Recombination of Hydrogen, Nitrogen and Oxygen Atoms on Copper and Silver Single Crystal Surfaces

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Hoping to get information about the bond strength of the chemisorption of hydrogen, the author et al.(1) carried out the recombination of hydrogen atoms on various metal surfaces including single crystal surfaces of copper. In the present work, experiments have been extended to cases of nitrogen and oxygen atoms on single crystal surfaces of copper and silver, considering the fact that comparatively simple electronic band structures of copper and silver will render the theoretical treatment of results possible in future. With regard to oxygen atoms, experiments were conducted only on single crystal surfaces of silver, because the probable formation of relatively thick oxide layers on copper surfaces might complicate the subject for consideration.

Since relatively much information about physical and physico-chemical properties of single crystal surfaces of metals with definite crystal indices are available, execution of any surface reaction on these surfaces seems to be advantageous in considering the mechanism of surface reaction through the comparison of catalytic activity with physical properties. With regard to the research along this line, the works of Gwathmey et al.(2), Sosnovsky(3) and Crocker et al.(4) are noteworthy.

However, few works have yet been undertaken except for the work of Gwathmey et al. in which detailed structures of surfaces during the course of and after the completion of the reaction are fully followed. In the work of Sosnovsky, where the decomposition of formic acid on single crystal surfaces of silver was dealt with, the natural free

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1) K. Nakada, T. Sugiura and S. Shida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 64 (1955); S. Sato, K. Nakada and S. Shida, ibid., **76**, 1308 (1955); K. Nakada, S. Sato and S. Shida, *Proceedings of the Japan Academy*, **31**, 449 (1955); K. Nakada, This Bulletin, **32**, 809 (1959).

2) R. E. Canningham and A. T. Gwathmey, *J. Am. Chem. Soc.*, **76**, 391 (1954).

3) H. M. C. Sosnovsky, *J. Chem. Phys.*, **23**, 1486 (1955).

4) A. J. Crocker and A. T. B. Robertson, *Trans. Faraday Soc.*, **54**, 931 (1958).

surface frozen from the melt was used as a reaction surface. The work of Crocker et al. in which the decomposition of formic acid on single crystal surfaces of copper was dealt with and that of Nakada et al. in which the recombination of hydrogen atoms on the same was dealt with were only concerned with the electropolished surfaces. Although the flatness of these surfaces on the atomic scale was ensured by Rhodin5) through the adsorption experiment by the use of microbalance technique, there seems still to be doubtful whether or not the electro-polishment would really give such an extreme flatness.

Accordingly, it is highly desirable to know detailed structures of surfaces on which the experiments were made. In the present work, the author devotes himself to the detection of the effect of various kinds of surface pre-treatments on catalytic activity. It seems probable that surfaces subject to such a treatment as chemical etching, which possibly roughen them, will comply with the purpose of this work better than the flattened surfaces, because for such a roughened electron diffraction technique may give the most detailed information on its surface structure. Conversely, it may be expected that from the change in activity resulting from various surface treatments, unknown surface structures lying beyond the limit of the power of the present scientific method, like electron microscopy or electron diffraction technique, would be made clear.

Experimental

An effusion method used in the preceding report* for determining the recombination activity of different transition metals was also adopted this time.

Apparatus. — The apparatus (not shown) described in the above was used without modification, but the sample metal slice was hung only with a Pt/Pt-Rh thermocouple (0.1 mm. in diameter) without any other lead.

Sample Gases.—The hydrogen, oxygen and nitrogen used were all commercial cylinder gases. Hydrogen or oxygen was allowed to bubble through a saturated sodium hydroxide solution and further to diffuse over the platinized asbestos (ca. 400°C) to remove oxygen and hydrogen included in hydrogen and oxygen as an impurity, respectively, but for nitrogen this procedure was not done. They were sent to the discharge tube through a capillary from a reservoir in which the gases were allowed to stay over the saturated sodium hydroxide solution to keep the humidity constant.

