

5. Holliday J. E., *J. Appl. Phys.* **33**, 3259 (1962).
 6. Fischer D. W. and Braun W. L., *J. Chem. Phys.* **43**, 2075 (1965).
 7. Sagawa, T., *J. Phys. Soc. Japan* **21**, 49 (1966).
 8. Weisweiler W., *Proc. Vth Int. Conf. X-Ray Optics and Microanalysis*, Berlin-Heidelberg-New York, Springer, Berlin (1969).
 9. Weisweiler W., *Ber. dtsh. Keram. Ges.* In Press.
 10. Coulson J. A. and Taylor R., *Proc. Phys. Soc.* **A65**, 815 (1952).
 11. Corbato F. J., *Proc. 3rd Conf. Carbon*, p. 173, Pergamon Press, Oxford (1957).
 12. Beardon J. A., *Rev. Mod. Phys.* **39**, 78 (1967).
 13. Ergun S., *J. Appl. Cryst.* **1**, 19 (1968).

Bureau of Mines, S. ERGUN
 U.S. Department of the Interior,
 Pittsburg, Penna. 15213, U.S.A.

Institut für Chemische Technik, W. WEISWEILER
 Universität Karlsruhe,
 Karlsruhe, Germany

Carbon 1970, Vol. 8, pp. 103-104. Pergamon Press. Printed in Great Britain

The Catalyzed Disproportionation of Carbon Monoxide

(Received 19 September 1969)

We report herein the results of a preliminary survey of some of the phenomenological aspects of the deposition of carbon from CO-H₂ mixtures (ratio used was 91:9) on sixteen different kinds of solid surfaces. Certain aspects of this reaction, which is of enormous importance in the steel and nuclear-reactor industry, has been studied [1, 2] in this laboratory previously. The stoichiometry is established to be $2\text{CO}_{(g)} \rightleftharpoons \text{C}_{(s)} + \text{CO}_{2(g)}$, and gravimetric and X-ray diffraction measurements have shown that the carbonaceous deposit, which may be filamentary or plate-like, contains appreciable quantities of the nutrient metal on which it grows, the percentage of metal in the carbon steadily diminishing with time. We have obtained supplementary information using time-lapse cinematography similar to that employed [3, 4] by us in the etching of graphite, and the catalysis of gasification of carbon, and not unlike the procedure [5] adopted by Gwathmey and his coworkers in their classic studies of deposition on metal single crystals.

The apparatus consisted of a 16 mm camera mounted on a microscope fitted with a long-working-distance objective and a (non-evacuable) hot-stage. Unpolarized light from a tungsten lamp served as (vertical) illumination; the net magnification on the film plane was *ca.* × 40 so that surface details in the range 1-3 μm could be resolved. All experiments were carried out at atmospheric pressure in a flow system (1600 cc min⁻¹), the pro-

cedure being to heat up the catalyst (*in situ*) to working temperature in an atmosphere of hydrogen, followed by introduction of the reactive gas. Deposition of carbon, and other changes were followed by time-lapse photography for periods ranging from 10 min to 5 hr after the introduction of the reactive gas. In this time, for the more reactive catalysts, several mg of carbon were deposited [1, 2]. The catalysts used were:

- | | |
|---------------|---|
| <i>Iron</i> | <ol style="list-style-type: none"> 1. electropolished, single crystal, (491) and (211) faces; 2. mechanically polished, single crystal; 3. polycrystalline foil-degreased; 4. polycrystalline foil, annealed so as to increase crystallite size, and wet-etched (nitric acid) to reveal grain boundaries and dislocations; 5. polycrystalline iron powder supported on iron single crystal; 6. electropolished 3% silicon-iron, (491) and (211) faces; 7. mechanically polished single crystal of 3% silicon-iron; |
| <i>Cobalt</i> | <ol style="list-style-type: none"> 8. mechanically polished, single crystal, with (0001) faces predominant; 9. polycrystalline cobalt powder on iron single crystal; 10. polycrystalline cobalt powder on cobalt single crystal; |
| <i>Nickel</i> | <ol style="list-style-type: none"> 11. electropolished single crystal, (110) oriented; 12. mechanically polished single crystal, (110) oriented; 13. iron powder on single crystal nickel; 14. iron powder, plus cobalt powder on single crystal nickel; |

Platinum 15. polycrystalline foil with grain boundaries etched thermally;

Quartz 16. fused quartz (silica) disc.

