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The Effect of Deformation on Catalytic Activity of Platinum in the Decomposition of Hydrogen Peroxide

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The decomposition of hydrogen peroxide has been studied on annealed and cold-worked platinum foils. The reaction was confirmed to be first order. The reaction rate constant was found to increase with the degree of cold work, and a direct relationship between the catalytic activity of the platinum and its deformation was established. The increase in activity is apparently due directly to deformation since the possible effects of preferred orientation and increased surface area proved to be negligible.

I. INTRODUCTION

There have been many experimental investigations reported in the literature on the role of defect structure in the catalytic activity of metals. Some investigations indicate that defect structure plays an important role in heterogeneous catalysis; others seem to show that the effect is minimal.

The purpose of this investigation has been to establish the role of defect structure in platinum on the decomposition of hydrogen peroxide. In this study attention was given to detailed metallurgical characterization of the Pt catalyst.

A. *Mechanism of the Reaction*

Platinum has received the greatest attention among the noble-metal catalysts for hydrogen peroxide decomposition. In their study of this catalyst Bredig and von Berneck (*1*) found, as have most other investigators (*2*), that the reaction is first order with respect to hydrogen peroxide concentration, but second order kinetics have also been reported (*3*). Several mechanisms such as a cyclic oxidation–reduction involving platinum oxides, formation of atomic oxygen, reciprocal depolarization of atomic hydrogen, and hydroxyl radical and electron transfer have been suggested to account for the catalysis of hydrogen peroxide decomposition by platinum. Rockstroh (*4*) reviewed this subject and concluded that the active form of platinum is the metal itself, which provides a site for reaction rather than entering into an oxidation–reduction scheme.

Rockstroh also concluded that the reaction proceeds by donation of an electron from the metal to the hydrogen peroxide molecule, which causes the latter to split up and form an OH molecule and an OH radical as in the following equation:

$$H_2O_2 + Pt = Pt^+ + OH + OH^- \quad (1)$$

The generation of the OH molecule is considered vital to the initiation of the decomposition, which then proceeds as follows:

$$OH + H_2O_2 = H_2O + HO_2 \quad (2)$$

The molecularity of this reaction scheme is two, and the first order kinetics generally observed is taken to indicate that the rate-limiting step is the diffusion of H_2O_2 molecules to the platinum surface.

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B. Defects in Metals and Catalytic Activity

Many attempts have been made to establish the relationship between surface-emergent defects on solids and their catalytic activity. This is very natural since it is thought that the activity of a heterogeneous catalyst resides chiefly at the interface between the solid catalyst and the reacting species. This interface is currently thought to lower the potential barrier between the reactants and products by activating the reactants and by increasing the probability of formation of the transition state (or states). Hence a change in the properties of the surface should have an effect on its efficiency as a catalyst.

Eckell (*5*) made the first experimental measurements showing that rolled nickel sheet has higher catalytic activity in the hydrogenation of ethylene than annealed nickel sheet. However, no quantitative correlation between work-hardening and activity was attempted. Cratty and Granato (*6*) explained the work by Eckell in terms of solid state theory by showing that the increased activity of nickel was of the same order of magnitude as the increase in dislocation density produced by cold-working the nickel sheet. Reinäcker (*7*) observed similar effects in nickel for the decomposition of formic acid.

Since Cratty and Granato's paper, several experimental observations have been made on both metals and nonmetals, and the results are somewhat contradictory. Krause and Hermannowna (*8*) found that scratching platinum foil increased its activity as a catalyst in the decomposition of hydrogen peroxide, but they could not obtain the same effect with gold. Uhara *et al.* (*9*) showed that cold-worked copper was a better catalyst than annealed copper for the dehydrogenation of ethanol and the decomposition of benzene diazonium chloride. They interpreted their data as indicating a contribution to the catalytic activity from both vacancies and surface-emergent dislocations.

On the other hand, in a recent paper, Bagg *et al.* (*10*) studied the catalytic activity of thin silver films amenable to examination by transmission electron microscopy. Their paper indicates that the concentration of emergent defects in the film had no effect on its activity in the catalytic decomposition of formic acid vapor at 180° and 260°C.

Studies of this kind have been extended to nonmetals used as catalysts for certain reactions. For example, Hall and Rase (*11*) have recently shown a direct correlation between dislocation density in LiF (as measured by etch-pit techniques) and catalytic activity in the dehydrogenation of ethyl alcohol.

