is quite distinct from that given by randomly oriented copper crystals, the (111) copper ring and the (100) graphite ring are very nearly co-incident; $d_{111}(Cu)/d_{100}(graphite) = 0.98$. Thus if only the inner diffraction rings are considered, the presence of an enhanced (100) ring in addition to an unchanged (002) ring might be attributed either to the development of graphite crystallites with some preferential orientation of the basal plane parallel to the film or to the presence of copper in addition to randomly oriented graphite.

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Effect of Oxygen Chemisorption on the Thermoelectric Power of Carbon and Graphite Artifacts*

RECENTLY it has been reported from this laboratory that the thermoelectric power (TEP) of molded, binderless natural graphite is sensitive to oxygen chemisorbed at temperatures between 335 and 452°C.[1,2] This effect was attributed to the trapping of negative carriers at the surface upon the formation of a carbon–oxygen bond, which has at least partial double bond character.[3] It was of interest to investigate whether the TEP of carbon and graphite artifacts (that is, bodies consisting of a filler and binder) are also sensitive to oxygen chemisorption.

The following samples were studied:

1. AGKSP spectroscopic graphite electrodes from Union Carbide.[3] The filler is a delayed needle petroleum coke; the binder is coal tar pitch. Electrodes were extruded and heated to *ca* 3000°C.

2. L113SP spectroscopic graphite electrodes from Union Carbide.[4] The filler is a lampblack; the binder is coal tar pitch. Electrodes were extruded and heated to *ca* 3000°C.

3. SP-1 natural graphite (as used in the previous study[1,2]) and coal tar pitch. Samples were molded from 87 parts SP-1 and 13 parts coal tar pitch and heated to 2900°C (courtesy of the Speer Carbon Company).

Prior to TEP measurements, the samples were first degassed at 950°C for 1 hr in He to remove most of the oxygen complex present on the sample. Degassed samples were then exposed to 1 atm of O_2 at temperatures between 350 and 450°C for varying lengths of time up to 25 hr to form various amounts of oxygen complex.

Gasification of carbon was small, amounting to less than 1 per cent for the 25 hr exposure to O_2 at 450°C. The TEP was measured against Pt, with the temperature gradient imposed $\perp$ to the molding direction or $\parallel$ to the extrusion direction of the sample, as previously described.[2] TEP was measured in 1 atm of He over temperature ranges where the oxygen complex was stable (that is, below its formation temperature). Following TEP measurement, each sample was degassed at 950°C (using an oil diffusion pump) to recover the complex as CO and CO_2.

Figure 1 presents the TEP results for the AGKSP graphite. The data represent measurements on a blank sample not heated in O_2 and twelve samples heated in O_2 for different times and temperatures. The maximum amount of oxygen complex formed was 1.1 μ moles/g (or *ca* 1.8 μ moles/m²) following exposure at 450°C for 25 hr. Lesser but significant amounts were formed at other conditions. As expected, for this highly graphitized material, the TEP of the blank is negative indicating dominance of the negative carrier.[2] However, oxygen chemisorption has no detectable effect on the TEP of this material, despite the fact that roughly six times as much oxygen could be chemisorbed (per unit of surface area) as was chemisorbed on molded, binderless SP-1.[1,2]

Figure 2 presents the TEP results for the L113SP carbon. The data represent measurements on three blank samples and four samples heated in O_2. The maximum amount of oxygen complex formed was 3.2 μ moles/g (or *ca* 2.0 μ moles/m²). As expected, for this poorly graphitized material, the TEP of the blank is positive. That is, its large defect concentration traps π electrons producing an excess of positive over negative carriers. Again oxygen chemisorption has not produced any significant change in TEP.

Figure 3 presents the TEP results for the bonded SP-1 graphite. The data represent measurements on three blank samples and three samples heated in O_2. The maximum amount of oxygen complex formed was 1.9
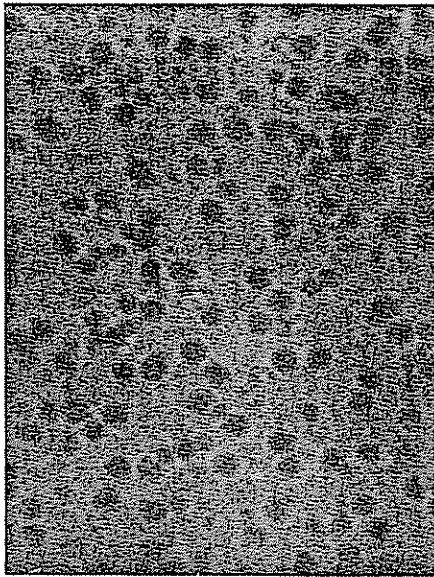
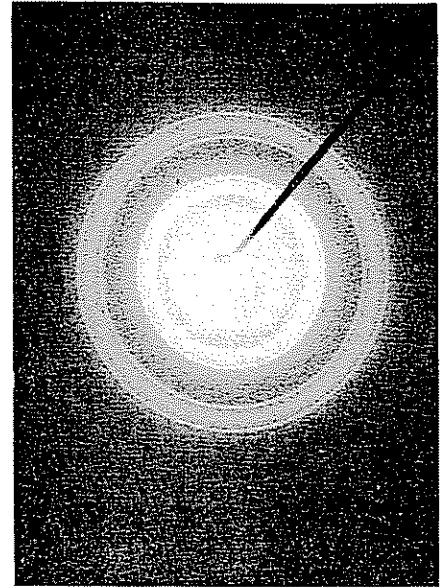FIG. 1. Electron micrograph of carbon film with copper crystals. (×140,000).

