Carbon 1967, Vol. 5, pp. 399–402. Pergamon Press Ltd. Printed in Great Britain

INTERACTION OF EVAPORATED CARBON WITH HEATED METAL SUBSTRATES

S. M. IRVING* and P. L. WALKER, Jr.

(*Received* 28 *April* 1967)

Abstract—Reaction between evaporated carbon and heated foils of Pt, Mo, W, Ti and Ta have been investigated at a substrate temperature of 1000±25°C. Evaporations were carried out in 5×10^{-5} torr of Ar. The films formed were separated from their substrates and examined by transmission electron microscopy and selected area electron diffraction. Over Pt and Mo, only carbon films were formed. Over W, Ti and Ta distinctive carbide particles as well as carbon films were formed. The carbon films show differences in crystallinity over the different metal substrates.

1. INTRODUCTION

FROM the time that BRADLEY described a technique for producing thin carbon films by the rapid evaporation of bulk carbon,$^{(1,2)}$ workers have investigated the structure$^{(3-5)}$ and electrical properties$^{(6)}$ of such films before and after heat treatment at elevated temperatures. Films deposited on glass and metal substrates at room temperature are of small crystallite size and turbostratic. Their electron diffraction patterns usually consist of three diffuse halos. When the films are separated from their substrate and heated to elevated temperatures, crystallite growth and ordering of basal planes in the c-direction occurs, as expected. BANNERJEE and WALKER$^{(5)}$ heated a carbon film, which was not separated from its nickel substrate, to 500°C in high purity He. Regions of NiO appeared which were attributed to the reaction of Ni with trace amounts of oxygen gettered by carbon species produced during carbon evaporation at a pressure of about 5×10^{-4} torr. More recently, SYKES and coworkers$^{(7)}$ heated carbon films supported on copper substrates to 700°C in an electron microscope. Crystals were observed to nucleate and to grow on the film. They were shown, by selected area electron diffraction, to be copper.

To the authors' knowledge, no studies have been reported on the interaction of evaporated carbon with heated metal substrates at the time of deposition. This paper presents some results on this subject.

2. EXPERIMENTAL

Evaporation was performed in a conventional, oil diffusion pumped vacuum evaporator at a pressure of 5×10^{-5} torr of Ar. The carbon source (spectrographic grade, $\frac{1}{8}$ in. dia. graphite rods) was positioned such that the carbon species were directed at the substrate at an angle of about 30°. Initially, the evaporation was attempted at 5×10^{-7} torr with only residual gas in the bell jar; however, the sticking coefficient of carbon was very low. CASWELL$^{(8)}$ reports that residual gas in a similar vacuum system contains about 50% water vapor and 5% O_2. It is well known that these species react rapidly with carbon at 1000°C, especially if a metal catalyst is present. For this reason, the unit was pumped to its ultimate vacuum (about 3×10^{-7} torr) and backfilled with Ar until its inlet rate equalled the pumping speed, producing a pressure of 5×10^{-5} torr. Argon was cycled through the system in this fashion for 1 hr before evaporation was started. Prior to evaporation, the metal foils were heated to 1000°C and held at this temperature for 30 min to allow the foil and contacts to outgas. The temperature was measured with a Leeds and Northrup optical pyrometer. The temperature was not constant along the foil, the ends being at a lower temperature than the center. All observations on the

---

*Present address: Signetics Corporation, Sunnyvale, California.

resultant films were made at the center of the foil, where the temperature was 1000±25°C. Carbon was evaporated at a slow enough rate so that the pressure did not rise above $5\text{–}7 \times 10^{-5}$ torr; the evaporation period was between 1–2 min. After evaporation was completed the heating current to the foil was turned off and the foil was allowed to cool to room temperature before being exposed to air. The films were removed from their substrates using the following solvents: Pt, aqua regia; Mo, HNO_3; W, $HF\text{–}HNO_3$ mixture; Ti, HCl; and Ta, HF. They were examined, in transmission, with a Hitachi HU-11 electron microscope.

The foils used as substrates were reagent-grade. In this preliminary study, the foils were not polished before use, and no information was obtained on the grain size or crystallographic orientation of the substrates.

3. RESULTS

3.1 *Platinum*

The resultant film consists of two distinct morphological forms of carbon—no carbide is detected. The first is a structureless film that appears similar to a normal carbon film evaporated onto any substrate at room temperature. This film forms a substrate for larger (500–1000 Å) particles. Figure 1 shows the appearance of both types of carbon. Feature (A) shows the substrate film and feature (B) shows a collection of larger particles. Shadowing, resulting from the angular relationship between the source and foil (30°), is seen around a "hill" (feature C) on the Pt foil.

