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Catalytic Etching of Pt/Rh Gauzes

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The catalytic etching of 90% (weight) platinum/10% rhodium gauzes in hydrogen/oxygen mixtures was studied. The gauzes were found to etch over exactly the same range of temperatures and gas stoichiometries as pure platinum. In contrast, pure rhodium etched in neither pure gases nor under reaction conditions. In a laminar flow type reactor weight loss of the Pt/Rh gauzes was found to be significant indicating rapid etching and the surfaces smooth and undifferentiated from the untreated material. In contrast, in an impinging jet reactor there was little weight loss, but the surfaces were found to be partially covered by complex particle structures, 1 to 10 μm across. Analysis of the particles showed them to have virtually the same composition as the original gauze. The application of a new model of catalytic etching of single metals to this system explained some, but not all, of the observations. The model explains the limited range of conditions under which etching was observed, as well as the formation of particles in the impinging jet reactor; however, the model failed to explain completely the presence of rhodium in the particles.

INTRODUCTION

Both single metal (*1*) and alloy gauzes (*2–5*) are known to be etched in a number of processes in which they are used as catalysts for high volume reactions. Recent work suggests that etching results from a type of homogeneous/heterogeneous catalysis (*6–9*). That is, it has been postulated that etching results from the interaction of homogeneously formed radical species with the metal surface, and the subsequent formation of a volatile, metastable metal complexes. A similar mechanism has been postulated to explain metal etching in plasma processes of the type used by the semiconductor industry for the fabrication of integrated circuits (*10–13*) as well as the etching of metals in the afterglow of microwave-generated plasmas (*14*).

Prior tests of the newly postulated mechanism of catalytic etching have been restricted to platinum foils (*6*), thin films (*7, 8*), and silica-supported particles (*9*). In this study the etching of Pt/Rh alloy gauze was studied in hydrogen/oxygen mixtures. This is of particular interest as alloy gauzes of this type are used industrially in the oxidation of ammonia (*4, 5, 15*) and the formation of hydrogen cyanide (*1*). In sum the recent model of etching explains many aspects of the results presented here, but some modification is required to explain rhodium enrichment of particles formed in the vapor phase.

EXPERIMENTAL

Reactors

Two different reactors were used in this study and both have been described previously in the literature. Reactor One was used to study weight loss. Essentially, this quartz reactor consists of a coiled preheating section, followed by a straight 10-mm i.d. tube (*6*). Small pieces of sample gauze were placed along the bottom of the straight tube section, attached to chromel–alumel thermocouples. The configuration of this reactor and the resulting flow pattern do not favor the deposition of particles on the gauze surface. The majority of the "volatilized" metal simply washes out of the reactor. (Efforts were made to "catch" volatilized metal on both heated

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and cooled downstream silica beds, but repeated chemical analysis indicated virtually no metal was trapped.)

Reactor Two was used to study the conditions under which etching took place as well as the morphology and composition of particles which formed in the vapor phase and subsequently redeposited on the gauze surface. This reactor has a preheater coil of approximately the same length as that of Reactor One, but at the end of the preheater section gas is forced through a small hole (approx. 1-mm diameter) and impinges on the alloy gauze which sits on a quartz stage about 5 mm below (*7*). This reactor is not useful for gauging weight losses or etch rates as most of the etched metal redeposits on the surface in the form of small particles.

Gas Handling

Ultrahigh purity oxygen, hydrogen, and nitrogen (99.999%), all obtained from Mitchell Industries, were used without further purification.

In all cases the total gas flow rate was 300 cm^3/min as measured at STP. The ratio of hydrogen to oxygen in the gas mixtures used are shown in Fig. 1. Note that reacting mixtures were always 90% nitrogen, with hydrogen and oxygen composing the balance.

Samples

The gauze samples used in this study were all taken from the same piece of Pt 90%/Rh 10% (99.95% purity) supplied by Strem chemicals. Rhodium foil (99.8% purity; 0.025 mm thick) was obtained from Johnson Matthey. In all experiments the gauze was prepared by washing in acetone, and then drying in air. The samples were then weighed on a Cahn microbalance.

The following procedure was employed. Gauze samples were placed in the reactor and the system evacuated to 1×10^{-3} Torr. The system was then filled with nitrogen to a pressure of 5 PSIG. Nitrogen flow was maintained for one hour at room temperature after which the temperature was rapidly raised (ca. 15 min.) to the experimental temperature. Only after the reactor reached the planned experimental temperature was the final gas mixture introduced. The gas mixture, flow rate, and temperature were held at steady values for 45 h (except where specifically noted), at which time the gas mixture was replaced by flowing nitrogen. After 1 h of nitrogen flow the system was cooled to room temperature.

