CHEMISTRY LETTERS, pp. 1247-1250, 1973. Published by the Chemical Society of Japan

MASS SPECTRAL ANALYSIS OF THERMALLY DESORBED GASES FROM DIAMOND SURFACES

Seiichiro MATSUMOTO, Yoichiro SATO, Nobuo SETAKA, and Masaru GOTO
National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 300-31

Mass spectral analysis was made of gases thermally desorbed from oxidized and hydrogenated surfaces of diamond up to 960°C. The chemisorbed oxygen desorbs as CO and CO_2, while hydrogen as H_2. The desorption in the form of CO occurs at least in two steps.

The diamond surface, likely to organic compounds, is expected to react with various foreign atoms forming stable surface compounds. Several authors studied the surface reactions or the kinetics of adsorption on diamond of such gases as hydrogen, oxygen and halogens.[1-3] This study was initiated as a preliminary study to determine the feasibility of a more detailed investigation of the chemisorbed diamond surfaces by thermal desorption method.

The thermal desorption of the surface oxide and hydride of diamond powders was studied by thermogravimetric and evolved gas analyses (TGA-EGA) from room temperature to 960°C.

The material used was finely pulverized natural diamond, which was treated by hydrofluoric acid and sulfuric acid and thoroughly washed by distilled water. The BET(N_2) surface area was measured to be 30 m^2/g. The apparatus used was composed of a torsion type vacuum thermobalance (sensitivity 50 μg) and a quadrupole mass analyser (Nihon Shinku MSQ-500). The sample (ca 10 mg) held in a quartz bucket was heated in an electric furnace.

Oxygen and hydrogen treatments were performed as follows: after outgassing at 2×10^{-6} Torr and at 900-950°C for 30 min., the diamond powder was kept in the oxygen gas of 10^{-2}-10 Torr at temperatures between 300-500°C for 1 hr., or in the hydrogen gas of 10^{-2}-2 Torr at 700°C for 1-3 hrs. After cooling and evacuation to 2×10^{-6} Torr, TGA-EGA was carried out by heating the sample from room temperature to 960°C at a heating rate of 20°C/min.

The results of EGA are shown in Figs. 1-3, where observed mass peak heights of evolved gases are plotted as a function of temperature. Sensitivity calibration of the mass spectrometer for each gas was not made. No significant difference in EGA was observed for the samples treated at the conditions described above. In Fig. 2, desorption spectra of the samples which adsorbed oxygen at room temperature are also shown. As a comparison, EGA of oxidized graphite powder was examined and the result is shown in Fig. 5. In these figures, M/e=28 and 44 correspond to CO and CO_2, respectively. However, the initial amount of M/e=28 is due to N_2 and some of hydrocarbons besides CO. Effect of possible reaction of diamond with residual gases was

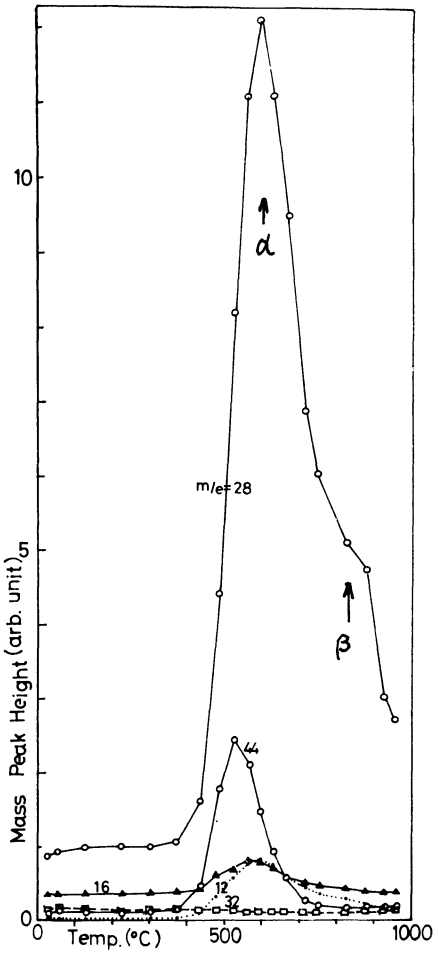

Fig. 1. EGA of oxidized diamond powder; 2×10^{-2}Torr O_2, 400°C, 1 hr (sample weight 11 mg)

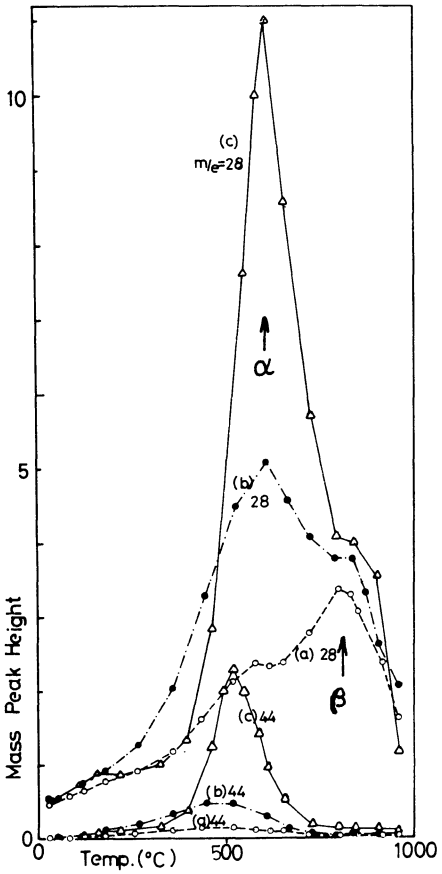

Fig. 2. EGA of diamond powder; (a) kept in leaked air ($\sim 10^{-1}$Torr) in the apparatus for 12 hrs at room temperature (11 mg), (b) kept in dry air for 12 hrs at room temperature (11 mg), (c) oxidized in 7 Torr O_2 for 1 hr at 415°C, then exposed to air at room temperature for 20 hrs (11 mg)

