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Catalytic Etching of Platinum in NH_3 Oxidation*

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The etching which occurs when platinum is heated in NH_3–air mixtures has been studied by exposing high purity wires to gases at different compositions and temperatures. Scanning electron microscopy indicates that etching is much more extensive and rapid in mixtures than in either pure O_2 or pure NH_3. Depending on the composition and temperature, etching produces either flat facets, curved surfaces, pitting, or a combination of several modes. A "phase diagram" for catalytic etching is constructed from micrographs of ~80 specimens.

The structures are similar to those observed when metals are heated in oxygen, but they develop in much shorter times and at lower temperatures. Crystallographic variations in surface tension and volatile oxide formation appear to be inadequate to explain these observations. A mechanism for catalytic etching which includes effects of both the surface reaction and the gas-phase boundary layer is proposed. Volatile oxide transport could be the transport mechanism under O_2-rich operation but surface diffusion is probably dominant in the NH_3-rich regime. Pit formation appears to be associated with preferential attack at line defects for certain temperatures and compositions.

INTRODUCTION

It is well known that metals frequently facet more readily and extensively when heated in certain gases than in vacuum (*1*). Oxygen is generally the most efficient gas for faceting, and the cause is probably the increased anisotropy of the surface tension in the presence of oxygen and facilitated transport through volatile oxides, although there is some question as to both the driving force and the transport path (*2*). Many years ago Gwathmey and Leidheiser (*3*) showed in an elegant set of experiments that copper single crystals were visibly faceted in H_2–O_2 mixtures at temperatures below 400°C. They also found that the types and extent of faceting varied strongly with the original crystal plane exposed.

Such effects can obviously be important in catalysis through development of particular crystal planes and surface structures and by alteration of crystallite size and surface area. Faceting processes are very obvious in the NH_3 oxidation reaction on Pt gauze where the wires of the gauze become visibly roughened in the first minutes of operation (*4–6*). This is accompanied by an increase in the selectivity for NO production. Metal loss is a significant cost factor in this reaction (*5*) and this is also related to formation of volatile species, mainly PtO_2 (*6, 7*).

We have recently reported (*4*) scanning electron microscope (SEM) observations of Pt gauzes used in NH_3 oxidation and in HCN synthesis. These showed extensive development of planar facets and in some cases formation of regularly shaped holes or channels. In the present paper we report a systematic study of etching of Pt wires and ribbons in NH_3–air mixtures measured as a function of wire temperature, time, and gas composition. These processes generally occur at faster rates and to a greater extent than is characteristic of thermal etching

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and should therefore be described as "catalytic etching."

Ammonia is oxidized to either NO or N_2 in this system through reactions whose stoichiometries are

$$NH_3 + \tfrac{5}{4}O_2 \rightarrow NO + \tfrac{3}{2}H_2O, \qquad (1)$$

and

$$NH_3 + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2O. \qquad (2)$$

The stoichiometric reactant feed in the first reaction is 14% NH_3-in-air, while for the second it is 21% NH_3-in-air. Both reactions are very fast with reaction (1) predominating for <10% NH_3 and reaction (2) for >20% NH_3. Apel'baum and Temkin (*9*) have shown that the rate of NO production correlates well with mass transfer rates to cylinders. Thus, it is probable that both reactions are mass transfer limited, and on either side of the stoichiometric feed concentration, boundary layer depletion can be expected to reduce the concentration of the limiting reactant to a very small value at the surface.

EXPERIMENTAL METHODS

In a Pyrex flow reactor NH_3 and dry air were mixed and passed over a high purity Pt wire or foil at flow rates typically 0.5 to 1.5 cm/sec and a total pressure of 1 atm. High purity platinum wires (99.99% obtained from Sigmund Cohn) of 0.010 in. diameter were used for most studies. A 3 cm loop was welded to tungsten support leads so that the wire could be heated resistively. The wire temperature was monitored with either an optical pyrometer or by resistive measurements using 0.004 in. diameter potential leads welded to the wire. Temperatures are regarded as accurate to ±20°C.

The NH_3 oxidation reactions are exothermic and the heat of the reaction provides a minimum or "adiabatic" wire temperature. For NH_3–air mixtures at atmospheric pressure this is indicated by a broken line in Fig. 1. Higher temperatures were obtained by dc electrical heating of the wire loop, and lower temperatures by

