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Direct Observation of Wetting and Spreading of Iridium Particles on Graphite

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Redispersion of sintered metal crystallites is one of the most important and least understood processes in the commercial operation of supported metal catalysts. In the present work we have attempted to gain a clearer insight into this process by following the behavior of a catalyst system inside an electron microscope. The system selected for this investigation was iridium/graphite in hydrogen. Wetting and spreading of iridium particles on graphite in hydrogen at 965°C has been observed directly using controlled-atmosphere electron microscopy. Quantitative measurements of the rate of particle disappearance and the change in contact angle, θ, between the particles and the surface have shown that the spreading can occur below the Tammann temperature of the bulk metal. The results are discussed in terms of a model in which particles have a cherry-like structure, consisting of a "hard core" surrounded by a "viscous" layer. Enhanced atomic mobility in the surface layers may be due to easier surface diffusion as compared to bulk diffusion, possibly due to a higher surface temperature resulting from exothermic processes occurring at the surface.

INTRODUCTION

The important role played by metal–support interactions, as well as by an ambient gas, in the determination of the behavior and bonding of metal crystallites to a support has been known for a long time (*1*). Metal–support interactions and gas pressures do influence the wetting behavior of the metal. Ruckenstein and Chu (*2*) have recently observed and discussed redispersion of platinum crystallites on alumina in the presence of oxygen and have emphasized the role of spreading by wetting.

In their studies, the formation of platinum oxides which are liquid-like at their experimental temperature account for the progressive redispersion of platinum on the support. Two situations are discussed, one in which spreading occurs over the entire surface available when the metal particle is completely oxidized, and another in which a two-dimensional fluid layer of platinum oxide(s) is formed on the platinum particle and moves towards the leading edge of the particle before wetting the support. Their data, obtained in a static fashion at 750°C, which is nearly the Tammann temperature of platinum, hence describe the behavior of metal particles of which the inner core presents some atomic mobility while the outer layer has to be considered a two-dimensional fluid.

We report in this paper quantitative data which describe the wetting behavior of iridium particles on graphite in hydrogen at 965°C, i.e., more than 100°C below the Tammann temperature of iridium. It will be shown that the wetting and spreading behaviors of such particles may be quantitatively described by assuming that the particles have, in such conditions, a cherry-like structure. It consists of an inner "hard core" surrounded by a "viscous" layer which exhibits some atomic mobility as its temperature probably is near, or above the temperature at which surface diffusion (mobility) becomes important. Evidence for such a structure is provided by wetting

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angle and spreading rate dependences as a function of time or particle size.

EXPERIMENTAL METHODS

The dynamic investigations described in this paper were performed in the controlled-atmosphere electron microscope (CAEM) previously described (*3*). The resolution of this technique is limited to 2.5 nm by the presence of a gas and the line scan of the TV monitor, a crucial link in the data collection facility. Reactive gas pressure was maintained at a desired level as measured by barometrically compensated gauges located at a position close to the gas entry port into the microscope. Temperature was measured by means of a Pt/Pt–13% Rh thermocouple spot-welded to the platinum heater strip at a point very close to where the specimen was mounted. Temperature variations across a given specimen were controlled to within ±10°C of the readings stated.

Single-crystal graphite substrates were prepared from crystals obtained from Ticonderoga, N.Y., by a standard method (*4*). Iridium was introduced onto the graphite as an atomized spray from a 0.01% solution of iridium dicarbonyl acetyl-acetonate in acetone. Transmission sections of graphite, 50- to 100-nm thickness, were positioned in such a way that the specimen covered half of the hole in the heater strip. With this arrangement one could simultaneously observe the subsequent behavior of particles supported on the basal plane and along edges of the graphite. The latter capability provided a unique approach to following the changes in interfacial characteristics of the metal and support accompanying reaction with a gas.

The reactant gas in this work, hydrogen, had a stated minimum purity of 99.999% (Scientific Gas Products Inc.) and was used directly.

