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The Surface Oxidation of Metals.

By

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INTRODUCTION.

A metallic surface exposed to chemical attack in dry or wet conditions soon becomes covered by a film formed by the chemical reaction. The initial film may be an oxide, or a hydroxide, or a basic or a normal salt.

The observed phenomena of the surface reactions caused by the attack are so varied that in order to consider them all adequately more than one point of view must be taken into account. If, however, the problem to be investigated is defined clearly enough all the phenomena may be considered easily from the aspect of this problem. The fundamental question may be asked: "What is the origin and nature of the reactions taking place on the metallic surface during the course of the chemical attack?"

In order to be able to answer this question, the influence of the following points must be considered during the corrosion experiments:

1. The thermodynamic properties of the metal surface depending on the crystallographic nature and the condition of the surface;
2. The chemical and thermodynamic properties of the attacking substance and of the initial corrosion products;
3. The electrochemical processes involved;

4. The influence of the structure and orientation of the initial corrosion products on the further course of the attack.

All the above points are connected so closely with the chemical attack on metals that all of them have to be considered for the investigation to be successful.

The influences of the above points 1, 2 and 3 have been investigated several times and are well recognised, but the influence of the nature of the initial film on the further course of the attack is less well known.

The development of the new research techniques such as electron diffraction and electron microscopy has now given the opportunity to determine the nature of the initial reactions which occur during a chemical or electrochemical attack on the metal surface. In particular electron diffraction (see, for example, Finch and co-workers [1-4]) is facilitating the identification of the initial reactions.

In the present investigation the influence of the structure and orientation of the initial oxide film on the further course of the corrosion has been examined. During the investigation, the other effects (thermodynamic properties of the surface and the reaction products, the electrochemical processes, etc.) have been considered in a broad sense.

The problem to be solved in the present work will be

defined as: "Of what kind are the origins and nature of the initial reactions taking place on a metal surface".

To answer this question it is clear that a study of the chemical reactions occurring on single crystal surfaces must be investigated.

PART I.THE NATURE OF THE METALLIC CORROSION.

Considering that in a corrosive attack the driving force is the change of the free energy between the initial and final states it is necessary to know the energy conditions before and during the attack in order to understand the course of the reaction. At the moment these demands are only partially fulfilled.

These energy conditions are determined by the nature of the metal, its structure and crystallographic nature, the surface finish, the nature and properties of the attacking compounds, the form and structure of the initial film, etc. The most important points are considered in the following sections.

1. The Thermodynamic Properties of the Metal Surface.

During a corrosion reaction the metal suffers a complete change of state. To explain theoretically the details of that reaction, it is necessary to define the initial state of the attacked surface as precisely as possible. Starting from the atomic arrangement, other effects such as those due to the texture, surface condition, and the influence of impurities have also to be considered. Until now these

high demands have been realised only partially. It is therefore necessary to carry out the investigation under conditions such that the number of variables is at a minimum. Hence single crystal surfaces must be our starting point. Polycrystalline material with its grain boundaries, deformed crystals, variable surface structure, etc. must exhibit a wide range of thermodynamic properties which will vary from place to place on the surface in an unknown manner.

Single crystals, too, show various effects depending mainly on their crystallographic nature and on the surface conditions; but such variations can largely be controlled.

a. The Metal and its Imperfections of Structure.

Metal physics relies upon the fact that the metal atom consists of a positive nucleus and a specific number of circumnuclear electrons arranged in characteristic envelopes. The outer electrons of the atoms provide not only the electric conductivity, etc., but also the binding of the atoms in the crystal lattice or in the molten state. In the metallic state there is no binding of the valency electrons; there is a lower valency like that of the Van der Waals', but with larger binding energy. For the metallic state the valency electrons are freely mobile between the atoms whence according to modern views the metal surface has associated with it "free" electrons.

The evidence of the regular distribution of the valency electrons as the "electron gas" throughout the whole crystal proved to be not quite right. Brill, Grimm, Hermann and Peters [5,6] carried out a Fourier analysis of X-ray patterns obtained from magnesium single crystals. Their results reveal the fact that a comparatively smooth electronic underground exists corresponding to a regular smearing-out of 1.75 electrons per Mg atom over the lattice. There are, however, in addition in the lattice discrete regions with accumulations of electrons, and in the neighbourhood of these regions a deficiency of electrons. More detailed evidence could not be obtained.

Brindley [7] obtained similar results on ruthenium. According to Griffith and Harris [8] there are accumulations of electrons on the cube edge of the lithium lattice. These experimental results proved the correctness of the previous theoretical conclusions arrived at by Sommerfeld [9].

This evidence of accumulations of electrons in the crystal lattice may now result in a different behaviour of different atoms during a chemical reaction. These properties are for the present purpose not very important, because they are outweighed by other more prominent effects.

Besides these irregularities on the atomic scale, a

real metal crystal has other irregularities, the so-called structure errors. These structure faults of a real crystal are associated with structure sensitive properties, that is, a metal single crystal shows a chemical behaviour which depends on the development of the structure. A single crystal is not in fact in a state of ideal thermodynamic equilibrium. In these places of structure errors corrosion occurs first, on thermodynamic grounds.

According to Renninger [10] these structure errors may be classified as follows:

1. Macroscopic defects of a size order $1 - 10^{-3}$ mm.
2. Mosaic or block structure of dimensions $10^{-3} - 10^{-5}$ mm.
3. Lattice faults (Smekal, Taylor) of dimensions $10^{-5} - 10^{-6}$ mm.

A characteristic difference has to be recognised between a single crystal grown from the molten metal and a single crystal obtained through recrystallisation. The crystals obtained through recrystallisation show more structure errors.

b. The Influence of the Crystallographic Nature.

It is well known that certain physical properties (hardness, friction, electric conductivity, thermionic and photo-electric emission, etc.) are due to the crystallographic

nature of the surface.

Several investigators have studied the chemical properties of single crystal faces, and the results obtained have an important bearing on the phenomena of the corrosion of metals. According to Fricke and Wagner [11], Haul [12], and Smoluchowski [13] the amount of the free surface energy of non-polar crystals (metals, rare gases) varies from one face to another with change in atom population density. According to Fricke [14] the free surface energy calculated from the heat of sublimation is as follows

	(100)-face	(111)-face
Al	1909 erg/cm ²	1618 erg/cm ²
Cu	2892 " "	2499 " "
Ag	1920 " "	1650 " "
Pb	871 " "	745 " "

The difference between total and free energy is small.

These differences in the free surface energy may result in different electrode potentials of the distinguished faces. Indeed, Sato and Maruyama [15], Druet and Jacquet [16] have shown that the standard potential of zinc and aluminium single crystal faces proved these suppositions. According to Sato and Maruyama [15] the standard potentials of zinc single crystal faces relative to the standard hydrogen electrode are as follows:

<u>Faces</u>	<u>mV.</u>
(0001)	870
(1010)	851
(1121)	809

and for aluminium single crystal faces according to Druet and Jacquet [16]

<u>Faces</u>	<u>Potential in V.</u>
(100)	- 1.15
(111)	- 1.20

Gwathmey and Benton [17] showed the difference in the solution potential in the case of electrolytic etching of copper single crystals. The distances between the opposite poles of the faces decreased in the following order:

(Electrolytic etching in a solution of phosphoric acid.
Time: 47 - 3/4 hrs. Current density: 0.006 amp./cm.²).

Poles of the faces	(100)	(111)	(110)
Decrease in mm. 1st Exp.	0.63	0.91	0.95
2nd Exp.	0.63	0.88	0.88

It was also observed that the rate of a chemical attack depends on the crystallographic nature of the surface.

Tammann [³⁰~~24~~] oxidised copper single crystal faces in air at a temperature of 260°C. and observed that the (110)- and (111)-

faces oxidised much faster than the (100)-face. Similar results were obtained by Benard and Talbot [20] heating copper single crystals at 900°C.

Leidheiser and Gwathmey [18] have shown not only that during a chemical attack the differently orientated faces have a different rate of attack, but also that the speed of a catalytic reaction depends on the crystallographic nature of the surface. They examined the catalytic properties of well defined copper single crystal faces on the reaction between H_2 and O_2 at a temperature of 400°C. According to these investigators the rate of the reaction on the (111)-face is much higher than on the (100)-face.

From the above results the important effect of the crystallographic nature of a surface on the rate of a chemical or electrochemical attack is shown clearly.

e. The Influence of the Previous Surface Treatment.

Besides the crystallographic nature and the texture the conditions of a metal surface have an important effect on a reaction taking place on it. The condensation of water vapour, the adsorption of gases, dust particles, etc. are facilitated at regions of higher free energy (edges, crystal boundaries, distorted areas, etc.).

On these points of higher activity the first reaction

takes place due to the thermodynamic irregularities. Very important information has been given by Erbacher [19]. He examined the effect of heating a catalyst. After heating the crystals in vacuo they showed, at a temperature of $2/3 F$ (F = melting point), a remarkable decrease in catalytic effect. The results obtained were explained by Erbacher in such a way that at a temperature above $2/3 F$ the structure faults have been healed. Etching resulted in an increase of catalytic properties. The etching evidently exposed extensive structural faults at the surface again.

