variations in AO parameters implies that both moment calculations require the incorporation of higher order terms[10] before good agreement with experiment will be obtained.

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Appendix

$$I_1 = \frac{R\rho^6}{192\sqrt{6}}(1 + \tau)^{5/2}(1 - \tau)^{7/2}[-5K^-{}_{64} + 6K^-{}_{62} - K^-{}_{60} + 8K^-{}_{53} - 8K^-{}_{51} - 11K^-{}_{42} + 6K^-{}_{46} + 8K^-{}_{31} - 5K^-{}_{20}]$$

$$I_2 = \frac{r}{30}(\alpha^3 + 6\alpha^2 + 15\alpha + 15)e^{-\alpha}$$

$$I_3 = \frac{\rho^7}{96\sqrt{6}R}(1 + \tau)^{5/2}(1 - \tau)^{9/2}[-5K^+{}_{54} + 6K^+{}_{52} - K^+{}_{50} + 14K^+{}_{43} - 9K^+{}_{41} - 20K^+{}_{32} + 6K^+{}_{30} + 14K^+{}_{21} - 5K^+{}_{10}]$$

$$I_4 = \frac{1}{20r}(\alpha^5 - 3\alpha^3 - 3\alpha^2)e^{-\alpha}$$

where

$$\alpha = r\zeta_{2\mathrm{p}} \text{ (r is the oxygen–oxygen distance)}$$

$$\rho = R(\zeta_{2\mathrm{p}} + \zeta_{3\mathrm{d}})/2 \text{ (R is the metal–oxygen distance)}$$

$$\tau = (\zeta_{2\mathrm{p}} - \zeta_{3\mathrm{d}})/(\zeta_{2\mathrm{p}} + \zeta_{3\mathrm{d}})$$

$$K^+{}_{nm} = A_n(\rho)B_m(\rho\tau) \pm A_m(\rho)B_n(\rho\tau)$$

$$A_n(\rho) = \int_1^\infty x^n e^{-\rho x}\mathrm{d}x$$

$$B_n(\rho\tau) = \int_{1-}^{1} x^n e^{-\rho\tau x}\mathrm{d}x$$

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Reaction of Sodium with Graphite at 400°

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Sodium lamellar compound formation at 400° in graphite that contained chemisorbed oxygen was followed by measuring changes in the magnetic properties of graphite as a function of the sodium content. Complete elimination of the diamagnetism of graphite was found when the sodium content approached 3 wt %. This agrees with the weight per cent of Na in the lamellar compound $C_{64}Na$. The sodium content of every sample consisted of at least three different components regardless of the amount of sodium present. Part of the sodium reacted with chemisorbed oxygen to form sodium carbonate. Another sodium component was reactive enough to liberate hydrogen from water. The third fraction was tightly bound and chemically inert. Only that sodium capable of liberating hydrogen from water strongly affected the magnetic properties of graphite. For complete elimination of the diamagnetism of graphite, 2 wt % reactive sodium was required, that is, a carbon to reactive sodium ratio of 96:1.

Introduction

Graphite is known to react interstitially with many substances[1] to form lamellar compounds. A sodium lamellar compound, $C_{64}Na$, has been reported, but disagreement exists concerning its formation. Asher[2] used X-ray diffraction to identify the compound $C_{64}Na$. Hennig[3] found reaction between sodium and graphite at 400° only when oxygen impurity was present in the system and suggested the possibility of a ternary system. Recht, *et al.*,[4] reported that if the graphite contains chemisorbed oxygen, any sodium that enters the graphite reacts to form sodium carbonate until all the oxygen available has been used.

In this work sodium lamellar compound formation at 400° in graphite containing chemisorbed oxygen was followed by measuring changes in the magnetic susceptibility of the samples as a function of the sodium content. Graphite is characterized by extremely high diamagnetism that arises from the presence of free electrons in giant π orbits. The formation of a lamellar compound eliminates the diamagnetism because electrons are donated by the intercalating sodium to these π orbits.[1] Early stages of the reaction were studied and amounts of different sodium components determined by chemical analyses.

Experimental Section

A Sartorius semimicrobalance adapted for below the pan suspension and mounted above a 4-in. Varian electromagnetic system was used to measure the diamagnetic force of a given sample. The diamagnetic force was the change in the apparent weight of the sample when suspended in a magnetic field. The

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TABLE I

MAGNETIC MEASUREMENTS AND ANALYTICAL RESULTS ON AGKSP GRAPHITE SAMPLES TREATED WITH SODIUM AT 400° DURING $NaNO_3$ ELECTROLYSIS