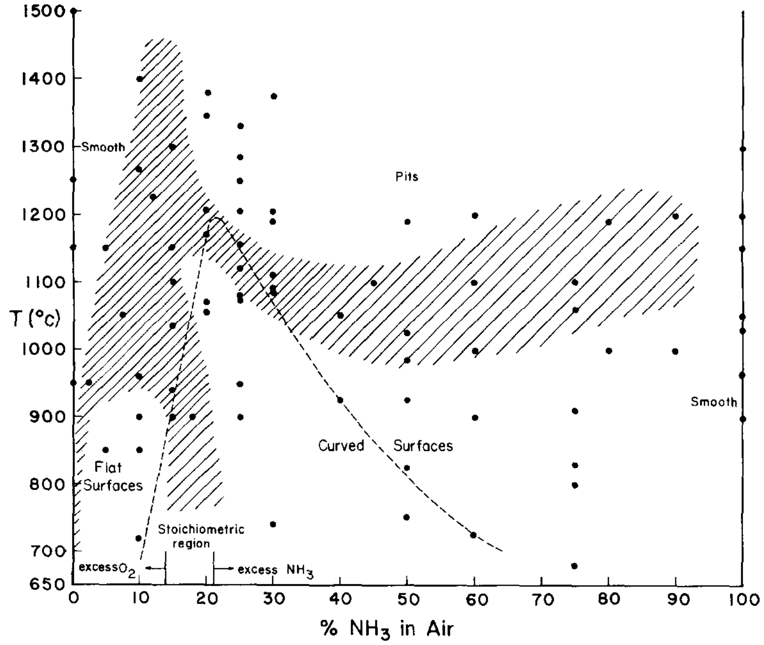

FIG. 1. Phase diagram for catalytic etching of platinum in ammonia oxidation. Points represent SEM observation of 0.010 in. diameter wires which had been heated in an ammonia–air mixture for 1 hr at the temperature and composition indicated. The regions of excess oxygen and excess NH_3 are indicated at the bottom of the figure. (- -) The wire temperature which would be obtained by reaction heat alone, the "adiabatic" temperature.

diluting with N_2 or mounting wires on heavy support leads (see below).

High purity NH_3 (99.99%) and dry air (20% O_2, 80% N_2, 0.1% impurities) were used for most experiments. On-line mass spectrometric analysis indicated no other species present at concentrations greater than 1% of the major species. A number of runs were made using lower purity gases to ascertain that contaminants had a negligible influence on the rate or types of etching. In some experiments gases were passed through coils at 195°K and were dried over KOH to remove water, and in other experiments the air was saturated with water. In essentially all experiments the rate and types of etching appeared to be a consistent function of the composition of the major constituents, temperature, and time alone.

A potential problem in such systems is contamination of the surface by S, C, Cl, metals, SiO_2, etc. We have analyzed the surface composition of samples which had been used in this and similar reactors by Auger electron spectroscopy (AES) and sputtering techniques (*8*). We found that, while contaminants are observed following improper procedures (sulfur from rubber stoppers and tubing, iron from stainless steel supports, etc.), the procedures used in these experiments yielded surfaces whose AES spectra were indistinguishable from clean Pt except for approximately a monolayer of oxygen and traces of nitrogen. This was in distinct contrast to surfaces not treated in oxygen; these surfaces generally are characterized as a thick graphite layer on the platinum surface.

Before each run, the wire was heated resistively in flowing N_2 for 15 min at temperatures greater than 1500°C to anneal each specimen, and thus assure that crystal defects were identical in all specimens. After heating in N_2, SEM showed that specimens were completely smooth except for grain boundaries separating crystal grains of ~ 100 μm diameter. After heating in the flowing gas mixture for a specified time and temperature, the sample was removed from the system and examined on a Cambridge Instruments scanning electron microscope (SEM).

RESULTS

We examined by SEM approximately 80 platinum wires which had been heated in NH_3–air mixtures. Each point in Fig. 1 indicates a separate experiment performed with a new wire. Except as noted, all runs were for 1 hr at the temperature and composition indicated.

Distinctive modes of etching are observed in excess O_2 and in excess NH_3. These concentration regimes are indicated at the bottom of Fig. 1. It is convenient to consider each of these regimes in turn.

Etching in Excess Oxygen

When platinum wires were heated in pure O_2 for 1 hr at temperatures between 800 and 1500°C (points indicated at the left of Fig. 1) the wires remained essentially smooth except for small pits (0.1–0.5 mμ) observed at temperatures above 1200°C. This is essentially in agreement with Fryburg and Petrus (*10*) who observed some etching in pure oxygen but only to a limited extent on samples which had been heated much longer than ours. Garton and Turkevich (*11*) also found that no significant etching occurs when platinum is heated in pure O_2 for short times.

Figure 2a, b, c, and d shows surfaces which had been heated in 5–18% NH_3 for 1 hr at temperatures at or below 900°C. Extensive faceting is evident. All runs in excess O_2 produced surfaces with predominantly flat facets, evidently exposing crystal planes of low surface energy. At higher temperatures ($T > 850$°C) some surfaces were curved as indicated in Fig. 2d.

The surface shown in Fig. 2a and b is a 0.035 cm wire which had been recrystallized to develop large grains (typically 20 to 50 μm). It is quite evident that some grains exhibit little or no etching while others are heavily faceted. Also visible in Fig. 2a and b are a number of grain boundaries. The enlarged view of a region of this surface in Fig. 2b shows one grain boundary at the left of the photograph and possibly one at the right. While characteristic etch patterns are associated with grain boundaries, etch-

