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Exfoliation of graphite–CrO_3 intercalation compounds in hydrogen peroxide solution

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This paper deals with the reaction of the graphite–CrO_3 intercalation compounds with hydrogen peroxide. As a consequence of this reaction, the exfoliation of the compound of the solvent as well as the impregnation-dry method has been observed. The swelling of the material results in a distinct decrease in bulk density of the compounds. It has been demonstrated that the split flakes of the exfoliated compounds can be transformed into a honeycomb-like structure if the reaction takes place in a more concentrated solution of H_2O_2. X-ray analysis has revealed that in spite of a partial leaching out of CrO_3 from the structure of graphite, the intercalation compounds are still preserved. Some contributions to the mechanism of exfoliation are discussed.

1. Introduction

New materials with many interesting properties are produced on exfoliating the graphite intercalation compounds (GIC). The compounds are formed due to the insertion of some elements or molecules, so-called intercalants, between the graphite layers. If, on heating GICs, the pressure of the gas intercalant increases excessively or the gas products are formed due to the decomposition of the solid intercalant then the bulk expansion takes place. This effect is caused by a multiple splitting of the graphite flakes and, consequently, harmony and/or honeycomb structures are formed. The exfoliated compounds consisting of very puckered flakes exhibit an increased specific surface area, increased adsorption ability, and a decreased specific density. These features make the exfoliated GIC very important from the technological point of view. For example, they can be used for making gaskets [1], electromechanical switches [2] and foils [3, 4]. The thermal exfoliation has been the most intensively examined [2, 4–11]. Significantly less attention has been paid to the exfoliation resulting from the chemical reaction of GICs. The exfoliation produced during the reaction between potassium–graphite compounds and water has been reported [12–15], and the exfoliation effected in GIC–$FeCl_3$ on contact with moisture has been observed by Hooley [16].

Graphite intercalation compounds with chromium trioxide (GIC–CrO_3) have also exhibited thermal exfoliation [16–18]. On heating, the intercalant itself undergoes decomposition to form oxygen and/or reacts with the graphite carbons to evolve CO_2. In both cases a new phase of lower chromium oxides is also produced. The exfoliation has also been observed on boiling GIC–CrO_3 with KOH solutions [20]. This process is accompanied by a partial leaching out of Cr (VI) ions from the compound structure into the solution. The electrochemical studies performed in aqueous acid electrolytes showed GIC–CrO_3 to be active in the red–ox reactions [18–21]. These results inspired us to examine the compounds in H_2O_2 solution.

The present work deals with the exfoliation of two compounds prepared by the solvent and the impregnation-dry method. A tentative proposal relative to the mechanism of exfoliation is presented.

2. Experimental details

2.1. Materials

The intercalation compounds were prepared from 99.7 wt % C graphite flakes from Graphitwerke Kropfmühl AG, West Germany. The material as-received from the producer was composed of particles of 67 to 1440 μm diameter, and was used for the intercalation process by the impregnation-dry method whereas the sieve fraction including the flakes of 170 to 283 μm diameter was used to prepare GIC–CrO_3 by the solvent method.

2.2. Preparations

The impregnation-dry method of intercalation comprised two stages. The first was the impregnation of graphite with 3 M aqueous solution of CrO_3 at 70° C until the water was evaporated. During the second stage the dried materials was heated in the temperature range 200 to 210° C. The intercalation reaction between molten CrO_3 and graphite proceeded for 10 h. To remove unreacted CrO_3 and lower chromium oxides not bound to the graphite, the product was severely treated first with boiling water and then with 6 M HCl at 100° C for 1 h. At the end, chlorides were washed out with water. Other details relating to this method were described in previous paper [19]. Intercalation by the solvent method was carried out according to the procedure of Platzer and de la Martiniere [22] using a mixture of 1 g graphite and 5 g CrO_3 in 50 cm^3 glacial acetic acid. After refluxing for 5 min the product was washed with cold glacial CH_3COOH. The compounds of both methods prior to examination

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were dried under vacuum to constant weight. GIC–CrO_3 were prepared using reagent-grade chromium trioxide produced by POCH Gliwice, Poland.

2.3. Experimental techniques

To determine carbon and hydrogen content, combustion analysis was used, while atomic absorption after pyrosulphate fusion was used for chromium.

