INTRODUCTION

Coal-tar pitch is an attractive precursor for the preparation of high-density polygranular carbons because of its capacity to generate mesophase microspheres of homogeneous size [1]. The obtention of mesophase suitable for sintering into polygranular carbons from coal-tar pitch includes several steps: (i) controlled thermal treatment to produce a partially anisotropic pitch; (ii) concentration of the mesophase microspheres and (iii) stabilization of the microspheres to produce a material with the appropriate thermoplasticity.

In the present work, polygranular carbons were prepared from the mesophase obtained from a coal-tar pitch and from a mesophase-based pitch. The structure and properties of polygranular carbons were related to the origin of the precursor and preparation conditions (mesophase stabilization temperature, pressure applied at the molding stage and carbonization heating rate).

EXPERIMENTAL

The mesophase used for the preparation of the polygranular carbons was obtained by the filtration [2] of an impregnating coal-tar pitch thermally treated at 430 °C for 4 h (M-A, 80 vol % of mesophase) and from a naphthalene-based mesophase pitch (M-B). Prior to sintering, mesophase samples were stabilized with air at 225 °C (M-A225) and 250 °C (M-A250 and M-B250), using a procedure previously described elsewhere [3]. The main characteristics of the parent and stabilized mesophase samples are given in Table 1.

After stabilization, the mesophase was finely ground (90 wt % of particles < 15 μm; 50 wt % of particles < 5 μm) and molded into prismatic blocks (50 x 10 x 3 mm) by the application of two different uniaxial mechanical pressures (50 and 80 MPa). Molded mesophase was then carbonized to 1000 °C following four different programs: (i) 1 °C min⁻¹ to 200 °C, 0.3 °C min⁻¹ from 200 to 300 °C, 0.1 °C min⁻¹ from 300 to 550 °C, 0.3 °C min⁻¹ from 550 to 1000 °C and after 30 min at 1000 °C at 1 °C min⁻¹ to 550 °C; (ii) The former program but heating at 0.3 °C min⁻¹; (iii) heating and cooling at 5 °C min⁻¹; and finally (iv) heating and cooling at 1 °C min⁻¹.

Polygranular carbons were characterized in terms of density and porosity determinations, changes in weight and volume during carbonization and microstructural/mechanical properties (optical microscopy, four-point flexural strength and scanning electron microscopy of the fractured surfaces).

RESULTS AND DISCUSSION

MESOPHASE PROPERTIES

The oxidative stabilization of mesophase with air involves a dehydrogenative process (Table 1). Hydrogen is removed as H₂O and oxygen is taken up to form different oxygen-containing functional groups [4]. Aliphatic hydrogen is preferentially consumed against aromatic hydrogen. This could be the reason why M-A is less reactive and can be stabilized in a wider range of temperature than M-B. At 225 °C, M-B undergoes considerable swelling. At 275 °C, M-A and M-B deform in the subsequent sinterization at 1000 °C. This deformation is more obvious for the M-B where both internal and external cracks are observed. A comparison of M-A and M-B stabilized at 250 °C shows that the values of the solubility parameters are similar in both samples (Table 1). However, the oxygen content is rather higher in M-B.
One of the properties that best defines the sintering ability of carbons is their thermoplasticity. Figure 1 shows the variation of the relative penetration with temperature for parent mesophases and samples stabilized at 225 and 250 °C. In the parent mesophases, relative penetration is completed below 270 °C. The temperature interval needed to increase the penetration from 10 to 90 % is 36 °C in M-A and 20 °C in M-B. This supports the idea previously mentioned concerning the higher flexibility of M-A during stabilization. Thermoplasticity is very sensitive to air treatment [5]. Stabilization at 225 °C leads to a significant reduction in the thermoplasticity of M-A (38.5 % of penetration). At the higher temperature of 250 °C penetrability is only 6.6 % in M-A and 3.6 % in M-B.

