SECTION V.

REDUCTION OF COPPER OXIDES BY MOLECULAR HYDROGEN.

INTRODUCTION.

It has long been known that catalytically active copper can be prepared by the reduction of copper oxides in molecular hydrogen. An extensive investigation of the reduction was carried out by Wright, Luff and Jennie (1878, 1879) who found that after a certain "induction period", reduction started at the bottom of the mass and spread upwards to the top. These results have been corroborated by the work of Pease and Taylor (1921), who also found that the reaction occurred at the copper/copper oxide interface and that the reaction
proceeded by the formation of copper nuclei. Hinshelwood (1923) suggested that the reaction proceeded by the formation of fresh copper granules and their growth around the nuclei of copper, at the expense of oxide nuclei. Palmer (1923) studied the oxidation of copper and the reduction of its oxides by hydrogen and carbon-monoxide and concluded that the reaction took place by the absorption of the gas by the metal followed by the reduction of the adjacent oxide layer. He also found that unless some metallic copper was present with the oxide, no reduction occurred until after a long 'induction' period. Hasegawa (1943) explained the reduction of cupric oxide on the assumption that the reaction between adsorbed hydrogen and the oxide took place at the interface of reduced copper, thus creating a reaction nucleus; these nuclei are small in number and are not in contact in the beginning, but as the reaction progressed, the nuclei grew both in size and number.

Garner and Stone (1946) and Aldred and Happy (1947) confirmed Hinshelwood's observations. Aldred and Happy also suggested that in the break-down of oxide crystals by reduction with hydrogen, extensive migration of the metal atoms was prevented due to the rapid dissipation of the heat of reaction caused by the high thermal conductivity of hydrogen. This resulted in the formation of a spongy matrix, which would account for its gaseous nature. Garner, Grey and Stone (1949) measured the
electrical conductivity of such films. According to Richardson and Dancy (1948), the reduction of cupric oxide proceeds by the formation of metallic copper which nucleates on the surface. In this case there is no inward diffusion of metal ions as observed in the case of certain other oxides (c.f. Gellner and Richardson, 1951). Tylecote (1956) found that the rate of reduction of cupric oxide in hydrogen-nitrogen mixtures at 320°C was dependent on the partial pressure of hydrogen up to 140 mm Hg.

Recently, Piggot (1952), studied the reduction of oxides and sulphides of copper, iron, nickel, lead; oxides of tin, chromium, tungsten and uranium and sulphides of silver and molybdenum by atomic hydrogen, at room temperature. He observed that there was no correlation between the reducibility of a substance by atomic hydrogen and the lowest temperature at which molecular hydrogen could reduce the oxides. In some cases, for example in Fe₂O₃, NiO, UO₂, etc, the reduction did not occur at all in atomic hydrogen while in molecular hydrogen they could be easily reduced to metal. He also found that, where reduction occurred in atomic hydrogen, epitaxially grown oxide or sulphide layers could sometimes be reduced to two-degree orientated metal. Goswami and Trehan (1956) reported the results of the reduction of cuprous and cupric oxide films formed on a Cu(110) face. They observed that the reduction of cuprous oxide produced copper films in which the orientation of the oxide was continued, while cupric oxide generally
Fig. 189. Diagram of apparatus used for the reduction of copper oxides in molecular hydrogen.
Fig. 164. Cu$_2$-d(110) Orn+K, by reduction of specimen of Fig. 8. Beam $\langle 110 \rangle$

Fig. 155. Polycryst. Cu formed by reduction of specimen of Fig. 17

Fig. 156. Cu$_2$-d(110) Orn. & twinning + polycryst. from specimen of Fig. 23. Beam $\langle 110 \rangle$

Fig. 157. Cu$_2$-d(111) + W(100) + twinning + polycryst. from specimen of Fig. 46. Beam $\langle 110 \rangle$

Fig. 158. Cu$_2$-d(111) + twinning + polycryst. from specimen of Fig. 38. Beam $\langle 110 \rangle$
Fig. 159. Cu$_2$S$\rightarrow$-d(100)+(111)+T+K, by reduction from specimen of Fig. 61. Beam $\langle 110 \rangle$

Fig. 160. Cu$_2$S$\rightarrow$-d(100)+(211)+T$\rightarrow$d(111)?, from specimen of Fig. 60. Beam $\langle 110 \rangle$

Fig. 161. Cu$_2$S$\rightarrow$Polycryst. from polycryst. Cu$_2$S on Cu(100). Beam $\langle 001 \rangle$

Fig. 162. Cu$_2$S$\rightarrow$-d(100) + W(111) Orn. from specimen of Fig. 62. Beam $\langle 001 \rangle$

Fig. 163. Cu$_2$S$\rightarrow$W, V, W, 1$\rightarrow$d(111) Orn. from specimen of Fig. 73
produced polycrystalline copper.

The present investigation was undertaken to study the growth of metallic films obtained on reduction, by molecular hydrogen, of oxides of copper formed on single crystal and polycrystalline copper substrates with a view to have a clearer understanding of the nature of the reduced surfaces and their relationship with the initial oxide layers.