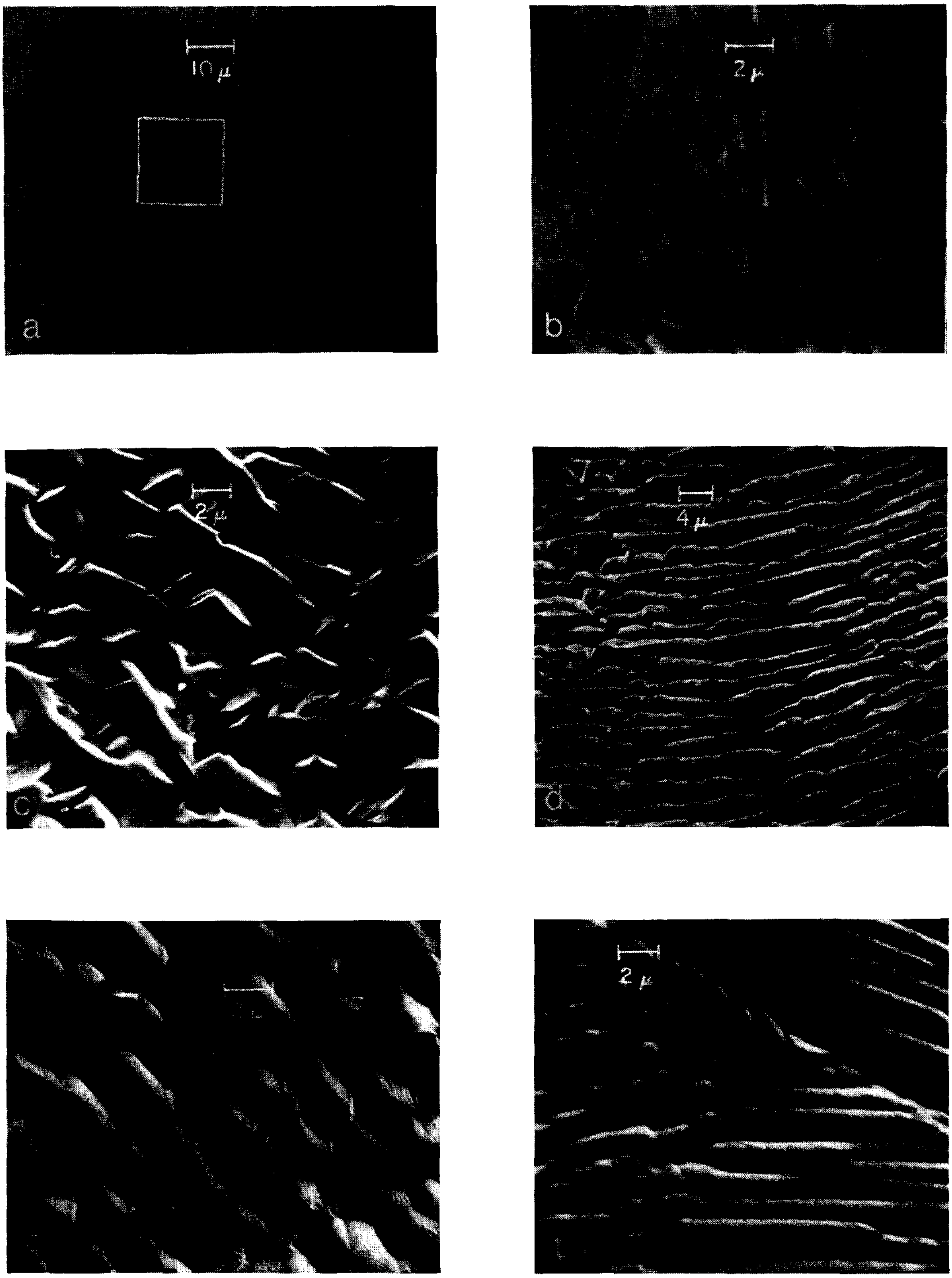

FIG. 2. Electron micrographs of platinum after heating in NH_3–air mixtures for 1 hr: (a) 18% NH_3, 900°C, 650×; (b) same, 3250×; (c) 5% NH_3, 850°C; (d) 10% NH_3, 900°C; (e) 60% NH_3, 725°C; (f) 60% NH_3, 830°C.

ing is no more extensive at grain boundaries than on originally flat single crystal surfaces.

At high temperatures ($T > 1100°C$) the surfaces exhibited less extensive etching, and in the regime indicated in Fig. 1 the surfaces remained essentially smooth. Etching was detectable in 5% NH_3 at a temperature as low as 400°C.

Etching in Excess NH_3

Figures 2e and f and 3a–d show micrographs of surfaces which had been heated in ammonia-rich mixtures. For temperatures less than approximately 1200°C, extensive faceting is again observed but in this case curved surfaces are generally produced. While the rates of etching are difficult to estimate using SEM, it appears that *etching is at least as extensive and rapid in excess NH_3 as in excess O_2*. A grain boundary is evident in Fig. 2f and, as before, etching is no more extensive in its vicinity than on single crystal planes.

In excess NH_3 etch patterns appear in general to depend on the underlying crystal structure just as they did in excess O_2. However, the influence of base plane crystallography is generally not as obvious as in excess O_2. In Fig. 2f ridge patterns are evident on two planes (note also the transverse ridges in the valleys between major ridges), while mound type structures are evident on the plane at the left. In Fig. 3a some preferred directions are evident, but there are no straight ridges or valleys, and all surfaces are curved. Figure 3b shows an apparently random array of cusped structures, but the walls and bottom of each depression have weakly visible structures of 2- or 4-fold symmetry.