II. Experimental Procedure

A. Apparatus and Materials

The experimental apparatus used in this study consisted of a thermostatically controlled, constant-temperature water bath in which a 1-liter Erlenmeyer flask was immersed. The contents of the flask were stirred by a stirrer driven by a variable-speed motor (Fig. 1). The velocity of the stirrer (27 rpm), the distance from the bottom of the stirrer, and the temperature of the bath remained constant during the series of runs. All decomposition runs were made at 37°C. The temperature was controlled to within ±0.15C°. A dark cloth was placed over the whole apparatus during a run.

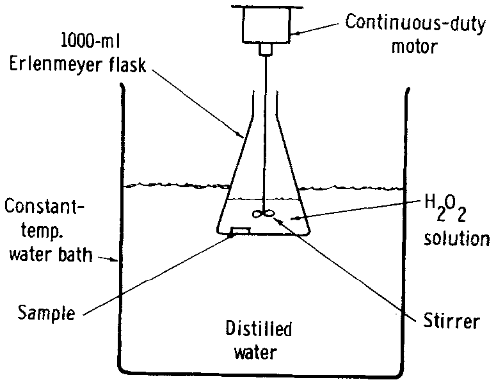

Fig. 1. Apparatus used for studies of hydrogen peroxide decomposition.

The hydrogen peroxide used was produced by Baker and Adamson (grade 1802), a 30% by weight solution in deionized water without any stabilizer or organic matter. The solution was diluted to 0.3% in our

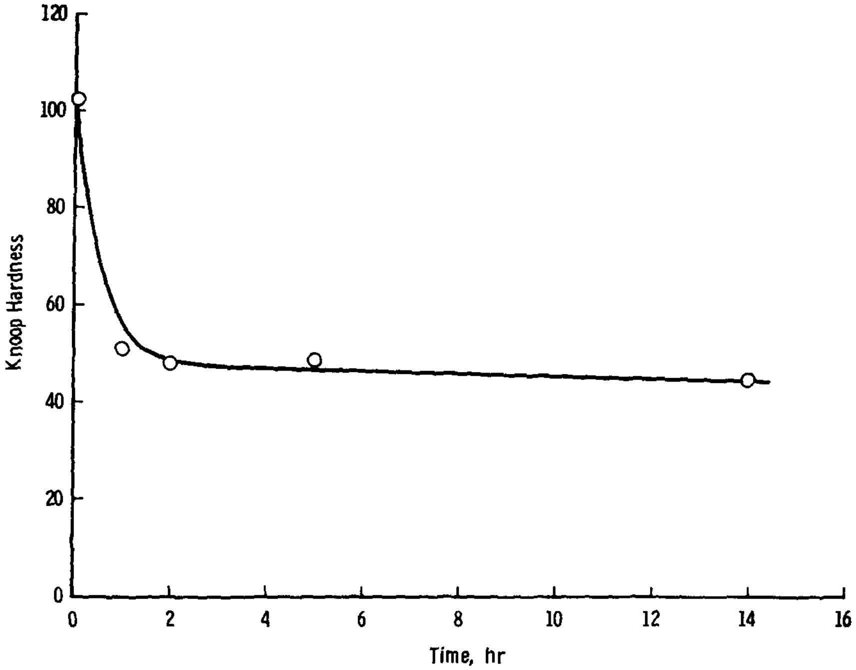

FIG. 2. Knoop microhardness vs. annealing time for Pt at 800°C.