The surface structure depends on the finishing of the metal. A mechanically polished surface is covered with the amorphous Beilby layer, whilst an electropolished surface shows an atomically smooth surface exposing the crystalline metal and an etched one is relatively rough.

It has frequently been noted [16-20] that the rate of an attack is much affected by the finish of an exposed metal surface.

2. The Chemical and Thermodynamical Properties of the Attacking Substances and of the Corrosion Products.

The application of thermodynamics in experimental chemistry as a helpful instrument has been limited too often to the study of reactions in the gaseous phase. Thermodynamics

can, however, also be applied with advantage to the consideration of heterogeneous reactions.

Pourbaix [25] has shown in an excellent way the application of thermodynamics in corrosion research. His book entitled "Thermodynamics of Dilute Aqueous Solutions" is a great help in examining the corrosion of metals. In particular, the diagrams in which the equilibrium potential is plotted against the pH show the domains representing "corrosion", "cathodic protection", or "passivation". He also has shown under what conditions in a complicated system the different corrosion products may be formed.

Feitknedt [26] showed that the formation of the different corrosion products during an attack on zinc in dilute solutions of sodium chloride obeys well-recognized thermodynamic principles.

3. Electrochemical Processes.

A metal surface exposed to a corrosive attack is actually a poly-electrode system caused by physical or chemical differences at different points on the surface. The differences are not only due to the properties of the metal but also to a different rate of supply of oxygen.

For example, consider the corrosion of zinc in a dilute solution of sodium chloride. On the anodic points zinc goes

as zinc ions into solution, on the cathodic points oxygen is depolarised and on a third set of points the corrosion product, zinc oxide in hydrated form, is precipitated. Zinc is consumed at one point, oxygen at a second and the product appears at a third one. The result is still the same, the combination of zinc and oxygen (and water). As the oxidation takes place in the indirect electrochemical way the corrosion product is not protective against a further attack because it is not precipitated where the attack is carried out.

These electrochemical processes during the corrosion of metals have been studied in detail by Evans and co-workers at Cambridge (see U.R.Evans: Metallic Corrosion, Passivity and Protection, 2nd Ed., 1946). These electrochemical processes not only occur in aqueous solutions but also in air containing water vapour, as has been shown by Feitknecht [27] and Leu [28].

4. The Influence of the Distribution, Structure and Orientation of the Initial Corrosion Product.

It is obvious that the distribution, structure and orientation of the initial corrosion product are very important for the further course of the attack. Amorphous or close packed crystalline material shows a good protection against a

further attack while a coarsely crystalline film shows less protection.

Despite the great volume of work devoted in the past to the study of corrosion little is known about the influence of the structure and orientation of the initial film on the further attack.

The following facts may be noted here :

1. A zinc cleavage face shows an excellent resistance against oxidation. After a long exposure to air at room temperature the metallic brightness is still visible. If a zinc cleavage face is heated up to a few hundred °C. the protection disappears.

2. Up to a temperature of about 680°C. the formation of an amorphous oxide film is observed on aluminium, showing an excellent protection. Above 680°C. the oxide becomes polycrystalline and the protection against a further attack has disappeared.

3. Lustman and Mehl [31] examining the oxidation of copper single crystal faces at temperatures between 105°C. and 118°C. observed that the rate of oxidation varied according to the different orientated faces. They suggested that the observed phenomena are due to the different orientations of the initial oxide film crystals. As the relations seem to be dependent on the oxidation temperature and other conditions,

they could not give more exact conclusions.

Other similar evidence has been observed. The reason for these uncertainties in formulating a theory of the influence of the structure and orientation of the initial film on the further attack may lie in the fact that insufficient experimental data has so far been obtained about the mechanism of the surface oxidation of metals.

II. The Mechanism of Oxidation of Copper.

In the present investigation the mechanism of dry and wet oxidation of metals was studied in the light of the theoretical considerations outlined in Chapter I. The experimental work has been limited to the system Cu/O_2 in dry and wet conditions.

The Mechanism of the Thermal Oxidation of Copper.

The oxidation of copper in air or oxygen at room or elevated temperature has been often investigated [20, 30-65]. Recently, Tylecote [66] has published a review entitled "Review of Published Information on the Oxidation and Sealing of Copper and Copper-Base Alloys". In that review an excellent summary is given and the problems concerning oxidation so that we may limit ourselves here to the main problem, that of the mechanism of oxidation.

The first investigators [30,32,37,39,40] suggested that the active part of the oxidation was due to the migration of oxygen along the grain boundaries or through the oxide crystals and that the reaction then occurs at the interface copper/cuprous oxide. The views of these investigators attributing the active role to the oxygen differ only in the interpretation of the diffusion relationship. They suggest a diffusion through the grain boundaries of the oxide or at high temperature also a diffusion of oxygen through the crystals.

The evidence that the active part of the oxidation is due to the migration of oxygen along the boundaries or through the oxide crystals could not hitherto be proved.

Wagner and Grunewald [54] examined the electric conductivity of the system $\text{Cu}/\text{Cu}_2\text{O}/\text{O}_2$ and from the results obtained they concluded that the active role during the oxidation is due to the migration of cuprous-ion through the oxide film, the reaction taking place on the oxide surface. Attempts were made to support this view by experiments in which radioactive copper surfaces were oxidised.^[55,56] The results, however, were indeterminate. Mott's [67] view that oxygen gains access to the metal only by the migration of copper ions through the oxide film is of doubtful validity.

From the formation of the initial oxide film up to the

complete oxidation of a piece of metal, so many different reactions are taking place side by side that in the writer's opinion it is impossible to come to a result with such a simple formulation of the question.

The oxide formed shows many variations in chemical nature, structure, orientation to the substrate, crystal size, etc. depending all on the experimental conditions. The following statement of the problem is much clearer and more real in investigating the mechanism of oxidation:-

Where are the sites of chemical reactions in the system $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}/\text{O}_2$ and how do the reactions proceed?



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PART II.THE DRY AND WET CORROSION OF COPPER SINGLE CRYSTALS.I. Experimental Details.1. Preparation of the Copper Single Crystal Faces.

The copper single crystal faces used in the present work were cut from a copper single-crystal rod, about 1 cm. in diameter. The crystal was carefully cut with a jeweller's saw lubricated with watch oil so as to avoid much distortion of the crystal. The cut pieces were ground carefully with emery paper of different grades so as to develop a face. This face was then etched deeply with HNO_3 1:1 to remove the distorted layers and then electropolished in a solution of phosphoric acid. After electropolishing the crystals were washed with distilled water and transferred under propyl alcohol into the electron diffraction camera. From the pattern obtained the crystallographic nature of the face was identified relative to the copper lattice. The faces were then ground on the crystals in the desired (110)-, (111)- and (100)- directions. The faces obtained were within about $2-3^\circ$ from the desired net-plane of the copper lattice.

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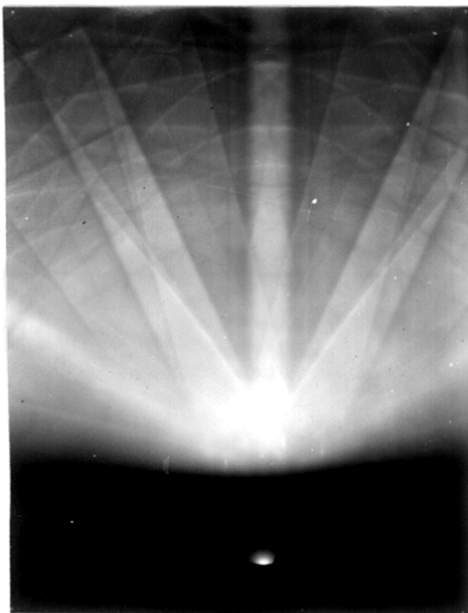


Fig. 1. (110)-face. Beam along the cube face diagonal.

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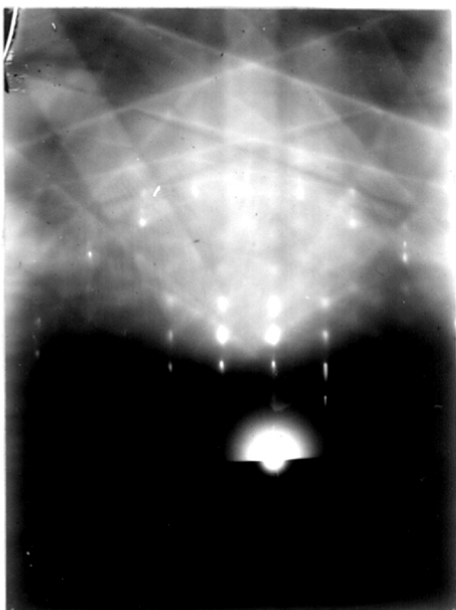


Fig. 2. (111)-face. Beam along $[\bar{2}11]$.

