The Copper Oxide Rectifier*

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The equilibrium diagram of the copper: copper oxide: oxygen system controls the conditions of formation of the cuprous oxide rectifier. The interface between the cuprous oxide and the copper from which it is formed can be studied with polarized light. Intimate contact exists for more than half the total area. The technique of preparing the rectifier has a marked influence on its characteristics. By using a method of measuring the resistance characteristic which did not cause an error due to current heating at the interface, unusual results were obtained from specimens made under various conditions. Measurement of the thermal conductance of the rectifier disclosed a new physical phenomenon, asymmetrical thermal conductance. This asymmetry is in the direction that would be expected from the electron theory of heat conduction.

INTRODUCTION

THE formation of cuprous oxide on copper at a high temperature produces a junction between the two that has an asymmetrical resistance. This asymmetry is utilized in the copper-cuprous oxide solid rectifier. The electrical resistance is lower in the direction of electron passage from the copper to the cuprous oxide than in the reverse direction. The junction between the cuprous oxide and the copper also has the property of developing an electromotive force when it is illuminated. This property is the basis of the copper-cuprous oxide solid photo-cell. The characteristics of the commercial cuprous oxide rectifier have been ably reported and discussed by Grondahl.[1]

THE SYSTEM COPPER: COPPER OXIDE: OXYGEN

The conditions that control the formation of the cuprous oxide rectifier and photo-cell can be determined from the equilibrium relations that exist between copper, cuprous oxide (Cu_2O), cupric oxide (CuO), and oxygen. These equilibrium relations are represented graphically by the pressure-temperature diagram of Fig. 1. The fixed points of the diagram, indicated in Fig. 1 by circles, and the data used for the calculation of the equilibrium triple curves were taken from the work of Roberts and Smyth,[2] Vogel and Pocher,[3] and Rhines and Mathewson.[4] The gas pressure plotted in Fig. 1 is the sum of the partial gas pressures of oxygen, cuprous oxide, and copper. The last two become appreciable only at very high temperatures or very low pressures. It is probable that at some very low pressure cuprous oxide sublimes. Feitknecht[5] has shown that the presence of N_2 or CO_2 has no effect on the equilibrium relations.

The temperature-concentration diagram of copper-cuprous oxide is given by Rhines and Mathewson.[4] The main point of interest in relation to the cuprous oxide rectifier is the eutectic mixture Cu—3.5 percent Cu_2O with a melting point at 1065°, corresponding to the vertical dotted line in Fig. 1. According to Vogel and Pocher,[3] below 375° cuprous oxide is not stable, and decomposes very slowly into a solid solution of oxygen in copper and into cupric oxide. The decomposition is extremely slow and cannot be found on the cooling curves. The existence of this decomposition has not been verified.

The partial pressure of oxygen in air is approximately 153 mm Hg. This is represented in Fig. 1 by the line *a–b*. The point *a* is the intersection of this gas pressure with the equilibrium curve of CuO, Cu_2O, and O_2, and corresponds to a temperature of 1026°. The point *b* corresponds to the eutectic temperature, 1065°.

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[1] Grondahl, "Copper-Cuprous-Oxide Rectifier and Photoelectric Cell," Rev. Mod. Phys. **5**, 141 (1933).

[2] Roberts and Smyth, "The System Copper: Cupric Oxide: Oxygen," J. Am. Chem. Soc. **43**, 1061 (1921).

[3] Vogel and Pocher, "The System: Copper-Oxygen," Zeits. f. Metallkunde **21**, 333 (1929).

[4] Rhines and Mathewson, "Solubility of Oxygen in Solid Copper," A. I. M. M. E., Inst. Metals Div. Tech. Pub. 534 (1934).

[5] Feitknecht, "Oxidation of Copper at High Temperatures," Zeits. f. Elektrochemie **35**, 142 (1929).

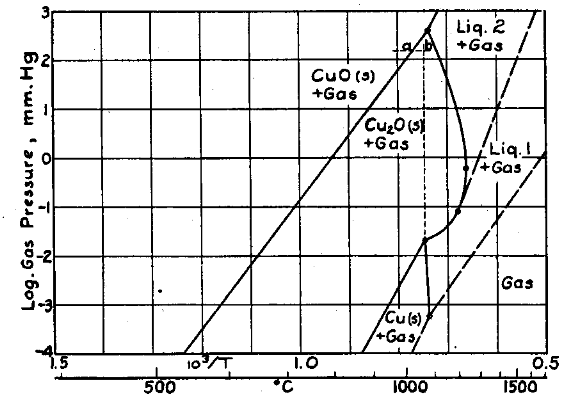
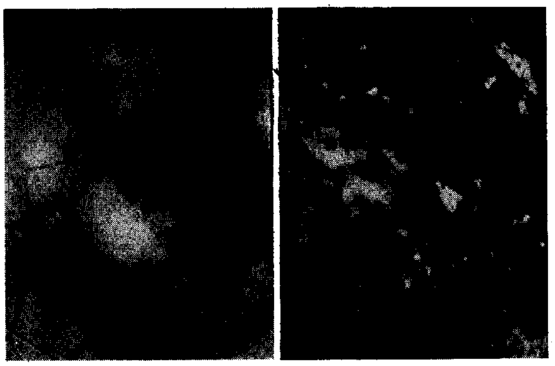


FIG. 1. Pressure-temperature equilibrium diagram of the system copper: copper oxide: oxygen.