The flakes were examined using a JSM 35 JEOL scanning electron microscope.

X-ray diffraction analysis was performed using filtered Cu*Kα* radiation. To reduce texture effects, the compounds subjected to analysis were pressed under 220 MPa.

The bulk density was determined in such a way that the sample flakes prior to measurement were shaken in a test tube for 1 min using a 50 Hz vibrator.

Exfoliation of GIC–CrO_3 with H_2O_2 solution was performed in an apparatus similar to that described in [23]. Because of the exothermic reaction, the temperature of the solution was continuously controlled to be 25° C. The experiments were carried out in a round-bottomed flask containing 2 g GIC–CrO_3 in 75 cm^3 15% solution of H_2O_2. After 5 days, water was evaporated under vacuum to a constant sample weight. In one case, after 24 h, a new portion of 10 cm^3 H_2O_2 solution was admixed with a primary solution containing compound A1-W1.

3. Results and discussion

On immersing GIC–CrO_3 in H_2O_2 solution, no changes within the compound flakes were initially observed. After some time, oxygen bubbles appeared at the edge surfaces of the flakes. The oxygen evolution accelerated gradually and the solution became more and more yellow, which was associated with the presence of Cr(VI) ions. When the oxygen was violently evolved, the flakes started to move from the flask bottom and collected at the surface of the solution. The number of the displaced flakes increased with time, and the colour of the solution intensified and changed to orange. It was noticeable that a colour change occurred only up to a certain time and then remained constant in spite of a continuous evolution of oxygen and an increased thickness of flake layer in the upper part of the solution. Microscopic analysis showed that flakes taken from the flask bottom were not exfoliated in contrast to those collected from the solution surface. The following day, gas evolution was less intensive but the reaction still proceeded. It was observed that after 24 h reaction all flakes had accumulated at the surface. After evaporation of water from the reaction bulk, the compound flakes were subjected to SEM analysis.

Figs 1 and 2 display the flakes exfoliated over 5 days, whereas Fig. 3 shows the flake of compound A1-W1 exfoliated for the same time, but with a solution of an increased concentration of H_2O_2. As can be seen from the scanning electron micrographs the flakes of GIC–CrO_3 treated with H_2O_2 solution appeared to be considerably exfoliated, exhibiting very puckered sheets. The bending of the flakes is especially pronounced near their edges (Figs 1 and 2). The extent of exfoliation was higher when the concentration of H_2O_2 was increased. In this case a honeycomb-like structure was obtained (Fig. 3).

It is worth noting that no distinct changes were observed in the morphology and bulk density of the exfoliation products depending on the method of intercalation, in spite of the differences in the intercalant

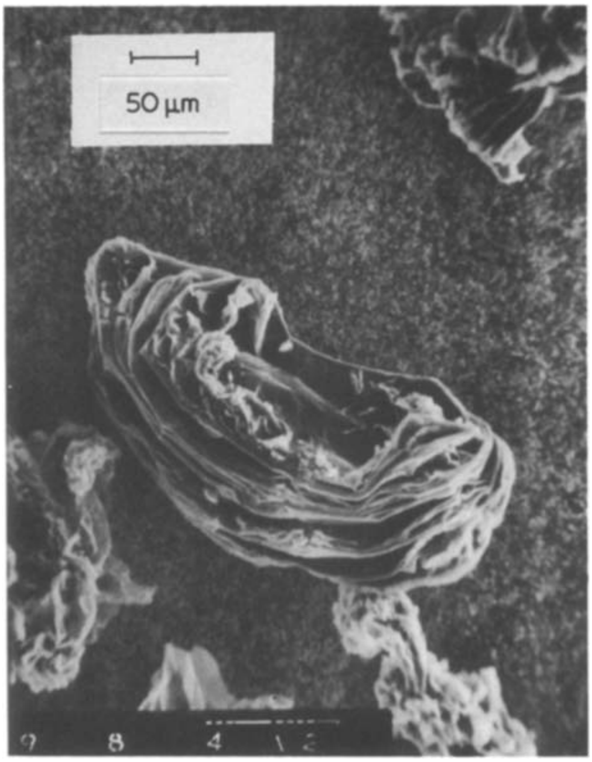

Figure 1 Scanning electron micrograph of exfoliated flake of intercalation compound A2-AC prepared by solvent method.