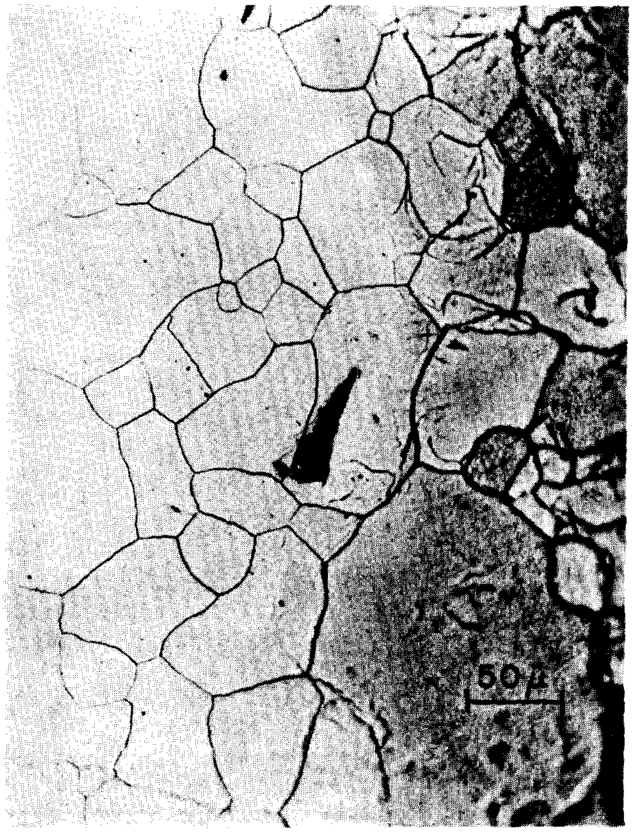

FIG. 3. Photomicrograph of annealed platinum sample electrolytically etched in 20% HCN solution.

laboratory by addition of deionized distilled water whose conductivity was 0.05×10^{-6} ohm^{-1} cm^{-1}. The solution was protected from light and heat during storage.

All of the glassware contacting hydrogen peroxide was passivated against H_2O_2 by soaking in 35% H_2SO_4 at room temperature for 1 hr followed by a thorough rinse in distilled water and drying in an oven at 110°C for 2–3 hr.

B. Catalyst Preparation

Commercially pure platinum sheet 0.005 inch (99.95% Pt) grade No. 1 M was obtained from the Engelhard Company. The platinum sheets were annealed in vacuum (5×10^{-7} mm Hg) at 800°C for 3 hr. The optimum annealing time and temperature for platinum were predetermined from heat-treatment experiments (see Fig. 2). After being annealed, the platinum sheet was cold-rolled to 0.004-inch, 0.003-inch, 0.002-inch, and 0.001-inch foils on a precision rolling mill used only for noble metals. From annealed and cold-worked platinum sheets, flat samples 2×2 cm were cut. All samples were washed in acetone, followed by a wash in 15% HCl.

C. Test Procedure

The flask containing 500 ml of 0.3% hydrogen peroxide solution was immersed in the bath water. After 30–45 min, the temperature of the solution reached the desired test temperature. The platinum sample was immersed in the solution, and a 10-ml sample of the H_2O_2 solution was withdrawn with a pipette for chemical analysis. This sample was then mixed with 10 ml of a 20% sulfuric acid solution and titrated against a 0.07 *N* potassium permanganate solution until a pink endpoint was reached (*12*). The corresponding concentration was recorded as the initial concentration c_0 and the time as

FIG. 4. Photomicrograph of 60% cold-worked platinum sample electrolytically etched in HCN solution.

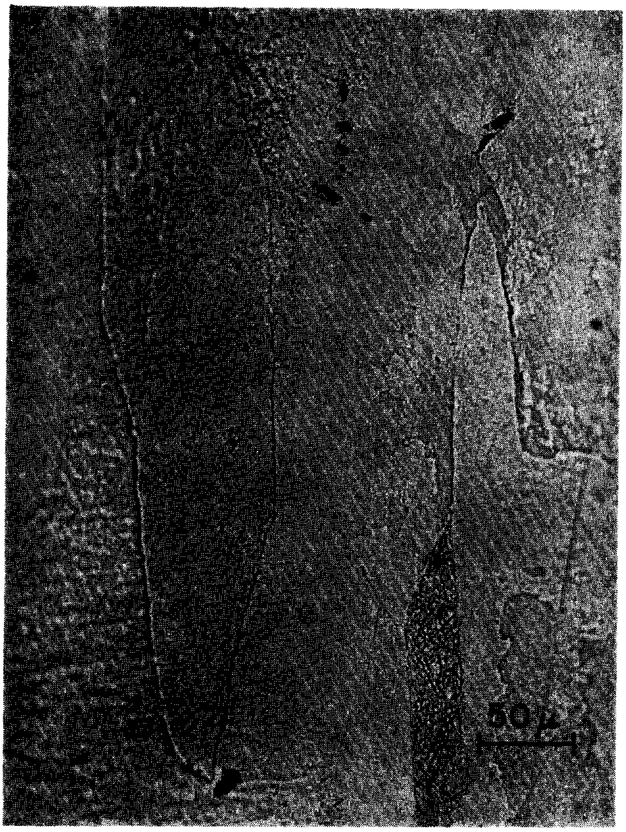

FIG. 5. Photomicrograph of 80% cold-worked platinum sample electrolytically etched in 20% HCN solution.

the initial time t_0. At regular intervals 10-ml aliquots were analyzed in identical fashion.

