

FORMS OF PYROLYTIC CARBON ENSUING ON THERMAL DEGRADATION OF COAL AND CARBONACEOUS ADDITIVES

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FORMY PYROLÝZNÍHO UHLÍKU V PROCESU TERMICKÉ DEGRADACE UHLÍ A UHLÍKATÝCH PŘÍSAD

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Abstrakt

Uhlí a uhlíkaté přísady jsou prekursory koksu a pyrolýzního uhlíku, který se tvoří jejich pyrolýzou v žárovém pásmu slévárenské formy. Při pyrolýze (900°C, 5°C/min) standardního vzorku černého uhlí a jeho směsi s uhlíkatými přísadami jen v 1.stupni byly zkoumány výtěžky koksu a těkavých produktů. Při 2-stupňové pyrolýze byl ve 2.stupni (1100°C) zachycován pyrolýzní uhlík, ze kterého byly separovány méně uspořádaný amorfni uhlík a vysoce uspořádaný (strukturovaný) uhlík. Srovnávací chemická charakteristika (C, H, C^{at}/H^{at}) a fyzikální charakteristika (hustota, rtg-struktura) dokládají výrazné rozdíly mezi uspořádaností koksu, amorfniho uhlíku a lesklého uhlíku.

Abstract

Pyrolysis of coal and carbonaceous additives in the glow zone of foundry moulds gives rise to coke and volatile products. This pyrolytical process was modeled and studied on two stages. In the first stage of pyrolysis (900°C, 5°C/min) of a standard sample of bituminous coal and its mixtures with carbonaceous additives, the yields of coke and volatile products were determined. The volatile fraction was then thermally degraded during the second stage of pyrolysis (at 1100°C). This resulted in two other products: less ordered amorphous carbon and highly structured lustrous carbon. The chemical analysis (C, H, C^{at}/H^{at}) as well as measurement of various physical characteristics (density, x-ray diffraction pattern) reveals remarkable difference between the degree of order in coke, amorphous carbon and lustrous carbon.

Introduction

In the process of thermal degradation of coal and carbonaceous additives in moulding mixtures [1], three different solid state substances having high content of carbon arise. Immobile pyrolytical product is coke located between the quartz grains and compensating for their volume

changes. The mobile products of primary pyrolysis - gas and tar - give rise to two different forms of pyrolytic carbon, which can be visually discerned and separated [2]. The dim, fine-grained form of pyrolytic carbon, which we call amorphous carbon, has less carbon and more hydrogen than the bright, flake-like form of pyrolytic carbon that we denote lustrous carbon [3]. These two distinct forms of pyrolytic carbon sprang up from the pyrolysis of pure coal as well as from the pyrolysis of coal enriched with 10% or 20% of additives. Traditionally, bituminous tar and its derivatives are used as the additives [4]. With regard to the present hygienic regulations and environment protection laws, industrial use of these additives is no more acceptable. But we still used them in our research performed within the framework of the project supported by the Grant Agency of the Czech Republic with the aim to be able to compare our results with the previous works [2,5]. In addition to it, we used natural resin as a representative of new types of additives, which do not contain polycondensed aromatic hydrocarbons (Table 1). Evaluation of gilsonite [6,7], which is a natural material closely related to asphalt, will be a subject of our future study.

Experiment

A standard sample of bituminous coal (from Dukla mine, OKR) has been used in our study, the characteristics of which being given in Table 2. This type of coal with low ash and sulphur content (4.2% and $S_0 = 0.49\%$, respectively) has an acceptable content of oxygen and yields a desirable high amount of volatile matter ($V^{daf} = 29.1\%$), which is the source of pyrolytical carbon produced during the second stage of pyrolysis. The caking properties and thermoplasticity are somewhat worse ($SI = 1$) but still satisfying to our purposes.

Fig.1 The morphology of lustrous (A) and amorphous (B) carbon (bituminous coal from Dukla mine)

Table 2 Properties of bituminous coal used

$$W^a = 1.3\% \quad A^d = 4.2\% \quad V^{daf} = 29.1\%$$

The spectrum of the traditional carbonaceous additives - coal-tar pitch and inden-coumarone (IC) tar fraction -has been supplemented by a natural material - the natural resin - having only little content of polycondensed aromatic hydrocarbons which are hygienically unacceptable. The Table 3 documents that both IC and natural resin have a high content of volatile matter (95% and 99%, respectively). The high oxygen content of the natural resin entails an increased production of oxides of carbon and water during pyrolysis. The two-stage pyrolysis of the mixtures of coal with additives has been performed in a laboratory pyrolytical unit described in [2,8]. During the first stage of pyrolysis (900°C, 5°C/min), immobile coke and volatile products (tar and primary gases) arise in a vertical quartz reactor. The volatile matter then flows to a horizontal quartz reactor, where the second stage of pyrolysis runs at 1100⁰C; the product of this process is pyrolytical carbon that settles down on the reactor wall. Two distinct phases of pyrolytic carbon can be discerned visually: a bright plate-like highly structured lustrous carbon on the reactor wall and a fine-grained amorphous dim carbon at the inner side of the deposited layer. These two phases can be manually separated, but the procedure is only semi-quantitative and that is why we indicated just the total yield of the pyrolytic carbon in the Table 4.