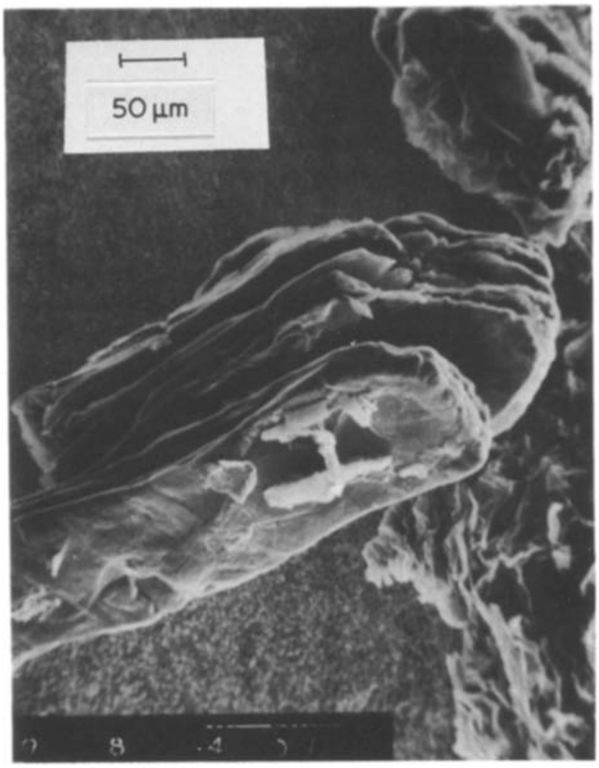

Figure 2 Scanning electron micrograph of exfoliated flake of intercalation compound A1-W1 prepared by impregnation-dry method.

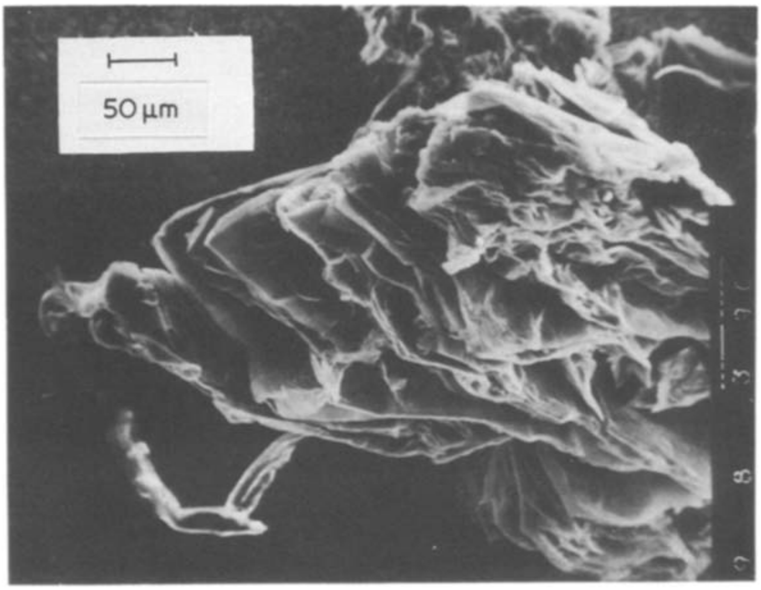

Figure 3 Scanning electron micrograph of exfoliated flake of intercalation compound A1-W1 prepared by impregnation-dry method. Concentration of H_2O_2 solution was increased during exfoliation.

concentration and X-ray data of the compounds used (Table I). The formation of a swollen material was reflected in a decrease of bulk density of the exfoliated compounds. As can be seen from Table II almost the same changes of this parameter were obtained on exfoliation for both compounds. Nevertheless there were some noticeable differences in kinetics of exfoliation. It was observed that the decomposition of H_2O_2 accompanied by the appearance of Cr(VI) ions in solution started earlier and gas was liberated more energetically for the compound in the solvent method (A2-AC). Explanation of this fact can be looked for in the structural differences resulting from the method of intercalation used. X-ray data listed in Table I show that the compound of the impregnation-dry method is less perfectly ordered compared with the other. The results obtained previously [18, 19] have suggested the latter compound to be a mixed structure containing intercalant localized in the more inner regions of the flakes. These suggestions are in a good agreement with the results of a more recent work [20] on alkaline deintercalation of the same compounds as used in the present work. It has been shown that the compound of the solvent method is also more readily deintercalated by KOH solution than that of the impregnation-dry method. Because the present paper is the first work on exfoliation with hydrogen peroxide at present, it is not yet possible to evaluate comprehensively the mechanism of exfoliation. Nevertheless, some possible reactions playing a role in the exfoliation process can be outlined.