III. EXPERIMENTAL RESULTS

A. *Metallography*

Figures 3, 4, and 5 are photomicrographs showing the grain structure in representative foils with different degrees of deformation. It can be readily seen that there is little difference in the ratio of grain surface area to grain boundary area between the annealed (0.005-inch) foil and the heavily worked (0.001-inch) foil. The grains have become elongated during the rolling process, and deformation lines are visible on some of the grains. Two-stage carbon replicas and palladium-shadowed replicas were made of all surfaces studied and examined in the electron microscope.

Figures 6, 7, and 8 are electron micrographs of annealed (0.005-inch) and cold-worked surfaces. As can be seen, all surfaces are clean of particulate matter.

B. *Catalytic Activity*

Most researchers have found that the decomposition of hydrogen peroxide proceeds in accordance with first-order kinetics. Accordingly, our data were analyzed by plotting log $c_0/c = k$ vs. time. The typical plot in Fig. 9 shows excellent agreement with the first-order assumption. On the same figure the reaction rate constant is shown for thermal decomposition at 37°C. If we define k_ϵ as the contribution of the catalyst to the reaction rate constant, then

$$k_\epsilon = k_t - k_{\text{blank}}$$

where k_t is the measured reaction rate constant; and k_b is the reaction rate constant measured without a catalyst in the solution.

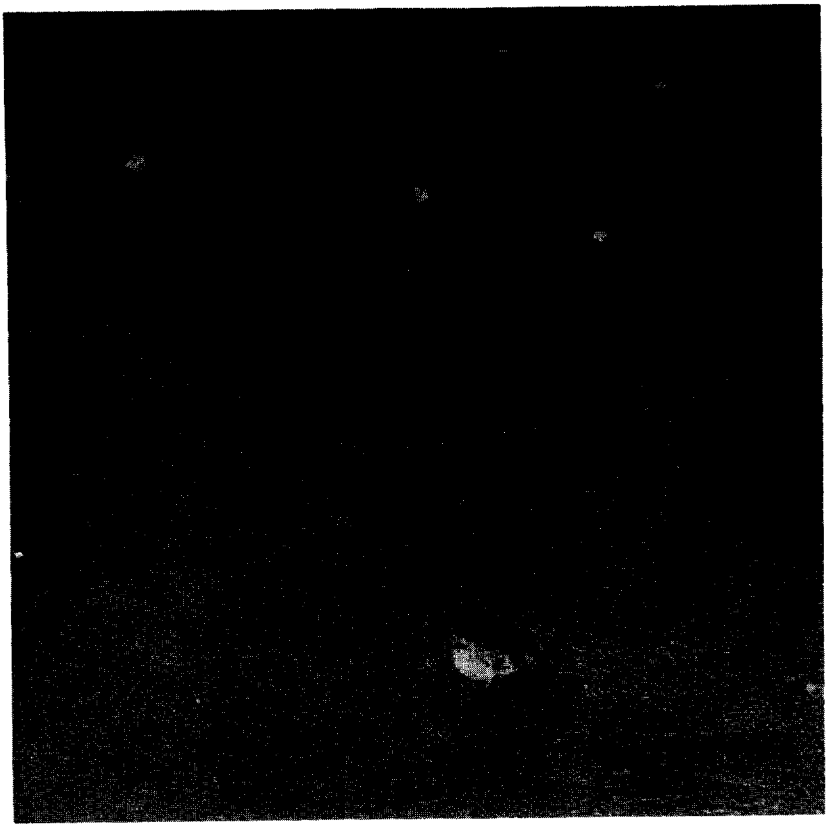

FIG. 6 Electron micrograph of palladium-shadowed Faxform replica of annealed platinum before reaction.

If we divide k_ϵ by the apparent surface area exposed to the reaction (area = 4 cm^2) we obtain

$$k'_\epsilon(\mathrm{hr}^{-1}\ \mathrm{cm}^{-1}) = k_\epsilon/4$$

which is the value reported for all of the platinum foils.

C. Relation Between Catalytic Activity and Deformation

The percentage of reduction R was calculated from the formula

$$R = [(H - h)/H] \cdot 100\%$$

where H is the initial thickness prior to rolling and h is the final thickness after rolling. The reported foil thickness is the average of five measurements taken at different locations on the foil.