There are three general types of curved surfaces in excess NH_3: V-shaped valleys with rounded ridges (Fig. 2e and f), U-shaped valleys with rounded ridges (Figs. 2f and 3a), and U-shaped valleys with sharp ridges (Fig. 3b). The type of structure was found to depend somewhat on temperature with V-shaped valley-rounded ridge structures generally found at temperatures below 1100°C while both the U-shaped valley-rounded ridge and U-shaped valley-sharp ridge structures were observed primarily at temperatures above 1100°C. However, crystal structure appeared to have a greater influence on the type of etching than temperature, and therefore it was not possible to indicate regimes for the various structures on the phase diagram of Fig. 1.

In pure ammonia consistently smooth surfaces were obtained below 900°C and slight etching and pitting at higher temperatures. Thus, in contrast to the situation for pure O_2, detectable etching occurred in pure NH_3 at high temperatures in the times of these experiments. It is possible, however, that this was due to traces of oxygen-containing species in the NH_3.

Pit Formation

In excess NH_3 for $T > 1000°C$ pits were observed in addition to, or in place of, the etching just described. One pit is evident in Fig. 3a, a few in Fig. 3b, and in Fig. 3c and d pits are the predominant structures. The regime of pit formation is indicated in Fig. 1.

At low temperatures the pit walls were generally flat, while at higher temperatures they were curved. Figure 3c and d show square and hexagonal pits, respectively. Symmetry implies that the walls of the square pits are (100) planes and those of the hexagonal pits are (111) planes, although both could have only 2-fold symmetry. The ends of shallow pits on these surfaces are faceted as inverted pyramids. The pits shown here were chosen to illustrate the shapes of the ends. Typically, pits penetrate the metal to depths many times the pit diameter. Walls of all pits appeared to be parallel.

Another characteristic of pits is that metal is deposited at the pit mouth. This is evident from mounds built up around pits in Fig. 3d, but is best illustrated by the arrows in Fig. 3c. In particular, the pit mouth in the lower right of the micrograph is a flat circular region built up around the square pit. Evidently, metal from the pit diffuses to the ledge where it is deposited. The mechanism of lip formation must be deposition of metal there after removal from the

