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THE EFFECT OF GASIFICATION ON THE DIAMAGNETISM OF GRAPHITE AND ARTIFICIAL CARBONS

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ABSTRACT

Magnetic susceptibility and magnetic anisotropy measurements by the Faraday method were carried out on samples of natural graphite, graphitized carbon composites, stress recrystallized pyrolytic graphite and on a graphitized carbon black (Graphon). The total susceptibility at room temperature ranged from -18.75×10^{-6} emu/g for graphon to -21.68×10^{-6} emu/g for the stress recrystallized pyrolytic graphite. The anisotropy ratios ($R = \chi_\perp/\chi_\parallel$) ranged from 1.02 for an extruded lampblack based carbon composite to 40 for the stress recrystallized sample. The temperature dependence of the susceptibility can be accounted for using a two dimensional degenerate electron gas model. From this model the values of T_o, the degeneracy temperature of the electron gas, the number of effective electrons per carbon atom and $\alpha = m/m^*$, the ratio of the electron rest mass to its effective mass were obtained. Within the spirit and limitations of this model the following estimates for T_o were obtained; 344°K for natural graphite, 379°K for stress recrystallized pyrolitic graphite and 500°K for Graphon. A strong correlation exists between T_o and the perfection of the graphitic material. Susceptibility measurements as a function of massive oxidation show that the effect of gasification in dry oxygen upon the susceptibility of the material reflects its perfection and preparation methods.

INTRODUCTION

Graphite possesses one of the largest diamagnetic anisotropies of any material known. When a single crystal of natural graphite is oriented such that the magnetic vector is perpendicular to the basal plane (aromatic plane) the specific susceptibility is $\chi_\perp = -21.75 \times 10^{-6}$ emu/g. If the magnetic field vector is oriented parallel to the basal plane the specific susceptibility is $\chi_\parallel = -0.30 \times 10^{-6}$ emu/g. The ratio $\chi_\perp / \chi_\parallel$ is a good measure of the diamagnetic anisotropy of the material and for selected natural single crystals is as high as 72.[1] The high diamagnetic anisotropy and the underlying physical phenomena have been fairly well known since the pioneering work of Ganguli and Krishnan in 1948.[2] They were able to interpret the high susceptibility for a magnetic field oriented perpendicular to the basal plane as being due to the contribution by quasi-free electrons in the π band.

The current models for the interpretation of the magnetic properties if graphitic materials are due to McClure[3,4] and to Marchand

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and co-workers.[5] McClure, using the rigorous formalism of band theory, derived explicit expressions for the diamagnetic anisotropy of graphite using the two dimensional band structure approximation. He also obtained computational results for the three dimensional band structure model. Marchand and co-workers, elaborating on a simple model proposed by Ganguli and Krishnan, noticed that the semi-empirical relation $y = 1 - \exp(-x)$ proposed to fit the experimental data, could be firmly grounded on existing theories of a two dimensional electron gas. In their theory the above semi-empirical relation takes the form

$$\chi_t/\chi_o = 1 - \exp\left(- T_o/T\right) \tag{1}$$

where $T_o = (\nu N h^2 \alpha)/(4\pi m k S)$ is the degeneracy temperature of the two dimensional electron gas, $\chi_o = [(\nu \beta^2 N)/(kT_o S)\ (1 - \alpha^3/3)$, N is the total number of carbon atoms, ν the number of holes per carbon atom in the band with effective mass $m^* = m/\alpha$, S the area occupied by the gas, and $\beta = eh/2mC$ the Bohr magneton. Their theory unjustifiably assumes ν to be temperature independent, implying no thermal excitation of carriers from the π band to the conduction band. According to Marchand's simple model, $T_o = \varepsilon_o/k$, where ε_o is the energy difference from the Fermi level to the top of the valence band and k is the Boltzmann constant. The present work was undertaken to see if magnetic susceptibility measurements could be used to characterize carbon materials and to investigate quantitatively their gasification in oxygen. This approach stemmed from earlier work which showed that the specific diamagnetic susceptibility χ_t is proportional to the position of the Fermi level with respect to the edge of the valence band[3] in carbon materials, and that gasification produces many forms of structural imperfections which can act as traps for electrons thereby lowering the Fermi level.