Figure 10 shows a plot of the first-order reaction rate constant k'_ϵ vs. reduction for all of the samples used. It is clear that k'_ϵ increases with increasing deformation of the platinum.

The microhardness of all samples was measured on a Reichert microhardness tester with a diamond pyramid (136°) as an indenter. Samples were backed with glass and with wax on separate sets of measurements to ensure the validity of the results. The microhardness values were taken with a very light load (5 g), and the resulting depths of penetration of the diamond intenter were about 1 μ. Hence, the hardness values do indeed represent hardness near the surface and are a reliable indication of the degree of deformation. Figure 11 shows the relation between the hardness and the reduction of the foil. The hardness increases rapidly with the reduction R and then levels off at a Vickers Hardness Number of approximately 123.

A semiempirical relation between micro-

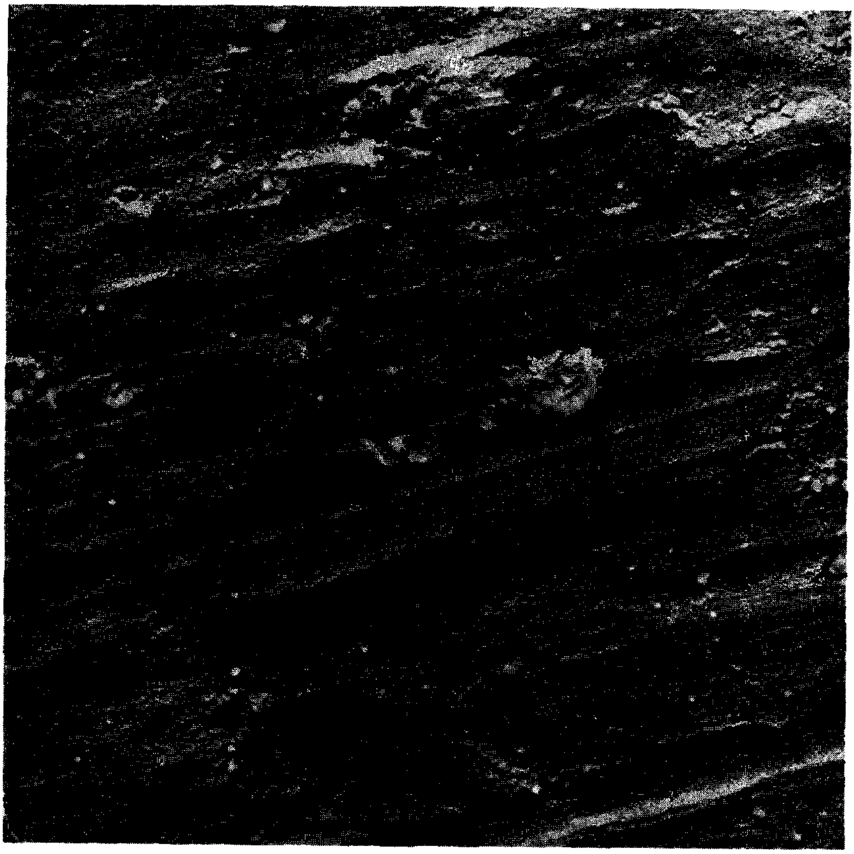

FIG. 7. Electron micrograph of palladium-shadowed Faxform replica of 60% cold-worked platinum before reaction.

hardness and yield strength was reported by Tabor (*13*). Yield strength of some of the platinum foils was determined in tension to correlate the mechanical properties of Pt catalyst.

TABLE 1

CATALYTIC ACTIVITY AND MECHANICAL PROPERTIES OF PLATINUM FOILS

Nominal sample thickness	Reduction (%)	Micro-hardness (VHN)	Tensile strength[a] (psi)	$k'_\epsilon \times 10^3$ (hr^{-1} cm^{-1})
0.005	0	88	23,000	4.76
0.004	20	122	32,000	7.21
0.002	60	123	32,000	8.36
0.001	80	123	32,000	8.11

[a] One sample only.

Table 1 shows catalytic activity k'_ϵ and mechanical properties of the platinum foils used. The values presented are averages for two different samples of the same thickness.

D. *Aging Effect*

It was noticed that the catalytic activity of all Pt foils decreased with time. However, the initial activities (measured over the first 24 hr) of samples containing the same amount of deformation were in agreement.