During the formation of cuprous oxide, the pressure of the oxygen surrounding the copper being oxidized should lie in the Cu_2O equilibrium region of Fig. 1. The temperature should not rise above the eutectic melting point, 1065°. For oxidation in air at atmospheric pressure, the temperature should not fall below 1026°. The customary oxidizing temperature is 1040°. With reduced oxygen pressure, attained by means of pumps or mixture with inert gases, the minimum temperature for proper oxidation is lowered, in accordance with the CuO, Cu_2O, O_2 equilibrium curve. During the cooling of the specimen from the oxidation temperature the region of formation of CuO (black oxide) is entered. Even if the rate of cooling is slow (furnace cooling) only a thin film of black oxide is formed on the surface of the Cu_2O (red oxide). If the cooling is very rapid (water quench) it is possible to prevent the formation of the black oxide, but the rapid cooling causes the red oxide to crack off the copper due to unequal thermal contractions. It was found that the use of inert gases, N_2 or CO_2, with a small amount of O_2, permitted water quenching without cracking. Such specimens had a glossy red surface. If the oxidation of the copper is conducted below 1026° in air at atmospheric pressure, a layer of CuO is first formed which reduces the oxygen pressure at the copper underneath so that Cu_2O may be subsequently formed, provided the temperature is not too low. If the temperature is too low, a black film is formed which will not adhere to the copper. Apparently an intervening layer of red oxide is necessary to cause the adherence of the black oxide.

STRUCTURE OF THE COPPER OXIDE INTERFACE

The nature of the contact between the cuprous oxide crystals and the copper from which they grew has been a subject for speculation. It was found that by observing a specimen with a glossy red surface under polarized light, it was possible to focus under the surface of the oxide and observe structure. The technique pertinent to the instrument used for these observations and the interpretation of observed structure has been discussed by Dayton.[6] A specimen oxidized at 950° in tank N_2 (contains a small amount of O_2) for 20 minutes and then water quenched, was observed in this manner. Fig. 2A shows the appearance of the surface of the rectifier, and Fig. 2B shows the appearance of the contact directly underneath the crystals seen in Fig. 2A. Both photographs were taken at 500 magnification with crossed Nicols. The thickness of the cuprous oxide layer was 0.066 mm. The structure under the surface could not be observed with parallel Nicols. The bright regions in Fig. 2B are the places where the cuprous oxide crystals have broken away from the copper, probably due to



A B

FIG. 2. Cuprous oxide rectifier, ×500, crossed Nicols. A, surface of the rectifier, showing the ends of the cuprous oxide crystals; B, copper-cuprous oxide contact at the base of the crystals shown in A.

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[6] Dayton, "Theory and Use of the Metallurgical Polarization Microscope," A. I. M. M. E., Inst. Metals Div. Tech. Pub. 593 (1935).

stress induced by the water quench. It is evident that intimate contact exists for more than half the total area. It does not seem, therefore, that the theories that assume point contacts between the copper and the cuprous oxide are tenable.

Determination of Rectifier Characteristics

The experimental work reported in this paper was performed on specimens one inch square prepared from electrolytic copper cut from 65 mil sheet. The applied metal contact was held against the surface of the rectifier with a pressure of 200 lbs./in.^{2} by means of a spring clamp. A constant temperature cabinet maintained the specimen at a temperature of 25°. The circuit used to measure the resistance-voltage characteristic was a resistance bridge. Since most of the rectifier resistance, in the high resistance direction, is concentrated in a thin layer at the natural interface between the base copper and the cuprous oxide formed from it, a small current flow in this direction raises the temperature of the interface markedly. This temperature rise appreciably lowers the resistance of the rectifier, so that the measurement of the resistance under a condition of continuous current flow gives too low a value (sometimes half the cold resistance) and the actual temperature of the interface is not known. In order to prevent this effect, a cam was used to periodically send a current through the bridge circuit. The period of the cam was 15 seconds, and the circuit was closed for about 1 second. This gave sufficient impulse to the galvanometer to allow the bridge to be balanced, but did not heat the rectifier appreciably and also allowed a long time for it to cool. After the bridge had been balanced, an equivalent resistance was substituted for the rectifier, the current circuit was closed, and the voltage across the equivalent resistance was measured with a potentiometer.