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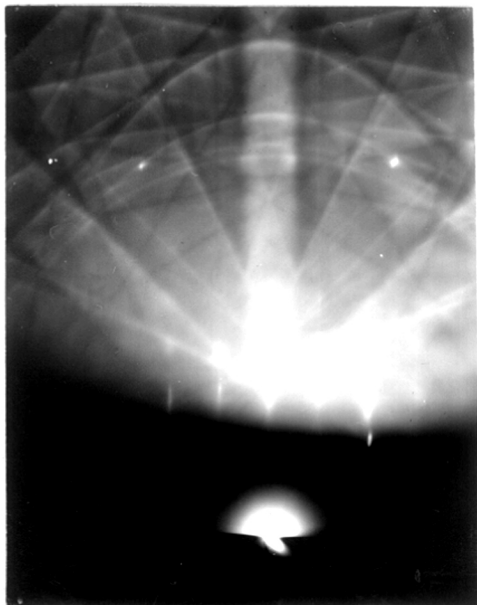


Fig. 3. (100)-face. Beam along a cube edge.

Electrolytically polished copper single crystal faces.

2. The Anodic Polishing of Copper Single Crystals.

Before carrying out any experimental work, the prepared copper single crystal faces were etched in HNO_3 1:1 so as to remove the distorted surface layer and then electropolished in an aqueous solution of phosphoric acid as recommended by Jacquet [68]. The conditions for the anodic polishing were as follows:

Bath: 2 parts phosphoric acid (S.G. 1.75) and 1 part distilled water.

Voltage: 2 - 2.2 volts.

Current Density: 0.05 - 0.1 amp/cm².

Time: 20 - 30 minutes.

After electropolishing, the copper crystals were taken out, thoroughly washed with a dilute solution of phosphoric acid followed by distilled water. To remove any traces of oxide formed on the surface during electropolishing or afterwards, the crystals were dipped for one minute into 2% KCN solution, then washed with alcohol followed by acetone. The faces were then transferred under propyl alcohol into the electron diffraction camera to avoid oxidation by exposure to air. The faces treated in this way yielded the patterns shown in Fig.1, Fig.2 and Fig.3. The sharp elongated spots

together with the sharp Kikuchi-lines show the atomically smooth nature of the surface and high lattice perfection of the crystals.

3. Etching of Copper Single Crystals.

Electropolished copper single-crystal faces were etched in HNO_3 1:1 at room temperature (time: 30 sec.). After etching the faces were washed with distilled water. To remove any traces of oxide formed on the surface after the etching the crystals were dipped for one minute in a 2% KCN solution, then washed with alcohol followed by acetone. In that way the faces were etched equally and had a not too rough surface.

Fig.4 shows the diffraction patterns obtained from an etched (110)-face, Fig.5 from an etched (111)-face, and Fig.6 from an etched (100)-face. These patterns reveal the comparative roughness of the etched faces.

4. Oxidation Experiments.

a. Dry Corrosion.

The experiments were carried out in laboratory air containing traces of impurities and water vapour. According to Dunn [60] and Pilling and Bedworth [32] traces of water vapour or carbon dioxide have little effect on the oxidation

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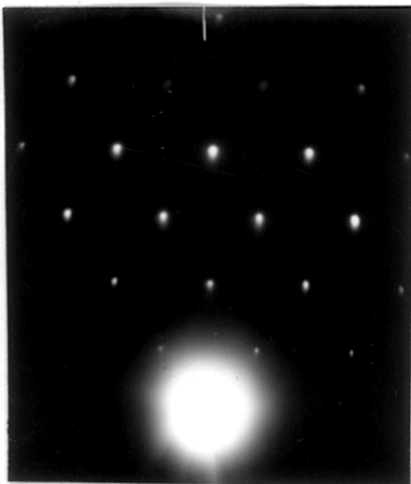


Fig. 4. (110)-face.
Beam along $[\bar{1}\bar{1}0]$.

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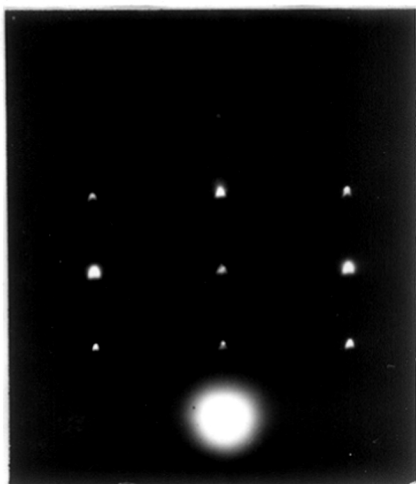


Fig. 5. (111)-face.
Beam along $[\bar{2}11]$.

F4988

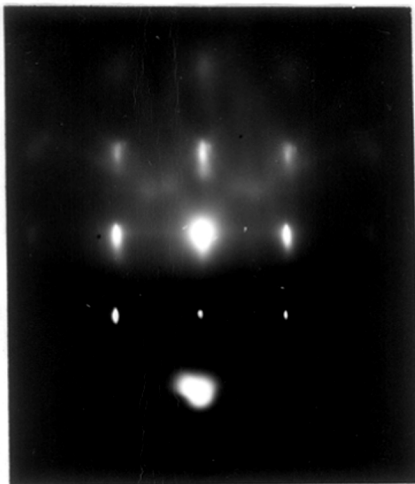


Fig. 6. (100)-face.
Beam along $[001]$.

Etched copper single crystal faces.

of copper up to a temperature of about 800°C. On the other hand Hudson and co-workers [64] have shown that traces of hydrochloric acid increase the attack noticeably.

The experiments were carried out in a furnace which was heated up to the desired temperature before inserting the copper single crystal. After heating the specimen for a certain time, the specimen was taken out and allowed to cool to room temperature.

The experiments were carried out within the temperature range between 0° and 250°C.

b. Wet Corrosion.

The experiments in distilled water, in dilute solutions of sodium hydroxide, sodium chloride, potassium bichromate or hydrogen peroxide were carried out at room temperature. The solutions contained dissolved oxygen.

Before examination in the electron diffraction camera the specimens were washed carefully with distilled water and acetone.

5. Measurement of the Film Thickness.

The thickness of the initial oxide films was estimated from the interference colours of these thin films. According to Evans [69] and Constable [43] the film thickness may be determined approximately in this way. For the present work that method has proved to be sufficient.

II. Experiments on the Thermal Oxidation.

1. The Thermal Oxidation of Electrolytically Polished Copper Single Crystal Faces.

Electropolished copper single crystal faces were oxidised in air at different temperatures. The faces used for the experiments were examined by electron diffraction before and after exposure to air. The results obtained are shown in Table 1.

Oxidation temperature 20°C. Anodically polished copper (110)-, (111)-, and (100)- faces showing a bright surface were exposed to air at room temperature. After a few hours the surfaces had become less bright and after an exposure of about 24 hours they were brownish in colour, not changing much during a further prolonged exposure (longest time: 40 days). Immediately after the exposure the initial film grew very quickly but after it reached a certain thickness (a few hundred Angstrom) growth ceased nearly completely. There was no noticeable difference observed in the rate of attack of the different orientated faces. The cuprous oxide film formed was ~~not~~ amorphous (Fig.7).

Oxidation temperature 100°C. At about 100°C., immediately after exposure the single crystal faces became less bright.

Table 1.

Thermal Oxidation of Electrolytically Polished
Copper Single Crystal Faces.

Nature of the Initial Oxide Film.

Product : Cu_2O

Thickness of the Film: less than
600 Å.

Temperature	Nature of the Oxide film formed		
	on (110)-face	(111)-face	(100)-face
20°C.	amorphous	amorphous	amorphous
100°C.	do.	do.	do.
130°C.	do.	do.	do.
135°C.	very small crystals random orientation.	do.	do.
140°C.	do.	very small crystals random orientation.	do.
145°C.	do. showing one- degree orient.	do. showing one- degree orient.	very small crystals showing one- degree orient.
150°C.	small crystals 2°-orientation [110]//[110] [100]//[100]	small crystals 2°-orientation (111)//(111) [110]//[110]	small crystals various orientations mostly (111) + (110)// (100)
160°C.	do.	do.	do.
180°C.	do.	do.	do.
200°C.	do.	do.	do.
250°C.	do.	do.	do.

After one hour they showed a brownish interference colour. After the oxide film had reached about 450 Å. thickness, its growth apparently ceased. The cuprous oxide formed was amorphous.

Oxidation temperature: 130°C. Immediately after the exposure the electropolished single crystal faces lost their brightness. After 30 minutes exposure to air the first interference colours appeared. The purple and blue colours were only observed after a prolonged exposure to air at 130°C. There was no noticeable difference in the rate of oxidation of the different faces. The oxide film formed at this temperature on electropolished surfaces was still amorphous.