checked by EGA of out-gassed samples as shown in Fig. 4. A gradual increase of M/e=2 and 28 values above 700°C was observed as shown in the figure. It is most probably caused by the decomposition of residual hydrocarbons and their reaction with H_2O, since the same behavior is observed in blank tests. Therefore, Fig. 4 represents, in effect, the background for the results given in this report. Desorption in the form of H_2O or OH was not detectable because of high background of these mass peaks.

The following points may be noted from the results obtained in the present experiment.

1) Oxygen adsorbed on the diamond surface desorbs in the form of CO or CO_2 as shown in Fig. 1. The weight loss due to the desorption was found to correspond roughly to monolayer capacity of oxygen as CO, assuming that the surface of diamond powder consists predominantly of (111), (110) and (100) faces.[2,3] As indicated in

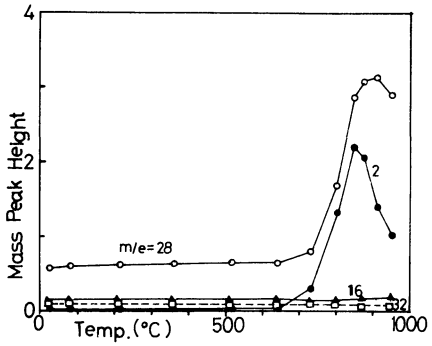

Fig. 3. EGA of hydrogenated diamond powder; 2.5 × 10^{-2}Torr H_2, 700°C, 1 hr (44 mg)

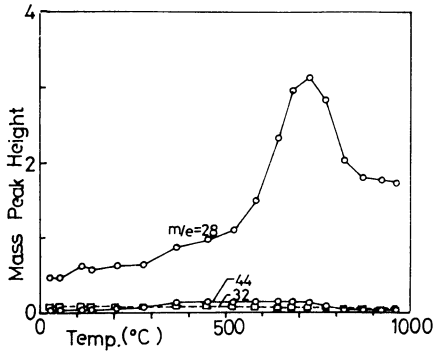

Fig. 5. EGA of oxidized graphite powder; 10 Torr O_2, 410°C, 1 hr (79 mg)

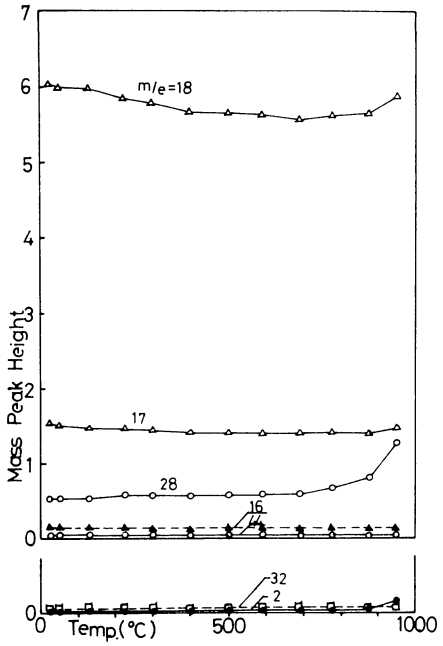

Fig. 4. EGA of outgassed diamond powder; 910°C, 10 min., at 3 × 10^{-6} Torr (11 mg)

Fig. 2, EGA of oxidized samples revealed at least two types of adsorption sites (α and β), and it is also shown that the amount of oxygen chemisorbed on these sites changes with the conditions of oxygen treatment. A desorption peak of CO_2 may indicate the presence of another sort of sites. However, it is not possible to conclude from these data only whether CO_2 is directly released from the surface or is produced by the reaction of released CO with adsorbed oxygen.

2) The samples oxidized at room temperature start to evolve CO at lower temperature giving much broader desorption curves. This seems to indicate the existence of more loosely bound, disordered carbon atoms as suggested by others,[2] which are burned off by oxygen treatment at higher temperature.

3) Oxidized graphite desorbs oxygen mainly as CO (Fig. 5). The peak position lies midway between α and β, indicating the activation energy of desorption is different from that of oxidized diamond.

4) Chemisorbed hydrogen is desorbed as H_2 (Fig. 3) rather than CH_4. A small amount of CO is also released and its desorption maximum lies close to the position of β peak. It was not possible to reduce this desorption to an unappreciable amount and it seems that the sites corresponding to this peak are highly active to oxygen. No appreciable CO desorption corresponding to α was observed even after exposure of the H_2-treated sample to air, indicating that the sites α are blocked by hydrogen

adsorption. Further oxygen treatment at 420°C in 10 Torr for 30 min. resulted in partial oxidation as revealed by the appearance of α peak of CO and the desorption peak of remaining H_2.

References

1) R. M. Barrer, J. Chem. Soc., 1936, 1256, 1261.
2) R. Sappok and H. P. Boehm, Carbon, 6, 283, 573 (1968).
3) R. C. Bansal, F. J. Vastola and P. L. Walker, Jr., Carbon, 10, 443 (1972).

(Received September 8, 1973)