SOME STUDIES ON RECOVERY AND OXIDATION CHARACTERISTICS OF COPPER BY THERMOELECTRIC PHENOMENON

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Abstract

It is well known that the junction of two dissimilar metals is the seat of thermoelectric force which can be used for the measurement of temperature. For this purpose usually dissimilar metals and/or alloys are used. In such cases the metals or alloys invariably differ in chemical composition. Although some work has been done to investigate the changes in the thermoelectric properties of the same metal or alloy due to some physical changes (without any change in chemical composition), not much of work has been done to study minute changes occurring in metals and alloys which do not appreciably affect either the microstructure or the mechanical properties. For example, neither the microstructure nor such mechanical properties as hardness, tensile strength and ductility undergo any appreciable change during the so-called 'recovery stages' of cold-worked metals and alloys or the so-called 'pre-precipitation stages' during ageing, tempering and other thermal treatments of metals and alloys.

An attempt has been made in this investigation to show that changes in the thermoelectric properties of metals and alloys may well be taken advantage of to detect minute changes in metals and alloys — be it on the surface or inside the volume. In a pure specimen of copper wire it has been shown that

(i) there are detectable and continuous changes in the thermoelectric properties throughout the recovery stage of the cold-worked specimen, and

(ii) there are very sharp discontinuities in the e.m.f. temperature plot in the initial stages of film formation during heating in air.

Further work is in progress to detect the changes in the initial stages of ageing, tempering and other transformations — isothermal or otherwise — in other metals and alloys.

Introduction

IT is well known that most of the mechanical properties like tensile strength, hardness and ductility are highly structure sensitive and depend on a large number of factors like grain size, orientation of grains, the shapes, sizes and distribution of micro-constituents, nature of the crystal lattices and so on. Nevertheless, the changes occurring in the initial stages of many phenomena like nucleation, precipitation, diffusion, phase transformation and so on can hardly be detected by changes in mechanical properties. Various methods, viz. magnetic, dilatometric and thermal analyses, electrical conductivity, X-ray and electron microscope studies, have been adopted by different investigators to find out some of the basic causes underlying the different phenomena occurring in metals and alloys. But the thermoelectric properties of metals and alloys under different conditions of thermal and mechanical treatments have not been studied so well. Apart from some studies in connection with the suitability or otherwise of thermocouple materials, very little work has been done to find out if the thermoelectric property can be utilized as a tool of research to throw some light on some of the different phenomena occurring in metals and alloys. An attempt has been made in this paper to show that changes in the thermoelectric properties may well be taken advantage of to detect changes in the so-called 'recovery' stages of cold-worked metals and alloys. It has also been shown that minute changes occurring in the surface of metals and alloys which could hardly be detected by any of the ordinary methods (except probably electron-diffraction) may well be detected by changes in the thermoelectric properties.

Some Basic Concepts

The contact point of two dissimilar substances develops a potential which is a function of the nature of the substances and the temperature. When zinc, for example, is placed in contact with copper, electrons flow from zinc to copper and the former acquires a positive charge. But this contact potential difference is not a 'driving potential', i.e. it cannot cause a further flow of current on completing the circuit of zinc and copper. If the junctions of two dissimilar metals or alloys are held at two different temperatures and the circuit completed, a current continues to flow in the circuit and several phenomena occur simultaneously in that circuit, viz. the reversible Seebeck, Peltier and Thompson effects, the irreversible Joule effect, and the conduction of heat. Thus the term 'thermoelectric properties' in general covers a number of different phenomena, including thermal effects of electric currents and the electrical effects of thermal currents. Under a given set of conditions, however, the same resultant thermoelectromotive force E is generated, i.e. so long as the temperatures of the hot and cold juctions remain the same and the metals or alloys concerned remain the same, the magnitude of E also remains the same. In actual practice, however, it is very difficult to obtain the same values of E even under apparently identical conditions, because the magnitude of E depends not only on the differences of the temperatures of hot and cold juctions and the chemical compositions of the thermocouple wires, but also on their physical condition in the region of temperature gradient. A slight bend or twist in a thermocouple junction is often supposed to disturb accurate calibration work. But the seat of the trouble usually lies not in the junctions but in the regions of temperature gradient.