Results and discussion

Addition of 20% of coal-tar pitch has in fact no influence on the mass balance (samples 1 and 2). Adding 20% of indene-coumaron tar increases the yield of pyrolytic carbon by 3.1% and the yield

of pyrolytic gas by 5.6%, while the yield of reaction water declines by 0.9%. Also the addition of 20% of natural resin has a positive influence, increasing the yield of pyrolytic carbon by 5.3% and the yield of pyrolytic gas by 3.5%. The rise of the yield of reaction water is in this case due to the high content of oxygen in the natural resin (14.22%). From the Table 4 it is seen that the use of the coal-tar pitch is not advantageous even from the point of view of the yield of pyrolytic carbon.

The technical and elemental analysis supplemented by density characterize coke (Table 5) and amorphous carbon (Table 6). As expected, neither the elemental composition nor the density of cokes have been significantly influenced by additives (see Table 5). Degassing of cokes (V^{daf} , H) is uniform. The mutual comparison of coke, amorphous carbon and lustrous carbon offer the tables 6 and 7.

Taking into account that the ash content in coke and in pyrolytic carbon are different, the degree of order of their organic matter should be compared by the content of carbon, hydrogen and the atomic ratio $H^{\text{at}}/C^{\text{at}}$ (aromaticity) in combustible matter. Tables 5, 6 and 7 prove that the structural regularity of the organic matter decreases in the sequence: lustrous carbon ($C_{\text{mean}} = 97.96\%$; $H_{\text{mean}} = 0.09\%$; $H^{\text{at}}/C^{\text{at}} = 0.0109$), amorphous carbon (97.07%; 0.31%;0.0381), and coke (95.71%; 1.26%; 0.1593).

The degree of structural order may be estimated also by oxyreactivity i.e. by profile of the DTA-peak corresponding to the burn of the sample in the air (Table 8). So, e.g., the mean temperature of the maximum of the DTA-peak is $t_{\text{max}} = 792.5^{\circ}\text{C}$ for the lustrous carbon (which is highly resistant to oxidation), while $t_{\text{max}} = 607.5^{\circ}\text{C}$ has been found for the amorphous carbon (with intermediate resistivity) and $t_{\text{max}} = 562.5^{\circ}\text{C}$ for the coke which is the least resistant species. And, taking for granted that the structural order is indirectly proportional to oxyreactivity, we obtain once again the sequence of lustrous carbon, amorphous carbon and coke arranged in decreasing order by their structural regularity.

Last, but not least, we estimate the degree of order (three-dimensional structural order/disorder *sensu lato*) in the structure of the lustrous and amorphous carbon by x-ray diffraction [9]. To this end, we used Fe-filtered CoK_{α} radiation and a 114,6 mm - diameter camera in the Bragg - Brentano semifocusing arrangement (25° angle of incidence) and Ge(111) - monochromatized CuK_{α}

radiation and a 500mm - diameter 120° position sensitive detector with 8192 channels. The following features were measured on the diffraction patterns: the position of the diffraction line (002), the broadening of the diffraction line (002) and the ratio $x = I(004)/I(10)$ of the intensity $I(004)$ of the diffraction line (004) and the intensity $I(10)$ of the diffraction band (10). Subsequently, with the help of these diffraction parameters, we calculated the following structural characteristics: the interlayer spacing $d(002)$, the coherent scattering domain size L along the direction of the sixfold axis and the so-called degree of graphitization $g = [0.344 - d(002)]/[0.344 - 0.3354]$. The results, which characterize the structure of the both forms of pyrolytic carbon, are summarized in the Table 9. Their discussion will be given in a forthcoming paper [9].

$d(002)$ = interlayer spacing;

$g = [0.344 - d(002)]/[0.344 - 0.3354]$ = degree of graphitization;

L = coherent scattering domain size along the direction of the sixfold axis;

$x = I(004)/I(10)$ = the ratio of the integrated intensity $I(004)$ of the diffraction line (004) and integrated intensity $I(10)$ of the diffraction band (10); it characterizes the structural distortion that consists in random displacements of carbon atoms from their equilibrium positions along the direction of the sixfold axis;

designation of samples - see Table 4

We assume that the advantageous effect of the lustrous carbon is enhanced by the structural similarity between quartz and graphite (carbon). This resemblance, expressed by the proximity of the values of the interplanar spacing of the graphite (002) lattice family - 0.335 nm - and quartz (101) lattice family - 0.334 nm, makes the surface tension between these two substances - when topotactically oriented - very low. Consequently, the quartz grains are well wetted by the carbon that insulates them from each other and from the melt. But this cannot happen in case of amorphous carbon due to its structural distortions that diminish the stability of the topotactical bond.

Conclusions

Our comparative analysis of the products of the two-stage pyrolysis of bituminous coal with 20% additions of coal-tar pitch, natural resin, and inden-coumaron tar fraction proved that

the largest yields 15.8% of the pyrolytic carbon were obtained with the 20% addition of natural resin, the high oxygen content of this additive having been converted mostly into the yield of the reaction water (6.8% - see Table 4);

the regularity of the structural arrangement of the organic matter rises in the sequence: coke - amorphous carbon - lustrous carbon, as is documented by the decreasing hydrogen content, increasing aromaticity (C^{at}/H^{at}), and decreasing reactivity with the aerial oxygen (values of t_{max} in the table 8);

to explain the difference between the values of $x = I(004)/I(10)$ corresponding to the amorphous and lustrous carbon (Table 9), we propose a model of structural disorder which consists in the deviation of the carbon atom from its equilibrium position in the direction of sixfold axis; in comparison with the lustrous carbon, these deviations are much greater in the amorphous carbon causing the lost of coherence (order) and structural decay (fragmentation).

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