Figure 12 shows a plot of the first order reaction rate constant versus cumulative exposure time for several samples exposed to the H_2O_2 solution. From the graph it is obvious that the heavily cold-worked samples maintained their higher activity compared with the annealed samples even though their absolute activity was decreasing with time.

The exact cause of this behavior is not

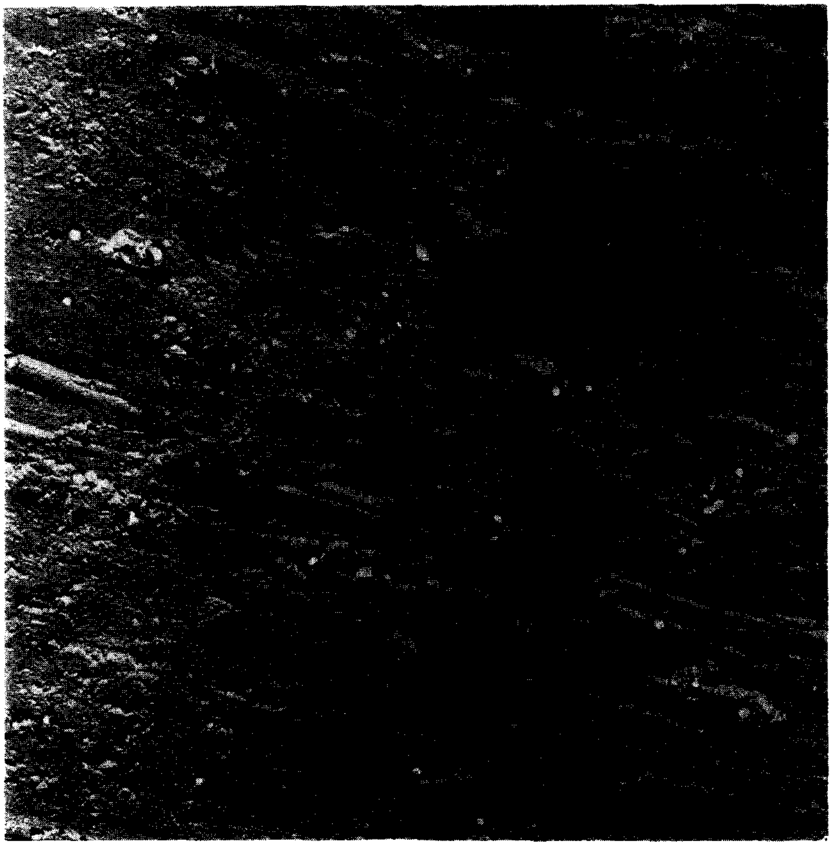

FIG. 8. Electron micrograph of palladium-shadowed Faxform replica of 80% cold-worked platinum before reaction.

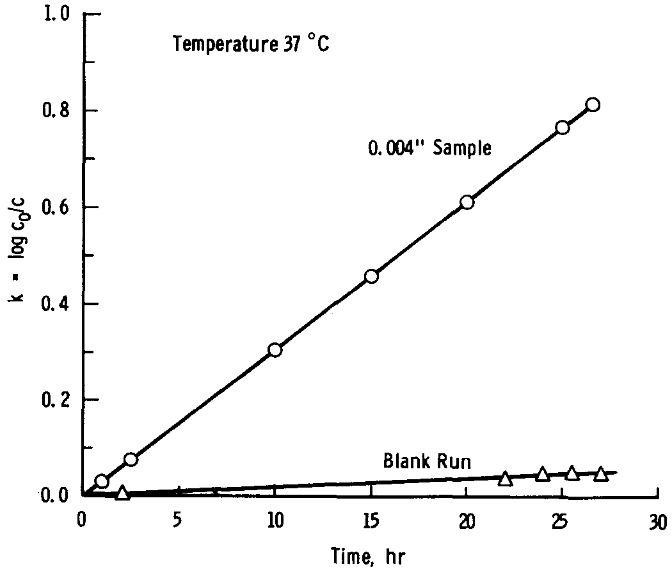

FIG. 9. Plot of log c_0/c vs. time for platinum sample and for blank run.