Neumann[1] has found that the so-called thermoelectric power $\frac{dE}{dt}$ may be as high as 2·6 microvolts per °C. for a thermocouple of wires of the same metal but one wire of which is rolled and the other annealed. Bridgman[2] has investigated the effects on thermocouples of the same wire but one being under tension and the other not. Wagner[3] has investigated the effects of pressure on thermoelectric properties. Bridgman[2] has considerably extended Wagner's work, but concluded that the thermoelectric effects were quite irregular and very complicated.

It has already been shown in a previous paper[4] that there are appreciable changes in the thermoelectromotive forces on different degrees of cold reduction and the rate of change of thermoelectromotive force is not a linear function of cold deformation. In this paper attempts have been made to study the changes in the thermoelectric properties of a cold-drawn copper wire on annealing under vacuum at different temperatures for different periods of time. A typical change due to oxide formation has also been studied.

Experimental Procedure

The thermoelectromotive force of a sample of pure copper wire was noted against constantan for a given temperature difference between the hot and cold junctions. The wire was cold-drawn through a clean die and the amount of reduction in cross-section noted. The thermoelectromotive forces against the same constantan wire for the same difference of temperatures were again noted. The hot and cold junctions were carefully made without introducing any twist, bend or solder. To increase the sensitivity of the tests, several thermocouples were used in series. To avoid disturbances during handling these were rigidly secured round a glass tube. A reservoir of warm water bath served as hot junction. The temperature of the bath could be easily controlled and measured by a sensitive thermometer. The cold-drawn thermocouple assembly was then carefully introduced inside a quartz tube which was evacuated. The entire assembly was then introduced inside an electrically heated tube-furnace whose temperature was kept constant at the desired temperature.

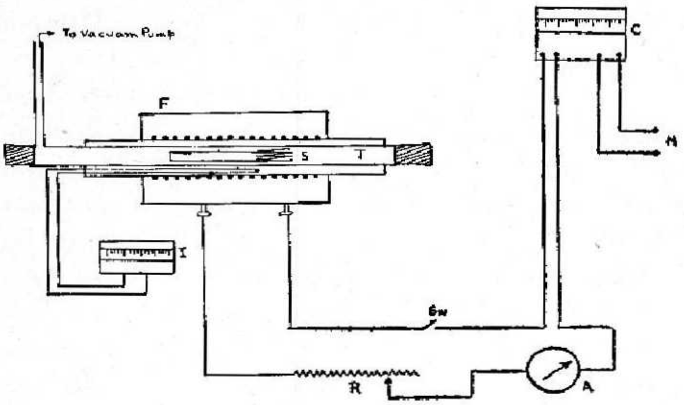

FIG. 1

F = Furnace; T = Refractory tube; S = Sample (copper wire drawn), I = Indicator, A = Ammeter, R = Resistance, M = Mains, C = Temperature controller, Sw = Auxiliary switch

The assembly of apparatus is shown in Fig. 1. After a given period of anneal the quartz tube was withdrawn, cooled and the thermocouple assembly carefully taken out. The thermoelectromotive forces were again measured. The process was repeated at different temperatures for different periods of time.

To study the oxide film formation a given set of copper-constantan thermocouples were slowly heated in air in an electrical resistance furnace. The temperature of the furnace was measured by a separate Pt-Pt.Rh thermocouple. Since the set of thermocouples were in series, any disturbance in any one of the couple junctions was detected by the sensitive galvanometer to which the couples were connected.

Experimental Results and Discussions

The experimental results are shown in Tables 1 and 2 and plotted in Figs. 2 and 3.

It will be obvious from Fig. 2 that the E-T plots, even within the narrow range of temperature studied in this investigation, are distinctly separate for each set of treatments. It may be noted that increasing the time of anneal at a given temperature reduces the E value. It is understandable, therefore, that if E be plotted as function of temperature

TABLE 1 — THE DIFFERENT TEMPERATURES AND TIMES OF ANNEAL OF A COLD-DRAWN COPPER WIRE

SAMPLE No.	TREATMENTS AFTER COLD REDUCTION
A	Annealed at 100°C. for 30 min.
B	Annealed at 100°C. for 1 hr.
C	Annealed at 190°C. for 15 min.
D	Annealed at 190°C. for 30 min.
E	Annealed at 250°C. for 15 min.