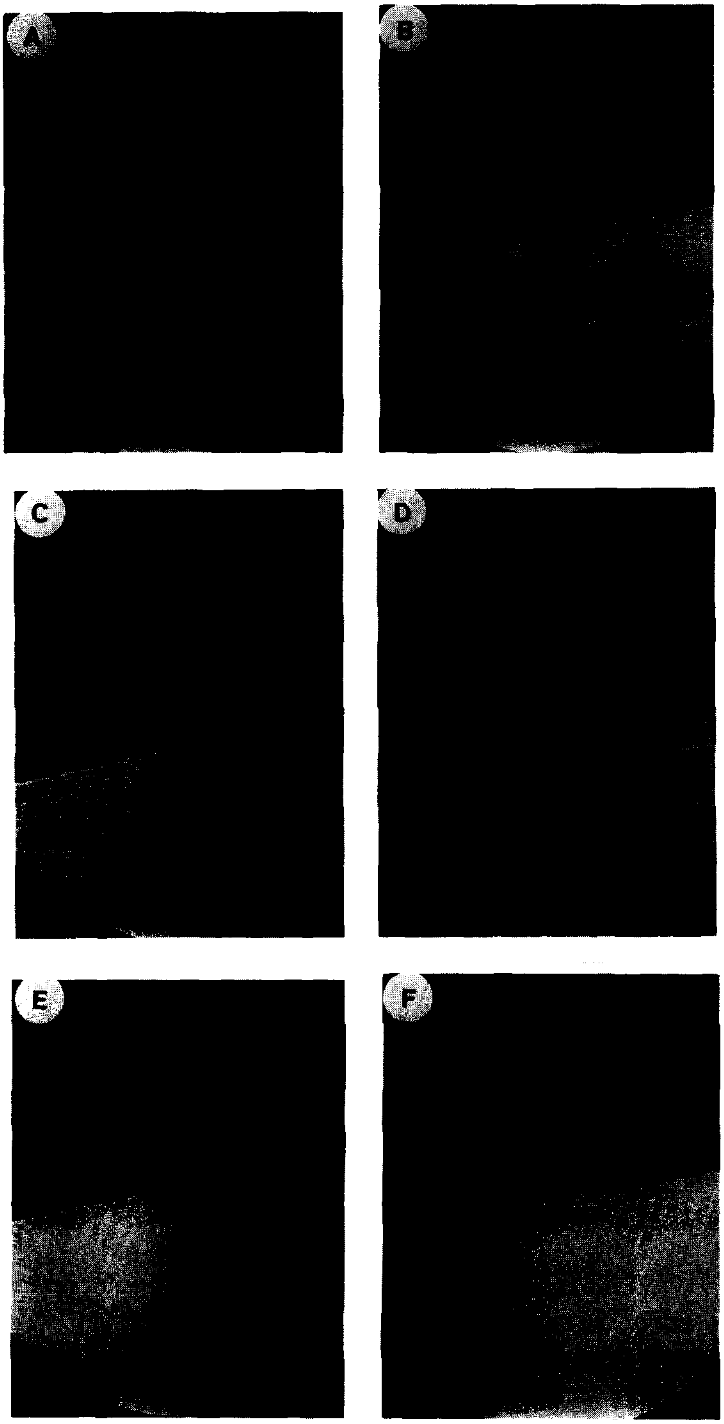
During reaction, changes in the appearance of the specimen were continuously recorded on videotape, and sections of particular interest were later transferred to 16-mm cine-film. Detailed quantitative measurements were made from this film by single-frame projection at a magnification of about 3×10^6.

RESULTS

Particle nucleation was achieved by heating the graphite specimens, coated with iridium dicarbonyl acetyl-acetonate, at 750°C in 1 Torr of hydrogen. Particles were in the range 5 to 80 nm in diameter. They tended to be very dense and had a faceted outline. Upon further heating, still in hydrogen, the particles continued to grow, maintaining the same form until the temperature reached 950°C. At this stage particles became smoother in outline; this feature was seen most easily from particles located on edges. Close examination of these particular regions showed that the contact angle between the particles and the surface was greater than 90°.