Selected area electron diffraction (SAD) shows only lines due to carbon. Figures 2 and 3 show the two types of SAD patterns obtained from carbon deposited on Pt. In Fig. 2, complete (10) and (11) rings are seen that are quite sharp. In addition, there are "bulges" on the rings which denote a tendency toward preferred orientation. Figure 3 shows an almost perfect single crystal pattern superimposed on a ring pattern. This was obtained from an area containing a number of large particles, such as feature (B) Fig. 1. It is apparent that the carbon has its basal planes aligned closely parallel to the substrate; that is, no (002) ring was detected in Figs. 2 or 3. For comparison with Figs. 2 and 3, Fig. 4 shows an SAD pattern from a carbon film that was evaporated onto a glass substrate at room temperature. Three very weak, diffuse halos from carbon are observed.

3.2 *Molybdenum*

Only poorly crystalline carbon films are found on Mo. Figure 5 shows the overall appearance of this film; its nature is more or less obscured by the shadowing effect of the underlying substrate. The film at high magnifications, is shown in Fig. 6. SAD patterns show (10) and (11) rings intermediate in sharpness between those in Figs. 2 and 4. A very diffuse (002) reflection is also found.

3.3 *Tungsten*

The resultant film on W shows a continuous, partially graphitized carbon substrate as well as WC, as seen in Fig. 7. The lath-like crystals of WC appear to be oriented perpendicular to one another, (the solvent used to dissolve the W also attacks the carbide, although slowly, and thus many of the crystals are partially dissolved). Figure 8 is an SAD pattern in which moderately sharp lines resulting from carbon are seen as well as arcs arising from WC. The *d*-spacings measured from the arcs are compared to the known spacings for WC in Table 1. No lines of $\alpha\text{-}W_2C$ were detected.

TABLE 1. SELECTED AREA DIFFRACTION RESULTS USED TO IDENTIFY WC IN FIG. 7

d-spacing (Å)		*hkl*
Measured	WC(ASTM Index)	
2·85	2·83	001
2·52	2·51	100
1·88	1·87	101
1·46	1·45	110
1·31	1·29	111
1·25	1·26	200

3.4 *Titanium*

Use of a heated Ti substrate results in quite spectacular carbide formation, as seen in Fig. 9. Again, the characteristic form of the crystals is lath-like with some crystals having good crystallographic terminations. Some of the crystals, up to 4 μ in length, are easily seen in the light microscope. It was difficult to prepare them for electron microscopic examination because the massive crystals broke the carbon substrate. No SAD

Fig. 1. Carbon film resulting from interaction of evaporated carbon with Pt at 1000°C (16,500×).

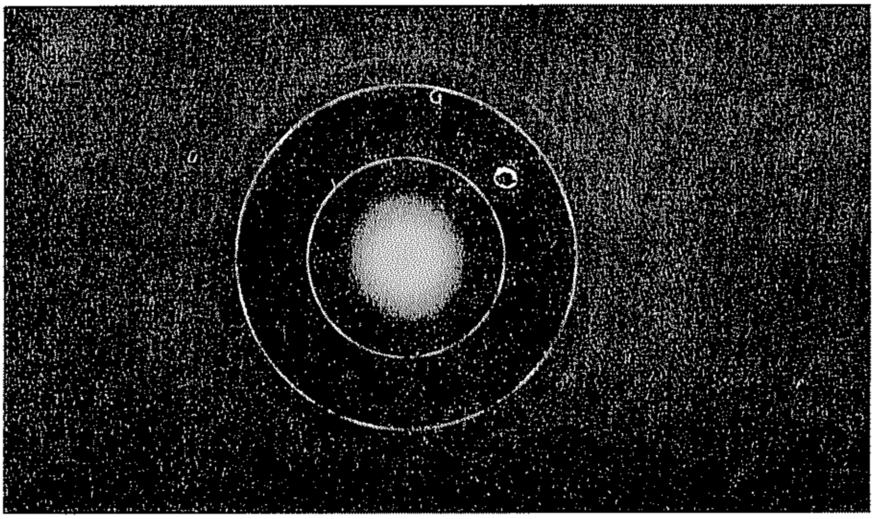

Fig. 2. Selected area electron diffraction pattern from region A in Fig. 1.

FIG. 3. Selected area electron diffraction from a region like B in Fig. 1.

FIG. 4. Selected area electron diffraction pattern from a carbon film resulting from deposition of evaporated carbon onto glass at room temperature.

FIG. 5. Carbon film resulting from interaction of evaporated carbon with Mo at 1000°C (16,500×).