TABLE 2 — GALVANOMETER READINGS AS FUNCTIONS OF TEMPERATURE IN °C. FOR THE SET OF THERMOCOUPLE SAMPLES AFTER DIFFERENT TREATMENTS AS SHOWN IN TABLE 1

HOT JUNCTION TEMPERATURE, °C.	GALVANOMETER READINGS WITH C.J. AT 23·0°C.				
	Sample A	Sample B	Sample C	Sample D	Sample E
30	85·0	70·0	56·0	45·0	25·0
29	76·0	58·0	48·0	37·0	20·5
28	57·0	46·0	39·0	28·5	16·5
27	46·0	33·5	30·0	20·5	12·0
26	36·0	23·0	21·0	13·0	7·8
25	22·0	12·5	11·0	6·0	3·5
24	10·0	1·4	0·5	0·2	0·1

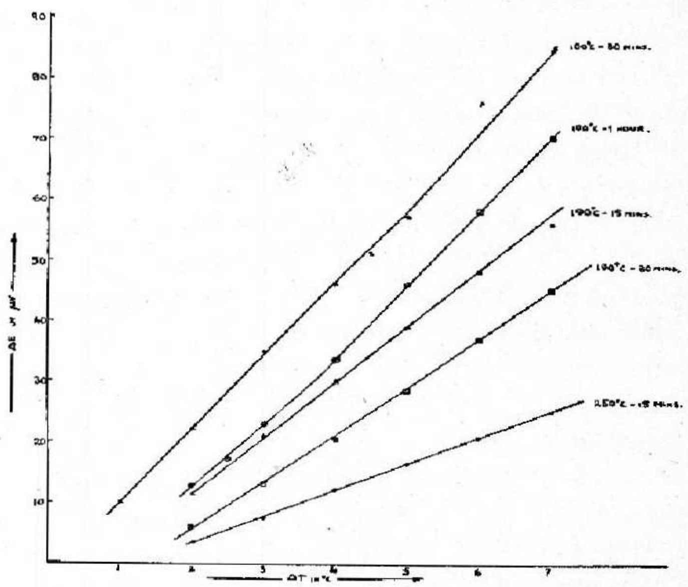

FIG. 2

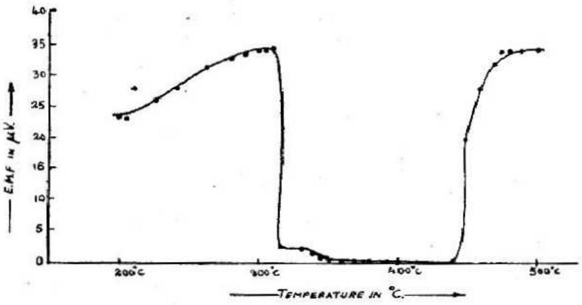

FIG. 3

of anneal (the time of anneal remaining constant), so-called 'Recovery stage' of cold-drawn metals and alloys may well be explored by changes in the thermoelectric properties. Further data are being collected in this connection and will be reported in future.

The phenomena of thermoelectric inversion in some metals and alloys have been studied by several investigators, but the study of film formations or other changes occurring on the surfaces of metals and alloys by means of changes in the thermoelectromotive forces offers many potential advantages both in sensitivity as well as simplicity. It is well known that cuprous oxide is used as a rectifier, i.e. the lattice of cuprous oxide permits the flow of electrons in certain specific directions. It is understandable, therefore, that if a series of copper thermocouples be set at known temperatures of furnaces, the critical temperature of formation of the oxide film as well as the behaviour of the film as function of time or temperature or both may be investigated.

A typical plot in this connection is shown in Fig. 3. The sharp discontinuity in the plot shows that there is a critical temperature at which the rate of formation of a particular type of film is maximum. It is quite likely that this critical temperature is a function of the nature of the alloying element present in the metal and also of the partial pressure of the reacting gases. How far this is true is worth further investigation.

Preliminary investigations by the senior author have shown that phase changes, initial precipitation stages as in ageing, tempering, etc., may well be detected by changes in the thermoelectric properties. Resistivity measurements are equally useful but usually involve comparatively more elaborate arrangements. Theory indicates that all factors which affect the specific resistance and/or the kinetic energy of the electrons in the different states and the number of states per unit energy should have comparatively larger effects on the thermoelectric properties. Thus changes in the grain size (other factors remaining the same) which do not usually affect appreciably the Fermi-levels are not expected to affect the thermoelectric properties to any serious extent. Preliminary investigations in our laboratories fully confirm this idea. Work is in hand in connection with ageing, tempering and some isothermal transformations in metals and alloys. These will be reported elsewhere in future.

