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Mobility of Metal Particles on a Graphite Substrate

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THE explanation formulated by Sears and Hudson¹ to account for the unexpected mobility of silver crystallites on surfaces of graphite and molybdenite² is of particular relevance to some observations made³⁻⁵ recently by us in the course of a study, using time-lapse photomicrography, of the influence of metal impurities on the oxidation of graphite monocrystals. It is possible^{1,5} that the mobility represents Brownian motion of the particles; and, according to Sears and Hudson,¹ the motion takes place over a chemisorbed layer of gas on the substrate, there being weak interaction between the mobile particle and the substrate itself. Moreover, the cessation of mobility is interpreted to indicate that true contact between the particle and the substrate has been established because, at the onset of immobility, the critical shear stress associated with the movement of the particles has increased abruptly.

In our experiments, motion pictures were taken (using a 16-mm movie camera mounted on a Leitz Panphot microscope fitted with a hot stage) of the movement of metal particles on the cleavage {0001} faces of Ticonderoga graphite crystals at temperatures in the range 630° to 850°C, and in a variety of gases. Cleaved crystals of graphite were produced by attaching the top and bottom faces of the natural graphite crystals to clean glass slides using Duco cement. The actual cleavage was effected by gentle rotation of the glass slides, and the cement was removed completely with acetone. Several metals were employed; the mean particle diameter varied from metal to metal, but was never greater than a few microns. The gases used (N₂, Ar, O₂, and CO₂) were all stringently dried beforehand.

In Ar and in N₂, particles of silver (at 630°C) and, to a lesser extent, particles of tantalum (at 720°C), were observed to execute rotary motion about an

axis perpendicular to the graphite surface. Some random translatory motion over the surface was also observed. Particles of iron, cobalt, nickel, and manganese on the other hand, remained immobile for periods of several hours under these conditions. Of the last named metals, cobalt displayed the most remarkable pattern of behavior. In the presence of O₂ at 720°C this metal, being a good catalyst for the oxidation of graphite, carved out channels a few microns deep across the graphite surface. This channeling seemed to persist for as long as the cobalt remained as the free metal. At 750°C cobalt particles situated on the graphite surface could be partially oxidized without at the same time oxidizing the graphite to any significant extent, by exposing the solids to an atmosphere of CO₂. When this was done the cobalt particles were seen not to move at all throughout the period of oxidation, which was 65 min. However, once the CO₂ was replaced by O₂, the oxide-coated cobalt particles became virulently mobile and also rotated briskly. No channels were now produced. In about one hour at 720°C a few large agglomerates, which continued to rotate and migrate, were formed from the numerous separated particles of oxide-coated cobalt originally distributed over the graphite surface.

We are not here concerned with the mechanism for the channeling of the cobalt particles along the surface during the oxidation of the graphite—this is a manifestation of the previously described^{6,7} crystallographically sensitive type of catalysis, the mechanism of which is still enigmatic. What is noteworthy in the present context is, (i) the mobility of certain metals and the immobility of others under apparently identical conditions, and, (ii) the profound influence of the nature of the gaseous environment on the mobility of some metal particles.

It is evident that, in order to explain (i) above, certain chemical factors must be incorporated into the physical interpretation of Sears and Hudson. Thus, the oxide film on the metal may well play an important role, it being conceivable that an oxide-coated particle may require a much smaller critical shear stress for mobility than does the metal particle itself. However, it is difficult to account for (ii) above, in terms of oxide layers alone, for the oxidized cobalt particles are immobile in CO_2 and mobile in O_2 atmospheres. To surmount this difficulty, and preserve the Sears-Hudson interpretation, we could postulate that the graphite surface is more likely to be extensively covered with chemisorbed oxygen upon exposure to O_2 than to CO_2 ⁸ at the same temperature. Caution is required here for it is doubtful whether the carbon atoms constituting the {0001} faces of graphite are capable of chemisorbing oxygen to any appreciable extent.⁹ However, the cleavage surfaces of graphite, especially those of partially oxidized crystals, often consist^{6,7} of numerous steps ranging in height from 10 to 1000 Å or more. The carbon atoms exposed at these steps are capable of

accommodating adsorbed oxygen which may, in turn, facilitate particle mobility.

Clearly, before we can interpret fully, in terms of Brownian motion, the movement of particles over a foreign substrate, the detailed chemical properties of the particle and substrate need to be taken into consideration. In particular, it is necessary to ascertain if, or how, the chemisorbed oxygen layer, over which the particle is thought to move, is displaced or removed and so engenders particle immobility.

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² G. A. Bassett, *Proc. European Regional Conf. Electron Microscopy*, Delft, 1960, **1**, 270 (1961).

³ J. M. Thomas, *Advances in Carbon* (to be published).

⁴ J. M. Thomas and P. L. Walker, Jr. (in preparation).

⁵ G. R. Hennig, *Proc. 4th Carbon Conf.*, Buffalo, 1959. **1960**, 145.

⁶ G. R. Hennig, *J. Inorg. Nucl. Chem.* **24**, 1129 (1962).

⁷ Glenda Hughes, Ph.D. thesis, University of Wales, 1963.

⁸ CO_2 is not chemisorbed as such, at high temperatures, on graphite. A surface oxide similar to the oxide produced by chemisorption of oxygen is produced: $\text{CO}_2 + \text{C} \rightarrow \text{C}(\text{O}) + \text{CO}$, where C(O) symbolizes the surface oxide.

⁹ N. R. Laine, F. J. Vastola, and P. L. Walker, Jr., *J. Phys. Chem.* **67**, 2030 (1963).