Oxidation temperature: 135°C. No noticeable difference from the experiments carried out at 130°C. was observed, except that the (110)-face seemed to oxidise a little faster than the (111)- and (100)- faces. On the (110)-face a polycrystalline film of cuprous oxide was formed, having random orientation (Fig.8). The oxide film formed on the (111)- and the (100)- face at this temperature was still amorphous.

Oxidation temperature: 140°C. At this temperature only a small difference in the rate of oxidation of the three faces was observed. The (110)- and the (111)- faces were oxidised

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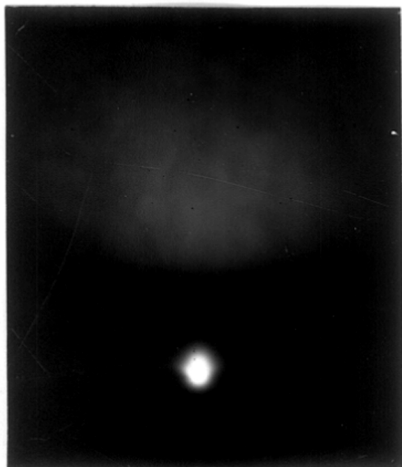


Fig. 7. (110)face; 1 day at room temperature. Amorphous Cu_2O - film.

F2 179

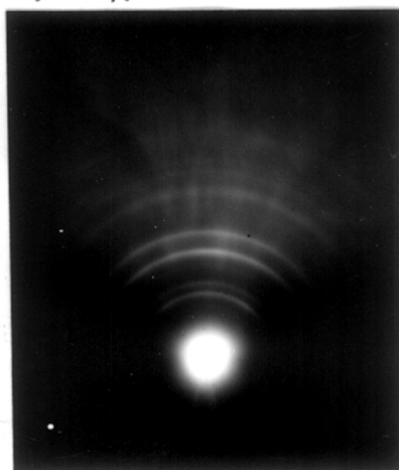


Fig. 8. (110)-face; 30 min. at 135°C . Crystalline film; random orientation.

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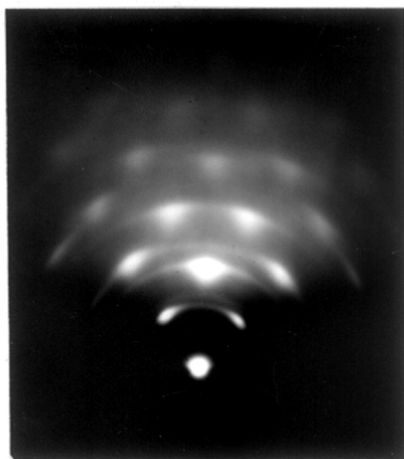


Fig. 9. (110)-face; 3 min. at 160°C . Crystalline film; two degree orientation.

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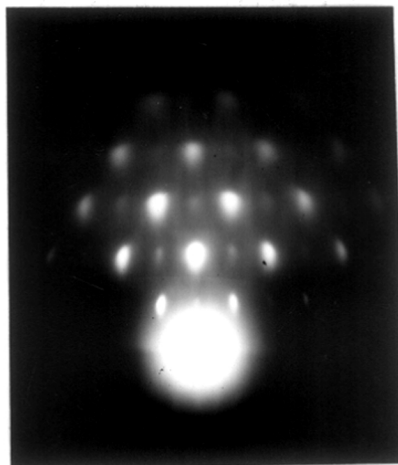


Fig. 10. (110)-face. 2 min. at 200°C . Crystalline film; two degree orientation.

Structure of the initial cuprous oxide film formed on anodically polished copper single crystal faces.

a little faster than the (100)-face. After 45 minutes heating in air the purple interference colours appeared on the (110)- and (111)- faces (thickness of the film: 450 Å.) while the (100)-face showed a red-brown interference colour (thickness of the oxide film: 420 Å.). The initial oxide film formed on the (110)- and (111)- faces was polycrystalline with random orientation. On the (100)-face the oxide film was still amorphous.

Oxidation temperature: 145°C. All the oxide films, including that formed at 145°C. on the (100)-face proved to be crystalline, with a slight preferred orientation relative to the substrate.

Oxidation temperature: 150°C. At this temperature the rate of oxidation was much higher on the (110)- and on the (111)-face than on the (100)-face. On the (110)- and on the (111)-face the initial cuprous oxide crystals had developed in a two degree orientation while on the (100)-face different orientations (mostly (111) and (110) parallel to the (100)-face) were observed.

Oxidation temperature: 160°- 250°C. The initial film at temperatures between 160° - 250°C. consisted of small cuprous oxide crystals, having on the (110)- and (111)- face an epitaxial relationship to the substrate (two-degree

F2 217

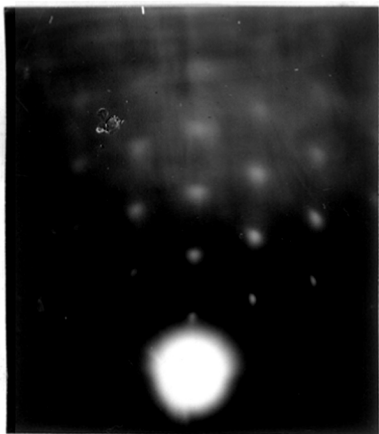


Fig. 11. (111)-face;
2 min. at 200°C.
Crystalline film; two
degree orientation.

F 5047



Fig. 12. (100)-face;
2 min. at 200°C.
Crystalline film; various
orientation.

Structure of the initial oxide film formed on
anodically polished copper single crystal faces.

orientation). On the (100)-face different orientations were observed, mainly the (111)- and (110)-face of the cuprous oxide parallel to the copper (100)-face. (Figs. 9, 10, 11 and 12). Increasing the thickness of the film resulted in formation of larger oxide crystals.

The (110)- and the (111)-face became oxidised faster than the (100)-face. Up to a film thickness of about 800 Å. the oxide film quickly grew in thickness but then growth practically ceased.

At about 200°C. after reaching a certain thickness the cuprous oxide on the surface was oxidised to cupric oxide. It is remarkable that on the (100)-face the formation of cupric oxide appeared on thinner cuprous oxide films than on the (110)- and (111)-faces. The thin cupric oxide film on the (100)-face sometimes showed interference colours and thus suggested that the rate of oxidation was higher than was actually the case.

The upper layers of thick cuprous oxide films (more than 1000 Å.) were slightly less strongly orientated than the initial film (Fig.13).

2. The Thermal Oxidation of Etched Copper Single Crystal Faces.

During the thermal oxidation in air copper single

F2 126

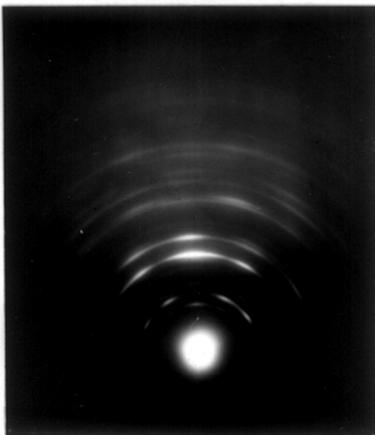


Fig. 13. Cu (110)-face;
anodically polished.
2 h at 180°C.
Decrease in orientation.

crystal faces were analogous in behaviour to the anodically polished faces, except for two differences:

1. The rate of oxidation on etched faces was a little higher than on electropolished faces.
2. Only at room temperature was the initial oxide film mainly amorphous (see Table 2).

Oxidation temperature: 20°C. At room temperature on etched copper (110)-, (111)- and (100)- single crystal faces there was a formation of mainly amorphous oxide film. A small part was crystalline in (110) and (111) one-degree orientation relative to the underlying metal (Fig.14). The crystalline part of the initial film was very small.

Oxidation temperature: 100°C. The initial oxide film formed at a temperature of 100°C. was polycrystalline on all three faces and showed one-degree orientation (Fig.15).

Oxidation temperature: 125°C. The results obtained at this temperature are similar to those obtained at 100°C. The cuprous oxide crystals on the (110)- and (111)- face had developed in one degree (110) and (111) orientation respectively. (Fig.16).

Oxidation temperature: 140°C. Similar results were obtained to those at 125°C.

Table 2.Thermal Oxidation of Etched Copper Single Crystal Faces.Nature of the Initial Oxide Film.Product: Cu_2O Thickness of the Film: less than 600 Å.

Temperature	Nature of the Oxide film formed on		
	(110)-face	(111)-face	(100)-face.
20°C.	mostly amorphous, small part crystalline, showing one-degree orientation.		
100°C.	polycrystalline showing one-degree orientation.		
125°C.	do.	do.	do.
150°C.	small crystals 2°-orientation (110)// (110) [100] // [100]	small crystals 2°-orientation (111)// (111) [110] // [110]	small crystals various orientations. mostly (111) + (110) // (100)
200°C.	do.	do.	do.
250°C.	do.	do.	do.

