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STUDIES OF THE REACTION BETWEEN THE AMORPHOUS CARBON AND SILICON

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The kinetic parameters and the mechanism of reaction carbon black-silicon was studied by DTA, QXRD and microscopic methods. The possibility of SiC micropowders production at temperatures below the melting point of silicon was proved.

The SiC micropowders can be produced as a result of the exothermic, self-propagating reaction between the active carbon component and silicon [1-3]. In the case of the hard carbon black application as a carbon-bearing reactant, the reaction is initiated at the temperatures below the melting point of silicon, and the mechanism must be different from that for the reaction between the molten silicon and carbon fibres [4, 5].

The DTA, QXRD and microscopic examinations were carried out in order to find the kinetic parameters and the mechanism of reaction carbon black-silicon.

Materials and methods

The carbon black component Sakap-6 (produced by Carbochem - Gliwice, Poland) and the ground, semiconducting silicon fractions 0-1 μm and 1-5 μm [4] were used as the starting materials. The mixtures at Si/C ratio 1:2 were prepared. The β-SiC powder from the silicon and carbon black [3] was synthesized as a QXRD standard [3]. The Setaram 2000 K thermoanalyser was used at the following parameters: temperature range 293-1873 K, heating rate 5 deg/min, vacuum ca. 1.3 Pa, T and DTA point registration at every 30 s, sample 70 or 100 mg in Al_2O_3 crucibles, Al_2O_3 powder as reference material. The following XRD peaks were measured by

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Philips diffractometer: for SiC-peak (111) at $2\theta = 35.60$ and for Si-peak (111) at $2\theta = 28.40$. The SiC grain size and phase composition by counting method were determined using Neophot-2 microscope at the reflected light and magnification 2000 x.

Results and discussion

The DTA curve typical for the samples with Si/C ratio 2 is shown in Fig. 1/a. The exothermic peak corresponding to the reaction carbon-silicon occurs usually at 1500-1650 K, i.e. below the silicon melting point. The relative rate of reaction as a function of temperature (Fig. 1/b) was determined following the procedure described earlier [5]. Taking into account the T and DTA registration (every 30 s) one can conclude that the rate of reaction becomes two times greater within 60 s. This reaction rate increase is 4-5 times smaller than for the reaction between the carbon fibres and molten silicon. Therefore the time of the reaction with carbon black becomes 4-5 times longer for the similar samples and the similar conditions. Taking into account that there is no molten silicon component present, it is evident that the change of the reaction mechanism occurs. The similar conclusion can be drawn from the apparent activation energy values calculated from the relation $-\ln k = f(1/T)$ (Fig. 1/c) for the initial stage of reaction ($E_1 = 1720 \pm 166$ kJ/mol) and final stage ($E_2 = 1006 \pm 40$ kJ/mol). The average in all the range is $E = 1379 \pm 58$ kJ/mol and the best correlation is achieved for the reaction of the first order (correlation coefficient $r = 0.98$). The errors of the procedure described above result from the small "dilution" of the reactants (Si:C = 2) and the differences of thermal properties between the standard and studied samples [6].

However, the change of concentrations from Si:C = 2 to Si:C = 1 brings about a slight temperature range lowering (ca. 40 K) accompanied by ca. 10% activation energy decrease. This small change indicates that the influence of the concentration is not significant. The area of the endothermic peak (Fig. 1/a) corresponding to the heat absorbed during the melting process of excess silicon in the samples with Si:C = 2 proves that the degree of reaction is ca. 90%. The microscopic observations show that this degree of reaction is higher; only ca. 1% of unreacted carbon black was observed and, respectively, 98% SiC. The similar results were obtained by QXRD. The measured Si residue was 3 ± 1% in the stoichiometric samples heated up to 1675 K. However, the SiC content in the samples heated to 1558 and 1675 K was 49% and 76% respectively.

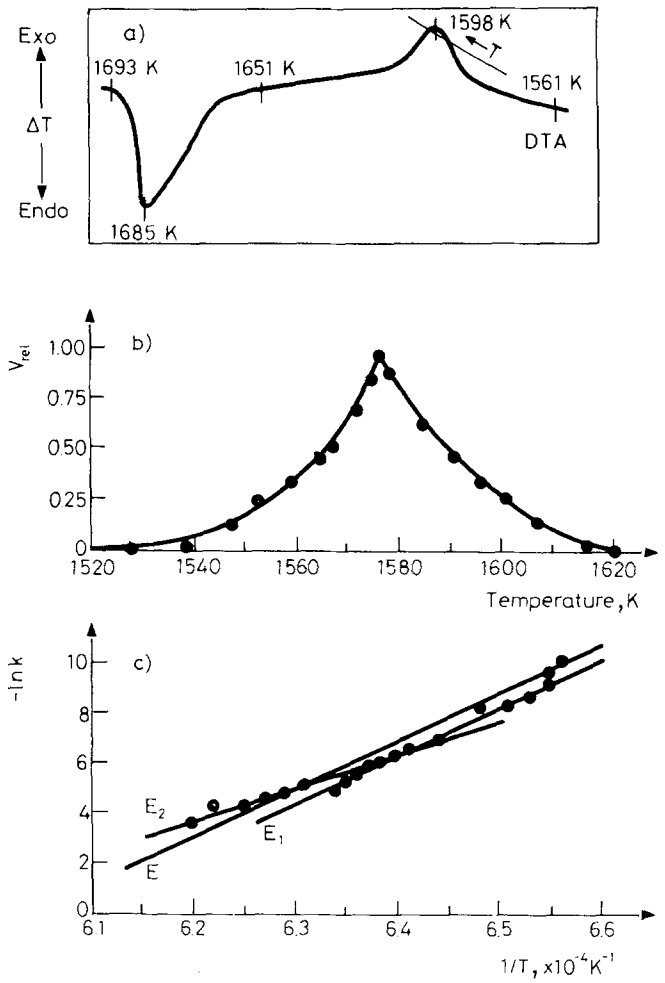

Fig. 1 a) - DTA curve of the micture carbon black-silicon, b) - the relative rate of reaction carbon black-silicon as a function of temperature, c) - the relation $\ln k = (-E/RT) + \ln A$ for the reaction carbon black-silicon

These discrepancies have not been explained until now but even these data indicate the high degree of reaction and possibility of SiC micropowders production below the silicon melting point. The SiC QXRD measurements in the samples heated below the observed endothermic peak (1500-1650 K), i.e. at 1223 and 1423 K indicate also small amount of SiC (0.3% and 0.5±0.2% SiC respectively). These results support the role of the gaseous phase in this reaction (though the surfacial diffusion of Si and solid

state reaction is not excluded), which seems to be significant in the light of the fact, that the intense evaporation of Si from the open crucibles takes place (12.8% weight loss at 1643 K). This Si gaseous phase can react with carbon black particles of high specific surface (92 m^2/g), which turn into the SiC grains. The SiC grain size measurements (after melting of excess Si) support this view. The diameter of more than 80% SiC grains is in the range 0.1-0.3 μm (the initial Si grains diameter is 1-5 μm). Therefore the reaction occurs in the area of carbon reactant, the same situation as in the case of carbon fibres and molten silicon. Further investigations in order to explain the mechanism of this reaction are continued.

References

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Zusammenfassung — Mittels DTA, QXRD und mikroskopischen Methoden wurden die kinetischen Größen und der Mechanismus der Reaktion Ruß-Siliziumdioxid untersucht. Es wurde die Möglichkeit der Herstellung von mikropulverisiertem SiC bei Temperaturen unter dem Schmelzpunkt von Silizium bewiesen.