FIG. 2. Diffraction pattern given by area shown in Fig. 1.
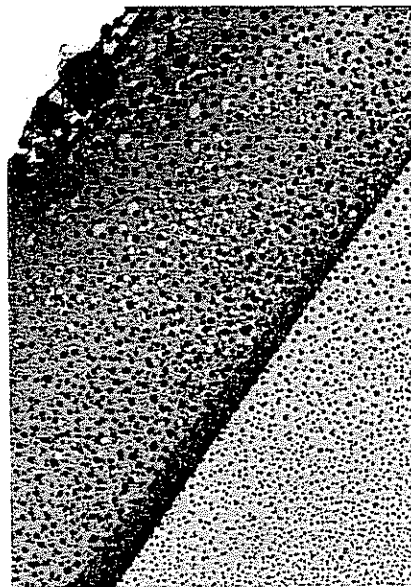
FIG. 3. Electron micrograph showing copper crystals obtained by heating sphere; darker regions are due to folds in the film. (×2800).
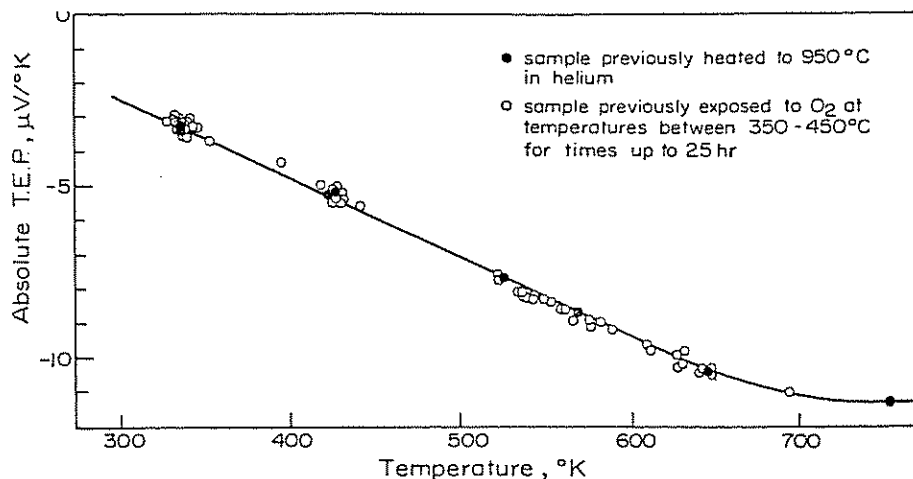
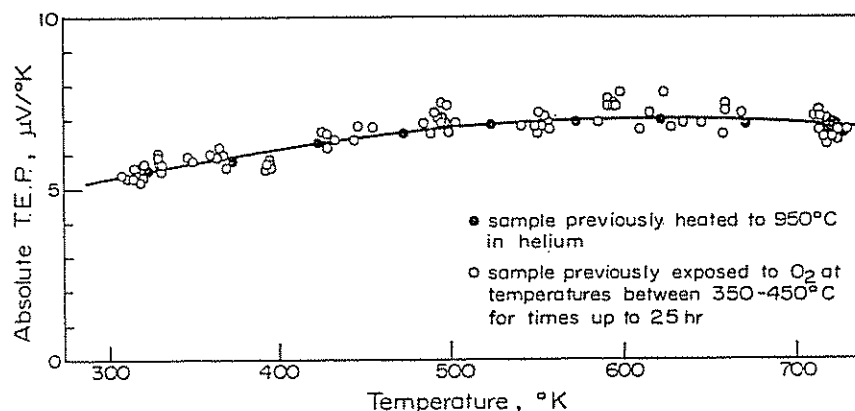FIG. 1. Absolute thermoelectric power of AGKSP graphite.