EXPERIMENTAL.

Copper single crystals, (110), (111) and (100) faces and polycrystalline copper discs were heated under various conditions (see Section III), and the oxides were then reduced in a stream of molecular hydrogen at about 300-310°C. The hydrogen was prepared in a Kipp's apparatus with dilute sulphuric acid and granular zinc, and purified and dried by passing successively through gas-bubblers containing (i) alkaline pyrogallol solution (KOH - 160 g, pyrogallol - 10 g, and water - 130 ml), to absorb acid vapour and oxygen and (ii) concentrated sulphuric acid, to absorb moisture. The last traces of moisture were removed by passing through a calcium chloride tower. A schematic drawing of the set up is shown in Fig. 153.

The specimens were kept inside the reaction vessel, through which a slow stream of hydrogen was kept
flowing. The temperature of the specimens was raised to about 300-310°C and maintained at this range for 20 to 60 minutes. The specimens were then cooled to room temperature in hydrogen atmosphere and examined by electron diffraction.

**RESULTS.**

The results of the reduction of different orientated oxide layers formed on copper (110), (111) and (100) faces and polycrystalline discs are set out in Table XXIV.

The amorphous or two-degree (110) orientated cuprous oxide formed on the Cu (110) face produced two-degree (110) orientated copper on reduction (Fig. 154), while random and one degree orientated cuprous oxide layers were reduced to random (Fig. 155) and one-degree orientated copper crystals. When the surface layers consisted of a mixture of two-degree orientated cupric oxide and two-degree orientated cuprous oxide, the reduced layer comprised of a mixture of two-degree (110) orientated and polycrystalline copper (Fig. 156). The presence of extra spots along the \(\langle 111\rangle\) directions at 1/3rd and 2/3rd distances from the main spot pattern is due to the formation of \(\{111\}\) twinned crystallites of copper as already discussed in Section III. Polycrystalline cupric oxide was reduced to polycrystalline copper (similar to Fig. 155).
### TABLE XXIV

**Reduction of Copper Oxides Formed on Copper Substrates**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Nature &amp; Orientation of oxide layer</th>
<th>Nature &amp; Orientation of reduced layer</th>
<th>Fig. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(110)</td>
<td>Amorphous</td>
<td>Cu$_2$O, 2-d(110), K</td>
<td>2154</td>
</tr>
<tr>
<td></td>
<td>Cu$_2$O, 2-d(110)</td>
<td>Cu, R</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu$_2$O, 1-d(110)</td>
<td>Cu, 1-d(110)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu$_2$O, 2-d(110) + CuO, 2-d.</td>
<td>Cu, 2-d(110) + T, R</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>CuO, R</td>
<td>Cu, R</td>
<td></td>
</tr>
<tr>
<td>Cu(111)</td>
<td>Cu$_2$O, 2-d(111), (100)</td>
<td>Cu, 2-d(111), W(100), T+K.</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>Cu$_2$O, R + CuO, R.</td>
<td>Cu, 2-d(111), T, R.</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>CuO, R</td>
<td>Cu, R</td>
<td></td>
</tr>
<tr>
<td>Cu(100)</td>
<td>Cu$_2$O, 2-d(111) + (100)</td>
<td>Cu, 2-d(100), W(100), T+K.</td>
<td>159</td>
</tr>
<tr>
<td></td>
<td>Cu$_2$O, 2-d(111) + (100)</td>
<td>Cu, 2-d(100) + (211) + T + 2-d(111)W</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>Cu$_2$O, R</td>
<td>Cu, 2-d(100), T</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>Cu$_2$O, 1-d S(111)</td>
<td>Cu, 2-d(100) + W(111)</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>Cu$_2$O, R + CuO, R.</td>
<td>Cu, R</td>
<td></td>
</tr>
<tr>
<td>Polycryst. Copper</td>
<td>Cu$_2$O, 1-d(111)</td>
<td>Cu, 1-d, W(111)</td>
<td>163</td>
</tr>
<tr>
<td>Polycryst. Copper</td>
<td>Cu$_2$O, R + CuO, R.</td>
<td>Cu, R</td>
<td></td>
</tr>
</tbody>
</table>

1-d = one-degree orientation  
2-d = two-degree orientation  
K = Kikuchi lines present  
R = Polycrystalline, Unoriented  
T = Twinning on \{111\} planes.
The two-degree \{111\} + \{100\} orientated cuprous oxide layer formed on the Cu(111) face were produced on reduced to two-degree \{111\} and \{200\} (weak) orientated copper films (Fig. 157). Twinned copper crystals were also formed. Polycrystalline cupric and cuprous oxide layers were reduced to polycrystalline copper films, though occasionally mixed with two-degree \{111\} orientated copper along with \{111\} twinned crystallites (Fig. 158).