Polygranular carbon properties

Table 2 summarizes the main properties of polygranular carbons prepared from M-A225, M-A250 and M-B250. The carbonization heating rate and pressure applied for molding have an important effect on the quality of the carbons. Thus, samples carbonized at 5 °C min⁻¹ show significant structural imperfections (large pores, cracks, swelling, etc.). This is because at high heating rates the release of gases takes place in a short interval of time, producing damage to the material. Likewise, molding pressures of 80 MPa lead to distorted materials. Only M-A250 molded under 80 MPa and carbonized at low heating rates (0.1 and 0.3 °C min⁻¹ between 300 and 550 °C) produced non-distorted materials. With the increase in molding pressure, the bulk density of the materials increases (Table 1), but at the same time, the network of pores that allows the release of gases is reduced. Consequently, gases need to open new pathways for their release, leading to dramatic damage of the material.

Although the three mesophase samples lose similar amounts of weight (18.0-19.5 wt %) and undergo similar volume shrinkage (35.0-37.9 vol %) during sintering, carbons derived from M-A225 and M-A250 develop more porosity accessible to helium than those carbons derived from M-B250. This could be related with the fact that in the temperature range of 300-700 °C, M-A250 and M-B250 lose ∼14 wt %, but this loss is more gradual in the case of M-B250, which makes that the release of gases would be more controlled in M-B250.

The carbonization heating rate and molding pressure also play an important role in the mechanical properties of the polygranular carbons (Figure 2). For the carbons that do not bloat during sintering, flexural strength...
strength improves with increasing heating rates and molding pressure, the effect of the latter being more pronounced than the effect of the former (Figure 2). An exception is the case of M-A225 (50 MPa) when it is carbonized at 0.1 and 0.3 °C min⁻¹. A possible explanation for this is that this mesophase is still excessively plastic, and consequently, requires low carbonization heating rates to avoid bloating. Under 50 MPa and the same heating rate, M-B250 gives rise to carbons with values of flexural strength higher than those of carbons from M-A250. However, M-A250 molded at 80 MPa produces carbons with values of flexural strength similar to those of carbons derived from M-250B, although lower heating rates are required.

Figure 3 shows the polarized-light micrographs of some selected carbons. An increase in the heating rate has a negative effect on the microstructure of the resultant carbons because it leads to materials with higher porosity, as observed under the microscope. It is interesting to note that M-B250 (50 MPa, 1 °C min⁻¹), which exhibits the highest flexural strength, shows regions where pores of ~8 µm (Figure 3d) can be observed. On the other hand, carbons derived from M-A250 molded at 80 MPa are homogeneous and the pores are <3 µm (Figures 2b and 2c). Bearing in mind that M-A250 carbons have more porosity accessible to helium, this seems to indicate that in these carbons the small-size porosity is more important than in the M-B250 derived carbons. This is corroborated by the scanning electron micrographs of the fracture surfaces of the carbons after flexural strength tests (Figure 4). By contrast pores in M-A225 derived carbons are more spherical in shape and have thicker walls than those of M-A250 derived carbons. The higher plasticity of M-A225 could be the main factor responsible for this behavior and for the higher values of flexural strength obtained for the derived carbons (Figure 2).

Conclusions

The differences in mesophase composition are the cause of the different behaviors during stabilization. Because of these differences M-A is able to stabilize over a wider range of temperatures than M-B. The higher the carbonization heating rate, the larger the size of the pores in the carbons. Carbons from M-A show a larger proportion of small-size porosity than those from M-B. Differences in porosity can also be observed between carbons from the same mesophase (M-A) stabilized at different temperatures (225 or 250°C).

The flexural strength of polygranular carbons improves with increasing molding pressure. With the same molding pressure, flexural strength improves if the carbonization heating rates are increased.

Acknowledgements

This research was supported financially by CICYT-FEDER (Project 1FD97-1657 MAT).

References

1. Blanco, C., Santamaría, R., Bermejo, J. and Menéndez, R. “Separation and characterization of the isotropic phase and co-existing mesophase in
thermally treated coal-tar pitches”. Carbon 2000, 38, 1169-1176.