At 965°C, however, this geometry rearranged, the contact angle decreasing to a value of 75–85°, showing that the particles were now wetting the surface. On prolonged reaction in hydrogen at this temperature a dramatic change occurred as particles rapidly subsided in the edge so that the original rippled appearance gave way to a smooth profile. This event is presented in a sequence of photographs, Fig. 1A–F, taken from the TV display. Smaller particles were seen to disappear first, and it was also apparent that the initial contact angle of 75–85° was maintained during the depletion of the iridium particles until a smaller and limiting size was reached. At this point, contact angles changed abruptly, ranging from 60 to 70°.

The continuous monitoring of the event (TV, videotape, and transfer to cine-film) enables one to measure the time dependence of the heights and apparent widths of several particles with different initial sizes. Some typical data for two particles presenting an original size of 90–100 nm are listed in Table 1. Figure 2 shows that a linear correlation holds between the width and the



FIGS. 1A–F. Sequence showing the gradual disappearance of iridium particles located on the edge of a section of graphite at 965°C in 1.0 Torr hydrogen.

TABLE 1

Progressive Diminution of Ir Particles on Graphite (P_{H_2} = 1 Torr; T = 965°C)

Time (sec)	W, Width (nm)	H, Height (nm)
0	98.0	65.5
2.72	97.5	61.5
7.21	81.5	53.5
11.70	70.5	45.5
14.14	61.5	37.5
15.37	60.0	33.5
16.59	52.0	27.5
17.68	48.0	22.0
18.77	42.0	14.5
19.72	31.5	7.5
0	96.0	64.0
2.86	95.0	64.0
5.30	83.5	53.5
8.57	76.0	52.0
13.33	62.5	34.5
15.10	53.5	28.0
17.14	42.5	18.5
18.36	36.5	9.5

height of particles belonging to a larger population, even during their progressive depletion as was illustrated in Fig. 1. The behavior of six different particles with initial sizes ranging from 20 to 98 nm was analyzed to obtain the data points of Fig. 2 and they are considered to be representative of the overall sample behavior. This correlation translates quantitatively the experimental observation that the depletion of the iridium particles is rather uniform for sizes larger than 50 nm, while the heights of small particles (<25 nm) collapse faster than their widths. Indeed, the plot does not extrapolate to the origin indicating that particles with nearly zero height still have a reasonable width.

DISCUSSION

The general correlation shown in Fig. 2 points to the existence of a common factor which determines the shape of the iridium particles on the graphite support and describes their progressive spreading.

The observed changes in contact angles, larger than 90° at 950°C, 75–85° when depletion occurs at 965°C, and 60–70° below a certain size indicate that one may be deal-

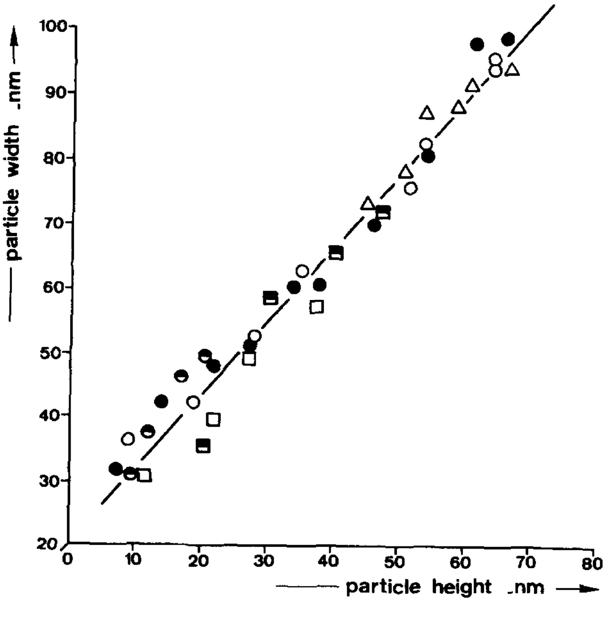


FIG. 2. Correlation between width and height of Ir particles on graphite. Symbols pertain to different initial particle sizes; ● = 98.1 nm, ○ = 96.1 nm, △ = 94.8 nm, ⬒ = 72.1 nm, □ = 58.7 nm, and ◓ = 49.4 nm.

ing with a wetting and spreading phenomenon.

