

EFFECT OF ADMIXTURE OF SILVER ON THE RECTIFYING PROPERTIES OF Cu-Cu₂O CELLS

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NUMEROUS 'Sperrschicht cells' or 'Barrier-layer rectifiers' are in commercial use; and it is very likely that this extremely useful device in its many forms will be increasingly employed to supply the demands for the direct current throughout the electrochemical and electrometallurgical industries. Unfortunately the precise details of construction have not been published,¹⁻³ nor are we familiar with the manner in which the physical conditions affect the rectification. This state of affairs results in the absence of a satisfactory theory of the rectifier action. In this field no material seems to have been studied more extensively than the copper-cuprous oxide rectifier; but even this material has not been the subject of a systematic investigation. We have undertaken to study systematically the various factors which alter the rectification of copper-cuprous oxide layers with a view that such a systematic knowledge will enable us to understand the mechanism of the rectifying action. In this paper the influence of a small percentage of silver impurity included in the copper block on the rectification is reported. But before we proceed to describe the experiments and their significance it would be better to give an outline of our present knowledge—both experimental and theoretical—of the Cu-Cu₂O cell.

A typical rectifying contact consists of a metal separated by a very thin almost insulating layer from a good semiconductor.⁴⁻¹¹ The Cu-Cu₂O rectifier is made by oxidising one face of a block of chemically pure metallic copper to an appreciable depth. The oxidation takes place in an electrical furnace at a little over 1,000° C. The block is usually polished flat before oxidation; this helps in making a good contact during its subsequent use. The oxidation converts the copper to Cu₂O. The cuprous oxide next to the mother copper is almost pure, but the subsequent layers are rich in oxygen. The pure Cu₂O forms the insulating layer and the pure cuprous oxide with the extra oxygen is a good impurity semiconductor. For efficient working the insulating layer should be about 10⁻⁵ cm. thick. Such plates are usually pressed together in a pile and possess another contact between the semiconductor (Cu₂O + O) and metallic lead. This contact between a good

semiconductor and a metal does not rectify appreciably. The efficiency of a rectifier is usually expressed by the ratio r_2/r_1 , r_2 and r_1 being the resistances observed when the current passes in the unwanted direction and in the wanted direction respectively, both resistances being measured at the same voltage.

The conduction electrons in a crystal lattice are supposed to occupy a band or a series of bands of energy levels.^{12 20} If the bands are completely filled there can be no conduction. A semi-conductor is formed when a new distinct band or set of levels of intermediate energy is supplied by the impurities present. In the system metal/semi-conductor/metal the two contacts are quite different, one forming an appreciable gap across which current has to flow and the other being a very intimate contact. If the potential of the metal is raised by V , the current transmitted across the gap can be obtained by applying the Schrödinger equation. Current = $\alpha e^{-\beta V} \{e^{eV/kT} - 1\}$ where α and β are constants. The current in the reverse direction will be $\alpha e^{\beta V} \{1 - e^{-eV/kT}\}$. The passage of the electrons across the potential barrier is explained in the above theory by the quantum-mechanical 'Tunnel effect'. But according to Mott^{21 22, 25} such a theory predicts a wrong direction of rectification; and he points out that the correct direction is secured by assuming that the electrons are able to go over the potential barrier when they are thermally excited, and not through it by the 'Tunnel effect'. Schottky²⁴ compares the metal/semiconductor/metal rectifier with a discharge tube working at low pressures. The metals take the place of the electrodes and the semiconductor of the space charge between the electrodes. The assumptions of Mott and Schottky are essentially similar and would give similar expressions for the current.^{21 25}

Procedure

Copper used in these experiments, was obtained from 100% pure copper wire (B. G. No. 14, made in Germany) available locally in $\frac{1}{2}$ lb. bundles. The silver was commercially pure silver, also available locally at a silver-smith's. The alloys were prepared by melting $\frac{1}{2}$ lb. of copper and the required amount of silver. The solid blocks were hammered to give plates about 3 to 4 mm. thick. The following plates were prepared in this way, Pure copper, 2 $\frac{1}{2}$ % Ag in Cu, 5% Ag in Cu,, 20% Ag in Cu.

