use of a micrometer to measure the diameter of fine wires directly can produce serious errors due to compression between the jaws. The method of weight and length measurements was therefore used to give relative values of the cross-sectional area when needed, but the results as expressed in the sixth column of Table 2 are independent of the wire dimensions. In this connection, the results of Rutter and Reekie (1950) should be noted. These workers measured the resistivities of spectrographic copper and aluminium as functions of deformation for temperatures of measurement of 20, 90, and 297 °K. They give no indication of the accuracy of their results nor of the apparatus used to measure the resistivities but their curves for the resistivity of aluminium as a function of deformation are of different shapes from those usually found (see, for example, Broom 1952). It is suggested here that this difference may be due to errors of measurements of specimen dimensions and that the accuracy of the results is probably at most 0·5 per cent. Within this accuracy, their results for aluminium agree with those in the present work, but the results for copper cannot be compared as sufficient data are not given.

The use of $\Delta\rho/\Delta T$ as a measure of $d\rho/dT$ in the present work does not depend on ρ being an exactly linear function of T in this temperature range, as the deviations from linearity are small and the equality of $(\Delta\rho/\Delta T)_D$ and $(\Delta\rho/\Delta T)_A$ therefore still implies parallelism of the two ρ *v.* T curves. This is, of course, the condition which allows separation of the resistivity into a part depending only on temperature and a part depending only on deformation.

It is of interest to note that, in the two cases where a deviation from Matthiessen's rule has been found, this deviation is such that the increase in resistivity with temperature is smaller in the deformed metal than in the annealed metal. According to theory, the electrical resistivity due to thermal vibrations, ρ_T, at not too low temperatures is given by

$$\rho_T = C\frac{T}{\Theta^2}\left(1-\frac{\Theta^2}{18T^2}\right),$$

where Θ is the characteristic temperature and C is a constant involving atomic constants and the number of conduction electrons per unit volume. Assuming that the deformation dependent part is unaffected by temperature changes, it follows that

$$\frac{d\rho}{dT}=\frac{d\rho_T}{dT}=C\left(\frac{1}{\Theta^2}+\frac{1}{18T^2}\right),$$

so that the slope of the ρ *v.* T curve depends mainly on Θ since Θ and T are of the same order of magnitude. If the number of conduction electrons is not altered by plastic deformation the observed change in $d\rho/dT$ on deformation can then be expressed in terms of an increase in Θ:

$$\delta(d\rho/dT)=-(2C/\Theta^3)\delta\Theta.$$

The fractional increase in $d\rho/dT$ can therefore be expressed as $-2\delta\Theta/\Theta$, so that, for the two alloys being considered, $\delta\Theta$ is positive and of the order of a few degrees.

This, of course, is only another way of expressing the experimental results but it does suggest a possible physical interpretation. Any deviation from Matthiessen's rule implies that the scattering of conduction electrons due to thermal vibrations is not independent of that due to lattice disturbances produced by plastic deformation. This may mean either that the scattering probabilities are not simply additive, or that the thermal vibrations in a distorted crystal are different from those in a perfect crystal. It is here suggested that the latter is the case and that the deviations from Matthiessen's rule indicate that deformation increases the maximum frequency of the lattice vibrations, thereby raising the characteristic temperature. A detailed calculation is required to show whether the inhomogeneous strain fields in a deformed crystal do have such an effect on the lattice vibrations. In this case a corresponding change in the relevant elastic constant would also be expected (Blackman 1951).

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