The reduction of two-degree \{111\} + \{100\} orientated cuprous oxide layers, formed on the Cu(100) face, produced copper films having a mixed \{100\} + \{211\} orientation together with the formation of twinned structures (Fig. 159). Sometimes a weak two-degree \{111\} orientation was also observed in the reduced layers in addition to these orientations and twinned structure (Fig. 160). One-degree \{111\} orientated cuprous oxide layers yielded a weak \{111\} orientated copper (Fig. 162). Similar results were also obtained on the reduction of oxide layers formed on polycrystalline copper substrate.

DISCUSSION.

The above results show that, in general, amorphous (fine-grained) or two-degree orientated cuprous oxide layers are reduced to two-degree orientated copper, following the orientation of the oxide reduced; polycrystalline cuprous oxide is reduced to polycrystalline copper and one degree
orientated cuprous oxide to one-degree orientated copper. On the other hand, cupric oxide crystals, whether two-degree orientated or polycrystalline, generally form polycrystalline copper on reduction.

Interesting results have been obtained during the reduction of two-degree \{111\} + \{100\} orientated cuprous oxide layers formed on the Cu(111) and Cu(100) faces. The reduced layers formed on the Cu(111) face consist of two-degree \{111\} + \{100\} orientated copper, while those on the Cu (100) face show a new two-degree \{211\} orientation in addition to the normal two-degree \{100\} orientation. Further, extensive formation of \{111\} twinned crystallites is also observed in both the cases. The formation of \{211\} orientation along with \{100\} orientated layers may be due to double twinning on \{111\} planes. Since extensive \{111\} twinning of copper was observed in the reduced films, the above suggestion is reasonable. It is not clear, why the \{111\} orientation of the oxide is not generally continued in the reduced film.

The orientations of the reduced films may be explained from a consideration of lattice structures of the oxides and the metal. In cuprous oxide (cubic, \(a_0 = 4.259\) Å) the copper atoms are at the coordinates \(\ldots, \ldots, \ldots, \ldots\), i.e. in a face-centred cubic arrangement, and the oxygen atoms are at \(000, \frac{1}{2}, \ldots\), i.e. in body-centred positions, each oxygen atom being surrounded by a
a regular tetrahedron of copper atoms (Syckoff, 1951). In copper (cubic $a_0 = 3.60 \AA$), also the copper atoms are arranged in a face-centred cubic lattice (Syckoff, 1951). Now, if the copper atoms, formed by the reduction of a single crystal of cuprous oxide, retain their initial lattice positions, the resulting lattice would be in a somewhat strained condition and hence they have to readjust to the normal stable configuration. Thus a single crystal of cuprous oxide would be reduced to a single crystal of copper, showing the same orientation as the oxide. This has indeed been observed in the present investigation. Further, since cuprous oxide has been observed to form \{111\} twinned crystallites during the growth of oxide crystals (Section III), it is reasonable that this twinned structure would be retained in the film obtained on reduction. This has also been observed in several cases. As the original copper crystal did not show the presence of twinned crystallites, the appearance of twinned crystallites in the reduced film can be explained on the above basis. Alternatively, the twinned crystallites may be formed in the metal-films, obtained by reduction, as a result of strain in the lattice due to the removal of oxygen.

When the oxide layer consisted of a mixture of two-degree orientated and randomly disposed cuprous oxide crystals, the reduced layers obtained from them consisted of two-degree orientated and polycrystalline copper and
thicker polycrystalline or one-degree orientated cuprous oxide layers were reduced to polycrystalline, and similarly one-degree orientated copper films. These observations indicate that the mobility of the copper atoms at the temperature of reduction (i.e. \( \approx 300^\circ C \)) was not sufficiently high to transform the polycrystalline or one-degree orientated copper to two-degree orientation. Alleman and Wilman (1949), have shown that a polycrystalline film of lead sulphide, formed on a rock salt single crystal substrate, can change to single crystal structure when heated to about 400°C. It would thus seem that the temperature of reduction in the present investigation was not high enough to impart adequate mobility to the copper atoms formed on the reduction of polycrystalline cuprous oxide layers to re-arrange epitaxially.

The results obtained from the reduction of cupric oxide films are not so easily explained. Cupric oxide has a monoclinic structure with \( a_0 = 4.684 \) Å, \( b_0 = 3.425 \) Å, \( c_0 = 5.129 \) Å; and \( \beta = 92^\circ - 28' \) (Swanson and Tatge, 1953), and have their copper atoms at the coordinates \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), and the oxygen atoms at \((0, u, 0)\), \((0, u, 0)\), \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\), where \( u = 0.584 \) (Tunnel, Fosnjak and Asanda, 1935). Here each oxygen atom is surrounded by a distorted tetrahedron of copper atoms (Myckoff, 1951). It will be seen that, because of the dissimilarity of the lattice positions of copper atoms or ions in cupric oxide and copper crystals, normally the reduction of two-degree
orientated cupric oxide would yield polycrystalline copper. If, however, the temperature of reduction is sufficiently high to impart enough mobility to the copper atoms, it is possible for the reduced film to take up a single crystal structure.

Experiments using single crystals of tenorite (cupric oxide) and cuprite (cuprous oxide) would throw better light on the mechanism of the reduction process and the growth of orientated layers. Work on these lines is being planned.