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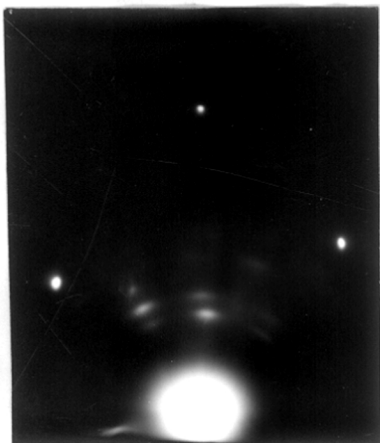


Fig. 14. (110)-face.
1 day at room temperature.
Film mostly amorphous.

F 4704

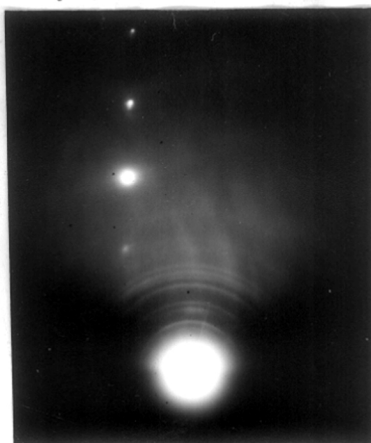


Fig. 15. (111)-face.
1 h at 100°C.
Crystalline film; one degree
orientation.

F₂ 183

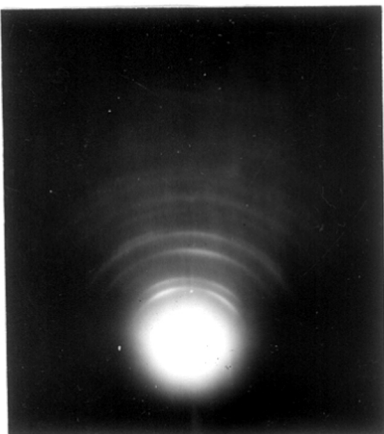


Fig. 16. (110)-face.
20 min. at 140°C.
Crystalline film; one
degree orientation.

F 4997

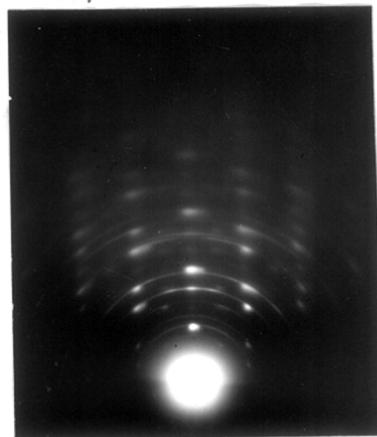


Fig. 17. (111)-face.
3 min. at 200°C.
Crystalline film; two degree
orientation. Deformation
through rotational slip.

Structure of the initial cuprous oxide film formed
on etched copper single crystal faces.

Oxidation temperature: 150°C. The (110)- and the (111)-face oxidised much faster than the (100)-face. The cuprous oxide film formed an epitaxial overgrowth (two degree orientation with Cu_2O (110)// Cu (110) [100]// [100] Cu; Cu_2O (111)// Cu (111) and Cu_2O [101]// Cu [101] respectively) on the (110)- and (111)- face while on the (100)-face various orientations of the oxide were observed.

Oxidation temperature: 200°C. The faces became oxidised much faster than at 150°C. but the other results obtained (rate of oxidation, nature of the initial film) were similar to those at 150°C.

On etched surfaces the initial cuprous oxide film sometimes showed a deformation. The reason for this deformation is that a state of strain exists at the cuprous oxide-metal interface due to lattice misfit. Mechanisms for the relief of this strain, which are now well-recognised in this laboratory, are twinning and rotational slip. [71-75].

3. Thermal Oxidation of a Mechanically Polished Single Crystal Face.

Mechanically polished copper single crystal (110) faces yielded quite different results from those obtained with electropolished or etched single crystal faces. This is due to the different surface condition (amorphous Beilby layer

Table 3.

Thermal Oxidation of a Mechanically Polished (110)-face
Metal Surface showing an amorphous Beilby-layer before
Oxidation.

Nature of the Initial Oxide Film.

Product: Cu_2O

Thickness of the Film: less than 600 Å.

<u>Temperature</u>	<u>Nature of the Oxide Film.</u>
20°C.	amorphous
100°C.	amorphous
150°C.	very small crystals random orientation.
200°C.	small crystals random orientation.

F 5060



Fig. 18. 1 h at 100°C.
Amorphous film

F 5070

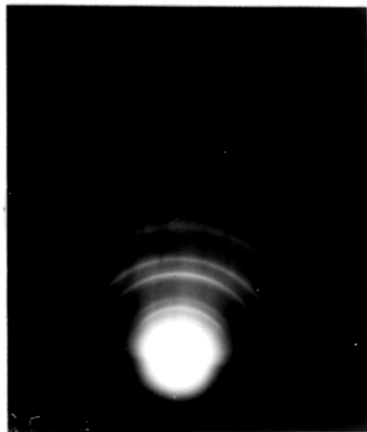


Fig. 19. 10 min. at 200°C.
Polycrystalline film; random
orientation.

Structure of the initial cuprous oxide film formed on
mechanically polished copper (110)-faces.

and its underlying work hardened crystalline layer).

The rate of attack was not so high as on electropolished surfaces.

At 20°C. and at 100°C. the amorphous Beilby layer was oxidised to an amorphous cuprous oxide film (Fig.18) while at 150°C. and above the cuprous oxide formed was polycrystalline with random orientation (Fig.19) (See Table 3).

4. Thermal Oxidation of Electropolished Single Crystal Faces in Presence of Traces of HCl Vapour.

Adding traces of hydrochloric acid vapour to the oxidising air had a remarkable effect. The attack at a temperature of 100°C. was much more rapid than usual.

After one hour's exposure at this temperature an electropolished (110)-face showed the interference colour blue 1st order. No cessation of the attack was observed during prolonged exposure. The cuprous oxide film formed in presence of traces of HCl vapour at 100°C. was polycrystalline showing a two degree orientation relative to the underlying metal (Cu_2O (110)// Cu (110); Cu_2O [100]// Cu [100]). No cuprous chloride could be identified (Fig.20).

5. Thermal Oxidation of a Deformed Copper Single Crystal.

Evans, Layton and Wilman [74] have shown clearly that

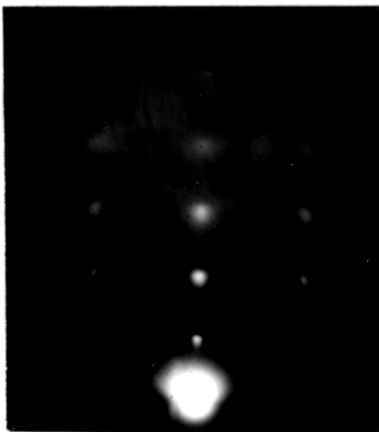


Fig. 20. Cu (111)-face;
anodically polished.
Oxidised 1 h in air at 100°C
in presence of traces of
HCl-vapour; polycrystalline
cuprous oxide film showing
two degree orientation.
Azimuth $[\bar{2}11]$.

if a single crystal surface is abraded unidirectionally the immediate surface region is heavily disorientated but those slightly below had mostly slipped rotationally about a well-defined axis [71,72,73]. The electron diffraction patterns obtained from such abraded crystals show at certain azimuths an arcing of the diffraction spots.

If such a unidirectionally abraded copper single crystal face is oxidised, the oxide film formed should show a change in the crystal orientation according to the nature of the mechanism of oxidation, i.e. migration of copper ions occurs through the oxide or oxygen diffuses through the oxide crystal boundaries.

To examine the nature and extent of lattice deformation caused by the abrasion, a copper (110) single crystal face was unidirectionally abraded with 0000 emery paper along $\langle 1\bar{1}0 \rangle$, etched carefully in HNO_3 1:1 and examined by electron diffraction. A similar (110)-face abraded along $\langle 1\bar{1}0 \rangle$ was oxidised in air at 180°C . for four hours. To examine the structure at different levels below the surface, the cuprous oxide film was etched progressively in a 2% KCN solution, with electron-diffraction examination at suitable stages. In Table 4, column 1, a section through an abraded copper single crystal face is shown. Column 2a shows the theoretical

Table 4.

Thermal Oxidation of a (110)-face, abraded along $\langle 1\bar{1}0 \rangle$

180°C.

Section through the Metal Surface.	Section through the Oxide Layer theoretically. $\text{Cu}^+ \uparrow$	$\text{O}_2 \downarrow$	Section through the Oxide Layer (Experimental Result).
Amorphous Beilby-Layer			
very small crystals random orientation.	Whole Film: small crystals.	very small crystals random orientation	very small crystals random orientation
small crystals showing rotational slip	random orientation	small crystals showing a little rotational slip	small crystals showing an increase in orientation and little rotational slip.
large crystals showing rotational slip		small crystals showing an increase in orientation and little rotational slip	small crystals showing an increase in orientation and little rotational slip.
Single crystal		two-degree orientation.	?