Typical results of the measurements are shown in Fig. 3 and Fig. 4. The figure captions give the preparation sequence of the specimens. Fig. 3, curve 1, shows the typical characteristic curve of a low resistance rectifier. The resistance has a maximum at about 1.6 volts. Grondahl[1] states that all the rectifiers have a similar maximum between 0.75 and 1.5 volts. That this is not so can be seen from the other curves. Fig. 4, curve 3, has a maximum at about 4 volts, curve 2 has a minimum at about 0.7 volt. Many specimens had no maximum below 5 volts. It is evident from a study of the curves that the treatment of the applied contact surface has a large effect on the shape of the rectification characteristic. This surface contact resistance does not behave like a series resistance. In many cases, a treatment of this surface contact that causes a resistance decrease in the low resistance direction causes a very much greater decrease of resistance in the high resistance direction. Fig. 3, curve 2, is of interest since it represents an attempt to remove from the Cu_2O of the rectifier as much CuO and O_2 as possible. The resistance char-

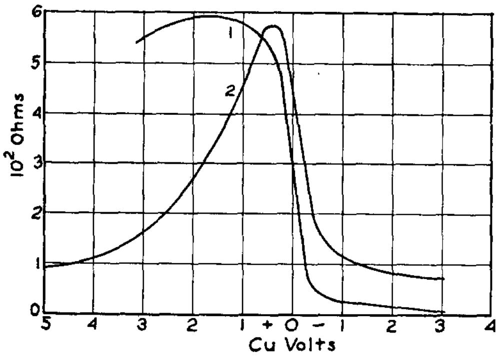

FIG. 3. Resistance-voltage characteristics. Curve 1, specimen oxidized in air at 1040°, furnace cooled, annealed in air at 500° for 3 hours, and water quenched. Aquadag on Cu_2O surface. Curve 2, specimen oxidized in tank N_2 at 950° for 20 minutes, water quenched, annealed in vacuum at 600° for 12 hours, and vacuum quenched. Aquadag on Cu_2O surface.

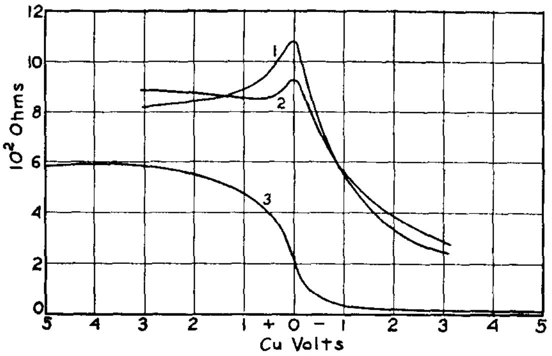

FIG. 4. Resistance-voltage characteristics of specimen oxidized in tank N_2 at 1000° for 10 minutes, and water quenched. Curve 1, CuO surface untouched. Curve 2, Cu_2O surface. CuO removed by $NaCN$ etch. Curve 3, Aquadag on Cu_2O surface.

acteristic is very unusual as very little asymmetry is present. Fig. 4, curve 1, shows a characteristic that was found to be quite general. All resistance curves for specimens that had CuO on the surface showed a maximum at or near zero voltage, and decreased exponentially on both sides of this maximum.

It has been definitely ascertained by Grondahl[1] and others that the resistance asymmetry occurs at the Cu_2O-Cu interface, and that the Cu_2O layer forms only a very small portion of the total resistance. It is evident from the experimental work here presented that the phenomenon is complicated by the behavior of the Cu_2O layer and the surface contact. A combination of the wave-mechanical action of a potential barrier at the interface and the action of a space charge in the Cu_2O might possibly explain the experimental results.

THERMAL CONDUCTANCE OF THE CUPROUS OXIDE RECTIFIER

No measurement of the thermal conductance of the cuprous oxide rectifier is reported in the literature. Vogt[7] measured the thermal conductivity of cuprous oxide. Using the comparison method, and quartz as the comparison substance, he found the thermal conductivity of cuprous oxide at −78° to be 0.019, at 0° to be 0.015, at 100° to be 0.017 cal./sec. cm² (°C/cm).

The apparatus used in this investigation to measure the thermal conductance of the cuprous oxide rectifier was similar to Vogt's. The only material available that had approximately the same thermal conductance as the rectifier was thin paper, of the type used to roll cigarets. This was used as a comparison standard. The arrangement of the apparatus is indicated in Fig. 5. The heat was supplied through a nichrome heating coil wound about the top brass block. The brass block at the cold end was cooled by a coil of copper tubing, embedded in Wood's metal, through which tap water ran. All faces had a cross section area of 1 in.², and were polished smooth with 3/0 emery paper. The rectifier used was the specimen whose resistance-voltage characteristic is shown in Fig. 3, curve 1.