The furnace was an electrical one prepared by winding No. 18 Nichrome wire. The temperatures were measured by a platinum-rhodium thermocouple and a calibrated millivoltmeter. The blocks were heated in a porcelain tube in vacuum, a hyvac pump was running all the time. The oxidation of the blocks was carried out by admitting air at a definite

pressure. The air was admitted through a capillary tube and was pumped out by the pump. This enables us to maintain a constant flow of air at a definite pressure. The pressure can be adjusted to any desired value by choosing a suitable length and diameter of the capillary tube as well as by changing the pumping speed.

The porcelain tubes used for heating were selected from those used by electrical wiremen for taking wires through walls, etc. Only such tubes were chosen as could stand vacuum at high temperature. The glazing material used for coating the inside of such tubes by the manufacturers decomposed and caused some trouble. This difficulty was overcome by baking the tube for half an hour at $1,100^{\circ}$ C. Such tubes are quite satisfactory and can very well replace the silica tubes used in similar experiments.

The porcelain tube is sufficiently long so that the two ends are well out of the furnace and are closed by rubber stoppers. In any experiment two blocks either of pure copper or one of pure copper and the other of alloy were placed at the centre of the furnace. The two blocks should not touch one another, otherwise silver from the alloy diffuses into pure copper. (This actually happened in one case, the silver creeping all along the surface of pure copper at a temperature of 800° C.) The blocks were reasonably flat, and were prepared by polishing them successively on 1, 2, 3 and 4 zero emery paper, with benzene or ether.

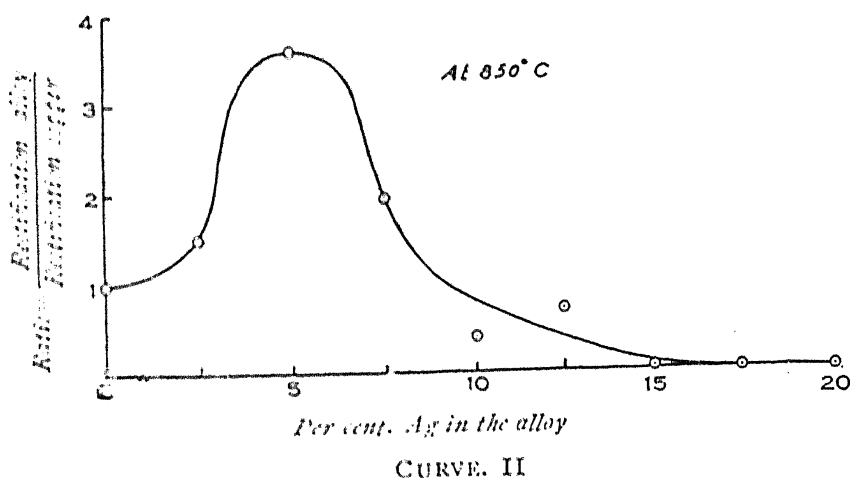
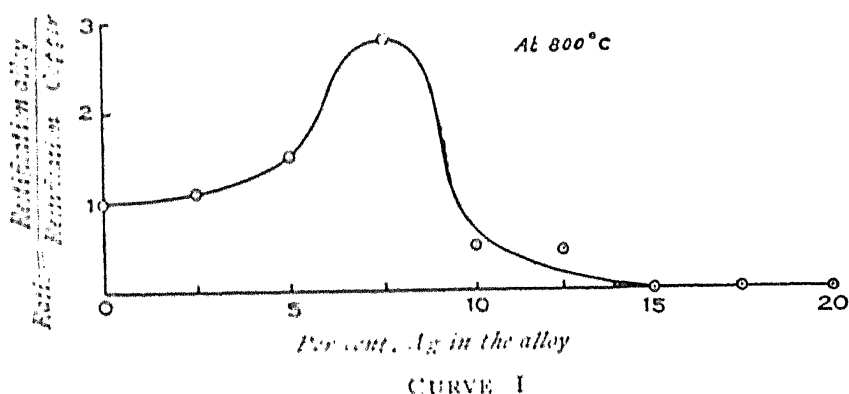
The layers of the oxide were formed in most cases by allowing air at 4 cm. pressure to flow intermittently for about 6 minutes. The blocks were allowed to cool down *in situ* to a temperature of 500° C., then they were taken out of the vacuum and cooled further by dropping in water. The layers formed at temperature of 750° C. and more adhered firmly to the base, whereas those formed at 700° C. and less peeled off easily on dropping in water, but did not peel off when cooled inside the vacuum system. The firmly adhering layer sticks so well that it can be removed only by filing.