Increasing Orientation \rightarrow

Increasing Orientation \rightarrow

Increasing Orientation \rightarrow

F 5128

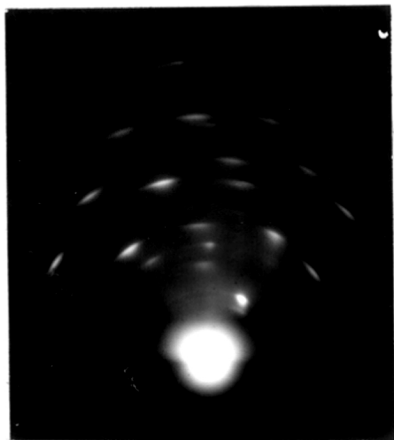


Fig. 21. (110)-face
abraded along $\langle 110 \rangle$;
etched. Deformed region.

F 5134

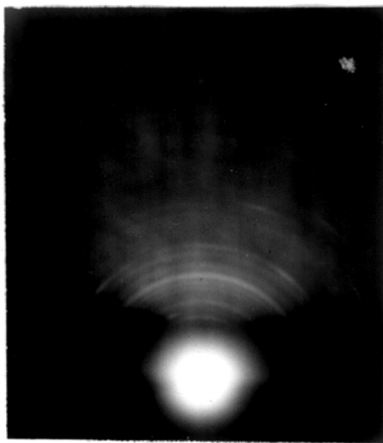


Fig. 22. (110)-face
abraded along $\langle 110 \rangle$.
Oxidised and etched.
Increase in orientation.

Thermal oxidation of an unidirectional
abraded (110)-face.

structure of the oxide formed in the case of a migration of cuprous ion through the oxide film and reaction with the oxygen at the surface; column 2b represents a theoretical section through the oxide film in the case of migration of oxygen through the crystal boundaries and following reaction with the underlying metal. In Column 3 are set forth the experimental results obtained.

III. Wet Corrosion of Electropolished Copper Single Crystals.

1. Introduction.

The corrosion of polycrystalline copper in aqueous solutions, especially in dilute solutions of sodium chloride, has been investigated several times [75-78]. Polycrystalline cuprous oxide was observed as initial corrosion product. A thicker film of cuprous oxide often changes after a further attack into a normal or basic copper salt. That second reaction depends on the concentration of the attacking solution. Further, it was observed that the rate of the initial attack depends on the surface conditions and on the salt concentration in the dilute solution.

Rauch and Kolb [79] examined the corrosion of copper in dilute solutions of cupric sulphate. They observed

cuprous oxide to be formed as initial corrosion product. According to them the rate of attack is not so high in a solution of cupric sulphate as in one of sodium chloride.

In the present investigation the formation of the initial film only was examined. The appearance of other corrosion products as the second stage of the corrosion was not investigated.

The experimental conditions were kept such that according to Pourbaix [25] and Feitknecht [26] an oxide was formed as initial corrosion product.

2. Results.

The results obtained are shown in Table 5.

a. Corrosion in distilled water.

The attack in distilled water (containing dissolved oxygen in equilibrium with the atmosphere) was very slow. The first interference colour (brown 1st order) appeared after several hours. The attack was continuous and after several days a thick film of cuprous oxide was formed showing the typical brownish-red colour of this oxide. The rate of attack was different for the three faces. The (110)- and (111)- faces became much more heavily oxidised than the (100)-face.

The cuprous oxide was crystalline and on the (110)-

Table 5.Wet Oxidation of Electrolytically Polished Copper Single Crystal Faces at Room Temperature.Nature of the Initial Films.

Thickness of the Films: less than 1000 Å.

Solution	Reaction Product.	Nature of the Film on		
		(110)-face	(111)-face	(100)-face
H ₂ O	Cu ₂ O	small crystals two-degree orientation (110)//(110) [100]//[100]	small crystals two-degree orientation (111)//(111) [110]//[110]	small crystals various orientations. mostly (111) (110) // (100)
0.5n NaOH	Cu ₂ O	do.	do.	do.
1 n. NaOH	Cu ₂ O	do.	do.	do.
0.01n NaOH	Cu ₂ O	do.	do.	do.
0.1n NaCl	Cu ₂ O	do.	do.	do.
0.001 m K ₂ Cr ₂ O ₇	Cu ₂ O(?)	amorphous	amorphous	amorphous
H ₂ O ₂ (20 Vol %)	CuO ?	amorphous	amorphous	amorphous

F₂ 140

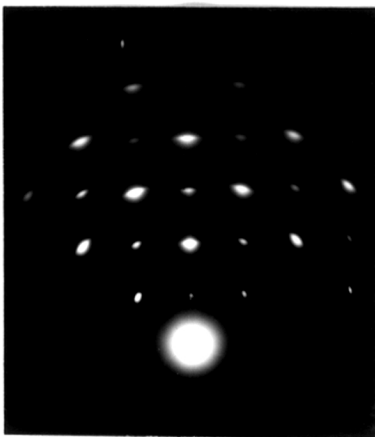


Fig. 23. Corroded in distilled water for 1 day. Cu_2O in two degree orientation. Beam along $[100]$.

F₂ 61

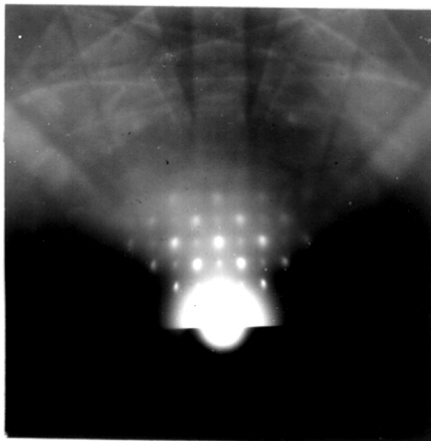


Fig. 24. Corroded in distilled water for 3 min. Kikuchi-lines of the copper substrate. Spot patterns of the formed cuprous oxide. Beam along $[100]$.

Corrosion of electropolished (110)-faces in distilled water.

and (111)- face was formed in a two-degree orientation.

Cu_2O (110) // Cu (110), Cu_2O [100]// Cu [100];

Cu_2O (111) // Cu (111), Cu_2O [101]// Cu [101] (Fig.23).

On the (100)-face the polycrystalline oxide shows various orientations, mainly (111) and (110) parallel to the (100)-face of the copper. The elongation of the diffraction spots show that the surface of the oxide film was virtually atomically smooth.

An electropolished (110)-face was exposed to the attack of distilled water for only 3 minutes, washed with acetone and transferred under propyl alcohol to the electron diffraction camera. The pattern obtained (Fig.24) shows clear "Kikuchi-lines" due to the metal surface and a strong spot pattern of the cuprous oxide formed. These patterns show clearly that the attack starts only on preferred points on the surface and not on the whole surface.

b. Corrosion in 0.5 n and 1 n Solutions of Sodium Hydroxide.

In solutions of sodium hydroxide (0.5 n and 1 n) the attack is analogous to that in distilled water, but is very rapid. The first interference colours appeared during the first hour of the exposure and after 24 hours the oxide film had become very thick and showed the typical colour of cuprous oxide. The structure and orientation relative to the

substrate are analogous to those found in the experiments on oxidation in distilled water (Figs. 25 and 26).

After the second day of corrosion in the 1 μ sodium hydroxide solution a thin black film of cupric oxide was formed ^{on the (100)-face}. The solution turned blue but remained clear. On the (110)- and the (111)- face the cupric oxide film was formed after the third day.

The formation of the cupric oxide was independent of the thickness of the film. As the (100)-face was attacked more slowly than the (110)- and (111)- face, it is shown that the nature of the cuprous oxide film is responsible for the beginning of the second reaction.

c. Corrosion in dilute Solutions of Sodium Chloride.

In 0.01 \bar{N} and 0.1 \bar{N} solutions of sodium chloride a polycrystalline film of cuprous oxide was the initial corrosion product. The properties concerning the structure orientation and rate of attack are similar to those obtained in the experiments carried out in distilled water or in a solution of sodium hydroxide.

The attack in the 0.1 normal solution was faster than the attack in the 0.01 \bar{N} solution.

Before a secondary reaction such as the formation of a basic or normal salt occurred, the cuprous oxide film had

F 4501

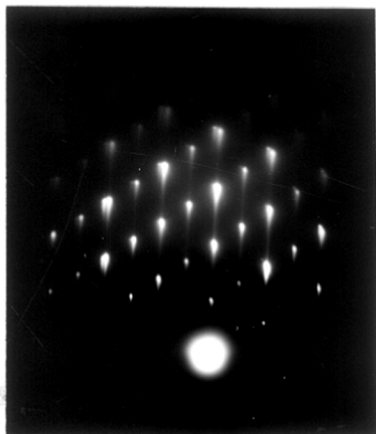


Fig. 25. (111)-face
corroded 3 days in 1n NaOH.
Crystalline cuprous oxide;
two degree orientation.
Azimuth $[101]$.