FIG. 6. Carbon film resulting from interaction of evaporated carbon with Mo at 1000°C (45,000×)

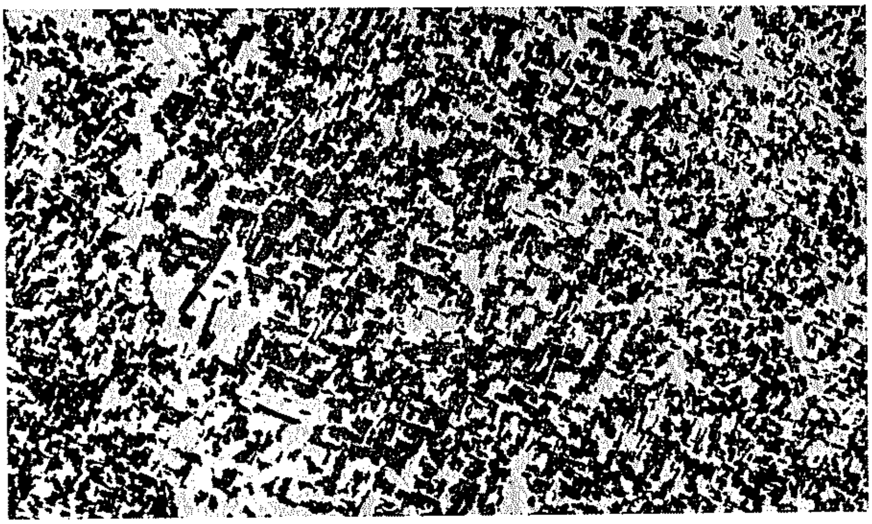

FIG. 7. Carbon film and WC resulting from interaction of evaporated carbon with W at 1000°C (11,000×).

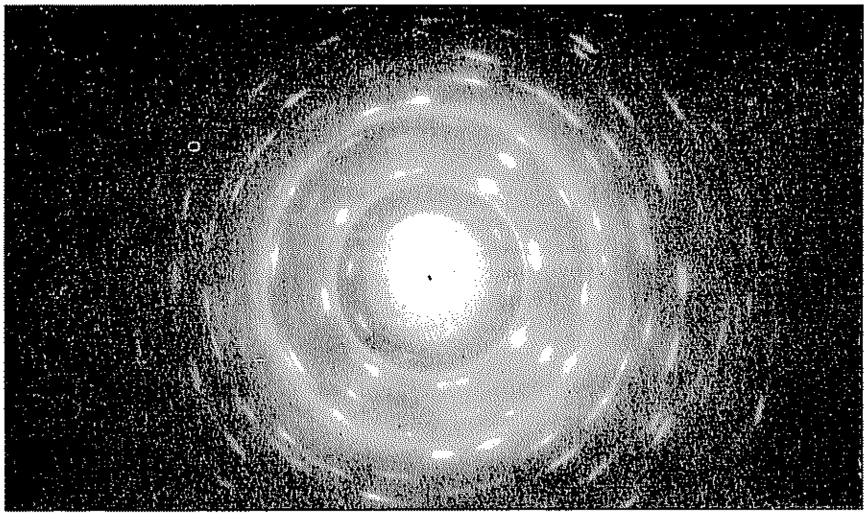

FIG. 8. Selected area electron diffraction pattern from part of carbon film and WC shown in Fig. 7.

FIG. 9. Carbon film and TiC resulting from interaction of evaporated carbon with Ti at 1000°C (7500×).

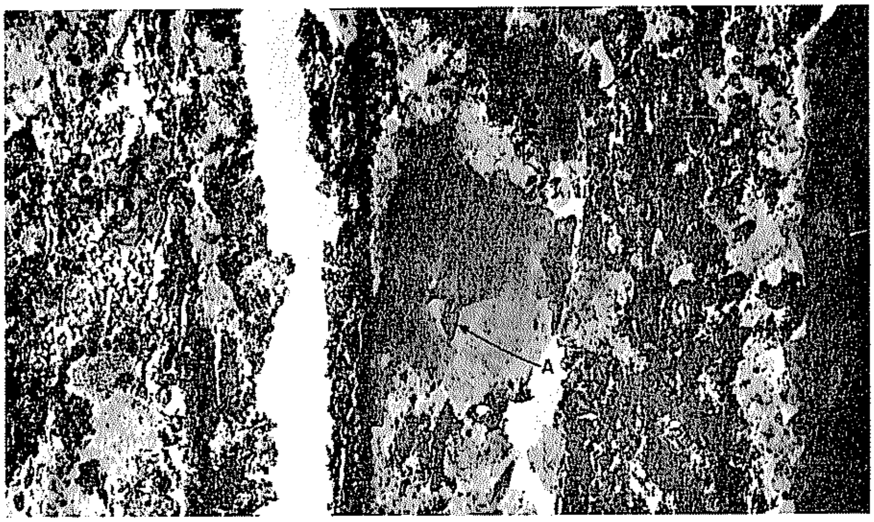

FIG. 10. Carbon film (area A) and TaC resulting from interaction of evaporated carbon with Ta at 1000°C (16,500×).