Sample Metal Slices.—Single crystals of copper and silver were produced by means of a slow cooling method from electrolytic copper and standard silver for analysis respectively. The single crystals thus obtained were of a cylindrical form (12 mm. in diameter and about 6 cm. long). Single crystal slices (generally in an elliptical form, about 2 to 3 mm. thick) were cut from a cylindrical single crystal in order that their macroscopic-cut planes might coincide with the three principal planes (100), (110) and (111), but in the case of silver only the (110) and (100) slices were prepared.

Pre-treatment of Surfaces.—Two surfaces of a sample slice were generally subjected to two different kinds of pre-treatments, e. g., one pre-treatment was electro-polishment and another, chemical etching with nitric acid or the like. The main conditions of pre-treatment adopted in this work were as follows:

1) Chemical etching was carried out a) in the nitric acid solution (1 : 1 by volume) for 3 min. and b) in the saturated ammonium persulfate solution for 15 min.

2) Electro-polishment of copper was done in the bath of phosphoric acid (90%) at the current densities of 6 to 8 amp./dm^2 for 10 min. and that of silver in the mixed solution of potassium cyanide (10%) and potassium ferrocyanide (10%) at the current densities of 1 to 3 amp./dm^2 for 3 min.

3) For the electric plating, solutions of potassium cuprous cyanide, potassium silver cyanide and ammonium aurocyanide were used as baths of copper-, silver- and gold-plating, respectively.

Procedure.—All free atoms were produced in a discharge tube by use of alternating currents. A sputtering of the electrode material (aluminum) occurred more markedly in the case of nitrogen than in oxygen. Since such a sputtering was localized within the neighborhood of electrodes even in the case of nitrogen, they did not become a serious obstacle to the present experiments.

In the reaction chamber, which was strongly pumped off, the sample metal slice was hung only by a Pt/Pt-Rh thermocouple (0.1 mm.) serving as the temperature measurements at the front of a small hole provided at the end of a side tube of the discharge tube. The temperature of a sample can be followed by measuring the electro-motive force by use of a K-type potentiometer. The electro-motive force was read at intervals of 5 min. The slice was allowed to turn over every twenty or thirty minutes. Before and after this procedure, the temperature was usually shifted from one value to another. From such a shift of the temperature the difference in activities of two surfaces of the same sample subjected to different treatments could readily be detected.

Results

In Fig. 1 is given a plot of temperature, expressed in terms of electro-motive force

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5) T. N. Rhodin, *J. Am. Chem. Soc.*, **72**, 5691 (1954).

* This Bulletin, loc. cit. in Ref. 1.