In our arrangement the oxide layers are formed on both sides of the block. The coating on one side is filed off by holding the specimen in a vice. The remaining layer is pressed against a lead block and the resistance is measured in both directions by applying a difference of potential of two volts. On dropping in water a layer of cupric oxide is usually formed on the surface, this was removed by gently rubbing the face on ether and 2 or 4 zero emery. The thickness of such a rectifying layer is of the order of one-hundredth of a millimetre and the resistance in the low resistance direction is of the order of 500 ohms/cm.²

Results

Copper blocks made from the same plate and treated under exactly identical conditions of temperature, pressure and cooling do not show identical rectification. The rectification is distributed about a mean value according to the Gaussian Law. Copper blocks prepared at about 600° C. just begin to show a perceptible rectification. The rectification goes on increasing apparently according to an exponential law as the temperature at which the layer is formed goes on increasing. This work has been done in our laboratory by Mr. S. G. Sharangpani and will also be soon published.

Curves I and II. The layers formed on alloys at 900° and 950° C. show the well-known phenomena of 'spitting' and the rectifying action of such blocks could not be measured. The layers were formed on alloys at 700° C., 800° C. and 850° C. and the rectifying action of these layers was compared with that of a layer formed on pure copper under identical conditions. The rectification as will be seen from Curves I and II goes on increasing at first as the percentage of silver increases, reaches a maximum at about 5 to 7% of silver and then diminishes and practically becomes zero for about 12% of silver.



The rectifying action of pure copper at these temperatures (700° C.–850° C.) is very small and lies roughly between 2 and 4. Whereas the rectification at 850° C. of 5% alloy can be as high as 15—a rectification which can be obtained with pure copper only if the temperature of the formation of the layer is about 1040° C.

Discussion

Copper and silver are both similar metals and crystallise in similar systems. The presence of a small amount of silver in the metallic copper is not likely to change its properties appreciably; even the lattice constant changes only by about 1% after the addition of 7% silver.²⁶ But it is quite likely that the electronic levels in consequence of the different atomic volumes of copper and silver are profoundly modified.²⁷ This modification is likely to allow a large number of electrons to go over the potential barrier. The large effect obtained with an alloy can be obtained with pure copper when the temperature of formation is increased considerably. It is but natural to expect that the modification of electronic energy levels produced by an impurity will go on increasing as the amount of impurity increases, and as a result the rectification should also increase with the impurity. But this is not observed to be the case, the rectification actually decreases when the amount of impurity increases beyond a limit. It may be that in such a case the unfilled bands overlap to such an extent that the direction of unrestricted motion is no longer a preferential direction.

Further some atoms of silver which are present along with the copper may be oxidised. Thus in addition to oxygen, silver oxide may be present as an additional impurity in the impurity semi-conductor Cu_2O . But when the amount of this impurity increases beyond a limit, it apparently no longer gives rise to a unidirectional current.

In this connection it is worth noticing that silver and copper are perfectly miscible in the liquid state but at a temperature of 779° C. only 7% of Ag is soluble in copper.²⁸ This probably means that at this temperature only 7% Ag can be included as an isomorphous inclusion in the copper lattice and is able to produce a maximum modification of the electron levels. Further if we consider a group of 27 elementary cells of copper, we see that the minimum number of silver atoms which can be included and will influence all these cells is 8. This gives a ratio of 8 Ag atoms to $27 \times 4 = 108 - 8 = 100$ Cu atoms as the ratio which is likely to give a maximum modification of the electron levels.

These experiments carried out with rectifying layers formed on pure copper and Ag-Cu alloy blocks appear to indicate that the process of rectification is probably governed by statistical laws.

Summary

The effect of including silver in copper blocks on which rectifying layers of Cu₂O are formed is determined experimentally. The rectification is maximum for 7% Ag when the temperature of formation of the layer is 800° C., but if the temperature of formation is 850° C. the maximum rectification is obtained with 6% Ag inclusion. It appears that the rectification is probably governed by statistical laws.

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