F 4972

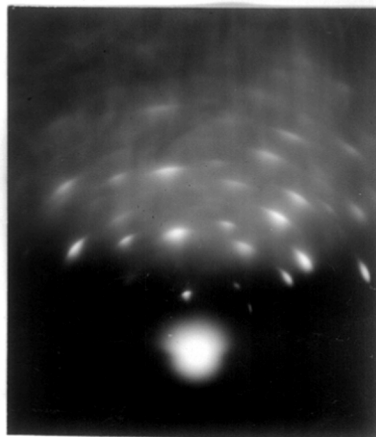


Fig. 26. (100)-face
corroded 1 day in 1n NaOH.
Crystalline cuprous oxide;
various orientation.

F 4498

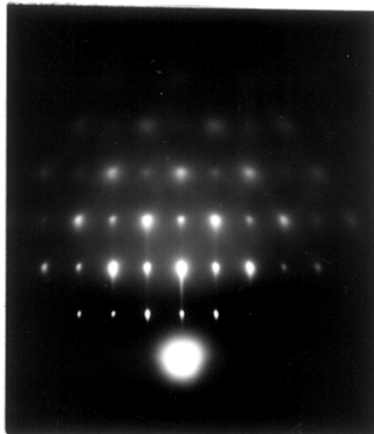


Fig. 27. (110)-face
corroded 1 day in 0,01n NaCl.
Crystalline cuprous oxide;
two degree orientation.
Azimuth $[1\bar{1}0]$.

Corrosion of electropolished copper single crystal faces
in aqueous solutions.

grown several thousand Angstroms thick.

The secondary reactions were not investigated in the present work. The conditions are completely different from those of the primary reaction.

d. Corrosion in 0.001 m Solution of Potassium Bichromate.

In a very short time a thin cuprous oxide film had formed. On reaching the thickness of approximately 400 Å. the film ceased to grow further. The initial film was amorphous and was very protective against further attack in distilled water or solutions of sodium chloride.

e. Corrosion in Hydrogen Peroxide (20 Vol %).

The exposed faces were soon covered with a black, spongy film showing no protection against a further attack. No coherent diffraction pattern could be obtained. The product was presumably cupric oxide and was amorphous.

PART III.GENERAL DISCUSSION.I. On the Mechanism of the Dry Oxidation of Copper.

The oxidation of copper has been investigated by many workers who have approached the problem from many different directions. Nevertheless the fundamental problem of the mechanism of the oxidation of copper still remains to be elucidated.

Before the fundamental problem is treated in greater detail it is desirable to give a short summary of the results obtained so far. We can confine ourselves to the following aspects:

1. Structure and orientation of the initial film.
2. rate of oxidation.

All investigators are agreed that cuprous oxide is invariably formed as the first corrosion product and that the rate of oxidation depends on a number of factors such as, for example, the state of the reacting surface and the temperature.

1. Structure and Orientation of the Initial Film.

Several workers [31, 35, 48, 53, 58, 80] have investigated the structure of the initial oxide film and its orientation with respect to the substrate, but the experiments

were not so detailed as those reported in the present work.

If the results reported by other workers are summarised and compared with those obtained by the writer, a clear picture about the conditions during the oxidation of copper in the temperature range between 0°C. and 250°C. can be formed.

If cuprous oxide appears in the crystalline form it exhibits its normal structure and, so far, no pseudomorphic oxide has been observed.

It is, however, significant that the crystallographic orientation of the metal surface as well as its state are of considerable importance.

A. Experimental Results on Single Crystal Faces.

a. Electrolytically Polished Surfaces.

On electropolished single crystal faces an amorphous oxide film is formed between room temperature and a temperature characteristic of the crystal face. Above this characteristic temperature the film is no longer amorphous, but is composed of very small crystals. This transition temperature for the different crystal faces was found to be as follows:

(110) - face	about 135°C.
(111) - face	about 140°C.
(100) - face	about 145°C.

If the temperature of oxidation is raised by a few degrees above the transition temperature, an orientated film begins to be formed.

At 150°C. and above, the oxide film shows two-degree orientation (Cu_2O (110) [100] // (110) [100] of Cu; Cu_2O (111) [101] // (111) [101] of Cu) when growing on the (110)- and (111)- faces, whereas various orientations (some of which are epitaxial) occur in the case of the (100)-face; in most cases the (111)- and (110)- planes of the oxide are parallel to the (100)-plane of the copper.

No reliable results by other authors exist for the oxidation of copper below 150° C., but above 150°C. the experiments carried out by the author are largely in agreement with previous work. Thomson [35], Moore [58], Yamaguti [53] and Gwathmey [80] found that the oxide grows in two-degree ((110) [100] of Cu_2O // (110) [100] of Cu) orientation on the (110)-face. Two degree ((111) [101] of Cu_2O // (111) [101] of Cu) orientation was also observed on the (111)-plane by Gwathmey [80].

The situation is different on the (100)-plane. Both Yamaguti and Moore were unable to observe any cases in which the (100)-plane of the cuprous oxide was parallel to the (100)-plane of the copper, but a number of other orientations (mainly (111) of Cu_2O // (100) of Cu) occurred. The

phenomenon observed by these workers was confirmed by the investigations of Gwathmey [80] and the author. In the only well developed orientation which has so far been definitely identified the (111) plane of the cuprous oxide is almost parallel to the (001)-plane of the copper substrate, with the cube face diagonal of the cuprous oxide parallel to the cube edge of copper.

b. Etched Copper Single Crystal Faces.

A predominantly amorphous oxide film is formed at room temperature on etched copper single crystal faces, but part of the film is crystalline and orientated. At 100°C. a film consisting of small crystals showing a not very pronounced one degree ((110) of Cu_2O // (110) of Cu; (111) of Cu_2O // (111) of Cu) orientation is formed.

At about 150°C. and above, an oxide film grown on a (110)- or a (111)- plane shows two degree ((110) [100] of Cu_2O // (110) [100] of Cu; (111) [101] of Cu_2O // (111) [101] of Cu) orientation, whereas various orientations occur in films grown on the (100)-plane.

The results obtained at temperatures above 150°C. are in agreement with those of Thomson [35] and Yamaguti [53].

B. Mechanically Polished Single Crystal Faces.

Mechanical polishing causes deformation of the single crystal surface and the experiments can no longer be regarded as affording information about single crystals but must be treated as experiments carried out on polycrystalline material.

B. Experimental Results on Polycrystalline Copper.

a. Electrolytically polished or etched surfaces.

Moore [58] found that the cuprous oxide film formed on electropolished polycrystalline copper at higher temperatures grows with its (110)-plane parallel to the metal substrate. The metal surface before oxidation showed (110) orientation. These results are in agreement with those obtained by Thomson [35]. The present experiments show that an amorphous oxide film grows on mechanically polished surfaces (exhibiting an amorphous Beilby-layer) both at room temperature and at 100°C., whereas a crystalline film of cuprous oxide in random orientation is formed at 150°C. and above.

2. The Rate of Oxidation.

According to Evans [69], three laws have been experimentally established expressing the increase of oxide film thickness "y" with time "t" in different cases:

1. $y = k_1 t + k_2$ (The Rectilinear Equation).
2. $y = k_3 \log (k_4 t + k_5)$ (The Logarithmic Equation).
3. $y^2 = k_6 t + k_7$ (The Parabolic Equation).

Broadly speaking two of these laws have been shown to be important for the growth of oxide films on copper.

According to Dunn [60] and Vernon [61] an oxide film below 150°C. grows according to the logarithmic law but above this temperature the parabolic law is obeyed.

It has been possible on several occasions to verify the validity of these laws experimentally but deviations frequently occurred, particularly at the beginning of the oxidation (Weitknecht [37]). Furthermore Dighton and Miley [62] were able to show that in the temperature range of 180°C. to 288°C. the oxide film first grows according to the parabolic law but later, i.e. after reaching a certain thickness, the logarithmic law is followed.

During the oxidation of polycrystalline copper, it can be said that at low temperatures the oxide film grows according to the logarithmic law. At intermediate temperatures (above 150°C.) the film grows first in accordance with the parabolic law and after reaching a certain thickness according to the logarithmic law, whereas at high temperatures (above 500°C.) the parabolic law is approximately obeyed throughout.

Precise investigations are not available for copper single crystal surfaces but it is to be expected that they will behave in a broadly similar way. The rate of oxidation, however, depends on the crystallographic orientation.

During the oxidation of copper single crystal faces Tammann [³⁰Et] had already found that the (110)- and the (111)-faces oxidise considerably more rapidly at a temperature of 260°C. than e.g. the (100)-face.

According to Bénard and Talbot [20] at a temperature of 850°C. the rate of oxidation of copper single crystal faces decreases in the following order

- (210) - (221)
- (211) - (110)
- (111)
- (100)
- (123)

These authors considered that the preparation of the surfaces also has a considerable effect on the rate of oxidation. Etched copper surfaces oxidise much faster than electropolished or mechanically polished surfaces.

