ANTHRACENE OIL-BASED SYNTHETIC GRAPHITES CONTAINING IRON NANOPARTICLES

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Introduction

Polygranular synthetic graphites are attractive materials for which applications are easily found in modern advanced technologies (eg., nuclear reactor walls, electric discharge machines, special containers, semiconductors). They are employed in various high tech fields because of their inherent electrical, mechanical, thermal and chemical properties (Rand, B., 2001), (Oya, A., 1997). This type of graphite is usually obtained from self sintering precursors, such as mesophase (Fanjul, F., 2004). The mesophase can be obtained from a variety of sources, coal-tar pitch and petroleum pitch being the most common. An alternative source is provided by highly aromatic fractions, such as anthracene oil. Anthracene oil can be polymerized by air-blowing, giving rise to pitches, which are able to generate mesophase when subjected to controlled thermal treatment. The mesophase obtained from anthracene oil pitches is totally free of solid particles. Moreover, the presence of light unreactive compounds in the reaction media favours both hydrogen transfer and the regulation of mesophase development, allowing highly thermoplastic condensed mesophase to be obtained. The final properties of the material can be enhanced by the addition of discrete nanoparticles (e.g. iron oxide). This is because the carbon matrix prevents iron oxide from oxidising and also because iron oxide in the form of discrete particles exhibits magnetic properties which are not visible at micro and macroscale.

This work deals with the preparation of self-sintering graphites from anthracene-oil based mesophase containing iron oxide nanoparticles. The effects caused by the presence of iron oxide nanoparticles in the steps involved in this process (oxidative stabilization of the mesophase, conformation and carbonization/graphitization) were studied by means of elemental analysis, plasticity and thermogravimetric analysis. The resultant graphites were characterized from a structural and mechanical point of view.

Experimental

An anthracene oil-based pitch, supplied by Industrial Química del Nalón, S.A., was used as mesophase precursor (softening point of 112 ºC; elemental analysis: C: 93.6 %, H: 4.4 %, N, 1.0 %, S, 0.5% and O, 0.5%). The mesophase (MAO) was obtained by thermal treatment of the pitch at 450 ºC for 4h and its subsequent sedimentation at 420 ºC for 1h to separate the mesophase from the isotropic phase.

The iron oxide nanoparticles were obtained by a toluene reflux of $Fe(CO)_5$ with Pluronic P127 in the presence of H_2 (Hyeon T., 2001).

Homogeneous dispersion of the iron oxide nanoparticles within the mesophase was obtained by mixing toluene solutions of mesophase and 10 wt.% of iron oxide nanoparticles. Distillation of the toluene leads to an iron doped mesophase (MAOFe).

Prior to sintering, the doped and undoped mesophases were stabilized with air at 225 (MAO-225 and MAOFe-225), 250 (MAO-250 and MAOFe-250) and 275 ºC (MAO-275 and MAOFe-275) using a multi-step temperature/time program (Fanjul, F., 2002). The samples were characterized by means of elemental analysis, plasticity determinations and TG/DTG experiments.

Finely milled stabilized mesophase samples were molded into prismatic specimens (50 X 10 X 3-4 mm) by applying a uniaxial mechanical pressure of 80 MPa at 140 ºC. The green materials were carbonized on a horizontal tube furnace at 3 ºC min^{-1} up to 1000 ºC. Polygranular carbons were labeled as PCFe-225/PC-225, PCFe-250/ PC-250, and PCFe-275/PC-275 depending on the presence or absence of iron oxide nanoparticles. Polygranular carbons were then graphitized up to 2300 ºC at a heating rate of 10 ºC min^{-1} to obtain the graphites PGFe-225/PG-225, PGFe-250/ PG-250, and PGFe-275/PG-275. Polygranular carbons and graphites were characterized by means of bulk/water densities (ASTM D20 standard), X-ray diffraction, four-point flexural strength (ASTM C651 standard), SEM and optical microscopy.

Results and Discussion

Composition and properties of the mesophase.

The total absence of primary QI particles in the anthracene oil pitch gives rise to a mesophase (MAO) with a predominant optical texture of flow domains. The treatment of MAO with iron oxide nanoparticles does not modify its optical texture. Thus, MAO and MAOFe exhibit the same optical texture after carbonization at 1000 ºC **(Figure 1)**.