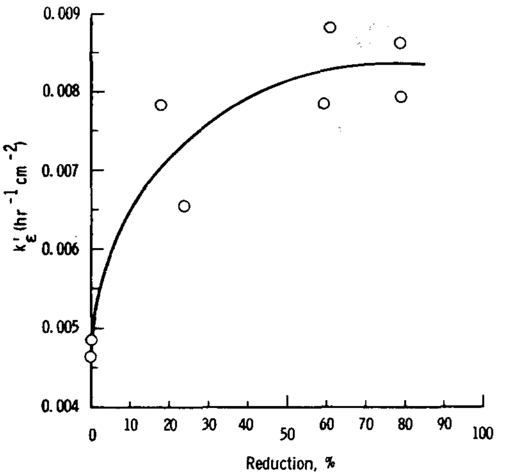

FIG. 10. Activity vs. per cent reduction for all samples.

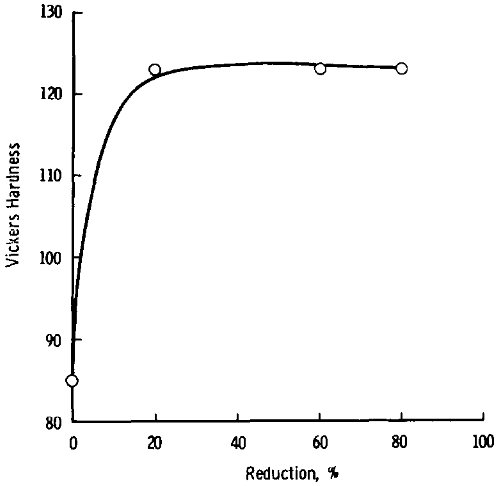

FIG. 11. Vickers hardness vs. per cent reduction for platinum foils.

known although a similar effect has been reported previously (*14*) for colloidal platinum. It was suspected that the catalyst was being etched or rearranged during the course of reaction. Therefore, samples were weighed on a Type FDJ Ainsworth microbalance (accuracy ± 1 μg) before and after reaction, and there was no measurable weight change up to 24 hr exposure. However, samples exposed for 160 hr did lose 8 μg, which is equivalent to an average depth of two atomic layers. Palladium-shadowed electron micrographs of replicas of the surface show

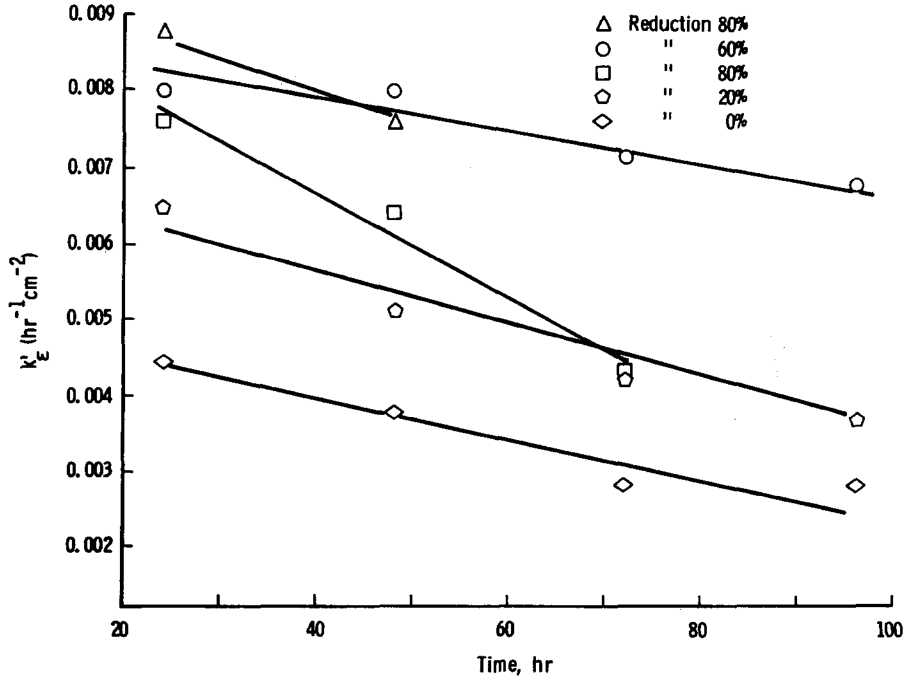

FIG. 12. Plot of k'_ϵ vs. total time exposed to H_2O_2 solution.

FIG. 13. Electron micrograph of palladium-shadowed Faxform replica of annealed platinum after exposure to H_2O_2.

considerable change in the topography of platinum after prolonged exposure (130 hr) to the H_2O_2 solution at 37°C (Fig. 13). In view of the refractory nature of platinum, it is apparent that this effect cannot be explained by the annealing out at room temperature of defects which may be responsible for enhanced catalytic activity.