TABLE I. INEQUALITY RELATIONS OF CATALYTIC ACTIVITY

No.	Species of slice	Method of pre-treatment: One side	Method of pre-treatment: The other side	Inequality relation	Kinds of atoms
1	Cu(100)	El. pol. :H_3PO_4	Mech. pol. 06 emery paper	Mech. pol.>El. pol.	N
2	Cu(100)	ditto	Chem. etch. : HNO_3	El. pol.>Chem. etch.	N
3	Cu(100)	Chem. etch.:HNO_3	Chem. etch. : $(NH_4)_2S_2O_8$	$HNO_3 < (NH_4)_2S_2O_8$	N, H
4	Cu(110)	El. pol. : H_3PO_4	Mech. pol. 06 emery paper	Mech. pol.>El. pol.	N
5	Cu(110)	ditto	Chem. etch. : HNO_3	El. pol.>Chem. etch.	N
6	Cu(110)	Chem. etch.:HNO_3	Chem. etch. : $(NH_4)_2S_2O_8$	$HNO_3 > (NH_4)_2S_2O_8$	N, H
7	Cu(110)/ poly.	Chem. etch. : HNO_3, single	Chem. etch. : HNO_3, poly.	poly.>single	N
8	Cu(110)/ poly.	Chem. etch. : $(NH_4)_2S_2O_8$, single	Chem. etch. : $(NH_4)_2S_2O_8$, poly.	poly.>single	N
9	Cu(111)	El. pol. : H_3PO_4	Chem. etch. : HNO_3	El. pol.>Chem. etch.	N, H
10	Cu(111)	Chem. etch., HNO_3	Chem. etch. : $(NH_4)_2S_2O_8$	$HNO_3 < (NH_4)_2S_2O_8$	H
11	Cu(111)	El. pol. : $CuSO_4$	El. pol. : H_3PO_4	$CuSO_4 \simeq H_3PO_4$	H
12	Ag(100)	El. pol. : $KCN+K_4FeCN_6$	Chem. etch. : HNO_3	El. pol.>Chem. etch.	H
13	Ag(100)	ditto	Chem. etch. : $(NH_4)_2S_2O_8$	El. pol.≃Chem. etch.	H
14	Ag(100)	ditto	Cu, Ag and Au-plating	(100)>Cu, Ag and Au	H, N
15	Ag(110)	ditto	ditto	(110)>Cu, Ag and Au	H, N
16	Ag(110)	Chem. etch.:HNO_3	Cu-plating	(110)>Cu	H, N
17	Ag(100)	El. pol. : $KCN+K_4FeCN_6$	Cu, Au-plating	Cu, Au>(100)	O
18	Ag(110)	ditto	ditto	(110)>Cu, Au	O

In this table the following abbreviations were adopted. For example, chemical etching in a nitric acid solution was abbreviated as Chem. etch. :HNO_3, electrolytic polishing as El. pol. :H_3PO_4 and electrical plating of silver as Ag-plating.

(μV), against the time (min.) for the case of Ag(110) slice, one side of which is the one electrically plated with silver, while the other side is electrolytically polished. Arrows in Fig. 1 show times when the sample slice was let turn over. From this plot the electrolytically polished Ag(110) surface is found to be more active than the electrically plated silver surface.

Inequality relations thus determined are shown en bloc in Table I. The first column shows species of macroscopic-cut planes of sample slices. In the second and the third columns are shown methods of pre-treatments applied to each side of the surfaces. In the fourth column are given the inequality relations about recombination activities of two surfaces. The last column shows kinds of atoms used.

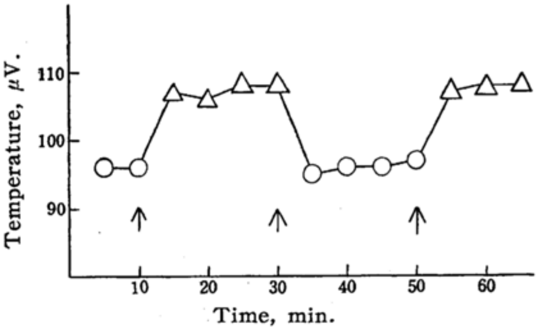

Fig. 1. The shift of the sample slice temperatures on the alternative exposure of two side planes to the reacting gas. This is an example about silver slice corresponding to Table I, No. 15.
○: Silver plating
△: Electrolytic polishing

Some Remarks on the Surface Structures

Since the main purpose of the present work is to make clear the effect of different surface structures on catalytic activity, several bits of information available to date concerning the surface structures of single crystals of some metals will be reviewed below in a little detail.

Among the works along this line the work of Yamaguchi[6] on single crystals of nickel is noteworthy. He made clear their detailed structures when they were etched by a mixed solution of ethyl alcohol and liquid bromine (1 : 1 by volume) by the cooperative uses of electron microscope and electron diffraction technique. In a similar way, structures of the single crystal of copper etched with ammonium

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6) S. Yamaguchi, *J. Appl. Phys.*, **22**, 983 (1951).