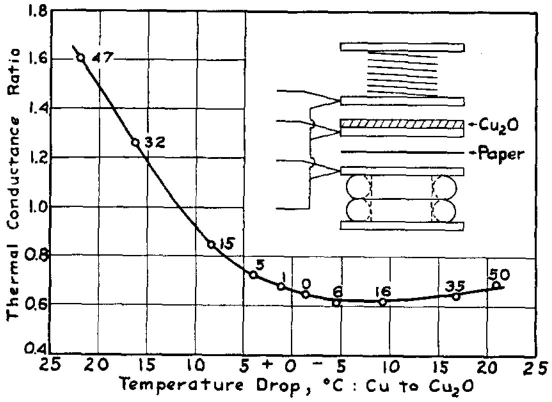

FIG. 5. Thermal conductance ratio, rectifier: paper, *vs.* temperature drop across the rectifier. The temperature above room temperature of the Cu_2O-Cu interface during the measurement of the ratio, is given beside each point.

Thermocouples of nichrome-advance wire were embedded in small holes in the sides of the brass blocks and in the copper of the rectifier, as indicated in Fig. 5. The advance wires of the thermocouples were connected together and the four leads brought to a cold junction held at room temperature. The whole assembly was held in a large *C* clamp, insulated from the jaws by asbestos board, and surrounded by a cylinder of asbestos paper to prevent air currents. The temperature gradient across the cuprous oxide was adjusted by varying the current through the heating coil. With the apparatus as arranged in the figure, the heat flowed from the Cu_2O to the copper, and with the rectifier reversed, so that the paper was above the copper and the Cu_2O was below, the heat flowed from the copper to the Cu_2O. The time required for the thermal equilibrium to be established was about 15 minutes. The thermocouple voltages were read with a Wolff potentiometer by using a galvanometer sensitive enough to allow the determination of microvolts.

When equilibrium was established, the ratio of the thermal conductances of the rectifier and the paper was equal to the inverse ratio of their temperature drops, assuming that the heat loss from the sides and through the center thermocouple was negligible. This assumption was tested after the measurements on the rectifier had been made by removing the cuprous oxide from the copper slab and placing paper in the

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[7] Vogt, "Electrical Determinations with Cu_2O," Ann. d. Physik **7**, 183 (1930).

top and bottom positions. Measurements of the ratio of the thermal conductances of the two papers were then made for different temperatures of the hot end. It was found that the ratio decreased by about 1 percent when the temperature of the hot end was raised from room temperature to 80° above room temperature. This error is of the order of the precision of the measurement, and so was disregarded. This measurement also indicated that the thermal conductivity of the paper did not change appreciably with temperature.

The results of the measurements are plotted in Fig. 5. Beside each point on the curve is given the temperature of the Cu_2O-Cu interface above room temperature.

The thickness of the cigaret paper was 0.026 mm. The *International Critical Tables* give as the thermal conductivity of paper 0.00011 cal./sec. cm^2 (°C/cm). The thermal conductance of the paper was thus 0.042 cal./sec. cm^2 °C. The thickness of the cuprous oxide layer of the rectifier, found from the thickness of the rectifier before and after removal of the oxide, was 0.0629 mm. With Vogt's[7] value for the thermal conductivity of the oxide, the thermal conductance of the oxide layer was 2.46 cal./sec. cm^2 °C at 24°. The measured ratio between the thermal conductances of the rectifier and the paper was about 0.66 at zero temperature gradient, or the total thermal conductance of the rectifier was approximately 0.028 cal./sec. cm^2 °C. The thermal conductance of the interface was thus 0.0283 cal./sec. cm^2 °C. Since the thermal conductance of the cuprous oxide layer is so much greater than that of the interface, the change of the thermal conductivity of the cuprous oxide with temperature can be seen to have a negligible effect.

The results indicate that there exists an asymmetrical thermal conductance characteristic in the cuprous oxide rectifier. The thermal conductance is larger in the direction in which the electrical conductance is larger, i.e., from the copper to the cuprous oxide. This would be expected from the electron theory of heat conduction. The asymmetry is apparently a property of the interface. The temperature characteristic of the interface is unknown, but while it probably affects the values of the thermal conductance it can not explain the observed asymmetry. As can be seen from the figure, for equal and opposite temperature gradients across the rectifier, the temperature of the interface was about the same, although the thermal conductances were different.

A more exact study of this phenomenon is necessary. The apparatus should be so arranged that the temperature of the interface remains constant throughout the measurement. A comparison material more reproducible than paper, and about which more is known, should be used.