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Thermochimica Acta 271 (1996) 163–177

thermochimica
acta

Thermoanalytical investigations on the formation, properties and reactivity of carbon modifications[1]

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Received 20 June 1995; accepted 23 June 1995

Abstract

Applications of thermoanalytical methods are demonstrated for the characterization and thermochemical reactivity of the carbon modifications fullerenes, diamond and graphite. In the first part synthesis pathways from charcoal to fragments of fullerenes and to graphite are presented. The second part sheds some light on the existence and specific textural and compositional characteristics of non-terrestrial, i.e. chondritic (meteoritic) carbon compounds. Finally, selected features specifying the thermochemical reactivity of all three modifications as function of temperature, pressure and atmosphere is described.

Keywords: Carbon modifications; Fullerenes, diamond, graphite; Combined thermoanalytical investigation; Thermochemical reactivity

1. Introduction

Carbon in its various modifications represents a most remarkable and ever growing field of contemporary research activities. This is readily explicable by the paramount importance of this element in its various forms, be it with respect to the technical, industrial as well as economic and even aesthetic relevance of the long-known modifications graphite and diamond, be it with respect to the recent findings on the third modification, the so-called fullerenes [1–3]. The controlled synthesis of this new modification was only rationalized in 1990 [4]. The subsequent studies on structural and physical properties of

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[1] Presented at the 11th Ulm Conference, Freiberg, 29–31 March, 1995.

SSDI 0040-6031 (95) 02609-6

pure and substituted fullerenes, but also of its fragments, brought to light a widespread and entirely new chapter of the phenomenology of carbon. Together with the data on the known modifications, some basic knowledge on the crucial aspects of general chemistry is achieved.

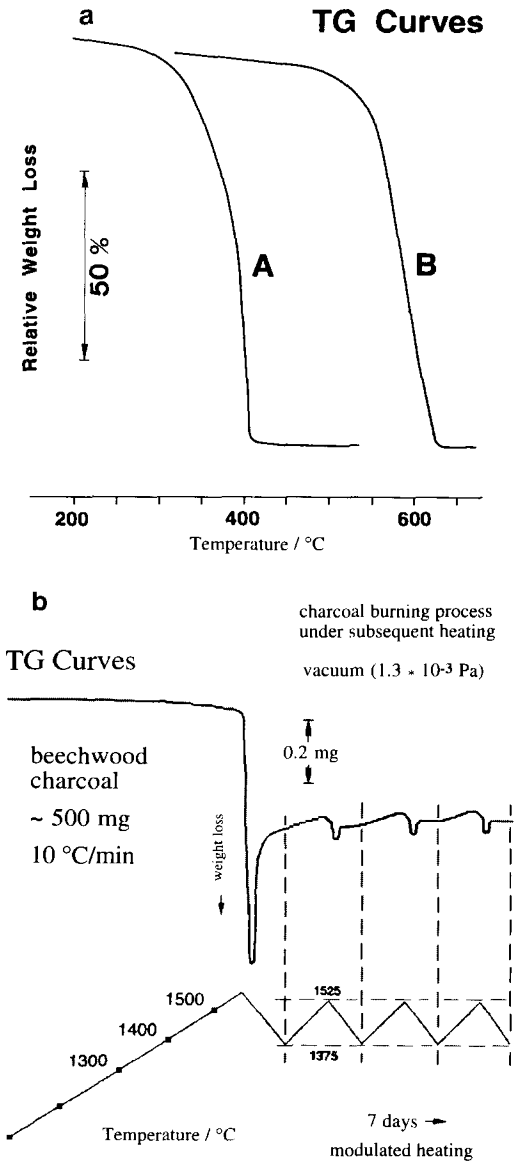

Fig. 1. Thermogravimetric measurement of the degradation of untreated (curve a) and pre-treated beechwood charcoal (curve b) in air (a). The pre-treatment procedure is depicted in (b).

The thermochemical reactivity as well as the formation pathways of the three modifications are not yet encompassed in full detail. In this field thermoanalytical methods prove to be very important tools, especially if they are combined with simultaneously measuring and/or observing complementary techniques such as mass spectrometry, light microscopy, etc. This contribution tries to shed some light on the formation of the various carbon modifications starting from terrestrial as well as from extraterrestrial sources [5,6]. Moreover, the thermochemical reactivity and the temperature dependence of specific properties of the different forms are described. The studies not only yield some insights into the chemistry of carbon but also afford new concepts and approaches to thermoanalytical instrumentation.

2. Investigations on the formation of carbon modifications

2.1. Degradation of beechwood charcoal in an inert atmosphere

The carbonization process of wood to charcoal, the historically important charring process, has been studied in detail using thermoanalytical techniques [7]. As essential degradation products of the natural carbonization lignite, bituminous coal, anthracite and poorly ordered graphite are obtained. Comparative thermogravimetric studies between the degradation of pure cellulose and the one of lignin reveal that time ageing preferably effects the degradation of lignin whereas thermal ageing, i.e. the said charring process, leads to the decomposition of cellulose and the transformation of lignin into charcoal [8].