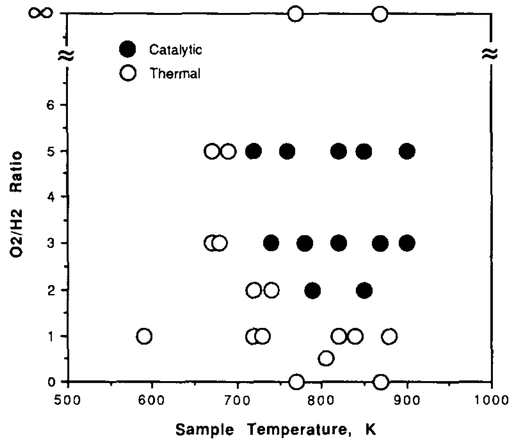


FIG. 1. *Etching conditions*. Etching was found to occur only over a limited range of gas stoichiometries and temperatures. These conditions are virtually identical to those in which pure platinum will etch (see text). A maximum etching temperature (if one exists) was not established, as the explosion hazard was too great at higher temperatures for safe testing.

Electron Microscopy

Two different scanning electron microscopes (SEMs) were used to examine the gauze samples. The ISI Model SX-40A was used simply to obtain clear images of the samples. The second microscope (Cameca Model SX-50 with a tungsten filament) was used for quantitative microprobe studies of cut and polished cross sections of the wire and to obtain quantitative local composition maps. That is, this instrument is equipped with energy dispersive X-ray analysis (EDX) which allowed the approximate local composition to be determined. The EDX was used in two fashions in this study. First, it was used in the "spot" mode in which an

TABLE 1

Weight Loss Experiments

Initial weight (mg)	Final weight (mg)	% Wt. loss	Time (h)	$N_2/O_2/H_2$	Temp. (K)
13.529	13.187	2.53	45	90/7.5/2.5	875
11.937	11.526	3.44	136	90/7.5/2.5	875
12.865	12.450	3.23	91	90/7.5/2.5	800
20.258	19.698	2.76	116	90/7.5/2.5	800
12.458	12.440	0.14	63	90/10/0.0	875
15.590	15.587	0.02	63	90/0.0/10	875
14.684	14.682	0.01	70	90[a]/0.0/0.0	875

[a] Nitrogen saturated with water vapor at 300 K.

area about 2 μm in diameter is sampled (15 kev, 18 nA). Second, it was used in the "map" mode in which a signal from the entire area appearing on the SEM screen is sampled. This mode yields a map of the composition over a large area.

X-ray Diffraction

A Cu*Kα* source in conjunction with a Scintag PAD 5 diffractometer with variable slit width and a lithium-drifted silica detector was used in the X-ray work.

RESULTS

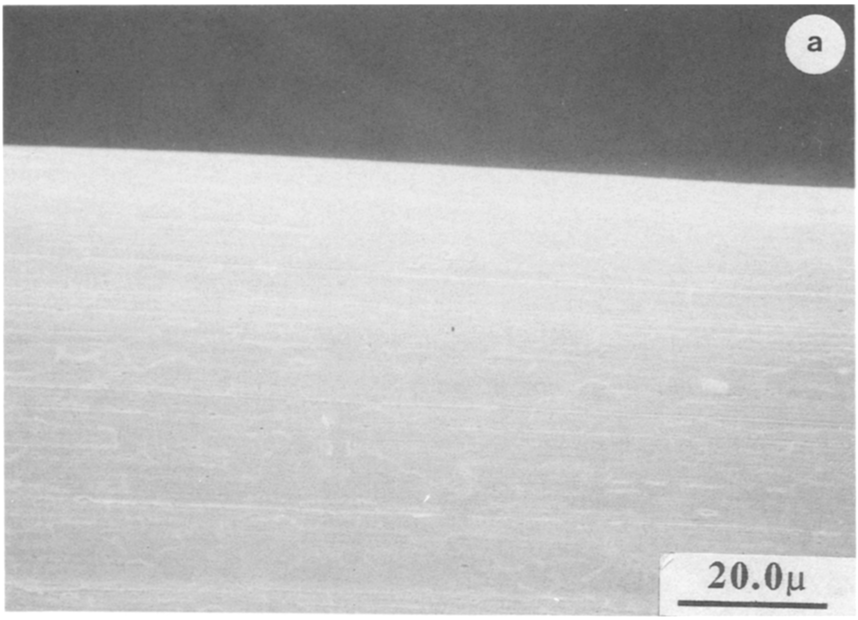
Reactor One

Weight loss experiments conducted in Reactor One clearly show that in hydrogen/oxygen mixtures gauze etching occurs only under those conditions under which platinum foil is found to etch (*8*). No significant weight loss was ever recorded in any of the control (single gas) experiments, or under reaction conditions at temperatures or in gas stoichiometries in which pure platinum does not etch. In Table 1 a list of recorded weight losses as a function of treatment conditions is given. Clearly, in the event that etching took place weight loss was quite significant.

The temperatures in Table 1 were those of the samples, measured with a chromel–alumel thermocouple immediately beneath. The temperature registered by this thermocouple was never more than 20° different, even in reaction conditions, than the temperature of the oven itself, which was measured with a second thermocouple. This result suggests that temperature gradients due to localized reaction on such highly conductive materials are not likely to be large. Extreme local temperatures would be required (ca. 1400 K) for significant metal loss via platinum (*16–18*) or rhodium (*19*) oxide volatilization.