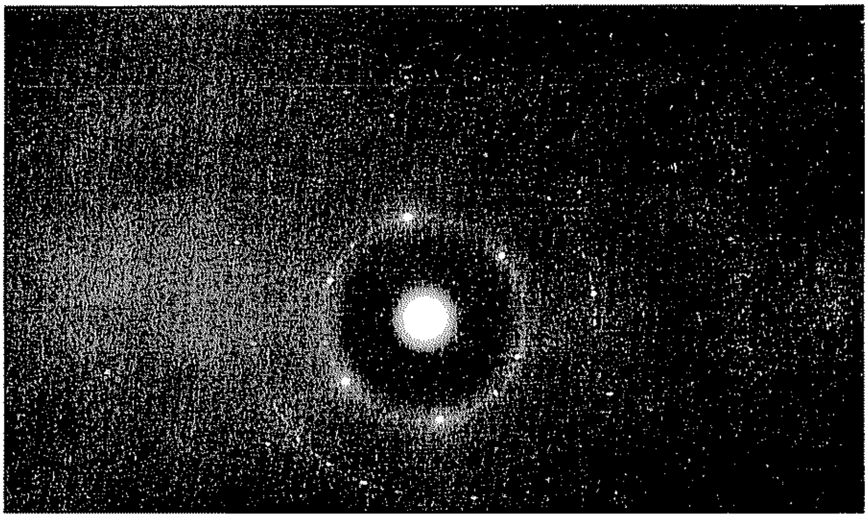

FIG. 11. Selected area electron diffraction pattern from region A in Fig. 10.

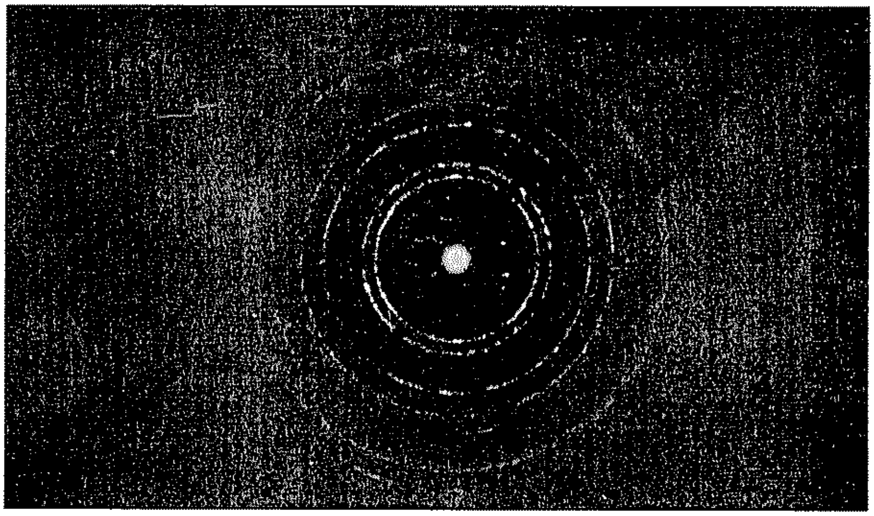

FIG. 12. Selected area electron diffraction pattern from a TaC area, such as shown in Fig. 10.

patterns could be obtained in transmission because the crystals were too thick. X-ray diffraction patterns clearly showed the presence of the strongest line for TiC ($d=2{\cdot}18$ Å).

3.5 Tantalum

The film formed on Ta is unlike that on any of the other metals studied. First, there is no continuous carbon film. Instead, areas of the film (Fig. 10, Area A) show masses of rather large single crystals of graphite that have an SAD pattern (Fig. 11) composed of spotty rings and no (002) line. Second, the carbide phase assumes all manner of interesting forms. A typical SAD pattern from the carbide phase is shown in Fig. 12. The measured *d*-spacings from the rings are compared to the known spacings of TaC in Table 2. No lines of Ta_2C were detected.