Conclusion

Changes in the thermoelectric properties of metals and alloys can be utilized as powerful tools of research to throw more light on some of the phenomena in metals and alloys which cannot otherwise be so easily detected by ordinary means. Not only volume phenomena but also surface phenomena may be easily investigated. Recovery and oxidation phenomena in copper show considerable changes in its thermoelectric properties. The method is simple but sensitive and many of the phenomena like those occurring in the so-called 'incubation' period, 'preprecipitation' stages and so on which do not produce appreciable changes in mechanical properties may well be investigated by changes in the thermoelectric properties.

References

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Discussions

MR. P. N. GANDHI (Indian Ordnance Factories)

It is considered that instead of adopting the thermoelectric method to study the phenomenon of recovery in copper it would perhaps have been preferable for Dr. Chatterjee to adopt the X-ray diffraction technique as thereby the changes taking place in the lattice structure of cold-worked copper on progressive annealing could be observed and followed more easily. This method would also permit the annealing treatment on the sample to be carried out progressively at different temperatures if the camera was provided with heating arrangement.

DR. G. P. CHATTERJEE (*Author's Reply*)

It is quite well known that X-ray diffraction methods have already been used by several investigators to study the changes in the lattice structure of cold-worked metals and alloys on progressive annealing. But the changes in the X-ray diffraction of lines or spots or even in the structures of individual spots cannot be detected visually due to *minute changes* occurring in the initial *stages* of any volume or surface phenomena in metals and alloys—be it recovery, recrystallization, precipitation or oxidation. Densitometric or other methods of detecting changes in the structure of X-ray lines or spots are somewhat more sensitive than the visual method, but are affected by the nature of the film, development conditions and other variables. Thus minute changes in the densitometer reading of X-ray diffraction spots may occur due to causes other than those occurring in metals and alloys. Even if these variables are kept within controllable limits, the fact remains that the sensitivity of the X-ray diffraction method is very much less than that of the thermoelectric method. Moreover, to incorporate heating arrangement and temperature measuring devices within an X-ray diffraction camera creates experimental difficulties well known to those who have worked in this field. Granted, however, that such an equipment is built up, the fact still remains that changes in the density of the line due to the thermal factor is superimposed on those due to changes in the lattice structure. Thus although a powerful technique otherwise, the X-ray diffraction method, far from being preferable and easy, as indicated by Shri P. N. Gandhi, is practically of no use for the detection of those minute changes in metals and alloys which can be detected by thermoelectric method.

MR. S. RANGANATHAN (National Metallurgical Laboratory, Jamshedpur)

The purpose of the paper as given at the beginning was to pursue minutely certain phenomena connected with recovery and recrystallization in metals. For this thermoelectric e.m.f. was employed. However, since e.m.f. readings may be affected by factors such as intercrystalline precipitation, conductivity characteristics induced by oxides, etc., even if these changes (which electron microscopy and electron diffraction analysis could not reveal) might become evident by this method, to correlate the fact of change with the cause so as to establish the nature of recovery and recrystallization would still leave us in the position of guessing.

DR. G. P. CHATTERJEE (*Author's Reply*)

With reference to Shri Ranganathan's question it may be said that thermoelectric force has been utilized in this investigation as a sensitive means of *indicating* positively the occurrence of some changes in metals and alloys and not to describe any detailed mechanism or nature of those changes. For pure metals treated in vacuum, intercrystallic precipitation, conductivity characteristics induced by oxides and other such variables are of minor importance. Nevertheless, by differential method or otherwise one has to guard against different sources of errors particularly due to the high sensitivity of the method. Electrical resistance and magnetic methods are sometimes equally sensitive, but there are some obvious advantages in the case of the thermoelectric method. Other methods like microscopy and X-ray diffraction, etc., do not even give an indication during the initial stages of the so-called incubation or preprecipitation period. True it is that a mere indication of a change without the mechanism or nature of that change leaves us in the *position of guessing*, but such a position, I hope, is better than that of 'no indication' — a position where *there is nothing even to guess*.