In Fig. 2b is shown a typical view of the surface of a sample which had great weight loss following treatment in Reactor One. There are no visible nonequilibrium structures (i.e., structures which increase the net surface area beyond that predicted on the basis of minimizing the Gibbs Free Energy of the surface). The surface has the same appearance following treatments in which great weight loss was recorded, and following treatments in which no weight loss occurred (Fig. 1a). It was concluded that in the simple configuration of Reactor One volatilized metal largely did not redeposit on the gauze surface. This could result from a variety of factors. Among the possible explanations are the following two: (i) the concentration of metastable species in the vapor phase above the samples never reached high enough concentrations for metal particles to nucleate and grow via gas phase collisional processes (*8*, *20–22*), and (ii) the flow pattern does not favor the deposition of homogeneously formed particles.

Results of EDX studies of the samples following extensive weight loss in Reactor One indicate that the concentrations of platinum and rhodium are virtually identical to those of untreated samples. This result was found, using the spot mode, to be the same whether the EDX was focused on the very edge of a gauze wire or at the center of a wire. This indicates that within the top 1 μm of the gauze there is no significant change in either the rhodium or platinum concentrations. It is important to note that the cross section of all cut and polished wires from Reactor One had smooth edges and regular eliptical shapes. There was no evidence of morphological



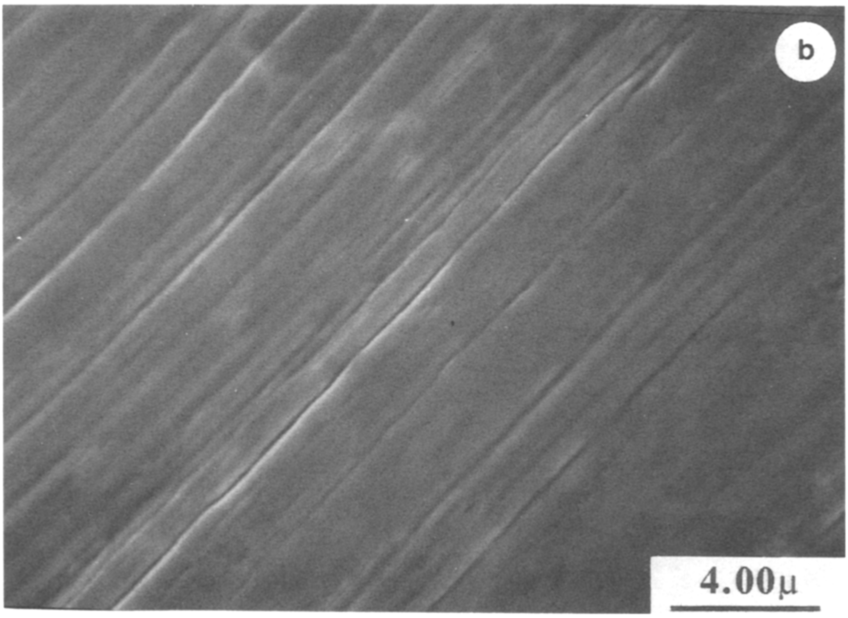


FIG. 2. *Etching without deposition.* (a) The gauze sample shown was treated in pure O_2 for 45 h at 875 K in Reactor One. It is indistinguishable in the SEM from untreated samples and samples treated in the same (laminar flow) reactor. (b) The sample shown was treated in a reaction mixture ($N_2/O_2/H_2$ = 90/7.5/2.5) at 875 K for 45 h in Reactor One, and had a 2.5% weight loss; yet, the surface is indistinguishable from untreated gauze and gauze samples treated in a single gas for the same length of time. Small ridges similar to those shown could be found on any sample treated in Reactor One.

TABLE 2

Rhodium Gauze Experiments

Sample number	Initial weight (mg)	Treatment		Final weight (mg)	X-ray analysis
1	9.280	90/7.5/2.5 875 K	$N_2/O_2/H_2$ 40 h	9.300	Rh_2O_3 formation
2	9.613	90/20/0 875 K	$N_2/O_2/H_2$ 46 h	9.631	Rh_2O_3 formation
3	8.976	90/0/20 875 K	$N_2/O_2/H_2$ 44 h	8.977	No. Rh_2O_3 peaks found

modification resulting from the preparation (cutting, polishing).

Reactor One was used for all control studies. In the case of the alloy samples no weight change was ever detected. In contrast, pure rhodium samples showed small weight gains both in oxygen–nitrogen mixtures and in excess oxygen reaction studies (Table 2). These weight gains could clearly be attributed to the formation of surface layers of rhodium oxide. That is, XRD analysis of these samples always showed the presence of rhodium oxide (Rh_2O_3), which was never present in any of the other samples.