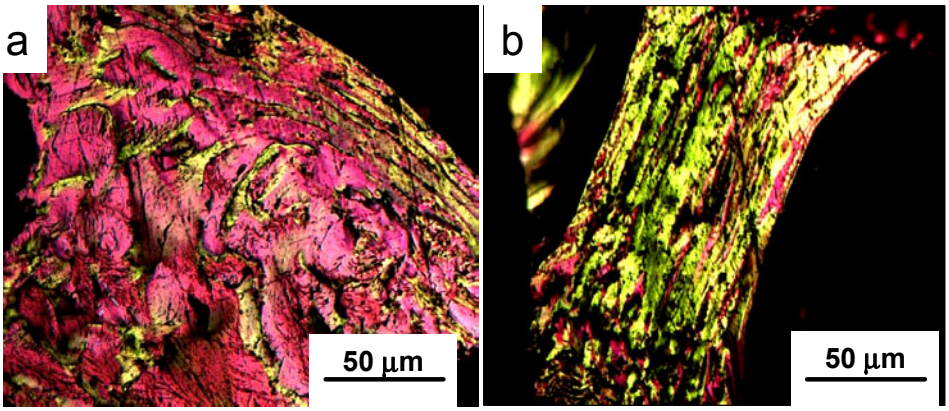

Figure 1: Optical micrographs of (a) the parent mesophase (MAO) and (b) the doped mesophase (MAOFe), carbonized at 1000 ºC.

However, both mesophases exhibit an excessively high plasticity which leads to deformation during the subsequent carbonization/graphitization. It has been demonstrated that stabilization with air is a suitable method for reducing plasticity, as the self-adhesive properties of the samples are maintained. The selected temperatures for the stabilization of MAO and MAOFe were 225, 250 and 275 ºC. It is well known that, depending on the temperature, the reactions involved are the formation of different oxygen-like functionalities and cross/linked structures (more polymerized structures and therefore, less plastic material) (Fanjul, F., 2004).

Table 1: Main characteristics of the anthracene oil based mesophases and derived stabilized samples.

Sample	Elemental Analysis (wt.%)					SP[1]
	C	H	N	S	O	
MAO	94.5	3.8	0.8	0.3	0.6	300
MAO-225	93.1	3.6	1.1	0.3	1.9	-
MAO-250	92.3	3.5	1.1	0.2	2.9	-
MAO-275	90.4	3.2	1.1	0.3	5.0	-
MAOFe-225	93.2	3.3	0.8	0.3	2.4	-
MAOFe-250	92.5	3.2	0.8	0.3	3.2	-
MAOFe-275	91.1	3.2	0.7	0.3	4.7	-

[1] Softening point (Mettler, ºC)

The mesophase used in this study is mainly composed of carbon and hydrogen (**Table 1**). All the stabilized samples show an increase in oxygen content and a decrease in the hydrogen content (3.8 wt.% in MAO to 3.2 wt.% in MAO-275 and 3.2 wt.% in MAOFe-275) as the temperature of stabilization increases. When the mesophases are doped with iron oxide nanoparticles, the oxidative stabilization affects the samples more strongly in addition. Thus, the hydrogen content decreases more strongly for the same stabilization temperature. In addition, the oxygen content at temperatures of 225 and 250 ºC is higher in the carbons doped with iron oxide nanoaprticles. However, at 275 ºC, the oxygen uptake is lower in MAOFe-275 (5 and 4.7 wt. % in MAO-275 and MAOFe-275, respectively). All these results seem to suggest that the process is modified by the presence of nanoparticles.

Thermogravimetric analysis of the undoped mesophases (**Figure 2 a,b**) shows that the stabilization causes a substantial reduction in weight loss. Moreover, the peaks corresponding to the maximum rate of weight loss shift to higher temperatures (**Figure 2b**). Similar effects are observed in the stabilized samples from the doped mesophase (**Figure 2 c,d**). However, in this case, the peak at 590-600 ºC is much more intense than in the undoped samples. This suggests that the oxygen uptake during the stabilization process leads to the formation of certain molecules that are thermally more stable and probably more polymerized than in the parent material. Moreover, the decomposition of the oxygen containing functional groups could be the factors responsible for the peaks observed in the stabilized samples above 600 ºC, these changes being more evident in MAOFe-275.

Determination of sample plasticity indicate that, MAO, MAO-225 and MAOFe-225 are completely fluid, while MAO-250, MAO-275, MAOFe250 and especially MAOFe-275 undergo a considerable decrease in plasticity. This could be related with the fact that oxygen uptake contributes to a decrease in plasticity as a result of the formation of cross-linking structures (Fanjul, F., 2004).