When a metal particle is in equilibrium on a solid support, Young's equation relates the three characteristic surface (interface) tensions: σ_{sg} (support–gas), σ_{mg} (metal–gas), and σ_{ms} (metal–support), such that

$$\sigma_{sg} = \sigma_{ms} + \sigma_{mg} \cos \theta, \qquad (1)$$

θ being the contact angle.

The surface tension of iridium at 965°C (temperature at which wetting is observed, $\theta < 90°$) can be estimated to be about 2920 ergs cm^{-2} (*5*). The surface tension of graphite is not very well known. In a rather recent and extensive discussion (*6*), it was proposed that adopted values for the *c* faces of graphite should be 4800 ergs cm^{-2} at 27°C and 4000 ergs cm^{-2} at 2727°C from which we evaluate σ_{sg} to be about 4500 ergs cm^{-2} at 965°C. The *c* faces of graphite should constitute the edge shown in Fig. 1A–F. No data are available for σ_{ms}, the surface tension between iridium and graphite. Considering an average contact angle of 80° at the beginning of the spreading at 965°C, one calculates a σ_{ms} value of 3990 ergs cm^{-2}. This value compares well with the corresponding data reported for Cu (3400–3700), Ag (3060–4210), and Au (4730) at temperatures near 1000°C (*7*). Hence, we can conclude that, the thermodynamic condition for wetting being fulfilled, wetting will occur provided that atomic mobility is present. It is worth mentioning at this point that the Tammann temperature of bulk Ir is nearly 1100°C.

The change in the particle geometry when the temperature is raised from 950 to 965°C, shown by the variation in contact angle which decreases from a value higher than 90 down to 75–85°, must be associated with a change in the (negative) sign of ($\sigma_{sg} - \sigma_{ms}$) (see Eq. (1)). Thus, either σ_{sg} increases or σ_{ms} decreases. An increase in the value of σ_{sg} may be accounted for by hydrogen spillover: hydrogen atoms produced by dissociation of hydrogen molecules on the metal particle surface diffuse to the support, performing a most efficient cleanup of the graphite surface by removing adsorbed species (*8*, *9*). Wetting of Ir on graphite hence occurs when the graphite surface is "activated" by atomic hydrogen produced on the metal particles (*9*).

Spreading Rate of Iridium on Graphite

In order to express the spreading of Ir as a function of time, with the calculation of spreading rates in mind, one has first to calculate particle volumes from characteristic particle dimensions, i.e., height and width. Two cases must be considered.

In the case of large particles, the contact angle stays rather constant during spreading, i.e., 75–85° (depending on the particle) down to a smaller and limiting size. The depletion of the metal particle also tends to be uniform and there exists a well-defined relationship between height and width as shown in Fig. 2. In this situation, the height, H, of the particle is also larger than its half-width, $W/2$, which we will also refer to as R' as it is the radius of the circumference that circumscribes the particles sitting on the support. The shape of such particles can be approached as depicted in Fig. 3(case 1): they consist of a cylinder of radius R' surmounted by a hemisphere of

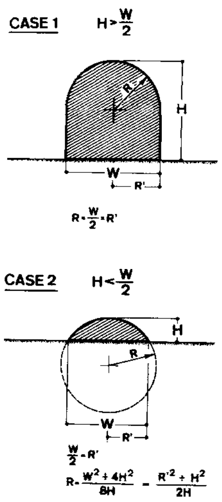


FIG. 3. Schematic representation of the shapes of case 1 (large particles) and case 2 (small particles).