Reactor Two

Following treatment under etching conditions in Reactor Two all samples were found to be covered with particles (Fig. 3). There was a pattern to the particle deposition. In the region of the sample surface directly under the impinging gas jet particles on the order of 1 μm across were found to cover the surface (Figs. 3b,c). In contrast, in a ring about 2 mm in outer diameter immediately outside of the region under the gas jet particle agglomerates were found to cover the surface (Figs. 3d,e). That is, the surface appeared to be covered by a layer of small "balls," each of the order of 5 to 10 μm across. On closer inspection it appears that the balls are actually composed of particles on the order of one micron across. Beyond about 1.5 mm from the center of the impinging jet particle concentration drops sharply, and beyond 2 mm from the center of the sample very few particles were found.

As with Reactor One, results of work carried out in Reactor Two showed that etching was restricted to those conditions under which platinum was found to etch in earlier work. Only under etching conditions (Fig. 1) were structures of the type seen in Fig. 3 discovered. Weight loss proved to be about an order of magnitude less than that detected in Reactor One and was not regarded as a means of distinguishing etching from nonetching processes. This is reasonable as it is clear that in Reactor Two a significant fraction of the initially volatilized metal redeposits on the surface in the form of particles.

The actual composition of the particles was precisely determined using the EDX method described in the experimental section. Distributions of Rh and Pt determined for one sample using EDX are shown in Fig. 4. From this figure it is apparent that the particles contain virtually the same concentrations of Rh and Pt as the wire itself. It is also clear that there are no significant concentration gradients within the wire itself. This same result was found repeatedly. Given the 1-μm sensitivity of the system, it was possible to focus the EDX in the beam mode on larger particles and clusters at the edge of the wires. The results consistently showed that the particles had virtually identical rhodium concentrations as the original gauze. Indeed, an average of eight measures

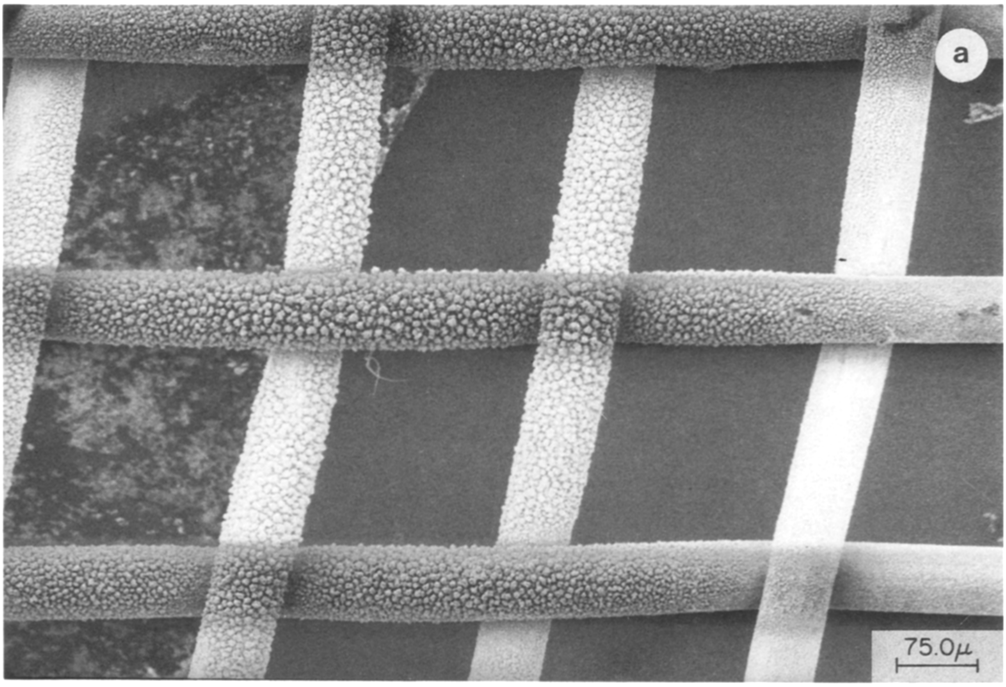


FIG. 3. *Deposition on etched samples.* Samples etched in the impinging flow reactor always had a surface partially covered with particles. The sample shown was treated for 45 h at 875 K in the following mix: $N_2/O_2/H_2$ = 90/7.5/2.5. (a) A long-range view showing areas covered with small particles close to the center of the impinging jet (right side of photo), and large particle agglomerates (left side). (b) and (c) Detail shot of the small particles in the region just below the impinging gas jet. (d) and (e) Detail shot of the large particle agglomerates.