Single crystals of nickel, single crystals of cobalt, and single crystals of both iron and silicon-iron along with the polycrystalline iron foil (etched or unetched), the polycrystalline powders of Fe, Co and Ni and various combinations of these solids all proved to be catalytically active (i.e. mg amounts of carbon were deposited in less than 10 hr at 800°C). Some of these surfaces, e.g. nickel, did not, however, yield any visible deposits of carbon on crystallographically well-defined faces in less than 5 hr. Whereas platinum and silica were totally inactive in the initiation of deposition, they could, nevertheless, sustain, for rather short periods, the growth of carbonaceous particles which had previously been deposited on iron. The more noteworthy features of the active catalysts were:

(i) Faceting of the catalyst, which entails rearrangement of the surface from one crystallographic orientation into two or more different kinds of orientation may occur during catalysis. This tendency is pronounced in cobalt, which appears to form a surface carbide phase rather readily.

(ii) Certain types of dislocation cores in iron function as active centers, see Fig. 1, which is a scanning-electron micrograph which shows filamentary carbon located at dislocation-etch pits. It is not yet clear whether the dislocation *per se* displays enhanced catalytic activity, or whether its role is simply to facilitate the growth of the carbon following deposition.

(iii) The deposited carbon can migrate over the surface, during catalysis, and the polycrystalline catalysts (especially iron) execute discontinuous movements (probably arising from unbalanced momentum transfer) during the deposition.

(iv) The catalytic activity of iron is dependent, in a complicated fashion, upon the oxide thickness. The precise nature of the interface, and the exact form of the oxide is of vital importance in this regard, which probably accounts for the conflicting reports in the literature [6, 7] on this subject.

(v) Mechanically polished iron and silicon-iron surfaces are better catalysts, and the activity is more uniformly distributed over the surface, than their electro-polished analogues.

(vi) No significant differences appear to exist between the {211} and {491} faces of iron and silicon-iron.

(vii) The activity of polycrystalline iron (mean diameter of particles 3 μm) appears to be influenced by the support material: it is less, by a factor of roughly three, on cobalt than on nickel.

(viii) With nickel as catalyst support, upon which there is no visible deposit, the ratio of the rates of deposition on polycrystalline iron and cobalt is 10:1 at 800°C.

More fundamental studies of some of these phenomena are now being pursued.

Acknowledgement—This study was supported by the Atomic Energy Commission on Project Number AT(30-1)-1710.

P. L. WALKER, JR.

*Department of Materials Science,
The Pennsylvania State University,
University Park, Penna. 16802, U.S.A.*

J. M. THOMAS

*Edward Davies Chemical Laboratories,
University College of Wales,
Aberystwyth, Wales, U.K.*

REFERENCES

1. Walker P. L., Jr., Rakszawski J. F. and Imperial G. R., *J. Phys. Chem.* **63**, 133 (1959).
2. Walker P. L., Jr., Rakszawski J. F. and Imperial G. R., *J. Phys. Chem.* **63**, 137 (1959).
3. Thomas J. M., In *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.), Vol. 1, p. 121. Dekker, New York (1965).
4. Thomas J. M. and Walker P. L., Jr., *J. Chem. Phys.* **41**, 587 (1964).
5. Meelheim R. Y., Cunningham R. E., Lawless K. R., Azim S., Kean R. H. and Gwathmey A. T., *Proc. 2nd Int. Congr. Catalysis*, Vol. 1, p. 2005. Technip, Paris (1961).
6. Akamatu H. and Sato K., *Bull. Chem. Soc. Japan* **22**, 127 (1949).
7. Everett M. R., Kinsey D. V. and Romberg E. In *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.), Vol. 3, p. 289. Dekker, New York (1968).