IV. DISCUSSION

A. Deformation of Catalyst

The platinum used in our studies was a polycrystalline solid. A polycrystalline metal may be considered macroscopically isotropic when the orientations are randomly distributed and the average dimensions of the individual crystals are small compared with the dimensions of the whole specimen. (For example, the grain size of our 0.005-inch material was about 5×10^{-3} cm compared with a sample size of 2 cm.)

Rolling was selected as the method of deforming platinum because, during rolling, the specimen is subjected to a large plane deformation. When a thin sheet of metal is deformed, the deformation is essentially a plane strain with the exception of narrow zones near the edges; therefore, samples from the middle of the rolled sheet were used in our experiments.

Such strain is regarded macroscopically as uniform but on a microscopic scale plastic deformation is highly inhomogeneous. Slip occurs by a process of generation and movement of dislocations. The dislocations remain in the metal and some of them emerge at the surface producing stepped regions (slip lines, deformation bands, or terraces). Dislocations moving through the metal leave in their wake vacant lattice sites and dislocation loops.

B. Possible Causes for Increased Catalytic Activity through Deformation

It has been pointed out that the deformation process is complex and introduces a number of changes in the metal properties.

The possible candidates for affecting the catalytic activity are: (1) surface contamination from the rolling operation or from handling; (2) increase in surface area due to formation of slip lines; (3) change in preferred orientation due to deformation in rolling; (4) dislocations emerging at the surface.

1. Surface contamination from rolling or handling. This factor can, in effect, be discounted because of the care taken in sample preparation, as previously described. Figures 6–8 show that foreign-metal pickup was negligible.

2. Increase of surface area due to slip-line formation. Plastic deformation is largely confined to narrow bands (slip lines) which are created by the passage along closely grouped planes of large numbers of dislocations. An increase in the surface area may be attributed to the formation of slip bands. Since this increase will be roughly proportional to the deformation, the catalytic activity should increase linearly with the deformation. This, however, is not the case (Fig. 10). The increase in catalytic activity is linear up to approximately 20% deformation and then continues to increase slowly with deformation.

It should be pointed out, however, that an average height of a slip step is about $2 \times 10^{-1}\,\mu$ (*15*) whereas the finish on the rolls cannot be better than 1 μ. This leads to the conclusion that the surface contour is much more a product of the rolling conditions than a result of the formation of slip bands. It is significant to note that slip bands were not observed by electron microscopy on freshly rolled platinum foils.

3. Anisotropy due to rolling operations. During plastic deformation the same crystallographic directions in each grain are gradually rotated toward a common axis. A preferred orientation is created, and the specimen becomes increasingly anisotropic. According to Hill (*16*) the anisotropy developed during rolling is usually negligible so long as the total strain is less than 30% reduction. We found, however, that a significant increase in catalytic activity occurs on 20% cold-worked samples, and this increase cannot be attributed to the effect of preferred orientation.

X-ray diffraction patterns were taken on annealed and on cold-rolled platinum samples. Line-broadening, which is a well established experimental fact for a cold-worked metal, was visible on all cold-worked samples. In addition to line-broadening, a slight increase in the diffracted intensity from the (220) plane was visible. This indicates a slight increase in the number of (220)-oriented crystallites; however, this increase is insufficient to account for a 100% increase in catalytic activity (*17*).

4. Lattice defects created during deformation. The dependence of catalytic activity on the degree of deformation, as shown in Fig. 10, suggests an increase in the dislocation density as a likely cause. Dislocations are areas of severe distortion of the crystal lattice. Thus the immediate locality around the core of a dislocation emerging from a surface will exhibit a range of interatomic spacings. If either chemisorption of the H_2O_2 molecule or desorption of the H_2O molecule is critically dependent on the interatomic spacing of the platinum atom (*18*), dislocations may provide sites where the ideal spacing is available.

During the rolling process, vacancies are created in the interior of the platinum crystal. Since their mobility at 37°C will be negligible (*19*), they will have no effect on the catalytic activity.

V. SUMMARY

The rate of the decomposition of 0.3% H_2O_2 on platinum foil has been found to be dependent on the degree of deformation of the catalyst. The results quantitatively confirm the findings of Krause and Hermannowna (*8*). The work suggests further studies on single crystals to determine quantitatively the role of dislocations on the catalytic activity of platinum.

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