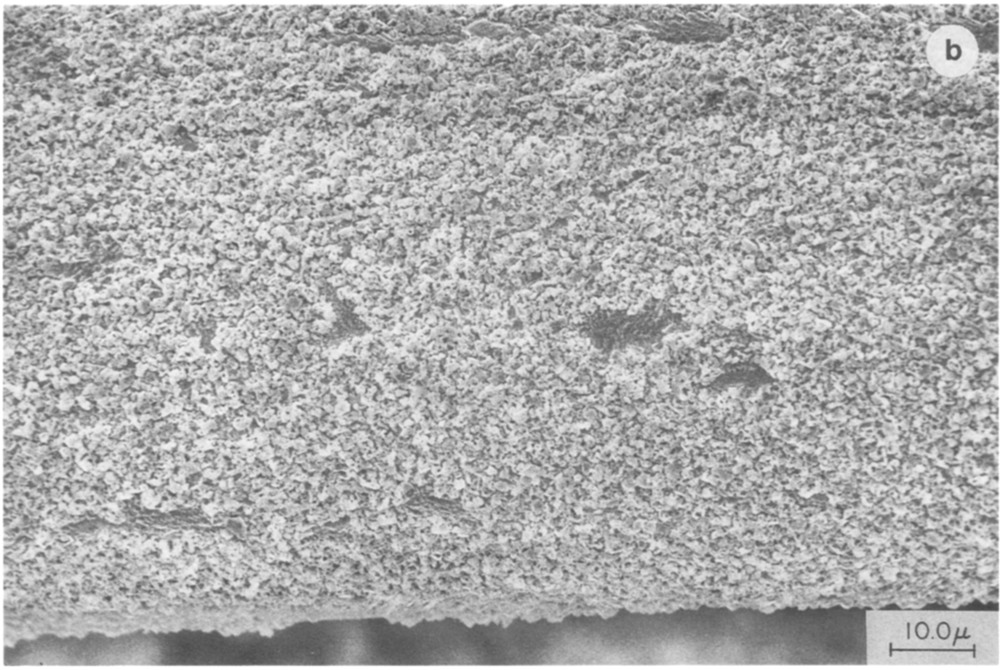
from various wire centers yielded 17.8 atomic% rhodium and an average of eight protrusion measurements yielded the identical result. The only difference was the spread of values. The centers yielded 17.8 ± 0.5%, whereas the protrusion compositions varied from 14 to 23 atomic% rhodium. The gauze itself in these samples had the same composition as untreated gauze. Moreover, there was no difference in composition for the gauze itself as a function of radial position. Compositions measured using the spot made at the edge of the wires were identical to compositions measured in the center.

In several cases, EDX studies of small areas (approximately 50-μm squares) of uncut and unpolished particle covered regions were carried out. In all cases the Pt/Rh ratio was nearly the same as that of the bulk wire. These measurements can only be considered qualitatively correct measures of particle composition as clearly, there is some sampling of the underlying wire.

It might also be argued that the sample preparation (cutting and polishing) "smeared" out the metals. However, as all data showed there was no morphological modification, it was concluded no chemical modification took place.

DISCUSSION

In summary, the following findings were made in the present work. First, pure rhodium is not found to etch in any oxygen/hydrogen mixtures. Second, platinum–rhodium gauzes are etched under the same



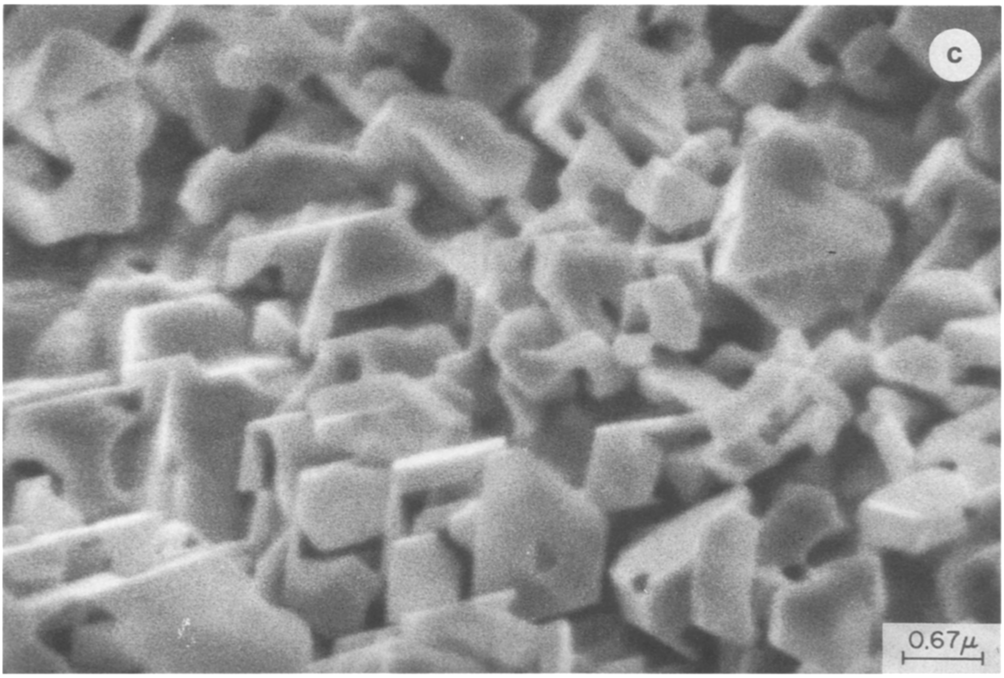
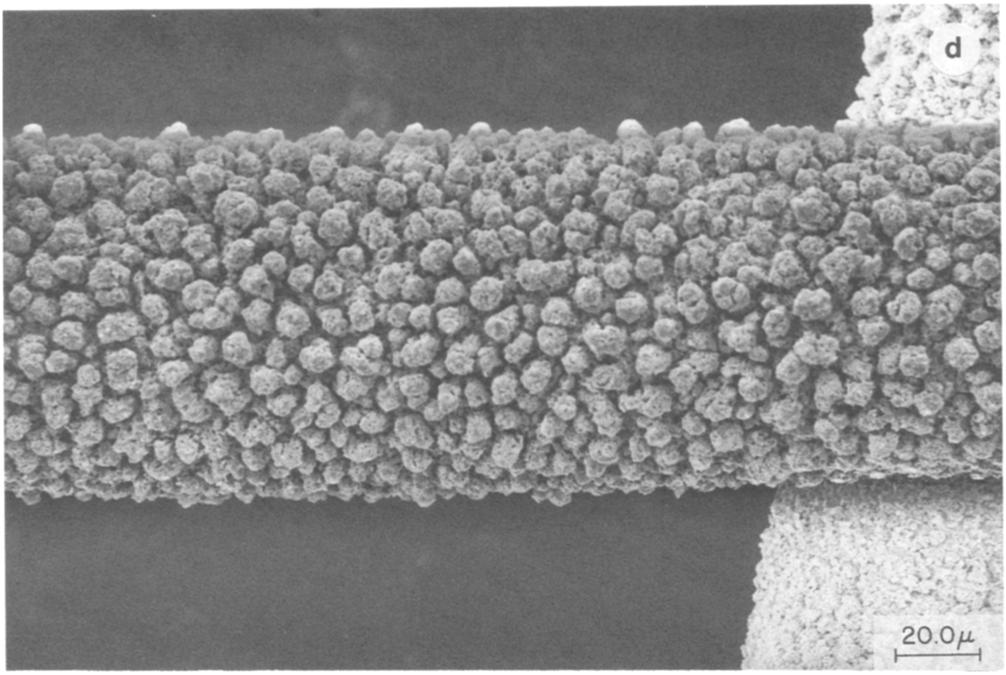