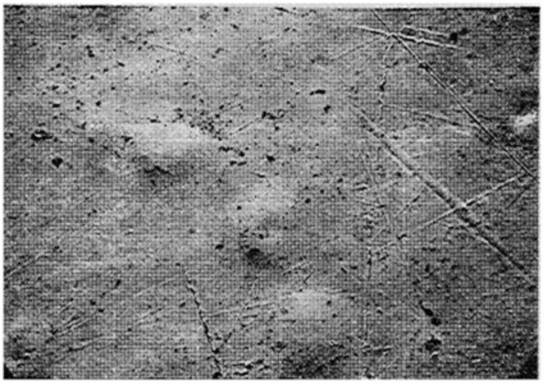
persulfate was made clear by Ueda et al.7) According to their result, the surface of a single crystal of copper etched by the saturated solution of ammonium persulfate exposes composite small facets, but all the faces of such facets have (110) family index irrespective of their directions.

Chalmers et al.8) examined the surface thermally etched in the presence of oxygen or nitrogen. According to their results, the surface heated to 500°C in oxygen was found to show a zonal orientation which should be ascribed to the exposition of (111) face, while surfaces heated in nitrogen show a flat surface having all desired orientations. Pashley9) examined the single crystal surfaces of silver parallel to the (100), (111), (110) and (311) plane when they were subjected to the electrolytic etching, electrolytic polishing and chemical etching by nitric acid (35%). In this work the electrolytic polishing was found to give very smooth surfaces, while the electrolytic etching or the chemical etching to give well-developed facets which were always of the (100), (110), (210) and (310) types and did not include (111) facets.

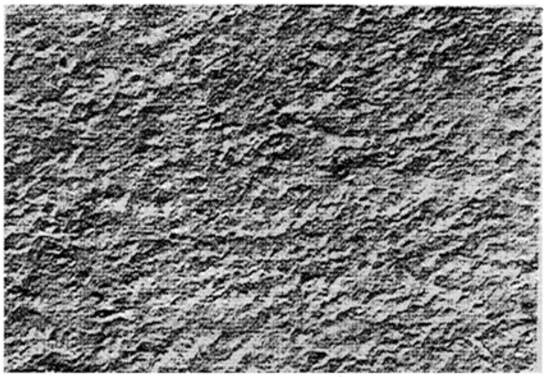
Less detailed and less reliable information can be drawn from the optical back reflection image obtained when a very intense light beam is spotted on the single crystal surfaces etched by chemical agents. This optical back reflection method was used in determining the crystal axes of single crystals in this work. Several pieces of information obtained by the use of this method can be found in old works of physicists who were engaged in the study of the anisotropy of work functions of metal single crystals. Farnsworth10) found that the electrolytic etching of a single crystal of copper at low current densities developed a (111) face and the same treatment at high current densities a (100) face. In the work of Rose11) the electrolytic etching of the (111) surface in a copper sulfate solution was stated to expose a (111) face and the chemical etching of the (100) surface in a nitric acid solution (65%) to produce a smooth (100) surface with very few undesired faces.

Discussion

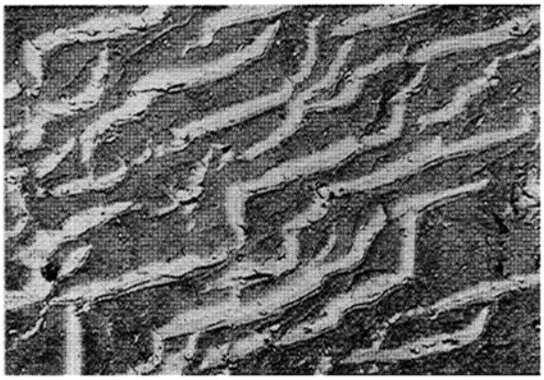
In Fig. 2 is given only a part of the electron micrographs of single crystal surfaces of copper and silver with different crystal indices. From Figs. 2b, c and d, it was clearly recognized that slices with different crystal indices were subjected to corrosion in a considerably different



a) The copper(110) surface electrolytically polished in a phosphoric acid solution (×2000).



b) The copper(100) surface chemically etched in a nitric acid solution (×3500).



c) The copper(110) surface chemically etched in a nitric acid solution (×3500).