the same radius. The volume, V_c of such particles is then equal to

$$V_c = \tfrac{2}{3}\pi R'^3 + \pi R^2(H - R')$$

or

$$V_c = \pi R'^2(H - R'/3). \tag{2}$$

The second situation (case 2 of Fig. 3) is encountered for small particles (<30 nm). The contact angles are now in the range 60–70° and decrease further with size. The height is smaller than R', and it decreases much faster than the particle width. The particle shape can now be approximated as a spherical cap. The radius, R, of the corresponding sphere is given by

$$R = (R'^2 + H^2)/2H \tag{3}$$

and the volume, V_{sc}, of the (spherical-cap) particle is

$$V_{sc} = \pi H^2(R - H/3). \tag{4}$$

Equations (2) and (4) have been used to compute, using the data of Table 1 as examples, the plots shown in Fig. 4. They represent the variation of particle volume as a function of time and enable the calculation of spreading rates at various time intervals. As shown in Table 2, the spreading rate is found to decrease with increasing time. The time dependence of R' (the particle half-width) is directly obtained from a plot of the experimental data; corresponding values are also listed in Table 2.

It is then possible to express the spreading rate as a function of R', or the particle width $2R'$:

$$\Delta V/\Delta t = k(2R')^n \tag{5}$$

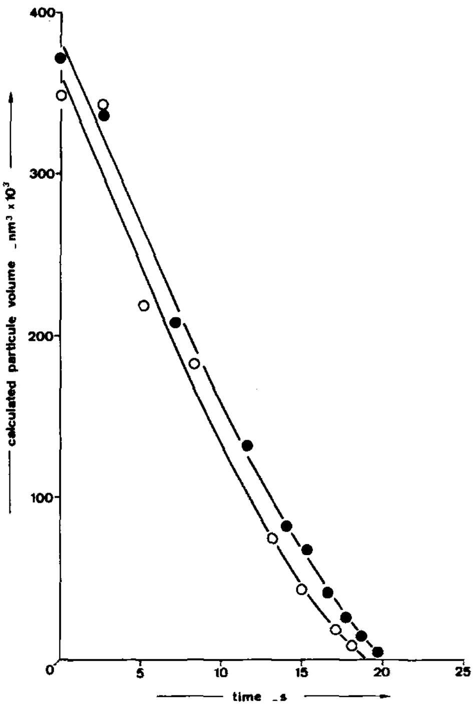


FIG. 4. Variation of calculated particle volume as a function of time, for two particles of initial size ● = 98.1 nm and ○ = 96.1 nm.

or

$$\log(\Delta V/\Delta t) = \log k + n \log(2R'). \tag{6}$$

Such plots are shown in Fig. 5. It is seen from these that $n = 0.5$ for particles larger than about 70 nm. and that $n = 1$ for smaller particles. The transition occurs when the particles have diminished to about one-third of their original sizes (for the 90 to 100-nm particles considered as examples). It is also at the same time that the contact angle charges abruptly from 75–

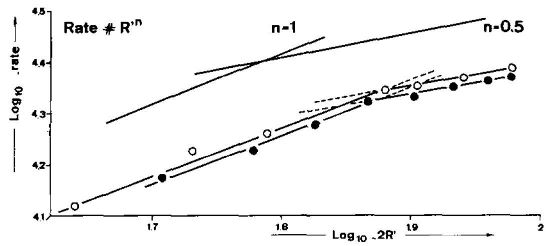


FIG. 5. Plot of spreading rate as a function of particle width, for the same particles as in Fig. 4.

TABLE 2

Time Dependence of the Spreading Rate of Iridium on Graphite[a]

Time (sec)	Volume, V (10^3 nm^3)	Width ($2R'$) (nm)	$\Delta V/\Delta t$ (10^3 nm^3 sec^{-1})
1	360	97.5	—
3	314	95.0	23.5
5	268	91.0	23.0
7	223	85.5	22.5
9	180	80.0	21.5
11	138	73.5	21.0
13	100	67.0	19.0
15	66	60.0	17.0
17	36	51.0	15.0
1	340	97.0	—
3	291	95.5	24.5
5	245	87.0	23.0
7	200	81.5	22.5
9	156	75.5	22.0
11	116	69.0	20.0
13	80	62.0	18.0
15	46	54.0	17.0
17	20	43.5	13.0

[a] Values calculated from the data of Table 1 as described in the text.

85° down to 60–70°, from where it further decreases smoothly.