EXPERIMENTAL

Average and anisotropic magnetic susceptibility measurements by the Faraday method were made on samples of SP-1 (natural graphite), AGKSP, L113SP spectroscopic grade artificial carbons from Union Carbide Co., SRPG (stress recrystallized pyrolytic graphite) and Graphon (a carbon black heat treated to a temperature of 2700°C). From the field dependence of the diamagnetic susceptibility (Honda-Owens plot), a negligible concentration of ferromagnetic impurities was determined. Traces from the diamagnetic susceptibility tensor $(\chi_\perp + 2\chi_\parallel)$ at room temperature ranged from -18.8×10^{-6} emu/g for Graphon to -21.6×10^{-6} emu/g for the SRPG. Other values for the room temperature trace were found to be -20.6, -21.0 and -21.2×10^{-6} emu/g for powdered SP-1, for L113SP and AGKSP extruded rod composites, respectively. The anisotropy ratios $(R = \chi_\perp/\chi_\parallel)$ ranged from 1.02 for the composite L113SP to 38.8 for the mosaic crystal of SRPG. Other values are presented in Table I.

Table I Principal Susceptibilities of Different Graphites and Graphitic Carbons in Units of 10^{-6} emu/g at Room Temperature

Sample		$-\chi_{\parallel}$	$-\chi_{\perp}$	$-\chi$	Total	Anisotropy Ratio
SP-1	Average χ = 6.86				20.58	not Measurable
SRPG		0.54	20.60*		21.68	38.2
AGKSP		8.33	4.60*		21.27	1.84
AGKSP#	Average χ = 7.10				21.30	not Measurable
L113SP		7.06	6.93*		21.06	1.02
L113SP#	Average χ = 7.01				21.03	not Measurable
Graphon	Average χ = 6.25				18.75	not Measurable

*Component parallel to c-axis, across the grain or in extrusion direction; whichever applies. #Powder

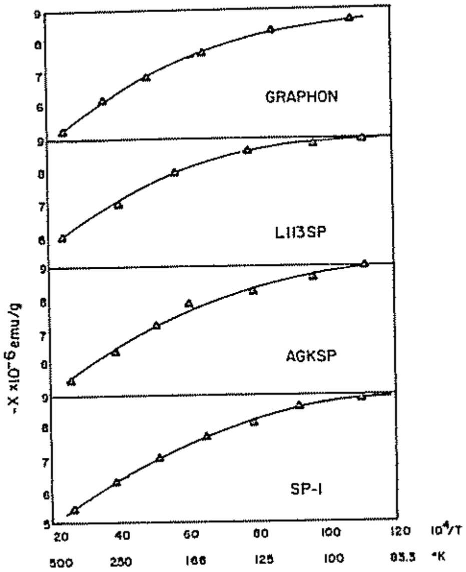

Fig. 1. Temperature Dependence of Diamagnetic Susceptibility.

Diamagnetic susceptibility as a function of temperature was measured from 77°K to 300°K and the results of these measurements are presented in Fig. 1.

The samples were gasified (or massively oxidized) in dry oxygen "in situ" in the Faraday balance. Gasification was carried out at temperatures selected so as to avoid a non-uniform, diffusion controlled reaction. Uniformly gasified samples were obtained, gasified to as much as 80% weight loss. The optimum gasification temperature increases with the perfection of the material to be gasified. These optimum gasification temperatures ranged from 450°C for SP-1 and Graphon to a high of 650°C for SRPG. Susceptibility as a function of gasification was measured for different sample orientation using the Faraday balance. Results of these experiments are presented in Fig. 2.