FIG. 3—*Continued*



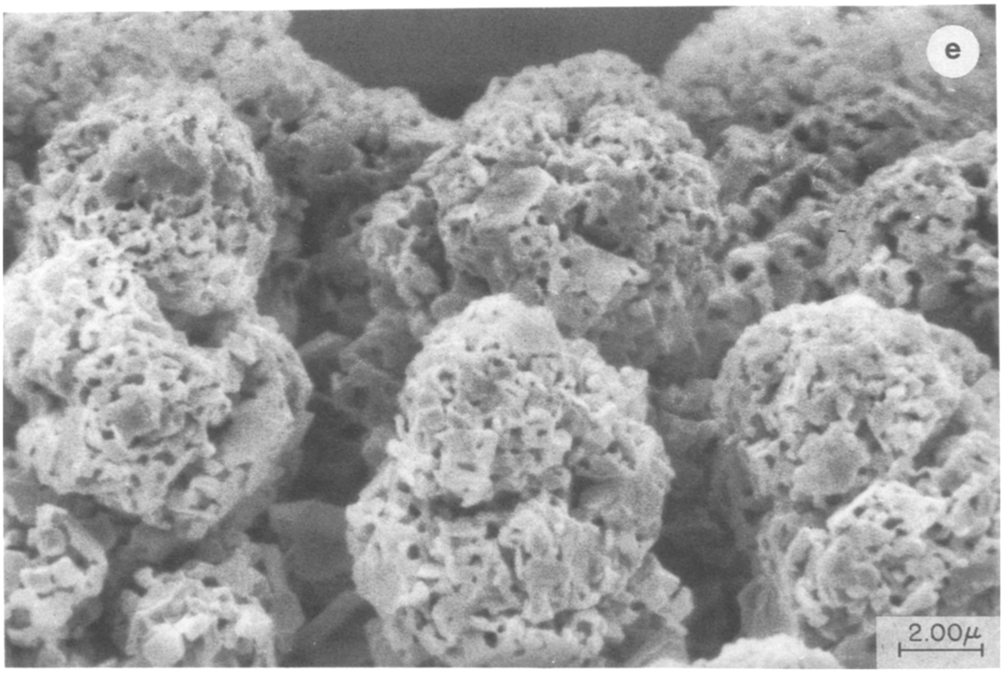


FIG. 3—*Continued*

conditions in oxygen–hydrogen mixtures as pure platinum. Third, all nonequilibrium structures found on the surface are not due to selective metal removal, or surface reconstruction, but rather to the deposit of particles formed via interactions between metastable volatile metal species in the vapor phase. Fourth, the particles which form in the vapor phase have a composition almost identical to the original gauze. These findings are discussed below.

Rhodium, silver (*23*), and palladium (*24*) have been shown not to etch in hydrogen–oxygen mixtures. In fact, it appears that platinum is, for some reason, particularly vulnerable to catalytic etching (*6, 25, 26*).

The finding that the conditions under which Pt–Rh etches are precisely the same as those under which pure platinum etches in the same reactors (*8*) suggests that it is the same homogeneously formed radical, possibly HO_2, is responsible in both cases. Research to test this hypothesis is underway.