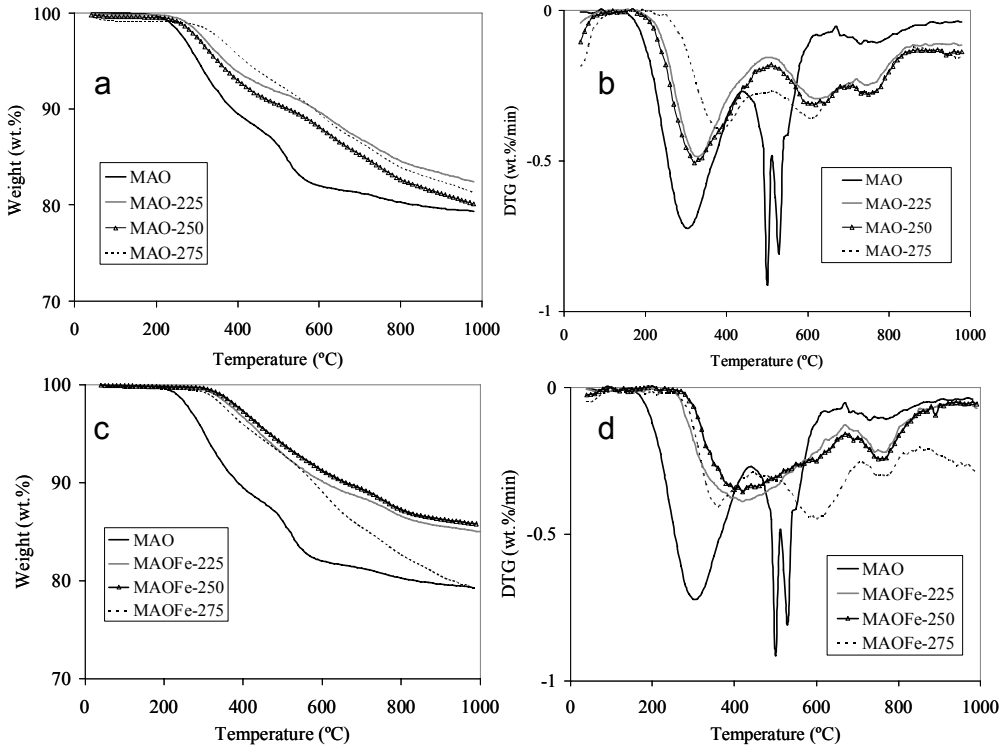

Figure 2: TG (left) and DTG (right) curves of: (a) and (b) parent mesophase (MAO) and stabilized mesophases MAO-225, MAO-250 and MAO-275; (c) and (d) parent mesophase (MAO) and stabilized samples from doped mesophases MAOFe-225, MAOFe-250 and MAOFe-275.

Polygranular carbons/graphites

The stabilized samples were molded into prismatic specimens and carbonized up to a temperature of 1000 ºC prior to graphitization to produce polygranular carbons. The graphitization of polygranular carbons to 2300 ºC leads to a more oriented and stacked structure in the materials, as can be observed from the XR diffraction data (**Table 2**). The d_{002} distance for PG-275 is 3.42 Å, while for PGFe-275 it is 3.44 Å. In both cases, this parameter is closer to the limit established for a turbostratic structure (Franklin, R.E., 1951). These results also agree with the fact that the parent material was stabilized at 275 ºC, giving rise to highly cross-linked structures that make the orientation and stacking of the pregraphitic structures more difficult. The higher d_{002} distance observed in PGFe-275 with respect to PG-275 could be due to the fact that the stabilization of MAOFe-275 was greater than the stabilization of MAO-275.

Table 2: XRD parameters and flexural strength values of polygranular carbons and graphites.

Sample	XRD Parameters			FS [4]
	d_{002} [1]	Lc [2]	La [3]	
PC-275	-	-	-	113
PG-275	3.42	13.3	37.3	91
PCFe-275	-	-	-	135
PGFe-275	3.44	15.1	41.9	121

[1] Mean interlayer spacing (002) (Å)

[2] Crystallite size along the c-axis (002) (nm)

[3] Crystallite size along the a-axis (110) (nm)

[4] Four-point flexural strength (MPa)

The mechanical properties of the polygranular carbons, evaluated by means of four-point flexural strength, shows that these materials can reach values of > 110 MPa. The presence of the iron oxide nanoparticles in the carbons causes a significant enhancement of the flexural strength (135 MPa). However, the transformation of the carbons into graphite is accompanied by reduction in this property (Table 2), which seems to be associated with a higher contribution of the delamination mechanism as a consequence of the higher structural order reached.

CONCLUSIONS

Polygranular synthetic graphites doped with iron oxide nanoparticles are easily prepared by the self sintering of stabilized anthracene-oil based mesophase. The mechanisms involved in the oxidative stabilization of the mesophase are modified by the presence of the nanoparticles, which results in an enhancement of the mechanical properties of the material.

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