The present experiments show that at low temperature (below 150°C.) there is no important difference in the rate of oxidation, but that above 150°C. the (110)- and the (111)-planes are oxidised much faster than the (100)-plane.

It appeared here also that the state of the surface has an important effect. The rate of oxidation decreased in the following order for differently prepared surfaces:

Etched surfaces
electropolished surfaces
mechanically polished surfaces.

It was also found that at 200°C. the attack became noticeably slower as soon as a thickness of about 800 Å. had been reached.

II. On the Growth of the Initial Oxide Film.

If the copper surface is exposed to oxygen a monomolecular film of oxygen is adsorbed. These adsorbed molecules are dissociated into atoms (chemisorption) almost immediately after the adsorption has taken place, provided that the temperature is not too low. These atoms gradually penetrate the metal and this penetration occurs above all at faults. The copper reacts with this oxygen and cuprous oxide is formed; according to the energy conditions this becomes amorphous or crystalline.

The attack probably begins at the faults and extends from there over the entire metal surface.

On an atomically smooth surface, and the electropolished surface may be considered as such, the mobility of the metal

atoms is too small to permit the cuprous oxide to form its normal crystal lattice and consequently the film is amorphous.

The mobility of surface atoms was first demonstrated by Volmer and Estermann [81] and later confirmed by Volmer [82], Muller [83] and Benjamin and Jenkins [84] who investigated their nature more closely. It was found that the mobility of the surface atoms depends on the temperature, the crystallographic orientation and the preparation of the surface.

If the temperature of oxidation is raised the mobility of the surface atoms increases accordingly. Once the transition temperature and hence suitable surface mobility is reached (e.g. for the (110)-face about 135°C.) the surface energy is sufficient to permit the cuprous oxide to form its normal small crystals.

If the temperature is raised further, i.e. if there is a further increase in the surface energy, the crystalline oxide may even grow epitaxially provided that there exists a suitable relation to the structure of the substrate metal.

The formation of the initial oxide film therefore occurred in all cases in practically the same manner, but its crystalline state (amorphous, crystalline either unorientated or orientated) depends on the mobility of the surface atoms, and is therefore determined by the temperature, the orientation and the state of the surface.

The oxidation of the copper surface occurs immediately after exposure to an oxygen atmosphere. Above all, the oxidation begins preferentially in certain regions (probably faults in the lattice) and spreads from these regions over the whole surface. The formation of the initial oxide film up to a thickness of about 30 Å. appears to occur in this manner.

This mechanism also explains the deviation from the laws of oxidation. At the start, i.e. until the entire metal surface is covered by an oxide film, the oxidation obeys an almost linear law and not the logarithmic or parabolic law.

III. The Growth of Thicker Cuprous Oxide Films.

When considering the growth of thicker oxide films it is necessary to distinguish clearly between the growth of an amorphous or a crystalline film.

a. Growth of the Amorphous Oxide Film.

The initial amorphous oxide film shows irregularities such as variations in thickness, pores or tears produced by mechanical forces. Fresh copper may be exposed along the tears and pores and may be changed into the amorphous oxide. As the thickness increases the faults are covered, it becomes increasingly difficult to expose fresh metal, and the growth of the film practically ceases.

Apart from oxidation along the tears or pores, the

attack can presumably occur in the manner suggested by Mott [67]: A strong field is set up in the oxide film, due to a contact potential difference between metal and adsorbed oxygen, which makes it possible for copper ions to move through the film without much help from temperature agitation.

b. Growth of a Crystalline Film.

If the initial oxide film is crystalline, i.e. if the surface energy is sufficiently high to permit the cuprous oxide to form its own crystal lattice, the conditions for further growth differ entirely from those for amorphous films.

The oxide film which consists of a large number of very small crystals allows oxygen to have access to the copper along the grain boundaries of the oxide. Apart from this access of oxygen along the boundaries of the oxide, two other mechanisms could come into play:

1. The assumption used by Mott [67] that copper ions migrate to the oxide surface and react there with the oxygen, or, (2) that oxygen migrates through the oxide crystals in the form of atoms or ions.

If a perfect cuprous oxide single crystal were to grow on a copper single crystal face, the mechanism of oxidation would have to occur in one of the above mentioned ways. Since however a large number of very small oxide crystals are formed

on copper single crystal surfaces a close mesh of crystal boundaries is present. These crystal boundaries result in a thermodynamically disturbed surface. The adsorption of oxygen is greatly facilitated for thermodynamical reasons, and therefore the oxygen can migrate along the crystal boundaries to the underlying metal. In other words the mechanism of oxidation during the growth of a crystalline film may be regarded as "micro intercrystalline corrosion".

This assumption has been proved to be correct by the present experiments on deformed single crystal surfaces (see p.31). Copper ions may migrate within the cuprous oxide crystals but this process is presumably of minor importance. A migration of oxygen through the oxide crystal is out of the question in the temperature range examined since this is impossible for spatial reasons.

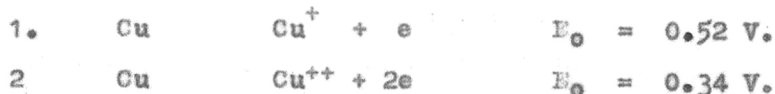
IV. On the Wet Oxidation of Copper.

1. On the Electrochemistry of Copper.

The wet oxidation of copper is an electrochemical process. The copper goes into solution as Cu^+ and Cu^{++} ions at the anodic points. Oxygen is depolarised at the cathodic points and the oxide formed is precipitated at a third point.

This oxide is precipitated at definite points and from these nuclei the oxide crystals grow until the entire surface is covered.

Since copper can go into solution at the anodic points as cuprous- or cupric-ions, the following reactions may therefore occur, at these anodic points:



from this follows



The following equilibrium relation is valid for equation (3)

$$\frac{[\text{Cu}^+]^2}{[\text{Cu}^{++}]} = K = 1.8 \cdot 10^{-6}$$

It is possible to deduce from this equilibrium relation that under normal conditions of corrosion (aerated distilled water, dilute solutions of sodium chloride, etc.) in the presence of or in contact with copper the cupric ion concentration is too small to exceed the solubility product of cupric oxide. For this reason either cuprous oxide or at higher concentrations of anions like Cl^- , Br^- , etc. the normal cuprous salts are formed.

2. The Structure and Orientation of the Initial Film.

The energy relations are such that the polycrystalline oxide generally occurs. This oxide shows how two degree

orientation on the (110)- and (111)-faces, whereas various orientations can occur on the (100)-face. Films as thick as several thousand Angstroms still show these pronounced orientations.

The influence of the orientation of the initial film and hence also of the substrate is analogous to that during dry oxidation. Amorphous films give good protection against further attack (corrosion in 0.001 M $K_2Cr_2O_7$) while crystalline films with good orientation afford practically no protection (oxide grown epitaxially on the (110)- and (111)-faces).

V. The Influence of Distribution, Structure and Orientation of the Initial Film on the Further Attack of Copper.

1. Correlation of oxide structure with its general rate of growth.

It appeared, both during the dry and the wet oxidation of copper, that the initial film has a very considerable influence on the further course of the attack.

If a closely packed film is formed as the first corrosion product any further attack is largely inhibited or at least greatly reduced, but a loosely packed material is only able to give little protection.

Even a closely packed film behaves differently according to its structure and orientation with respect to the

substrate.

a. Amorphous film: An amorphous oxide film affords some protection, although some further attack can take place along tears or pores. If these faults are healed, the growth of the film can be presumed to be almost arrested.

b. Unorientated film consisting of small crystals: An oxide film consisting of close packed small crystals in random orientation gives considerable protection against further attack. Since an attack can only occur along the crystal boundaries both during dry and wet corrosion the further attack is made very difficult in the case of random films. The crystals are mixed up and the access of oxygen to the substrate metal is therefore obstructed.

c. Epitaxial films consisting of small crystals: An oxide film showing two degree orientation gives little protection. Small "channels" are formed between the well orientated crystallites and consequently oxygen can easily gain access to the surface.

2. Correlation of oxide structure with the detailed growth rate observations.

The structure of the film can be used to explain the laws governing the growth of the oxide film. If the oxide film is amorphous or consists of small random crystals the logarithmic law is broadly applicable. These films give some

protection after they have reached a certain thickness.

Epitaxial films often give little protection, i.e. oxygen can easily reach the underlying copper and react there. Their growth should then evidently be governed by the parabolic law as, indeed, has been found to be the case.

It has been shown above that an amorphous or crystalline but random film is formed when the logarithmic law applies (below 150°C.) but that an orientated film is formed when the parabolic law applies (above 150°C.).

The effect of orientation becomes important during the oxidation of copper at about 200°C. If the surface film shows pronounced two degree orientation it gives little protection. As soon as the film loses its two degree orientation in the course of the oxidation the rate of oxidation becomes noticeably smaller, i.e. in this case the films afford protection.

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