C.V.D. CARBON COMPOSITES :

PREPARATION, ELECTRONIC AND THERMAL PROPERTIES

A. PACAULT, P. LOLL, P. DELHAES

Centre de Recherches Paul Pascal, Université de Bordeaux I, 33405 TALENCE (France)

and

A. PIERRE

S.N.I.A.S.-AQ, Centre d'Issac, 33160 SAINT-MEDARD-EN-JALLES

1 - Introduction

Carbon densification processing (1) of porous or fibrous substrates have been studied during these recent years because of the aerospace applications (2). We have prepared and investigated a family of carbon felt-carbon matrix composites. In relation with the different microstructures we have studied the electronic and thermal properties.

2 - Deposition technique and characterization

- *Experimental* : the isothermal process with a resistor-graphite furnace working between 1000 and 1300°C has been used. The hydrocarbons is methane diluted in nitrogen and sometimes with hydrogen additions. The substrate is a carbon felt.

- *Existence diagram* : the pyrolysis of methane occurs under conditions far from thermodynamical equilibrium. In order to describe such a process it is useful to distinguish (3).

The constraints : variables which might be controlled by the experimenter ; they are either fixed by the method (shape and size of the furnace, no thermal gradient because of the isothermal process, constant pressure of gases) or adjustable (deposit temperature T_D, composition and flow (D) of gases, time of deposit t_D).

The responses : variables measurable by the experimenter, all the observations and the physical properties which are involved in the study (see table I).

The system is the whole set of response and depending on the processing constraints an existence diagram can be established in the constraints space. In order to do that a response must be chosen as pertinent : this is the nature of the microstructure determined by optical microscopy under polarized light illumination (4). Differents microstructures have been characterized : rough laminar (L.R), smooth laminar (L.L), granular (L.G), isotropic (I) and mixture of them in agreement with previous investigations (5) except a difference quoted for the granular microstructure (4). For a quasi-constant flow a section of the existence diagram characteristic of the carbon felt is drawn with only 15 responses (figure 1).

- *Physical properties* : they are presented on table I for the CVD as deposited :

- the apparent and powder densities, the X-ray informations which are in agreement with results on similar composites (3)(5).

- the magnetic properties have been examined for the first time : the EPR line widths are characteristic for each microstructure and the diamagnetism furnishes a very interesting result. There is significant differences between the characterized microstructures (see figure 1). Furthermore the relative diamagnetic anisotropy ($\Delta\chi\%$) allows us to confirm quantitatively the optical anisotropy of the different samples.

- the electrical and thermal conductivities confirm the picture : the thermal variations of the thermal conductivity give further evidence of two classes of materials (figure 2).

- *Graphitization process* : after heat-treatment at 2500°C during 1 h 30 mn the studies of structural and physical properties confirm that only the rough laminar microstructure is graphitized the other ones behave as hard carbons.

3 - Conclusion

The model proposed by LIEBERMAN (6) which relates gas phase conditions to the structure of deposit is discussed in the frame of the established correlations between electronic properties and microstructu-

res. We show in this study that a graphitable microstructure (L.R) exists between the non-graphitable ones (see figure 1). This behavior could be correlated with the formation of a mesophase from the gas phase reaction processes which might occurs only for these constraint conditions.

The existence diagram shows up how to obtain the desired microstructures under defined conditions. They change with the fixed and adjustable constraints. Finally we proposed a method to analyze the parameters which define an evolution and to make possible a selection of a specific material for a given application.

(1) W.V. KOTENLSKY - *Physics and Chemistry of Carbons, vol. 9, p. 183. (Ed. by P.L. WALKER, 1973).*

(2) B. GRANOFF, H.O. PIERSON and D.M. SCHUSTER - *J. Composite Materials, vol. 7, p. 36 (1973).*

(3) A. PACAULT, P. MANUSSE, P. DE KEPPER, C. VIDAL and J. BOISSONADE - *Accounts of Chemical Research p. 438 (1976).*

(4) P. LOLL - *Ph. D Thesis, Bordeaux 1976.*

(5) B. GRANOFF - *Carbon, vol. 12, p. 681 (1974)(and previous publications from SANDIA Laboratories).*

(6) M.L. LIEBERMAN - *Proceedings of the 3rd Conference on Carbon vapor deposit, p. 95 (1972).*