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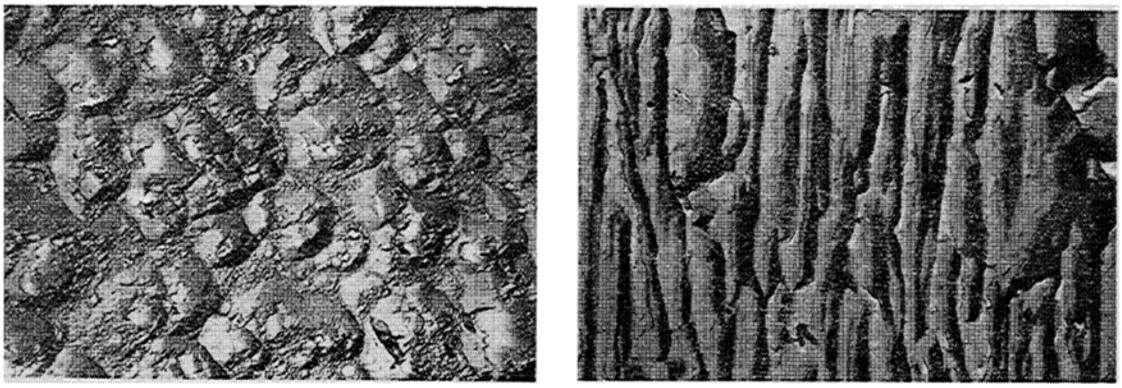
7) R. Ueda et al., presented at the Meeting of the Physical Society of Japan, Osaka, November 2, 1953 (unpublished).

8) B. Chalmers, R. King and R. Shuttleworth, *Proc. Roy. Soc.*, **A192**, 465 (1948).

9) D. W. Pashley, *Proc. Phys. Soc.*, **A64**, 1113 (1951).

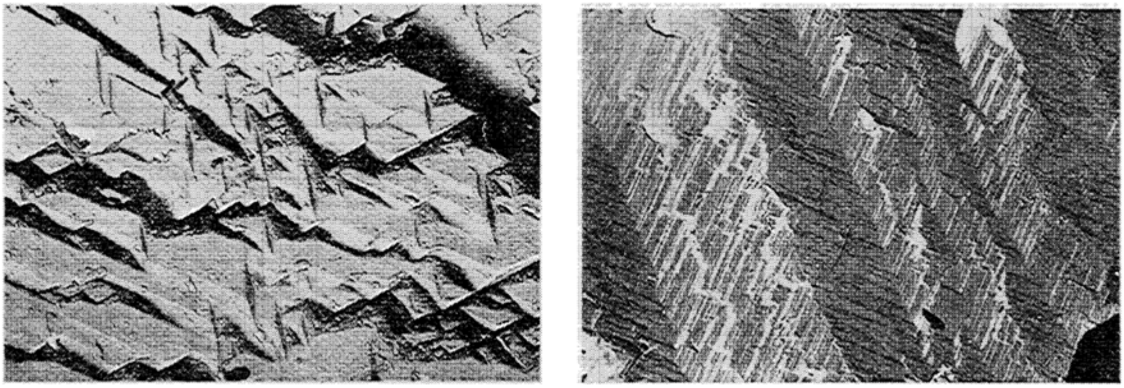
10) H. E. Farnsworth, *Phys. Revs.*, **40**, 684 (1932).

11) B. A. Rose, ibid., **44**, 585 (1933).