			Sodium components, mg					Diamagnetic forces, mg			% change	
Sample no.	Initial wt, g	Total wt gain, mg	Carbonate	Reactive	Tightly bound	Wt % sodium	Wt % reactive sodium	Initial, f_1	With Na, f_2	After H_2O, f_3	$[(f_1 - f_2)/f_1] \times (100)$	$(f_3/f_1) \times (100)$
1	2.408	15.0	5.0	6.0	4.0	0.62	0.25	96.3	81.8		15.0	
2	2.393	19.1	3.1	7.1	8.9	0.79	0.30	97.5	64.2		34.2	
3	2.421	27.0	7.6	9.3	10.1	1.10	0.38	92.7	57.3		38.2	
4	2.415	39.5	9.6	13.1	16.8	1.61	0.54	92.7	33.6	89.0	63.7	95.7
5	2.386	50.6	8.6	21.2	20.8	2.08	0.88	94.3	15.5	89.1	84.7	94.5
6	2.401	53.3	7.2	25.2	20.9	2.18	1.04	93.4	8.3		91.1	
7	2.390	70.0	6.7	33.2	30.1	2.84	1.37	96.5	5.0	89.8	94.7	93.0
8	2.433	68.8	4.3	36.7	27.8	2.76	1.49	93.8	3.1	87.5	96.2	93.4
9	2.402	86.2	5.2	43.7	37.3	3.46	1.80	94.0	2.6		97.5	
10	2.407	78.0	13.8	41.1	23.1	3.12	1.65	94.1	0.9		99.0	
11	2.411	113.5	12.2	68.0	33.3	4.50	2.74	95.0	1.2	82.4	98.8	86.7
12	2.404	107.3	18.4	55.4	33.5	4.27	2.25	94.4	0.7		99.3	
13	2.427	145.6	44.0	51.0	50.6	5.66	2.08	92.5	0.3		99.7	
14	2.391	10.93		4.8		0.45	0.20				23.2	

magnetic anisotropy of graphite did not cause difficulty. As shown in Table I, the initial magnetic force measurements for graphite samples suspended in the same magnetic field agreed well with each other. The samples used were 2 in. long, 0.25-in. diameter AGKSP National Carbon spectrographic graphite electrodes guaranteed to contain no more than 6 ppm of impurities. Powdered samples were not suitable because physical attack as well as changes in magnetic properties was of interest. The Gouy method was used to determine the diamagnetic force exerted on the rod in a magnetic field.

Sodium was introduced into graphite by electrolysis of Allied Chemical reagent grade sodium nitrate. The graphite specimens were attached to a nickel current lead and placed inside a 10 in. long, 0.5-in. diameter soft-glass cell made of Corning No. 0080 glass. This cell served as the cathode in the electrolysis cell. Electrical contact and a sodium path between the graphite and walls of the soda-glass cell was provided by graphite powder packing that completely covered the sample. The packed cell was evacuated at room temperature and filled with dry argon. The argon environment was maintained in the cathode cell by a flexible rubber cap through which the nickel current lead was passed. The cathode cell was immersed in a fused sodium nitrate bath controlled at 400°. All current passage during electrolysis was attributed to sodium ion migration through the soda glass. The soda-glass cell enabled complete separation of the graphite specimen from the fused electrolyte. The diamagnetic force and weight of the graphite rods were determined in an argon environment before and after electrolysis. These are tabulated in Table I.

Chemical analyses of the sodium-treated graphite showed that part of the sodium content of every sample liberated hydrogen from water even when excess sodium was not present. This sodium is listed as reactive sodium in Table I. Another part of the sodium content was found as sodium carbonate. The amounts of these components were determined by double-indicator titrations of the alkaline solution produced by immersing the sodium-treated samples in water. The water solutions contained dissolved sodium carbonate and the sodium hydroxide that accompanied hydrogen generation. The reaction with water was not violent; roughly 12–18 hr was required before hydrogen evolution ceased. Standard HCl titrations were carried out to phenolphthalein and methyl orange end points. At all times an argon environment was maintained over the water reservoir to prevent conversion of hydroxide to carbonate through carbon dioxide pickup from air. The carbon and oxygen that reacted to form sodium carbonate was assumed to be part of the original weight of the sample. A third fraction of the total sodium content was so tightly held by the carbon that it resisted leaching in concentrated HCl at room temperature. This sodium is designated in Table I as the tightly bound component. The existence of the tightly bound sodium content was demonstrated by pulverizing water-treated samples, leaching the powder in fuming sulfuric acid at 400°, oxidizing the carbon away in a muffle furnace at 500°, and analyzing the ash for sodium by the triple-acetate gravimetric method. Because such analyses proved the presence of the tightly bound sodium, its amount was usually obtained by the difference between the total weight gain and the sum of the two water-soluble sodium components. Satisfactory agreement was found for amounts of tightly bound sodium determined by chemical or gravimetric analyses.

Discussion

The weight gain of the AGKSP graphite rods is attributed to sodium absorption during the electrolysis of sodium nitrate at 400°. No visible evidence of physical failure or breakage of the graphite specimens was observed in any of these tests regardless of the total sodium content introduced into the graphite. The change in the diamagnetic force of graphite is rapid until the total sodium content approaches 2 wt %. At about 2 wt % sodium the diamagnetism of the original graphite rod has been reduced 90%. With additional sodium absorption the diamagnetic force continues to change but at a reduced rate. The elimination of the diamagnetism of graphite occurs at about 3 wt % sodium in good agreement with the sodium content of the lamellar compound $C_{64}Na$. Only a negligible additional change in the magnetic force is produced by sodium absorption in excess of 3 wt %. This change is attributed to the additive contribution of an increasing weight fraction of free sodium to the magnetic susceptibility of the sample.