There are several reasons for believing that the particles found on the surface of samples treated in Reactor Two were formed in the gas phase. First, there is precedent. Particles of a very similar appearance and size range were found to form homogeneously when pure platinum foils and thin films were etched in the same reactors in the same reaction mixtures. It was established in the earlier studies (but in ethylene/oxygen mixtures) that the platinum particles were forming homogeneously on the basis of a number of findings. For example, individual particles were found as far as a centimeter "downstream" from the nearest platinum.

The second reason for believing that the particles form homogeneously is based on a comparison of the behaviors observed in Reactors One and Two. In Reactor One no particles were found and the rate of weight loss increased with time. In contrast, in Reactor Two very little weight loss occurred, but particles were found on the surface. This can be easily explained on the basis of the proposed model. In Reactor One the flow was steady and laminar, possibly leading to a low concentration of metastable species such that particles do not form. The volatile metal species were simply washed out of the reactor. In Reactor Two (impinging gas jet), very possibly there was a high local concentration of metastable species with a relatively lengthy residence time in the vicinity of the gauze. Particles could nucleate and grow in the vapor phase. Some metal was lost, but most returned to the surface in the form of particles.

The third argument is a thermodynamic one. Initially the total surface area, and thus the surface free energy is at a minimum. There is no known driving force for a surface to spontaneously reconstruct in such a manner that its net surface area increases several fold. In contrast, the formation of particles in the vapor phase and subsequent redeposition is a thermodynamically rational explanation for the observed increase in surface area.

The last point of discussion is the composition of the particles. On the basis of control studies with rhodium and earlier studies with platinum it was anticipated that in an etching environment only platinum would be volatilized, and thus only platinum would be found in the particles. There are a variety of potential explanations for the presence of rhodium in the particles.

The first potential explanation is that only platinum is volatilized and forms particles. Subsequent to particle deposition, rhodium-enriched surface (platinum having been preferentially removed), diffuses and alloys with the platinum. However, this model does not explain the fact that EDX indicates there is no composition profile apparent in the main wire. Even in a sample which lost more than 3% of its total weight EDX did not show a change in wire composition. A 6% loss of platinum only is equivalent to the depletion of all platinum from the top 1 μm of a wire with a 50-μm radius. This would be readily de-

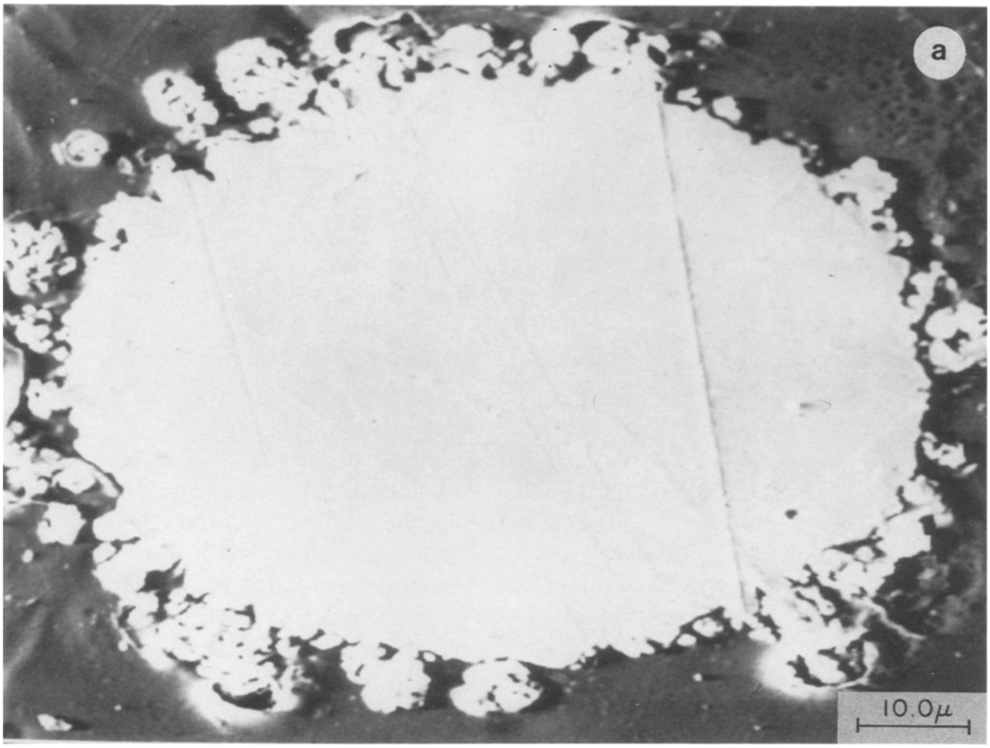


FIG. 4. *Distribution of platinum and rhodium.* (a) SEM photo of a polished cross-section of an area of a sample covered with large particle agglomerates produced during etching in Reactor Two. (b) EDX map of the platinum distribution for the same cross section. (c) EDX map of the rhodium distribution for the same cross section.

tected with EDX unless there was rapid platinum diffusion from the bulk.

