INTERCRYSTALLITE ELECTRICAL AND THERMAL CONDUCTIVITY OF POLYCRYSTALLINE CARBONS HEAT TREATED AT HIGH HTT

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Introduction

Although most polycrystalline carbon materials heat treated at high temperatures (above 2000°C) contain a high amount of graphite-like crystallites, they show electrical and thermal conductivities values different from those of the graphite single crystal along its main direction of conductivity (along the *a*-axis). This behaviour differs from other conductive polycrystalline materials, such as metals, where the values of electrical and thermal conductivities are similar to the those found in their respective single crystals. The objective of this work is to present a model for the electrical and thermal conductivities of heat-treated polycrystalline carbons in which the intercrystallite (or intergranular) conductivity is a main variable. The conductivities are determined in terms of microscopic structural parameters obtained from x-ray diffraction, and the theoretical predictions, valid for high heat treatment temperatures (HTT), are applied to a graphitizable and a non-graphitizable carbon.

Intergranular conductivity

The electrical and thermal conductivities of the graphite single crystal [1] are 1/0.45 μΩm and 1850 $Wm^{-1}K^{-1}$ along the *a*-axis and $1/10^2$-10^3 μΩm and 8-80 $Wm^{-1}K^{-1}$ along the *c*-axis. Since the conductivities of the graphite single crystal along the *a*-axis are much higher than those along the *c*-axis, it can be shown that by assuming a random distribution of orientations of the crystallites, the process of conductivity through the crystallites of the polycrystalline carbons occurs fundamentally along the *a*-axis.

The room temperature electrical conductivity of carbon materials before the stage of graphitization was discussed by Carmona and Delhaes [2] and Emmerich et al. [3]. We will analyse here the behaviour of the electrical and thermal conductivities after the heat treatment temperature HTT_a [4,5], where the coalescence of crystallites along the *a*-axis starts, that is, where the important side by side junction of their graphite-like layers occurs and the material may begin to present 3D XRD graphitic lines.

Above HTT_a the process of coalescence of crystallites along the *a*-axis suggest that most crystallites may be "linked" with each other through their lateral surface. We will assume that this is the shortest and main circuit where the process of conductivity along the material takes place. Thus, the conductivity of the polycrystalline carbon materials heat treated at high temperatures is obtained from the association in series of two main types of contribution: the conductivity of their graphite-like crystallites and the intercrystallite conductivity.

Since the polycrystalline carbon materials at high HTT present a high volume fraction of graphite-like crystallites and values of electrical and thermal conductivities of the order of $1/10^1$-10^2 μΩm and 10^1-10^2 $Wm^{-1}K^{-1}$, which are at least one order of magnitude lower than those of the single crystal along the major direction, we will make here a simplification by assuming that the conductivities are governed by the intergranular conductivity among crystallites. This means that the equivalent conductivity of the association in series of the two contributions is limited by the intercrystallite conductivity.

If we assume that for each carbon atom of the lateral surface of the crystallites there is one link with a carbon atom of the lateral surface of an adjacent crystallite, and this connection presents a constant conductance k_i, then the equivalent conductance k_{eff} is inversely proportional to the number of crystallites per unity volume (N_{cr}) and the lateral surface of the crystallites (S_l).

$$k_{eff} = f_t \, k_i / N_{cr} \, S_l \ , \qquad (1)$$

where f_t is a factor that will depend on the texture of the material. Among other properties, f_t depends on the angular distribution of the intercrystallites contacts in relation to the direction where the conductivity k_{eff} is being measured and the fraction of crystallites that may be not contributing to the conductivity. Substituting the expressions for N_{cr} [5] and S_l [6], we obtain:

$$k_{eff} = C_i \, L_a / (L_a)_{vg}^2 \ , \qquad (2)$$

where $(L_a)_{vg}$ represents the value of L_a vegetative [5] and C_i is a constant for the material.

Results and Discussion

The theoretical expression (2) was applied to the Petroleum coke (a typical graphitizable carbon) and to the Akabira coal (a nongraphitizable carbon), which were extensively studied by Honda and co-workers [7]. Since above 2000°C HTT the value of $K\times\rho$, where K is thermal conductivity and ρ is electrical resistivity, is nearly constant for the Petroleum coke ($K\times\rho$ = 0.0013 ΩWK^{-1}) and for the Akabira coal ($K\times\rho$ = 0.0017 ΩWK^{-1}) [8], we will only present here results for the room temperature electrical conductivity.

The experimental values (obtained from [7]) and our theoretical predictions for the inverse of the electrical conductivity are shown in Figure 1. Since HTT_a for the Petroleum coke and the Akabira coal are 1500°C and 2700°C respectively [4], we are only showing the theoretical predictions above these temperatures. In the case of the Petroleum coke, we observe that initially, from 1500 to 2000°C HTT, our model does not explain satisfactorily the behaviour of the resistivity. On the other hand, above 2000°C, there is a very good concordance between the experimental behaviour and predictions of the model, showing that our assumption on the importance of the intercrystallite conductivity may be valid in this range. In the case of the Akabira coal, although the HTT measurement interval is relatively short, the accordance of the results may be considered reasonable good.

Acknowledgements

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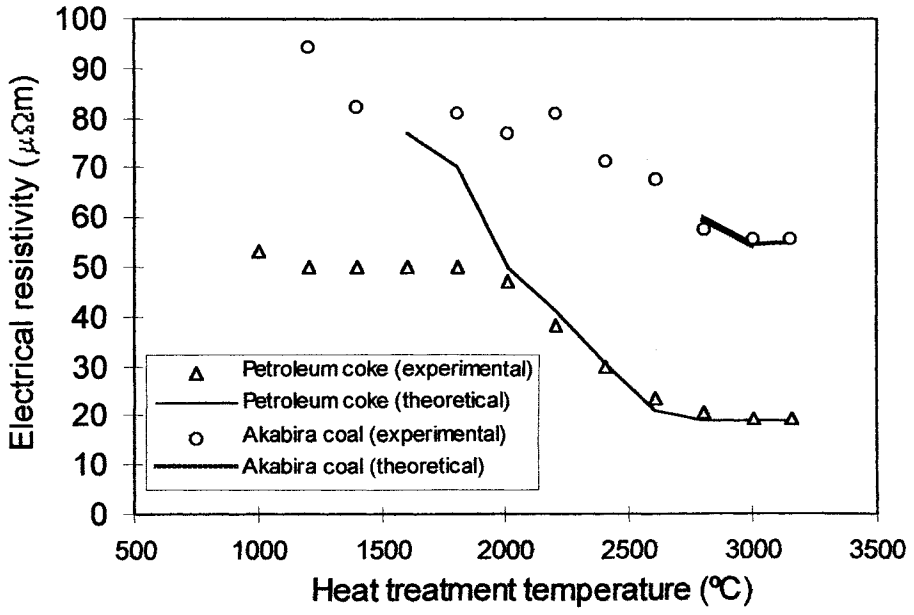

Figure 1. Electrical resistivity of Petroleum coke and Akabira coal as a function of HTT.