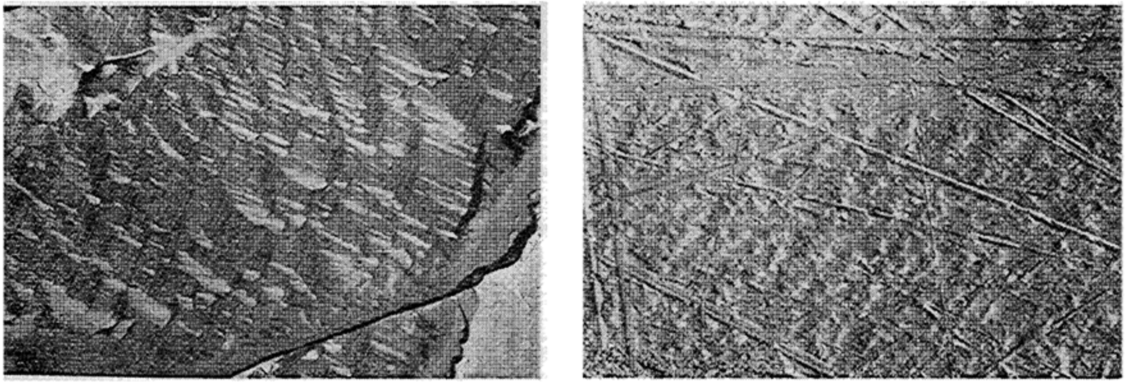
d) The copper(111) surface chemically etched in a nitric acid solution (×3500).

g) The silver(100) surface chemically etched in a nitric acid solution (×3500).



e) The silver(100) surface electrolytically polished in a mixing solution of potassium cyanide and potassium ferrocyanide (×3500).

h) The silver(110) surface chemically etched in a nitric acid solution (×3500).



f) The silver(110) surface electrolytically polished in the same bath as in e) (×3500).

i) The electro-polished silver(110) surface aged under contact with oxygen atoms(×3500).

Fig. 2. Electron micrographs of copper and silver single crystal surfaces subjected to various kinds of pre-treatment.

manner on the attack of the same etching agent. As known from Figs. 2e and f, it seems rather reasonable that the electrolytical polishing of silver surfaces in the bath used in the present work is considered as the electrolytical etching in an electron-microscopic scale. In spite of the significance of determining crystallographic planes of the small facets exposed to the reacting gas, further approach to the true surface structures could not be attained without getting an opportunity to use the electron diffraction method.

No results were obtained in which inequality relations of relative activities for hydrogen atoms and nitrogen atoms disagreed with each other. This suggests that the recombination of hydrogen atoms and nitrogen atoms may proceed probably through the similar mechanism.

In the case of both Cu(100) and Cu(110) slices, the mechanically polished surfaces were more active than electrolytically polished surfaces (Table I, No. 1 and 4). It is supposed that this difference in activity might have originated in strains of Beilby layers formed on the surface. Experiments of No. 7 and 8 were made about the special sample of the Cu(110) slice, the back side of which was changed to a polycrystal state by rapid cooling of only one side after re-heating, while another side remained to be the original single crystal state. From the comparison of activities of these two surfaces for the recombination of nitrogen atoms, both of which are subjected to the attack of the same reagent (nitric acid or ammonium persulfate), were obtained results showing that the polycrystal surface was always more active than the single crystal surface. It seems, however, to be premature to accept the existence of the effect of the crystal boundaries on the catalytic activity.

Bearing in mind the statement of Rose, an experiment of No. 11 was done to know whether the Cu(111) surface electrolytically polished in a copper sulfate solution may be more flat (accordingly less active) than the electrolytically polished surface in phosphoric acid, but any difference in these two treatments could not be detected.

In the previous work of the present author et al. about the recombination of hydrogen atoms on single crystal surfaces of copper which was electrolytically polished, it was made clear that the (110) face is the most active, the (100) face less active than this, and the (111) face the least active. In view of Ueda's work cited above, in which single crystal surfaces of copper etched by ammonium persulfate were shown to be composed of only the (110) family facets, it may be expected that surfaces etched by ammonium persulfate will be more active than those etched by nitric acid which was known to develop the (100) face. Present results show that with the Cu(100) slice this is certainly the case (No. 3), whereas with the Cu(110) slice the reverse order of activity has been obtained (No. 6). These results show that copper surfaces subjected to the chemical etching by nitric acid or ammonium persulfate seem to have more complex structures than expected from the information given above.