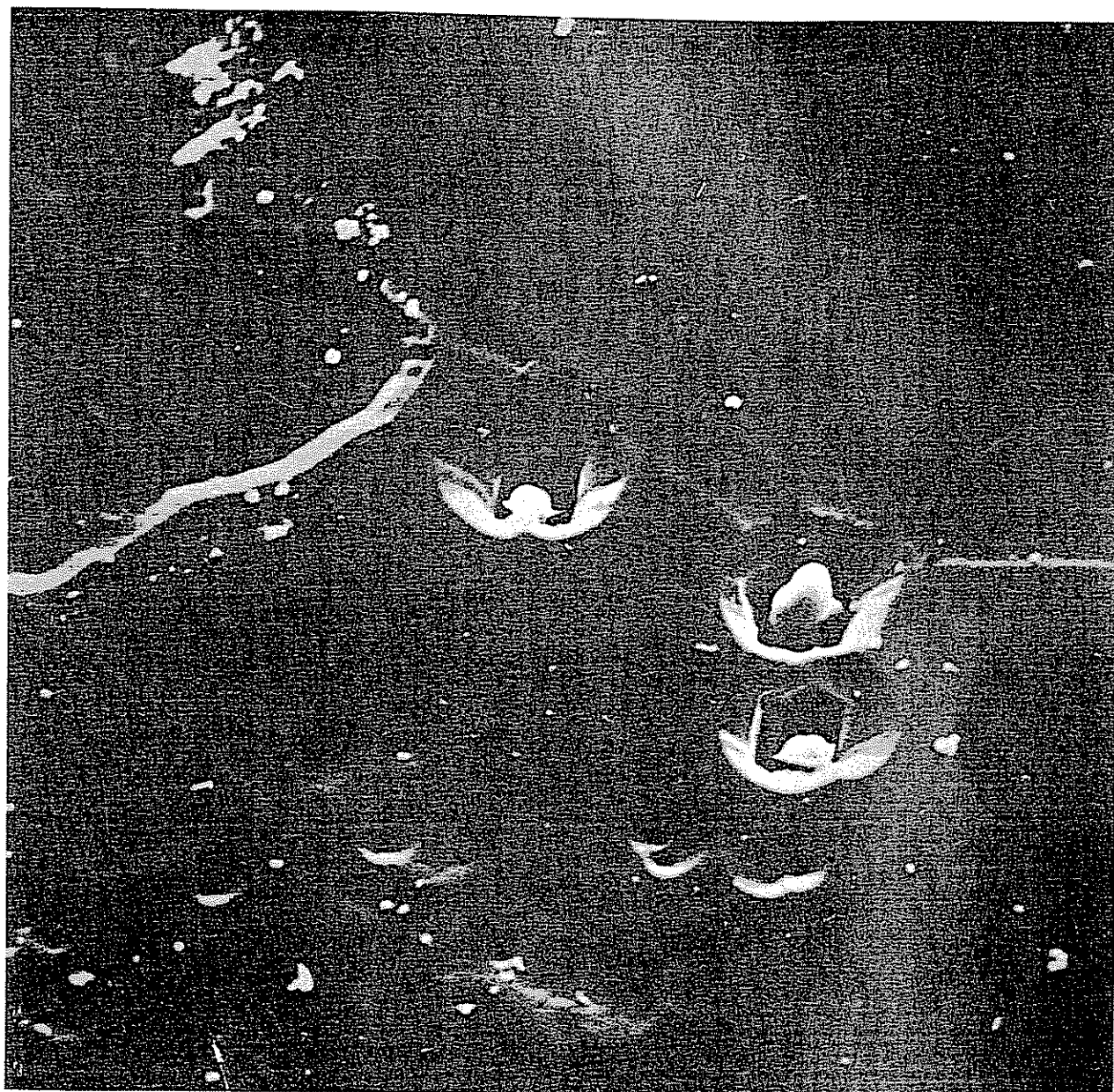


Fig. 1. Scanning-electron micrograph of iron crystal (previously etched to locate emergent dislocations) showing preferential concentration of deposited carbon at dislocation cores (magnification $\times 40,000$).