It is reasonable at this point to recall some features related to the compounds examined. It has been reported [24] that compounds of the solvent method very easily lose CrO_3 on immersion in water. In contrast to this, compounds of the impregnation-dry method appeared to be stable not only in water but also in acids [18–20]. This may be one of the reasons why, at the beginning of the reaction with hydrogen peroxide, Cr(VI) ions are released easier from the compound of the solvent method than from the other. The fact that some portion of the intercalant can also be dissolved with water from the compounds of the impregnation-dry method provided they are pressed and/or milled [18–20], allowed us to assume that the intercalant exists in these compounds in an island form [25] being caged within graphite pockets or crystalline boundaries. In the case of thermal exfoliation the opening of these pockets starts from their centre as the effect of the gas overpressure. This mechanism cannot be applied to the exfoliation occurring in H_2O_2 solution. In this case the exfoliation process starts from the flake edges. In the initial period of reaction the catalytic decomposition of H_2O_2 seems to play a significant role in the peripheral disruption of graphite layers. If the layers pinned peripherally are separated as a result of oxidation effected by oxygen evolving catalytically, the first portion of the intercalant will be released from graphite pockets to take part in homogeneous reaction with H_2O_2. The deformation of graphite layers facilitates the penetration of hydrogen peroxide molecules into the more inner regions of the flakes. Except for the catalytic decomposition taking place at the edges, dislocations and/or grain boundaries, H_2O_2 can also react with the intercalant. On contact with water, CrO_3 forms a mixture of chromate and dichromate

TABLE I Physicochemical data of graphite intercalation compounds with CrO_3

Sample	Intercalation method	Formula*	Main X-ray lines	
			d(nm)	I/I_0
A1-W1	Impregnation-dry process [19]	$C_{28}CrO_3$	0.335	100
			0.352	17
A2-AC	Solvent process [22]	$C_{44}CrO_3$	0.335	100
			0.360	95

*Intercalant is assumed to be CrO_3 only.

TABLE II Changes in bulk density effected by exfoliation

Sample	Bulk density (g dm^{-3})	
	before exfoliation	after exfoliation
A1-W1	496	205
A2-AC	642	232

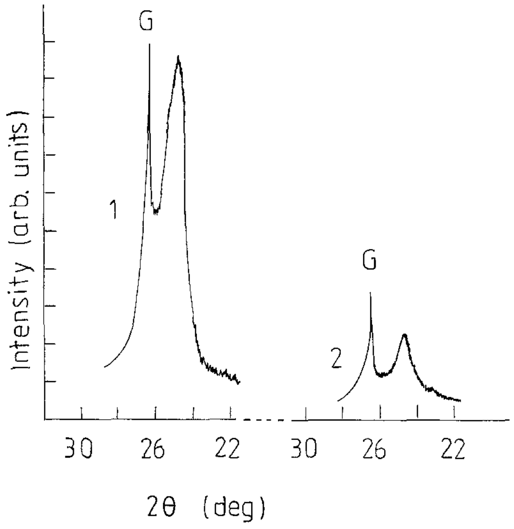

Figure 4 Sections of X-ray diffractometer recordings of graphite intercalation compound A2-AC prepared by solvent method. G = graphite 002 reflection, (1) before exfoliation, (2) after exfoliation.

anions, whereas the solution is strongly acidified. It is well known that these anions accelerate the catalytic decomposition of H_2O_2 [26]. On the other hand, before anions diffuse out of the graphite structure, they can take part in the reaction with H_2O_2. In acidic solution, H_2O_2 reacts with dichromate, yielding an unstable peroxyacid of chromium which decomposes with evolution of oxygen [26, 27]. When the tensile stress of oxygen exceeds the graphite pocket strength the buckling of layers takes place.