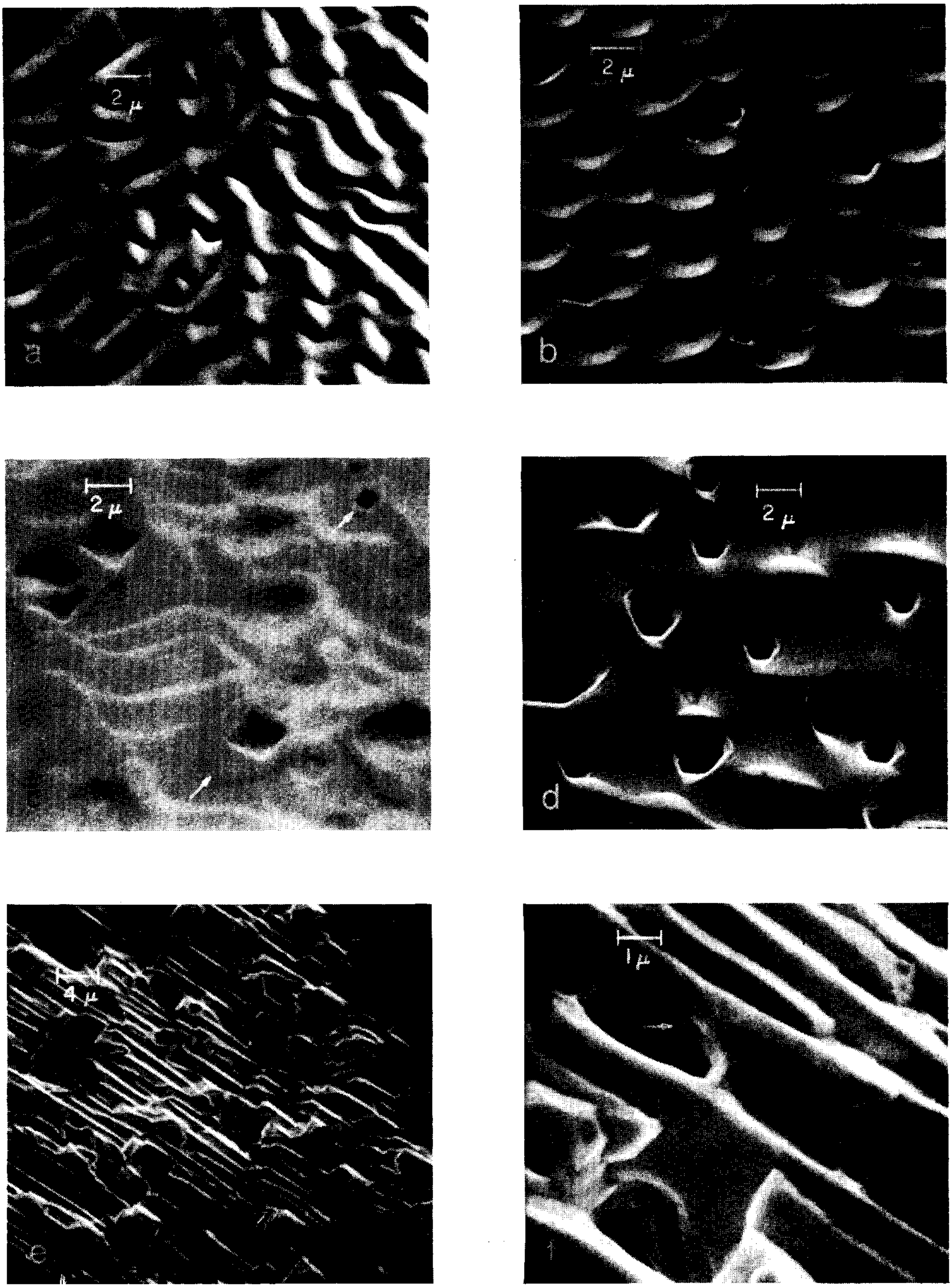

FIG. 3. Electron micrographs of platinum after heating in NH_3-air mixtures for 1 hr: (a) 90% NH_3, 1200°C; (b) 80% NH_3, 1190°C; (c) 18% NH_3, 1200°C; (d) 25% NH_3, 1250°C; (e) 25% NH_3 at 1375°C for 1 hr followed by 4 hr at 10% NH_3 at 700°C, 1625×; (f) same as (e), 6500×. The arrows in (c) indicate material deposited at pit mouths while that in (f) indicates facet formation within a pit.

pit, either by vapor or surface diffusion transport.

Additional Experiments

Several experiments were carried out in an effort to further elucidate the mechanism of etching. These are described below.

Dilution. One possible mechanism of etching is faceting which results from microscopic temperature variations over the surface caused by crystallographic variation in reaction rates. To test this hypothesis, several measurements were carried out comparing a surface exposed to NH_3-in-air for 1 hr with one exposed to the same NH_3/O_2 ratio but diluted with N_2 so that the reactant concentrations were one-half of those used previously. To attain the same total flux a reactant time of 2 hr was employed. Surface morphologies appeared similar, indicating that etching is a function of the total transport of NH_3 and O_2 to the surface. Due to the difference in fluxes in the two cases, any temperature variations over the surface would be much smaller for the diluted situation. Further, since transport steps are probably activated, these experiments suggest that surface temperature variations do not play a dominant role in catalytic etching.

Flow conditions. The extent and modes of etching were insensitive to both flow velocity and orientation of the surface with respect to the gas flow direction. The latter was demonstrated by observing the upstream, downstream, and sidestream sides of a wire. Crystallographic variations were much more marked than those which may be associated with flow direction and velocity. These results suggest that the rate of transport of reactants to the surface is not significantly affected by the flow pattern around the wire.

Metal loss. A possible mechanism of etching involves transport as gaseous PtO_2:

$$Pt(s) + O_2(g) \rightleftharpoons PtO_2(g). \tag{3}$$

Etching is as extensive, or more extensive, in excess NH_3 compared to excess O_2, while volatilization of PtO_2 should be much more rapid in excess O_2 than in excess NH_3, especially since the boundary layer resistance depletes the limiting reactant. We qualitatively measured the metal loss by positioning a glass plate a few millimeters downstream from the wire and heating to ~1400°C in various gas compositions. An opaque film of the metal deposited in 1 hr in pure O_2, some deposit was noted in 5 and 10% NH_3, and no deposit was visible in excess NH_3.

Control of surface morphology. The reproducibility of the etching modes (Fig. 1) suggests that it should be possible to prepare surfaces with various structures by suitable exposures and temperatures. We heated a wire first for 1 hr in the pit forming regime (25% NH_3 at 1375°C) and then for 4 hr in the facet forming regime (10% NH_3 at 700°C). The resulting surface is shown in Fig. 3e and f. The external surface is etched into flat planes and the surface is permeated by pits. In fact, Fig. 3f shows that the *pit walls have also been faceted.* The experiments indicate that it is possible to form a surface with a desired morphology by suitable choice of etching conditions.

Size of etch structures. An important consideration in deciding the mechanism of etching is the dimensions of the structures formed. We measured distances between repeating etch structures and pit diameters for all micrographs to determine whether they were a systematic function of temperature and/or composition. Figure 4 shows that *all structures are between 0.5 and 3 μm* and that only weak correlation exists between the characteristic size of structures and the temperature and composition which produce them. However, a few general trends were noticeable. Higher temperature produced larger structures of a given kind. For example, planar facets produced at 5% NH_3 and 450°C were approximately 0.5 μm across, whereas facets observed at temperatures ranging from 700 to 900°C were 1–3 μm.