The second possible explanation is that rhodium is volatilized from alloy surfaces. For example, possibly platinum helps maintain rhodium in the reduced state when it is part of an alloy. Indeed, it is well known that one noble metal can have a significant impact on the oxidation state of another (*27, 28*). It can then be postulated that rhodium metal can be attacked and volatilized by radical species. This would not be detected in control studies, because in those studies surface rhodium is oxidized and thus protected from volatilization.

A third possibility is that clusters of atoms surrounding a central platinum atom are removed from the surface by attacking radicals. The notion that clusters and not individual atoms are volatilized is consistent with the general understanding of Ostwald ripening (*9, 29*). Thus, in this model platinum and neighboring rhodium atoms are volatilized collectively and the multi-atom clusters which form subsequently interact in the gas phase to form particles containing both metal species.

The major caveat with the last two models is that there is no direct evidence to support them. Thus, in conclusion it can only be reported that some aspects of the catalytic etching of alloys is still not understood.

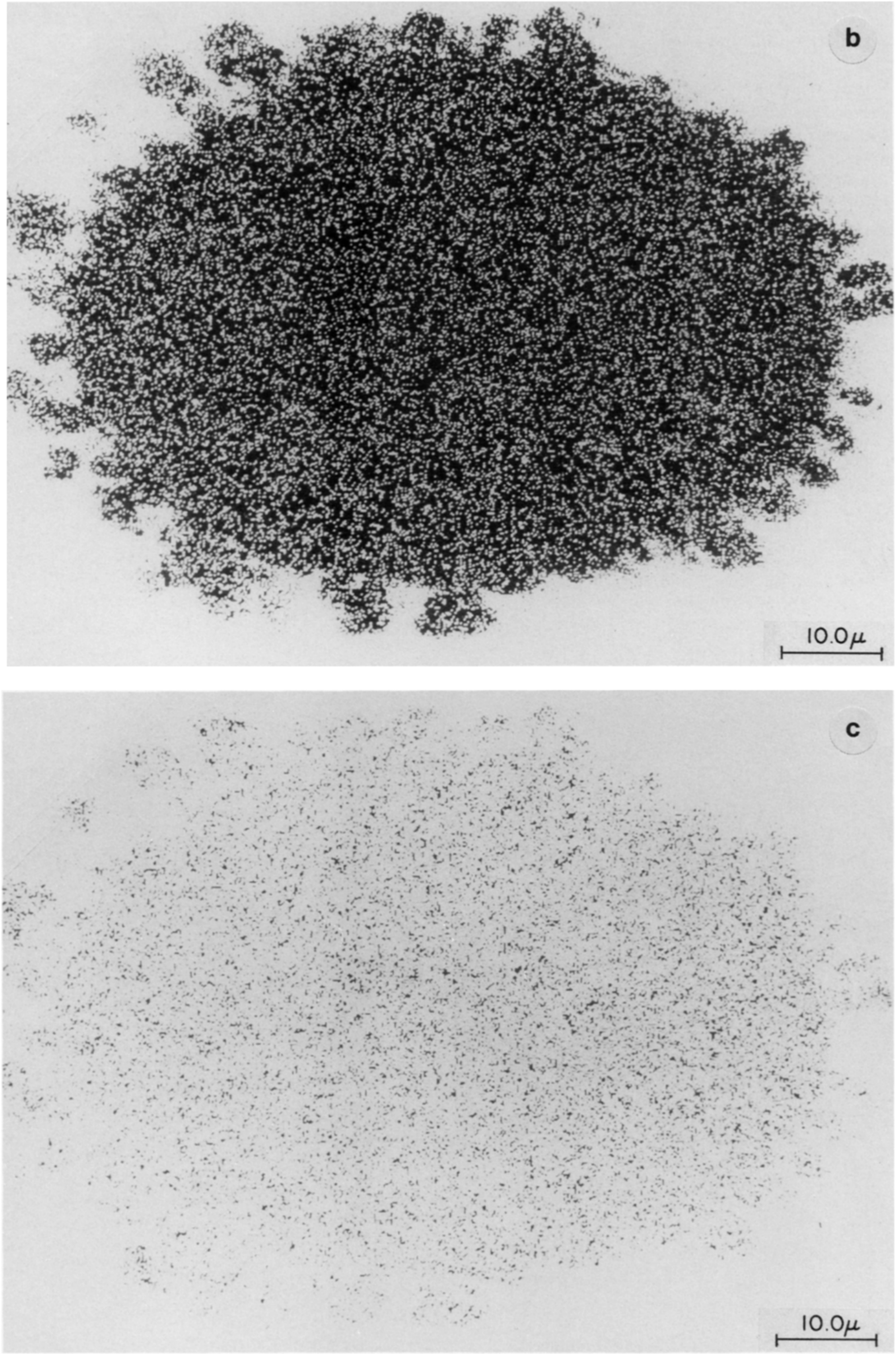


FIG. 4—*Continued*

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