The "Hard-Core" Model

Ruckenstein and Chu (*2*) have recently discussed the spreading of Pt crystallites on alumina in terms of wetting, explained by the formation of platinum oxide in the presence of oxygen. Two types of behavior were observed. In the first one, no wetting angle can exist between the crystallites and the surface, and spreading must therefore occur on the entire available surface. In the second case, crystallites are coated with a thin layer of platinum oxide as a "two-dimensional fluid, a bilayer, or a multilayer." This platinum oxide was supposed to spread onto the oxide support "through the leading edge of the crystallite." Spreading was observed to occur in oxygen at 750°C, which is also near the Tammann temperature for Pt, and at which platinum oxides are known to be in the liquid state.

Our observations for iridium on graphite are at variance with the former one, in the following way:

1. As shown previously one may reasonably propose that iridium will wet a clean surface of graphite at 965°C, this without the need of an adjuvant gas.
2. At 965°C, iridium will not form with hydrogen a compound that could wet the surface by spreading.
3. Spreading of iridium on graphite in H_2 occurs at an experimental temperature which is about 100°C below the Tammann temperature.
4. The rate of spreading decreases with size, while from the model of Ruckenstein and Chu one could expect an increase of the spreading rate for smaller particles because of a Kelvin-type effect.

Also, we have to account for additional and quantitative data obtained in dynamic conditions:

1. the dependence of the spreading rate on particle size;
2. the change in contact angle that accompanies the change in spreading regime;
3. the general relationship which correlates the height and width of various particles.

For a wetting phenomenon to occur and to be observed, both thermodynamic (Young's equation) and kinetic (atomic or molecular mobility) requirements must be realized. Such requirements are easily accounted for in the Pt–Al_2O_3 experiments of Ruckenstein and Chu; we, however, must explain the iridium atom mobility observed at an experimental temperature below the Tammann temperature of the bulk metal. A reasonable assumption in this respect is to consider that the actual temperature (of the surface) of the metal particle differs from the set-temperature because of an external extra-heat input. As Ir spreading is observed only in the presence of H_2, no gasification of graphite being however observed in these conditions, we propose that the extra heat is that provided by the continuous chemisorption on iridium of hydrogen which eventually spills over to the graphite surface. The particle can then be viewed as depicted in Fig. 6A. It consists of a "hard core" which has a temperature below the Tammann temperature and of a mobile "surface layer" above the Tammann temperature, in which some mobility does exist. We will refer to this as the "cherry" structure.

The spreading phenomenon, as well as its essential and quantitative features, is then easily depicted. Atoms in the mobile surface layer are spreading to the graphite through the leading edge, as iridium is wetting graphite in our conditions. This leads to a depletion of iridium and a decrease of particle size, without a change of the wetting angle that is determined by the skeleton of the particle, i.e., its "hard core." As the particle volume progressively decreases, the proportion of atoms in a mobile state will increase because of an increase in surface-to-volume ratio and overall particle temperature. This is shown in Fig. 6B. Ultimately, as depicted in Fig. 6C, the hard core will disappear. This transition point is easily observed as it implies an abrupt change of the wetting angle (which decreases experimentally from 75–85 to 60–70°). Indeed, the temperature of iridium in the mobile state is higher than that of the hard core, meaning a lower σ_{mg} surface tension and a lower wetting angle according to Young's law (see Eq. (1)). The spherical-cap particle, at a temperature higher than the Tammann temperature, will then spread further.

This qualitative description is supplemented quantitatively by the spreading rate data. As shown in Fig. 7, three different regions can be considered to describe the depletion of iridium from a cherry-like particle sitting on a graphite surface. In region I, atoms move towards the leading edge of the metal particle. In region II, Ir atoms hop across the iridium–graphite boundary (which implies the existence of an energy barrier) and it is logical to assume that the "hopping" rate, r_h, is proportional to the length of the leading edge, i.e., $2R'$:

$$r_h \propto k_h R'. \tag{7}$$

In region III, Ir atoms diffuse on graphite; the rate of this process is not affected by the intimate nature of the original metal particle (cherry-like or cap-like) and should be rather high as Ir wets graphite.