The most significant observation concerning structure size was the effect of composition and temperature on pit size. Average pit diameter was 1–3 μm, with the largest occurring with compositions from 20 to 30% NH_3-in-air. At higher and lower NH_3

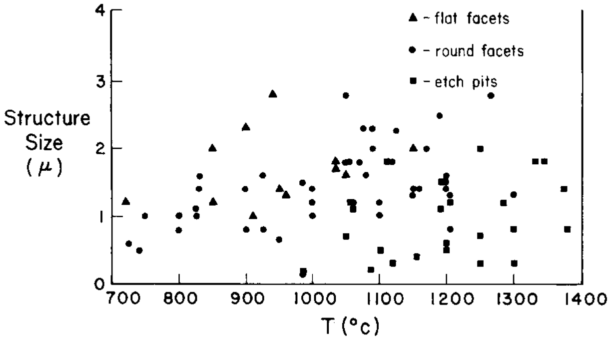

FIG. 4. Plot of average size of etch structures versus temperature for specimens indicated in Fig. 1. All structures have dimensions of 0.5 to 3 μm. Sizes are nearly independent of temperature although a slight increase with increasing temperature is evident.

compositions average pit size was typically less than 1 μm. Similarly, pits formed in the lower temperature range of the pitting region (Fig. 1) were found to be about 0.5 μm in diameter, whereas pits formed at higher temperatures were typically 1–3 μm.

DISCUSSION

In this section we shall consider various mechanisms of catalytic etching and discuss their feasibility. Any experiment which relies largely on microscopy must of necessity be qualitative, and the present study is no exception. However, the experiments clearly demonstrate that three distinct modes of etching occur, depending on temperature and composition. These produce either flat facets, curved surfaces, or pits. The conditions under which these occur are sufficiently distinct that it is possible to construct a phase diagram for catalytic etching.

Etching of solids is an old and much studied phenomenon which includes thermal etching (primarily in oxygen) and gas and electrochemical corrosion. Many investigators have reported structures similar to (and perhaps even more baroque than) those shown here. The remarkable features of these results, however, are the *low temperatures* and *short times* required for them to occur and the strong dependence on *mixture composition*. The only comparable situations appear to be in electrochemical etching and in the experiments of Gwathmey and Leidheiser (*3*); in all cases reacting mixtures are also involved. We also note that, since no definitive explanations exist for these phenomena after many years of investigation, probably no simple explanation will be adequate for the present situation.

The major difference between the present system and etching in nonreactive gases is the existence of many species—product, reactant, and intermediates—and a gas-phase boundary layer near the surface. These provide a number of possible driving forces and transport paths which are not present in nonreactive systems.

The driving force for etching must be a variation in the chemical potential between surface regions ~1 μm apart. Since this is much less than crystal grain size, etching must involve the breakup of initially smooth surfaces (macroscopically) into faceted surfaces. There are three obvious potentials: surface free energies, temperature variations, and concentration variations induced by the surface reactions. We note that these can exist and cause gas or surface metal transport even though the distances involved, ~1 μm, are comparable to the gas-phase mean free path.

Temperature variation. One might speculate that there could be significantly higher temperatures in concave regions (pit or valley structures) with a concomitantly enhanced transport of metal out of those regions, but this seems unlikely considering the rapid thermal relaxation between surface and bulk for these low surface-to-volume metal catalysts. Furthermore, comparable etching in diluted mixtures and in mixtures far from the stoichiometric NH_3:O_2 ratio—where essentially all of the heat was supplied electrically rather than reaction generated—argues against the importance of local heating. Edwards, Worley, and Luss (*12*) have looked for temperature fluctuations of Pt in this reaction with a spatial resolution of 40 μm. All fluctuations could be attributed to improper mixing and turbulence.

Surface free energy variation. Herring's classic paper (*13*) on the equilibrium shapes of crystals for which the surface tension depends on crystallographic orientation gives theoretical criteria for the stability of plane surfaces with respect to break up into hill and valley structures and for the existence of flat and curved surfaces. Thermal etching has been interpreted almost exclusively in these terms (*14–16*). It is postulated that, in the presence of oxygen, adsorption increases the anisotropy in the surface tension and this, in turn, makes hill and valley structures more stable thermodynamically. To what degree these equilibrium considerations apply to catalytic etching, or even thermal etching, is unknown. It is now known that metal surface atoms interact dynamically with the gas phase under most etching conditions and, hence, the surface cannot be considered closed in the thermodynamic sense.

Nevertheless, in catalytic etching there are even greater possibilities for large variations in surface tensions between crystal planes because, with multiple adsorbate species, one expects coadsorption configurations which may be highly specific to substrate atom configurations. However, surface tension anisotropy appears to be incapable of explaining all the structures observed. For example, the structures in Fig. 2d exhibit parallel facing walls, a configuration impossible in terms of minimum surface energy ideas. Also, the region on the right of Fig. 2f shows structures with parallel rows, but in the valleys between the rows there also exist hill and valley structures perpendicular to the major structures. Thus, while hill and valley structures on some planes are certainly predicted from minimum surface free energy considerations, secondary structures on the same plane are not.

Finally, we note that the tendency toward rounding of corners and smoothing at high temperatures are qualitatively as expected from minimum surface free energy considerations—the anisotropy is reduced because the entropy term becomes important at high temperatures. Another cause for reducing the anisotropy at high temperatures is that fewer species adsorb and the adsorbate influence on surface tension anisotropy is thereby reduced.

Boundary Layer Considerations

Because a fast, exothermic reaction is occurring at a surface with a gas pressure sufficiently high that the mean free path is short ($\sim$1 μm), there are large temperature and concentration gradients in the boundary layer near the surface. These are, of course, the defining properties of the boundary layer and it seems likely that they play an important role in catalytic etching. Unfortunately one cannot determine concentrations and temperatures with sufficient precision to describe quantitatively the processes occurring.