Because all the mentioned reactions with H_2O_2 are exothermic, a local overheating within the graphite layers can occur, in spite of a thermostatted solution. The temperature increase acccelerates the course of the reactions and, in addition, can give rise to the exfoliation effected by thermal decomposition of the intercalant in the reaction with graphitic carbons. It has been observed earlier [21] that such a reaction occurs already at temperatures lower than 200° C. It is expected that on releasing oxygen from the flake, cooling the reaction sites and/or exhaustion of H_2O_2, a collapse of graphite layers will take place. In such a case the intercalant could again be caged in graphite. X-ray results obtained for compound A2-AC before and after exfoliation are in accordance with this presumption. Fig. 4 reveals a reduction in the intensity of the line corresponding to graphite (0.335 nm), as well as a line characteristic of the intercalation compound (0.360 nm). However, as can be seen, the peak positions remain unchanged whereas a reduction of the intercalation line effected by exfoliation is somewhat greater than that of graphite. This suggests that the exfoliated sample is still the intercalation compound, in spite of the decreased intercalant concentration in the graphite structure and the presence of very puckered layers of graphite. Comparison of Figs 2 and 3 leads to the conclusion that the enrichment of the reaction solution with H_2O_2 transforms a harmony structure into a honeycomb one.

The results of this paper throw new light on wide practical perspectives of using the presented method of exfoliation to prepare exfoliated GIC–CrO_3 of different properties. On the other hand, one can expect that more thorough studies on the process made in the future will reveal many technological applications of the exfoliated compounds.

References

1. R. K. FLITNEY, *Tribology Int.* **19** (1986) 181.
2. D. D. L. CHUNG and LAN W. WONG, *Carbon* **24** (1986) 639.
3. J. E. SHANE, R. J. RUSSEL and R. A. BOCHMAN, US Pat. 3404061 (1968).
4. M. B. DOWELL and R. A. HOWARD, *Carbon* **24** (1986) 311.
5. J. E. BROCKLEHURST, *Nature* **194** (1962) 247.
6. W. H. MARTIN and J. E. BROCKLEHURST, *Carbon* **1** (1964) 133.
7. L. C. OLSEN, S. E. SEEMAN and H. W. SCOTT, *ibid.* **8** (1970) 85.
8. R. E. STEVENS, S. ROSS and S. P. WESSON, *ibid.* **11** (1973) 525.
9. C. MAZIERES, G. COLIN, J. JEGOUDEZ and R. SETTON, *ibid.* **14** (1976) 176.
10. S. H. ANDERSON and D. D. L. CHUNG, *ibid.* **22** (1984) 253.
11. N. MURDIE, I. A. S. EDWARDS and H. MARSH, *J. Mater. Sci.* **20** (1985) 171.
12. D. E. BERGBREITER and J. M. KILLOUGH, *J. Chem. Soc, Chem. Commun.* **913** (1976).
13. *Idem, J. Amer. Chem. Soc.* **100** (1978) 2126.
14. R. SCHLÖGL and H. P. BOEHM, *Carbon* **22** (1984) 351.
15. L. B. EBERT, *ibid.* **23** (1985) 585.
16. J. G. HOOLEY, *ibid.* **10** (1972) 155.
17. J. G. HOOLEY and M. REIMER, *ibid.* **13** (1975) 401.
18. J. M. SKOWROŃSKI, *Electrochim. Acta* **30** (1985) 989.
19. *Idem, Carbon* **24** (1986) 185.
20. *Idem, Synth. Meth.,* **22** (1987) 157.
21. *Idem, Electrochim. Acta* **32** (1987) 1285.
22. N. PLATZER and B. DE LA MARTINIERE, *Bull. Soc. Chim. France* **177** (1961).
23. K. APPELT and J. M. SKOWROŃSKI, *Metalloberfläche* **27** (1973) 323.
24. L. B. EBERT, R. A. HUGGINS and J. I. BRAUMAN, *Carbon* **12** (1974) 199.
25. N. DAUMAS and A. HEROLD, *C. R. Acad. Sci. Ser.* **C268** (1969) 373.
26. G. M. PANTCHENKOV and W. P. LIEBIEDIEV, "Kinetyka chemiczna i kataliza" (WNT, Warszawa, 1964) p. 244.
27. R. B. HESLOP and P. L. ROBINSON, "Inorganic Chemistry" (Elsevier, Amsterdam, London, New York, 1963) p. 387.

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