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Short Communication

REACTION BETWEEN CARBON FIBRES AND MOLTEN SILICON: HEAT DETERMINATION USING DTA

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The highly exothermic reaction between carbon fibres and molten silicon, which is the basis of SiC—Si composite production, was investigated using a Setaram 2000 K thermoanalyser. DTA curves were recorded in 1.3 Pa vacuum and up to 1770 K, i.e. under the conditions of composite production. The results allowed calculation of the heat of the reaction, which ranged from 91 to 115 kJ/mol.

The reaction between carbon fibres and molten silicon is the basis of the production of composites with the silicon matrix reinforced with fibrous silicon carbide (β-SiC). The reaction is very fast: it lasts for 4–6 minutes and is carried out in a vacuum of 1.3 Pa at 1700–1800 K [1].

The production of SiC—Si composites by this method is more economical than the production of self-bonded Refel SiC with similar thermomechanical properties.

Investigations of the mechanism of the reaction between carbon fibres and molten silicon [2, 3] prove that the temperature and carbon concentration oscillations at the fibre-molten silicon interface cause the precipitation of small ($\sim$0.1 μm) β-SiC crystals to occur. Subsequently, these small crystals are transformed by the recrystallization into fibrous, polycrystalline β-SiC, which results in the advantageous mechanical properties of the composites. These fibrous SiC crystals grow at the sites originally occupied by carbon fibres.

The temperature oscillations occur owing to the reaction heat emission, determination of which is therefore necessary for a rational explanation of the process.

Moreover, the highly exothermic silicon-carbon reaction is utilized to synthesize a special refractory material in a self-propagating solid-state combustion process [4].

The carbon-silicon reaction heat values determined in the thirties and forties ranged from 44 to 160 kJ/mol. Recent thermochemical calculations [6] gave a value of 115 kJ/mol, while in [7] a reaction heat of 247 kJ/mol was taken in the calculations.

These discrepancies led us to carry out new measurements of the carbon fibre—molten silicon reaction heat by using DTA.

Experimental

Materials

For sample preparation, semiconductive silicon with a total Al, Mn, Cu, Pb, Cr and Ni content of less than 10^{-1} ppm and an Fe content of about 20 ppm was used. Fibres with a diameter of 12.4 μm, a Young's modulus of 152 GPa and a density of 1.7 g/cm^3, obtained by carbonization of the polyacrylonitrile precursor at 1275 K [8], were applied.

Method

The measurements were carried out with a Setaram 2000 K thermoanalyser in a vacuum of 1.3 Pa at 293–1873 K at a rate of temperature increase of 5–20 deg/min. The weight of the samples studied was about 70 mg, and they were placed in cylindrical alumina crucibles. As inert material, alumina or silicon was used. The coincidence of the melting points and the heats of fusion for silicon and nickel allows determination of the heat transfer coefficient K. This was done by comparison of the melting and solidifying effects of these elements, assuming that the heats of fusion and the melting points of silicon and nickel were 46.5 ± 1.7 kJ/mol, 1683 ± 5 K and 17.7 ± 3.3 kJ/mol, 1723 ± 5 K, respectively [5, 9].

Procedure

In the range of the carbon–silicon reaction temperature, oxidation of the silicon by oxygen from the alumina crucible occurs. This brings about an increase in the surface tension of the liquid silicon, impeding infiltration of the liquid silicon into the carbon fibres and markedly slowing down the reaction. In order to prevent silicon oxidation, the inner walls of the crucible were covered by a thin layer of the powdered carbon fibres. The mixture of cut fibres (2 mm long) and comminuted silicon (grains ~2 μm) was then placed in the crucible. The carbon : silicon weight ratio ranged from 0.2 to 0.3. The phase composition of the samples after the reaction was determined by the microscopic method. The fibrous silicon carbide in the silicon matrix and some quantity of unreacted carbon fibres are present in the samples. The presence of the latter phase hampers interpretation of the DTA results, and the heat of reaction was therefore calculated for the samples containing silicon carbide and silicon only.

Results and discussion

A typical DTA curve for carbon fibres—molten silicon is shown in Fig. 1. The emission of the reaction heat brings about sample self-heating, which influences the reaction course. A temperature increase of from a few K to several hundred K is observed, depending on the weight of the sample [3].

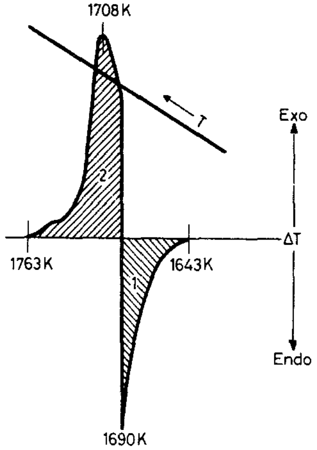

Fig. 1 DTA curve of the reaction between carbon fibres and molten silicon (inert material: α-Al_2O_3). 1 – Endothermic effect due to silicon melting. 2 – Exothermic effect due to reaction between carbon fibres and molten silicon

The heat of reaction Q_R was calculated by taking into account the quantity of silicon, the areas of the exothermic and endothermic effects (Fig. 1) and the heat transfer coefficient K. Its value ranges from 91 to 115 kJ/mol and depends on the measurement conditions and on the nature of the inert material of the reference sample. Assuming for the calculations a mean value of the reaction heat $Q_R = 102.8 \approx 103$ kJ/mol, the heat balance can be performed. It is known that the reaction starts from the endothermic dissolution of carbon in molten silicon and the heat of this process—Q_s is 247 kJ/mol [10]. Next, owing to supersaturation, the crystallization of silicon carbide occurs, with emission of the crystallization heat Q_c.

Thus, $Q_R = Q_s + Q_c$, and next the heat of crystallization can be calculated, $Q_c = -350$ kJ/mol. This result indicates that the exothermic effect of the reaction is caused by the silicon carbide crystallization and an increase of temperature can be expected in areas where the crystallization occurs. This is of importance when the mechanism of the carbon fibre–molten silicon reaction mechanism is discussed.

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