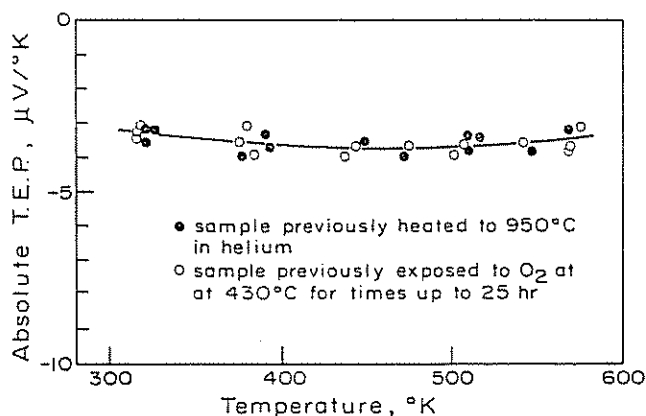
FIG. 2. Absolute thermoelectric power of L113SP carbon.

FIG. 3. Absolute thermoelectric power of bonded SP-1 graphite.

μ moles/g (or ca 1.0 μ moles/m^2). As expected, the TEP of the blank is negative. Oxygen chemisorption has no detectable effect on the TEP of this material, even though the amount of oxygen complex formed was roughly three times that which could be formed on molded, binderless SP-1.[1,3]

Klein has concluded that TEP is not influenced by preferred orientation (except when orientation is perfect and one can measure separately an a and c direction TEP) and bulk density and that the TEP of bonded carbons and graphites reflects basal-plane contributions originating from organized phases of the material with no or very little perturbation by intercrystallite potential barriers.[5] Henisch and Francois have shown that TEP can be considered a true property of the bulk of the crystallites.[6] Therefore, the measured TEP of our samples is expected to represent that of the crystalline regions in the filler and binder phases. Since the filler represents greater than ca 85 per cent of the sample weight in each case, the TEP of the filler should dominate.

Obviously, oxygen chemisorption will have no detectable effect on TEP if the carbon on which it adsorbs contains a large defect concentration and, consequently, a large number of trapping states for negative carriers. It is felt that our results are explicable on the basis of this consideration. For L113SP, as just discussed, its positive TEP indicates a large defect concentration in both the filler and binder phases. For the other two samples, the negative TEP values indicate

a reasonably low defect concentration in the filler. However, as discussed by NODA and INAGAKI,[7] among others, the binder phase does not graphitize well, primarily because of the physical limitation of its being in a relatively thin film. It is suggested that the binder phase covers most of the accessible filler surface area in the AGKSP and bonded SP-1 samples. Consequently, oxygen chemisorption primarily occurs on the binder carbon, where a negligible effect on TEP would be expected.

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Graphite Intercalation Compounds with Chlorides of Manganese, Nickel and Zinc

GRAPHITE reacts with numerous anhydrous chlorides to form intercalation compounds. This class of graphite compounds was recently reviewed.[1,2] In a paper by CROFT[3] there are listed various metal chlorides, which, according to his investigations, cannot be intercalated. RÜDORFF and coworkers[1,4] have shown that the reaction between metal chlorides and graphite occurs only if free chlorine is present. They have found that some chlorides for which Croft's experiments gave negative results can still form graphite compounds if the reaction is carried out in an atmosphere of chlorine. Some attempts have been made therefore to obtain compounds with other metal chlorides which are reported[3] not to react. This paper describes briefly three new graphite compounds with the chlorides of manganese, nickel and zinc.

These compounds result when graphite is heated with the anhydrous metal chlorides in sealed tubes filled with chlorine. In the absence of free chlorine no reaction occurred. After heating, the reaction mixture was washed with dilute hydrochloric acid to remove the excess of metal chloride. For analysis the samples were burned in a stream of oxygen saturated with water vapour. The hydrogen chloride and chlorine evolved were absorbed in an alkaline sodium sulfite solution. Chlorine and the residual metal oxides were determined by standard procedures.

The compositions of the compounds with the highest content of metal chloride which could be obtained hitherto are presented in the following table, which contains also the reaction conditions and the results of X-ray investigations.

TABLE 1. COMPOSITIONS OF SOME METAL CHLORIDE–GRAPHITE COMPOUNDS

	$MnCl_2$	$NiCl_2$	$ZnCl_2$
Reaction temperature °C	400	500	400
Reaction time (days)	7	4	7
Maximum content of metal chloride (%)	61,5	49	40,8
Ratio metal atoms/carbon atoms	1:6,6	1:11,3	1:16,5
Stage	1	2	3
c-axis (Å)	$2 \times 9,51$	12,68	$2 \times 16,39$

The data refer to compounds made from natural graphite (from Passau, Germany) with grain sizes 0,07–0,09 mm. The ratio metal to chlorine was found to be slightly higher than in the starting metal chlorides. It varied within 1:2,05–1:2,11. Such values have been reported for some other intercalated divalent metal chlorides.[1]

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