Hence, for small cap-shaped particles, it is foreseen that step II will be rate determining (as region I does not exist) and therefore

$$\Delta V_{sc}/\Delta t \propto R' \tag{8}$$

as observed experimentally (see Fig. 5). Larger particles present a hard core and the spreading rate will be affected by the features of both regions I and II. An iridium atom must now first diffuse to the leading edge of the particle and then hop onto the graphite surface. By analogy with classical reaction kinetics for consecutive processes, one may write as a first approximation that

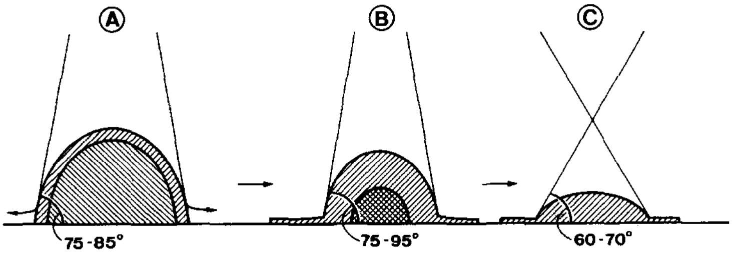


FIG. 6. Iridium particle depletion on graphite. The "hard-core" model.

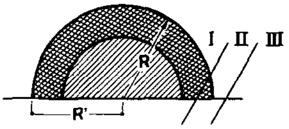


FIG. 7. Schematic representation of the three diffusion regimes operative in particle spreading on a support.

$$\Delta V_c/\Delta t \propto r_I \cdot r_h, \tag{9}$$

where r_I is the rate-determining factor in region I, r_h being given by Eq. (7). It is observed experimentally that $\Delta V_c/\Delta t \propto R'^{1/2}$ for large particles, which leads to

$$r_I \propto R'^{1/2}. \tag{10}$$

This indicates that for large "hard-core" particles, there will exist a deviation of the rate of spreading from the linear dependence on particle size. The larger the particle size, the larger the discrepancy will be. It is tempting to identify the behavior in region I to that of iridium atoms, in a "viscous" layer supported by a "hard core," diffusing towards the leading edge of the particle. The ($R'^{1/2}$) dependence of the rate of this process would eventually support such a proposal.

The "hard-core" model is essentially different from the models discussed by Ruckenstein and Chu (*2*) as it describes the behavior of a metal particle which is spreading below the Tammann temperature, because of an enhanced atomic mobility in its surface layers. The latter may be at or above the Tammann temperature as a result of an external heat input. In the case of Pt on Al_2O_3, mobility was virtually present everywhere in the metal particle: the Pt core was nearly at Tammann temperature, Pt oxides were liquid or volatile at the same temperature.

The "hard-core" model should also apply in principle to systems composed of small particles, for which surface diffusion will ensue at 0.3–0.37 of the melting point T_m (*10, 11*) compared to 0.5 T_m for bulk diffusion. At an intermediate temperature, atomic mobility being enhanced in the surface layers, the cherry-like model can also be maintained due to the high surface-to-volume ratio. However, the concept of surface and core diffusions alone can not explain the data for the iridium-on-graphite system, as spreading is observed only in hydrogen, for rather larger particles (90 nm) and at a temperature (965°C) well above those (550–743°C) at which surface diffusion is expected to occur.

CONCLUSIONS

The present work has shown that metal particles on a support, e.g., iridium particles on graphite in the present case, can actually spread by wetting below the Tammann temperature. Higher atomic mobility may be present in a surface region possibly as a result of exothermic surface processes which increase the local temperature. Such particles present a cherry-like structure consisting of a "hard-core" and a "viscous" layer, above a certain size. The presence of the "hard core" affects the spreading rate as well as the wetting characteristics of the metal particles. It is shown that the depletion of the small iridium particles is kinetically controlled by particle size.

The "hard-core" model complements the observations recently reported by Ruckenstein and Chu (*2*). It brings in quantitative kinetic data and enlarges the scope of theories of spreading by wetting towards lower operating temperatures.

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