The chemical reactivity of sodium-treated samples indicates that the sodium content is chemically bonded in three distinct and different ways in addition to elemental sodium which is assumed to be present when the total sodium content exceeds 3 wt %. The three different sodium components are designated: sodium carbonate, nonreactive sodium, and reactive sodium. Regardless of the total sodium content, some of each component was found in every sample.

The amount of sodium carbonate found appears to depend on the amount of oxygen available for its formation. Air leakage into the argon-filled cathode cell accounts for the high-carbonate fractions in samples from the longer electrolyses. The carbonate fractions in the shorter tests appear relatively constant compared to the gradual increase with time of the other sodium components. Although the amount of sodium carbonate present is significant in all cases, it does not effect a measurable change in the magnetic properties of graphite. This suggests that the carbonate is present as a separate phase and not chemically bonded to the graphite.

The tightly bound nonreactive sodium component exhibits behavior similar to the phenomena of "residue compound" described by Hennig and co-workers. The difficulty encountered in chemically analyzing for the tightly bound sodium fraction suggests that it possesses chemical bonding that is different from the other sodium fractions. Magnetic force measurements on water-treated samples that still contain the tightly bound nonreactive sodium show a 90% return of the original diamagnetism of graphite. These measurements and the earlier conclusions concerning the negligible effect of carbonate on the magnetic properties of graphite indicate that only the sodium component capable of liberating hydrogen from water has a strong effect on the magnetic properties of graphite.

In Figure 1 the lowering of the magnetic properties of graphite is plotted as a function of the reactive sodium content. Because of the strong effect on the magnetic properties of graphite, the reactive sodium presumably donates electrons to the π orbits of graphite. The diamagnetism of graphite is completely eliminated at about 2 wt % reactive sodium, or a carbon to sodium ratio of 96:1. This ratio of carbon to alkali metal atom is the same as that reported[5,6] for metal-poor potassium and rubidium lamellar compounds. Because of this analogy, the arrangement of reactive sodium atoms in the graphite lattice ought to be similar to that proposed[2] for the $C_{96}M$ metal-poor compounds.

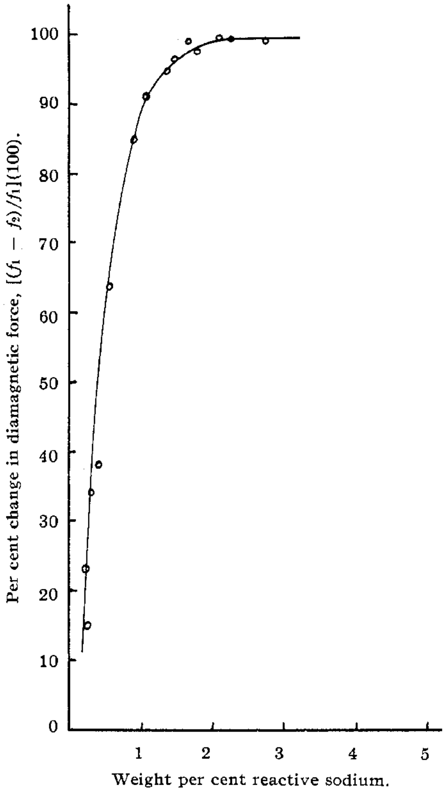

Figure 1.—Change in the diamagnetism of graphite rods as a function of reactive sodium content introduced at 400°. $C_{96}Na$ = 1.95 wt % sodium.

Conclusions

The complete elimination of the diamagnetism of graphite at about 3 wt % sodium is attributed to lamellar compound formation in graphite containing chemisorbed oxygen. The chemisorbed oxygen reacts to form sodium carbonate which appears to be a separate phase that does not undergo electron transfer with the graphite. The carbonate probably serves as a spacer to stabilize the lamellar compound. The reaction of chemisorbed oxygen to form sodium carbonate appears to be accompanied by the simultaneous formation of lamellar compound. Even at low levels the sodium content of graphite samples was found to be present in three different forms, each chemically bonded in a different way. Only reactive sodium, capable of liberating hydrogen from water, undergoes electron transfer with the π-orbit electrons of graphite. It is possible that the reactive sodium occupies sites in the graphite lattice similar to those of the metal-poor lamellar compounds $C_{96}Na$. This arrangement is different from that of $C_{64}Na$ in that the metal layers between every eighth graphite layer contain less metal. At this time it is impossible to ascertain whether the difference between the reactive and tightly bound sodium fractions arises during lamellar compound formation or during attempts to remove sodium from the sample. The reaction of the sodium lamellar compound with water is not violent. In the presence of only trace amounts of carbonate, the reaction may be represented as

$$3C_{64}Na + 2H_2O \longrightarrow 2NaOH + H_2\uparrow + C_{192}Na$$

where $C_{192}Na$ is a residue compound designated in this work as the tightly bound sodium component. In this case all the sodium which is neither in excess or present as carbonate is present as an intercalation compound.

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