TABLE 2. SELECTED AREA DIFFRACTION RESULTS USED TO IDENTIFY TaC IN FIG. 10

d-spacing (Å)		*hkl*
Measured	TaC(ASTM Index)	
2·58	2·57	111
2·23	2·23	200
1·58	1·58	220
1·37	1·35	311
1·27	1·28	222

4. DISCUSSION

Catalysis of graphitization of carbon in the presence of metals is of much fundamental and practical interest at the present time. Enhanced graphitization is thought to occur by one of two mechanisms. In one, the metal acts as a solvent for carbon, the solubility increasing with increasing temperature. In the presence of a temperature gradient, carbon atoms (or ions) continually enter the metal at the higher temperature and leave the metal at the lower temperature. The atoms leaving the metal have high mobility and a good probability of participating in the growth of highly crystalline graphite. In the second mechanism, the interaction of carbon with the metal forms the carbide. At some temperature, the carbide decomposes to the metal and carbon, which is usually highly crystalline.

It is thought that enhanced graphitization observed in this study can be attributed to the solution of carbon in the metal substrate for two reasons. First, Mo was not observed to significantly catalyze graphitization. The solubility of carbon in Mo is very low; FEW and MANNING(9) report it to be only 0·005 wt. % even at 1650°C. Tungsten was not a particularly good catalyst for graphitization. The solubility of carbon in W is reported to be only 0·05 wt. % at 2400°C.(10) In contrast, the solubility of carbon in Ta and Pt, both of which promote graphitization, is about 0·2–0·3 wt. %.(11) Second, decomposition of the carbides of the metals studied (to yield a crystalline carbon) takes place only at temperatures approaching or exceeding the melting point of the carbides;(12) in all cases this is considerably in excess of 1000°C.

The very rapid rate of carbide formation for W, Ti and Ta in this study is worthy of note. Commercially, WC and TaC are produced by reacting metal powder with carbon black between 1300–1600°C over a period of hours; TiC is produced by reacting TiO_2 with carbon black between 1700–2100°C. In this study, massive deposits of carbides were formed at 1000°C in about 1 min. This indicates that the small vapor species of carbon are highly reactive with these metals. By contrast, massive particles of carbon black are much less reactive. It is interesting that although the rate of formation of carbide increases with increasing temperature, in commercial practices the lowest practical carburization temperature is usually employed to restrict grain growth. It would be of interest to compare the grain size of the carbides produced in this research with the size in the commercial carbides, which are produced at much higher temperatures.

It is not understood why the formation of Mo_2C and Pt carbide was not observed. Mo_2C is made commercially by reacting Mo with carbon black between 1400–1500°C.(13) It is possible that Mo_2C was undetected, because the solvent (slightly warm HNO_3) used to dissolve the substrate also slowly attacks the carbides of molybdenum.(14) KONIG(11) has made an electron-diffraction study of a Pt carbide produced by alternately depositing carbon and Pt on a thin collodion film and heating this preparation *in vacuo* for several hours at 1100°C. The final film was only 100 Å thick. It is true that very thin films frequently show reflections that are normally forbidden by the structure factor, because of the presence of large strains.

5. CONCLUSIONS

1. At 1000°C, evaporated carbon reacts rapidly with Ta, Ti and W foils to form a mixed carbide–carbon film. Over Pt and Mo, only carbon films are observed.

2. The carbide phases show textured growth patterns.

3. The carbon films formed over the metals show increasing crystallinity in the order: Mo, W, Pt and Ta.

REFERENCES

1. Bradley D. E., *Brit. J. Appl. Phys.* **5**, 65 (1954).
2. *Ibid*, 96 (1954).
3. Cosslett A. and Cosslett V. E., *Brit. J. Appl. Phys.* **8**, 374 (1957).
4. Kakinoki J., Katoda K., Hanawa T. and Ino T., *Acta Cryst.* **13**, 171 (1960).
5. Banerjee B. C. and Walker P. L., Jr., *J. Appl. Phys.* **33**, 229 (1962).
6. Blue M. D. and Danielson G. C., *J. Appl. Phys.* **28**, 583 (1957).
7. Becker J. J., Pritchard J. and Sykes K. W., *Carbon* **4**, 535 (1966).
8. Caswell H. L., *Physics of Thin Films*, Vol. 1, p. 49. Academic Press (1963).
9. Few W. E. and Manning G. K., *J. Metals* **4**, 271 (1952).
10. Schwarzkopf P. and Kieffer R., *Refractory Hard Metals*, p. 155. MacMillan (1953).
11. Hansen M., *Constitution of Binary Alloys*, pp. 377 and 380. McGraw-Hill (1958).
12. Ref. 10, p. 50.
13. Ref. 10, p. 132.
14. *Handbook of Chemistry and Physics* (43rd edition), Chemical Rubber Publishing Co., Cleveland (1962).