Under the conditions of our experiments, the boundary layer thickness is nominally 10^{-2} cm. It should be noted that this is much greater than the size of the etch structures and is comparable to the wire diameter. Also, under the flow conditions used here, the flow around the wire is not turbulent. Thus near the surface the gas phase should be essentially stagnant. The temperature and concentration fields should be uniform (parallel to the surface) over distances large compared with the dimensions of the etch structures, but there may be microscopic variations in their vicinity. These variations would be caused by inhomogeneities in the surface and, hence, in the surface reaction rates.

It is to be expected that only that portion of the boundary layer within a few mean free paths of the surface can affect the etching process. This is consistent with the observation that etching appears independent of orientation with respect to the overall direction of gas flow. The reaction creates temperature variations and transport *perpendicular* to the surface, but the transport process responsible for etching involves transport and/or temperature variation *parallel* to the surface. It is the latter which must be considered to describe the etching process.

Transport Mechanisms

Of the three modes of transport generally considered as possibly operative in thermal etching—volume diffusion, surface diffusion, and vapor-phase transport (*17*)—the first has always been discounted as having too high an activation energy. Although this work extends the temperature range yet studied to 1500°C, the remarkable rapidity of the etching process under our reaction conditions would appear to exclude volume diffusion once again. Furthermore, except for a very few studies which included vapor-phase transport for completeness in presenting a highly idealized mathematical model of thermal etching (*17, 18*), the bulk of the thermal etching literature considers surface diffusion only. The reason for this is that the vapor pressures of the pure metals were known to be negligible under most of the experimental conditions employed. In the early 1960's some consideration was given to the possibility of metal transport via volatile oxides. Indeed, Hondros and Moore (*2*) gave evidence that etching may be associated strictly with net metal loss via metal oxides. Thermodynamic and kinetic data on the O_2–Pt system obtained in the last 15 yr (*10, 19*) strongly support our belief that gas-phase transport via volatile PtO_2 plays a role in the catalytic etching of Pt in O_2-rich atmospheres at least as strong as surface diffusion.

For the reaction,

$$Pt(s) + O_2(g) \rightleftharpoons PtO_2(g),$$

the vapor pressure of PtO_2 under 1 atm of O_2 is $\sim 10^{-3}$ Torr at 1000°C. This is sufficient to account for metal loss in excess oxygen atmospheres. We propose a mechanism for etching in catalytic oxidation reactions. It includes effects of both the boundary layer and the surface reaction in facilitating metal transport parallel to the surface. The reasoning follows that of the volatile oxide mechanism of platinum loss in commercial ammonia oxidation reactors. Some background on this may be helpful.

Fryburg and Petrus (*10*) were the first to suggest the strong limiting effect of gas-phase diffusion of PtO_2 at atmospheric pressure. Previously in Pt oxidation studies mass transfer had not been considered a factor since the surface reaction rate is extremely slow (probability of reaction between an impinging O_2 molecule and a surface Pt atom $<10^{-7}$ at 1000°C). However, the instability of the PtO_2 molecule had not been taken into account—it dissociates with essentially unit probability on striking the platinum surface. Hence, at high pressure, a large fraction of the evaporating PtO_2 is reflected back and decomposed. Fryburg and Petrus determined an "escape probability" of 0.002 at 1 atm for their system.

Of course, at high pressure, any such escape probability is dependent on the system geometry and oxygen flow rate. Bartlett (*7*) used standard mass transfer correlations and the reaction kinetic parameters obtained by Fryburg and Petrus at low pressure to calculate overall oxidation rates for the entire pressure range. They compare well with the experimental rates. Nowak (*6*) took the final step of applying the reaction kinetic parameters and mass transfer correlations for wire gauzes in calculating platinum metal loss rates in industrial ammonia oxidation converters. He made his calculations for some of the conditions of Handforth and Tilley's pilot plant studies (*20*) and found the calculated loss rates too high by a constant factor of about 4. However, it appears that he used the oxygen pressure of the feed stock in his calculation—0.18 atm for 10% NH_3-in-air at 1 atm—totally neglecting the very important reaction competing for oxygen, NH_3 oxidation itself. Since this is many orders of magnitude faster than the metal oxidation, the effective oxygen pressure available for platinum oxidation is 0.055 atm. Thus his calculated loss rates should be reduced by a factor of 3.3 and the comparison with the experimental rates becomes quite good. We noted previously that the rate of metal loss decreases markedly in NH_3-rich mixtures. Furthermore, in commercial HCN synthesis from NH_3, O_2, and CH_4, with the reaction mixture usually oxygen deficient, no metal loss is noted even at temperature 200°C higher than those in commercial NH_3 oxidation (*4*).

We now propose that a similar competition for oxygen may be operating between microscopic regions of the surface—when the fast, catalytic reaction proceeds preferentially on one or more active regions. Thus, with a given oxygen partial pressure at the surface, as determined by the overall reaction rate and boundary layer resistance, a significantly larger fraction of the PtO_2 in the gas phase will have evaporated from the catalytically inert regions. Since redeposition is likely to be isotropic, a net transfer of platinum from inactive to active regions results. Moreover, since catalytically active regions *must* grow at the expense of inactive regions, this process describes a *mechanism for catalyst activation.* Because the transport path from facet to facet is very short, facet growth could be very rapid, as the experimental evidence indicates it must.