Samples	Deposit conditions: flow (l/h) CH_4	H_2	% CH_4	temperature T_D(°C)	residence time t(h)	microstructure	density: apparent	of powder	R.X. Structures: L_c(Å)	L_a(Å)	d_{002}(Å)	Static magnetism: χd(10^6 emu CGS/g)	Δχ%	E.P.R.: g-factor	S(gauss)	Conductivities: electrical Ω(Ωcm)$^{-1}$	thermique K(Wcm^{-1}K^{-1})
PLB	38	347	8	1150	74		1.50	2.05				- 3.53	16				
PLD	15.5	347	4.7	1100	123		1.65	2.07	80	90	3.430	- 3.28	18		55		0.36
PLE	16.5	347	4.7	1050	179	L.R.	1.60	2.07	72		3.432	- 3.31	16	2.0005	65		
PLH	16.5	347	4.7	1110	181		1.73										
PLI	16.5	347	4.7	1135	105		1.65	2.07	87		3.424	- 3.42	21	2.0034	20	890	
PLL	16.5	347	4.7	1080	200		1.80	2.06	70	75	3.436	- 3.26	22	2.0026	34	840	0.36
PLF	36.4	327	10	1080	97		1.75	1.98	65	70	3.438	- 2.75	16	2.0027	27		0.34
PLG	54.6	305	15	1080	85	L.R.+L.L.	1.75	1.98	57		3.447	- 2.47	15	2.0019	26		
* PLQ	36.4	327,6	10	1110	21		1.33	1.91	74		3.432				66	490	
PLJ	109	255	30	1080	59	L.L.	1.70	1.87	42	< 70	3.447	- 2.10	12	2.0031	6.8	555	0.145
PLN	73	291	20	1050	120		1.80	1.95	43	< 70	3.458	- 2.25	12	2.0030	12.5	570	
* PLK	7.3	357	2	1230	67		<1	1.51	49		3.433	- 3.75	7		∿ 55	230	
PLM	6	294	2	1150	160		1.25	1.67	68		3.428	- 3.66	8		46	290	0.16
PLO	4	196	2	1150	154	L.G.	1.19*										
PLP	2	98	2	1150	205		1.20	1.52	50		3.428						
PLR	16.5	347	4.7	1150	69		1.30	1.51	85	75	3.428	- 3.65	8	2.0022	12	175	
PLS	2 +H_2=6	96	2	1225	116		1.05	1.51	54		3.440	- 4.15	5	2.0021	9.4	155	
PLT	2 +H_2=12	96	2	1230	257	I	1.22	1.46	52	90	3.440	- 4.42	2.5	2.0021	6	135	0.225

* These samples are not completely densified.

Table I : Structural and physical properties measured at 295 K of the C.V.D. composites.

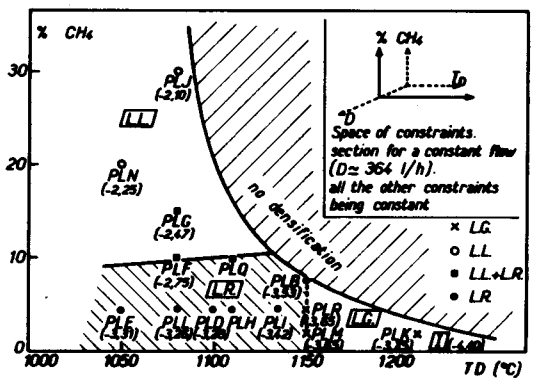

Fig. 1 : *Existence diagram in the constraint space. The dashed part represents the graphitable L.R microstructure zone and the numbers between brackets are the diamagnetic susceptibilies measured at room temperature.*

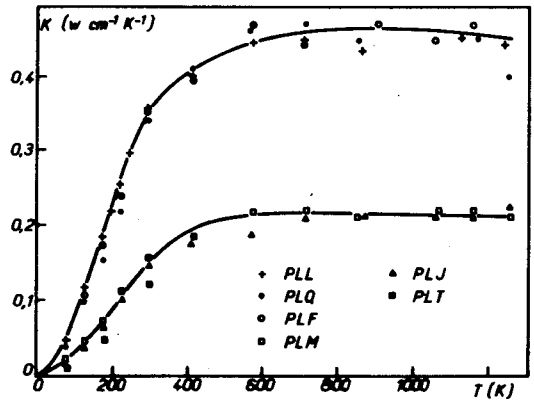

Fig. 2 : *Thermal conductivity versus temperature between 80 and 1300 K for several characteristic composites.*