Throughout every three slices (100), (110) and (111), electrolytically polished surfaces were found always to be more active than chemically etched surfaces (No. 2, 5 and 9). This suggests that there may exist some other faces with relatively high activity than these principal faces. It is instructive that chemically etched surfaces having a rather complex microtopography are less active than flat surfaces electrolytically polished. This implies that the recombination does not proceed on the corners or edges of small crystal facets, but rather mainly on plane faces. This has probably originated in such a special circumstance as that reactants are only composed of free atoms which need not be activated further.

Next, let us examine the results on single crystal surfaces of silver. As for the Ag(100) slice, surfaces chemically etched by nitric acid are also less active than those electrolytically polished in accord with the experiment of No. 2 (No. 12), whereas between surfaces chemically etched by ammonium persulfate and those electrolytically polished, no difference in activity was observed (No. 13). Combining the result of the experiment No. 12 with that of No. 13, the surface etched by ammonium persulfate is known to be more active than the one etched by nitric acid in accord with experiment No. 3 about copper. Consequently, it may be said that these chemical agents will have, to some extent, a similar corrosive action against both copper and silver.

For both the recombination of hydrogen atoms and that of nitrogen atoms, Ag(100) and Ag(110) surfaces electrolytically polished were together more active than the electrically plated surfaces of copper, silver and gold (No. 14 and 15). This shows firstly that activities of these three kinds of metals do not show any wide diversity and secondly that the character of surfaces plays a significant role when the activities of these metals were compared. From the combination of No. 14 and 15, no conclusion could be drawn as to which of the Ag(110) slice and the Ag(100) slice would be more active. With reference to the earlier results of the present author et al. about the recombination of hydrogen atoms on single crystal surfaces of copper, the author has been inclined to ascribe the higher activity to the (110) face.

For the recombination of oxygen atoms on single crystal surfaces of silver subjected to the electro-polishment, inequality relations

$$\mathrm{Ag(110)} > \text{Cu or Au plated surface} > \mathrm{Ag(100)}$$

were obtained (No. 17 and 18). The relation Ag(110) > Ag(100) is in good accordance with the case of the recombination of hydrogen atoms on single crystal surfaces of copper so far as the order is concerned. This accordance seems, however, to be fortuitous in view of the considerably larger nuclear distance of an oxygen molecule, 1.20 Å, than that of a hydrogen molecule, 0.75 Å, even though the larger lattice constant of silver, 4.08Å, compared to that of copper, 3.61 Å, would work favorably for this reaction.

With the recombination of oxygen atoms it was noticed that a kind of polishing action becomes appreciable in repeated runs. Comparing the micro-photograph of Fig. 2a with Fig. 2i, it is immediately perceived that such an aged surface under the contact with oxygen atoms resembles the electrolytically polished surface of copper in its micro-topographic appearance, except that the former possesses somewhat worse flatness than the latter. Experiments No. 17 and 18 are obtained with respect to such aged surfaces, while experiments No. 12 to No. 15 with respect to surfaces polished afresh.

Though it appears probable that this kind of polishing will come from any particular property of oxide layers, such changes of surface structures were not studied further, because this problem is not concerned with the main theme of the present work.

Summary

Recombination of hydrogen atoms, nitrogen atoms and oxygen atoms was carried out on single crystal surfaces of copper and silver subjected to various surface pre-treatments.

With both the recombination of hydrogen atoms and that of nitrogen atoms, copper surfaces electrolytically polished have always higher activity than those chemically polished. The Cu(100) surface chemically etched by ammonium persulfate was more active than that etched by nitric acid for both hydrogen atoms and nitrogen atoms, whereas with the Cu(110) the opposite order of activity was obtained. For both silver and copper, no evidence was found to show the different order of activity between the recombination of hydrogen atoms and that of nitrogen atoms. Concerning the recombination of oxygen atoms on single crystal surfaces of silver, the (110) face was found to be more active than the (100) face in accord with the result of our earlier work about the recombination of hydrogen atoms on single crystal surfaces of copper.

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