The volatile oxide mechanism is inadequate, however, as an explanation for the etching observed well into the ammonia-rich regime. It is possible to speculate on the existence of other volatile platinum compounds or even a chemical vapor transport process (*21*), on a microscopic scale, in which volatilized platinum compounds are decomposed by reaction in the boundary layer, with the platinum eventually replating itself. Without further evidence, though, we tend to reject all such speculation on the grounds that such processes would inevitably lead to significant platinum loss—loss never observed in oxygen-deficient operation.

We are left, then, solely with the surface diffusion mechanism for etching, at least in the NH_3-rich regime. Surface diffusion of platinum has been studied by Blakely and Mykura (*22*) using scratch healing techniques. They measured diffusion coefficients in the temperature range of 900 to 1300°C and times of 30 to 100 hr at pressures of $\sim 10^{-5}$ Torr. A random walk model predicts diffusion over the observed structure dimensions (1 μm) in less than 1 sec. However, Blakely and Mykura required much longer times than employed here even though temperatures were comparable. Evidently if transport coefficients are comparable in the two experiments, the driving forces must be considerably larger in ours.

Since the faceted structures obtained are roughly equivalent in size to those obtained in O_2-rich operation, the transport rates are apparently comparable. The major difference in the etch structures is that the facets from the NH_3-rich operation are notably rounded compared to the sharply defined crystallographic planes obtained in O_2-rich operation. We surmise that such sharp-edged facets could well be the predominant structures obtained when the mass transfer driving force is, in a certain sense, a difference in a crystallographically specific chemical reaction potential. The driving force for the surface diffusion mechanism is a difference in surface chemical potential between platinum atoms exposed on different crystal planes.

While it has long been assumed that adsorbed oxygen increases the anisotropy of metal surface free energy [sharpening the cusps in the polar γ-plot of surface tension vs orientation (*13*)], it may be that adsorbed ammonia decreases this anisotropy while yet facilitating transport by lowering the effective activation energy for surface diffusion. Thus the rate of metal transport could be enhanced with the final structures being more rounded due to the lowered anisotropy. Obviously more progress is required in determining these critical surface parameters and the effect on them of adsorbed and reacting gases.

Mechanism of Pit Formation

Pit formation could occur either through attack at line defects or through instabilities on initially defect-free planes.

A mechanism for pit formation on silver in the presence of H_2S has been suggested (*23*) which notes that a plane may be unstable with respect to pit formation if crystallographic anisotropies are of a certain type. If there exists an outward pointing cusp in the polar plot of surface tension versus orientation, then the plane at the point of the cusp will be unstable with respect to vicinal planes, and pits may be the equilibrium structures. This situation could arise if sulfur adsorbed preferentially on steps of a low index plane and thus reduced the surface tension of the stepped planes.

Arguments against such intrinsic instabilities in the present case are that our pits generally have parallel walls and that pits are frequently clustered in regions of the wire in a linear array. Parallel walls are not obviously predicted by an outward cusp in the γ-plot, and clusters of pits suggest that they be associated with regions of strain left in the wire after annealing.

We feel that preferential attack at line defects adequately explains the pits we observe here. On a heavily pitted surface (Fig. 3d for example) the density of pits is $10^6/\text{cm}^2$. Dislocation densities on well-annealed crystals are typically 10^6–$10^8/\text{cm}^2$, in good agreement with our observed pit densities.

We have no explanation for preferential attack at line defects. Perhaps the reaction rate is higher in the region of strain near the defect and metal migration is enhanced. The pit would have a width determined by the size of the strain field and a depth determined by the length of the defect. No such attack is observed at grain boundaries where strain should also be present.

The fact that pits are formed only in excess NH_3 suggests that impurities such as sulfur may be involved. In excess O_2 this would be removed as SO_2, but otherwise sulfur may be adsorbed on the surface. However, we have no evidence for sulfur contamination. Data appeared to be strictly reproducible, and pitting could result from action of the major gas species in the proper temperature and composition range.

SUMMARY

The objectives of this paper are, first, to describe conditions leading to catalytic etching and the types of structures produced and, second, to discuss possible mechanisms by which these structures may be formed. The results summarized in Fig. 1 show the correlation between reaction conditions and modes of etching.

While data on catalytic etching are, at present, confined to the NH_3 and H_2 oxidation systems, metal migration during surface catalytic reactions may be a very general effect, at low temperatures as well as high, and may not even require the presence of oxygen or an exothermic reaction. Such processes may be operative in catalysis on supported metals, perhaps causing sintering or, possibly, preventing it by dispersing metal into high area structures. The lower temperatures employed in supported catalysts do not preclude such processes on the time scales of their operation.

The present experiments have, hopefully, narrowed the possible mechanisms for catalytic etching. However, further study using single crystal planes, different gas mixtures, and techniques for direct surface chemical analysis are necessary for further elucidation of the processes. Experiments along these lines are in progress.

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