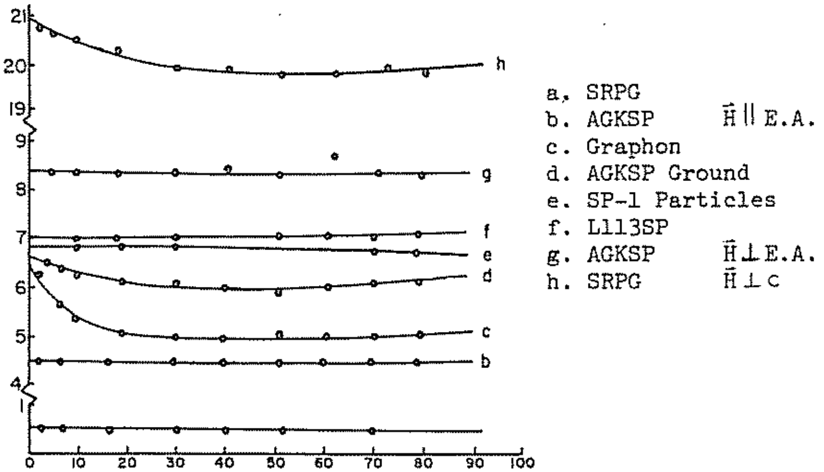

Fig. 2. Diamagnetic Susceptibility vs. "Burn-off" for Various Graphitic Carbons

DISCUSSION

From the susceptibility vs. temperature measurements and using Marchand's model for the susceptibility of a degenerate two dimensional electron gas, values for the ratio $\alpha = m / m^*$ of the rest mass (m) to the effective mass (m^*) of the free carriers, and the degeneracy temperature (T_o) were calculated. The following degenercy temperatures were estimated: For SP-1 powder sample, T_o = 344.2°K; Graphon T_o = 506°K and SRPG, T_o = 379.3°K. The other carbon materials under study, the composites (filler plus binder) AGKSP and L113SP, possessed a degeneracy temperature of 389.4°K and 402.0°K respectively. The effective masses derived from this model ranged in value from m^* = 0.003m for SP-1 to m^* = 0.005m for Graphon. These values are smaller than the magnitude usually assumed for the effective masses in graphitic materials.

Now that the sign of γ_2 (an overlap integral in the band theory of graphite) has been definitely stablished (γ_2<0) and the heavy carriers identified as electrons[6], Spain[7] has found from galvanomagnetic data that the light holes close to the H point in the first Brillouin zone (the top of the Fermi surface extending into the next zone) may be identified with the effective minority carriers. It is possible that only the carriers with the smallest effective masses are responsible for the magnetic susceptibility of graphite and graphitic carbons, the contribution of charge carriers with larger m^* values being negligible. This possibility, as previously pointed out by Marchand[5], could account for the small m^* values found in this work and for the temperature independence of ν. One should point out that Schoenbert[8] also found small values for ν of the order of 10^{-5}. Using susceptibility measurements as a characterization tool, one found that the SRPG sample with the lowest T_o of the artificial materials has better over-all metallic properties than the other artifical carbon samples (AGKSP, L113SP and Graphon).

CONCLUSIONS

The results on the effect of gasification upon the susceptibility of the materials were shown to depend on the origin and preparation of the individual samples. For the commercial carbon composites, the susceptibility was found to remain constant with gasification. This behavior was observed for AGKSP and the lampblack based L113SP samples. This was explained on the basis that the electronic effects of carrier trapping would not be significant, since the material was known to contain too many carrier traps, due to their highly disordered structures and created by plastic deformation during fabrication, which mask any gasification effect. For the highly anisotropic SRPG mosaic crystal, when oriented with the field perpendicular to the basal plane, the specific susceptibility ($\chi_\perp$) vs. burn-off (gasification) curve was seen to decrease with burn-off. The susceptibility decreases steadily to 45% burn-off and then remains constant thereafter. However, for the magnetic field parallel to the basal plane of the crystal there was no measurable change in the susceptibility ($\chi_\parallel$) with burn-off. In this material the effect of gasification upon the susceptibility was significant and could be attributed mainly to the formation or enlargement of defects upon gasification which are effective charge carrier traps. Since Graphon has the largest specific surface area for chemisorbing oxygen when activated, it is suggested that the observed decrease in the susceptibility during gasification was a result of chemisorbed oxygen acting as surface trapping sites.

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