ESR in Carbons: Studies of Temperature Dependence and of Neutron Irradiation*

G.M. Arnold and S. Mrozowski

Carbon Research Laboratory, State University of New York at Buffalo, Buffalo, New York

In continuation of the work of the senior author on ESR in polycrystalline graphites[1], experiments on temperature dependence[2] and on neutron irradiation of the ESR for two carbon blacks, P33 and Thermax, were performed in the range of heat treatments from 1600°C to 3000°C. As shown in the work referred to, the spin resonance of incompletely graphitized materials is due to both conduction carriers and to localized spin centers (vacancies, peripheral dangling bonds, interstitial ions etc.). A single absorption line is observed due to presence of exchange interaction between both types of spin which leads to mixing of the g-values. A study of temperature dependence of intensity permits to evaluate the contributions of both types of spins and thus establish their variation with heat treatment. The results show that while for HTT 1600°C the concentration of localized spins is about 1.6×10^{19} per gram (both P33 and Thermax show similar behavior), this concentration decreases with increase of HTT so that for HTT 3000° the concentration for P33 drops to 3.5×10^{17} per gram, while for Thermax becomes so small that no reasonable estimate can even be obtained. The absorption due to conduction carriers at HTT 1600 is about 50% larger than for localized spin and also decreases fast with increase of HTT - however, it goes through a minimum at around HTT 2600°C (7.5×10^{18} equivalent spin per gram) and then increases toward a limiting value 8.5×10^{18} spins per gram corresponding to a perfect crystal of graphite. Since the absorption is proportional to the density of conduction states n(E) at the Fermi level, it seems that for incompletely graphitized materials the band overlap must be smaller than for graphite. By correcting the g-values for the mixing effect, the dependence of the true g-value can be obtained for conduction carriers on the HTT and on the density of states n(E) at the Fermi level.

A similar analysis of the data obtained for these materials all irradiated to the same dose shows that like in the case of incompletely graphitized materials the increase in ESR absorption is mainly due to formation of localized spin centers with some increase caused by the depression of the Fermi level. The total number of localized spins created by irradiation increases with decrease in heat treatment (100% increase between HTT 2600 and 1600°). This is undoubtedly due to a larger mobility of the displaced carbon atoms in highly graphitized materials and in consequence to a considerable annealing taking place at the temperature of irradiation. While samples of partially graphitized material show strong annealing below 400°C, for lower heat treated samples only 50% more centers are annealed between irradiation temperature (50°) and 400°C and thus lower heat treated show relatively a much greater stability reminding the one of samples of polycrystalline graphite irradiated to higher doses. After a 400°C anneal the number of localized

centers remaining is still about 3-4 times greater than the number of centers originally present in the material. Some results and their analysis are condensed in the table below where the fractional contribution x of conduction electrons was calculated from the formula $R = 3.75\ (1 - x) + 0.88\ x$[1]

Table

HTT	Nonirradiated P33				Irradiated P33			
	I_o	$R = I_{LN}/I_{RT}$	Cond	Loc.	I_o	$R = I_{LN}/I_{RT}$	Cond.	Loc.
1600	400	2.0	240	160	1405	3.3	260	1145
1800	310	2.0	188	122	1350	3.2	290	1060
2000	242	2.1	141	101	1100	3.2	250	850
2200	186	2.1	108	78	915	3.25	180	735
2400	122	1.7	86	36	775	3.4	155	620
2650	92	1.4	75	17	(610)	(3.25)	(120)	(490)

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+ present address: LaVerne College, La Verne, California
1. S. Mrozowski, Carbon 3, 305 (1965)
2. S. Mrozowski, Tokyo Symposium (1964)