As thermogravimetric measurements elucidate (see Fig. 1a), the degradation of beechwood strongly depends on the thermal pretreatment; untreated beechwood decomposes in air with a temperature onset of around 400°C. By a pre-treatment, i.e. modulated heating under a vacuum in the temperature interval of 1375–1525°C (see Fig. 1b), structural and compositional transformations are induced. This leads to a remarkable enhancement of the thermal stability. As high resolution electron microscopy (HREM) reveals, these structural transformations can be interpreted in terms of graphitization as well as in terms of formation of fullerene fragments (see Fig. 2a,b) [9]. The formation of these carbon modifications is influenced by the presence of inert by-phases; metal oxide crystallites such as CaO, silicates, etc. act as support materials, on which epitaxial or at least topochemical formation of preferably graphite layers is observed (see Fig. 2b).

The findings give evidence that sophisticated thermoanalytical studies provide insights into the mechanistic course of temperature dependent structural reorganizations in carbonaceous matter. This is of importance for the following.

2.2. Carbon modifications from extraterrestrial sources: combined thermoanalytical investigations on chondrites

Among the meteorites which have been found and analyzed only a few contain organic carbon compounds. These meteorites are called chondrites. The discovery of amino acids and hydrocarbons in the Murchison meteorite has initiated extensive scientific activity and speculation over the past two decades. In his book *Kleine Meteoritenkunde*, F. Heide gives the following statements [10]:

"Die primitiven kohligen Chondrite, vor allem Typ C1 und C2, enthalten auch organische Substanzen. Das sind Verbindungen von Kohlenstoff mit Waaserstoff, Sauerstoff, Stickstoff und Schwefel, wie sie in lebenden Organismen gefunden werden. Man glaubte früher, sie könnten nur von solchen Organismen erzeugt werden, aber heute kann man sie auch im Labor aus den Elementen oder anorganischen Verbindungen herstellen. Deshalb sind die organischen Stoffe in den Meteoriten noch kein Beweis für die Anwesenheit von Leben auf ihrem Mutterkörper."

And later on: "Ausserdem konnte gezeigt werden, dass die meisten organischen Verbindungen der kohligen Chondriten durch katalytische Reaktionen an wasserhaltigen Silikaten oder Magnetit (die in kohligen Chondriten vorkommen) unter den Bedingungen

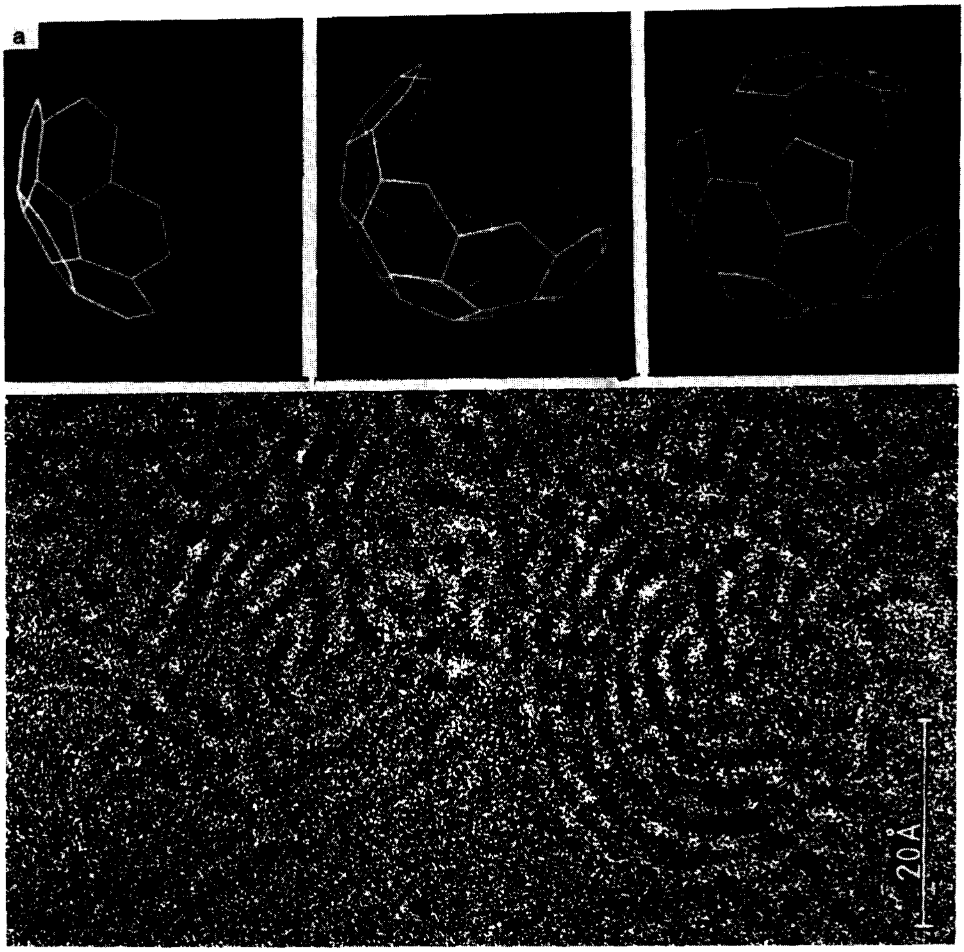

Fig. 2a.

Fig. 2. High resolution electron micrograph showing icospiral growth of carbon during charcoal surface graphitization (a). This process can be interpreted in terms of the formation of shell-like fragments of fullerenes (b). In the presence of inert nanocrystals such as calcium oxide (c), "enwrapping", highly orientated graphite layers are formed.

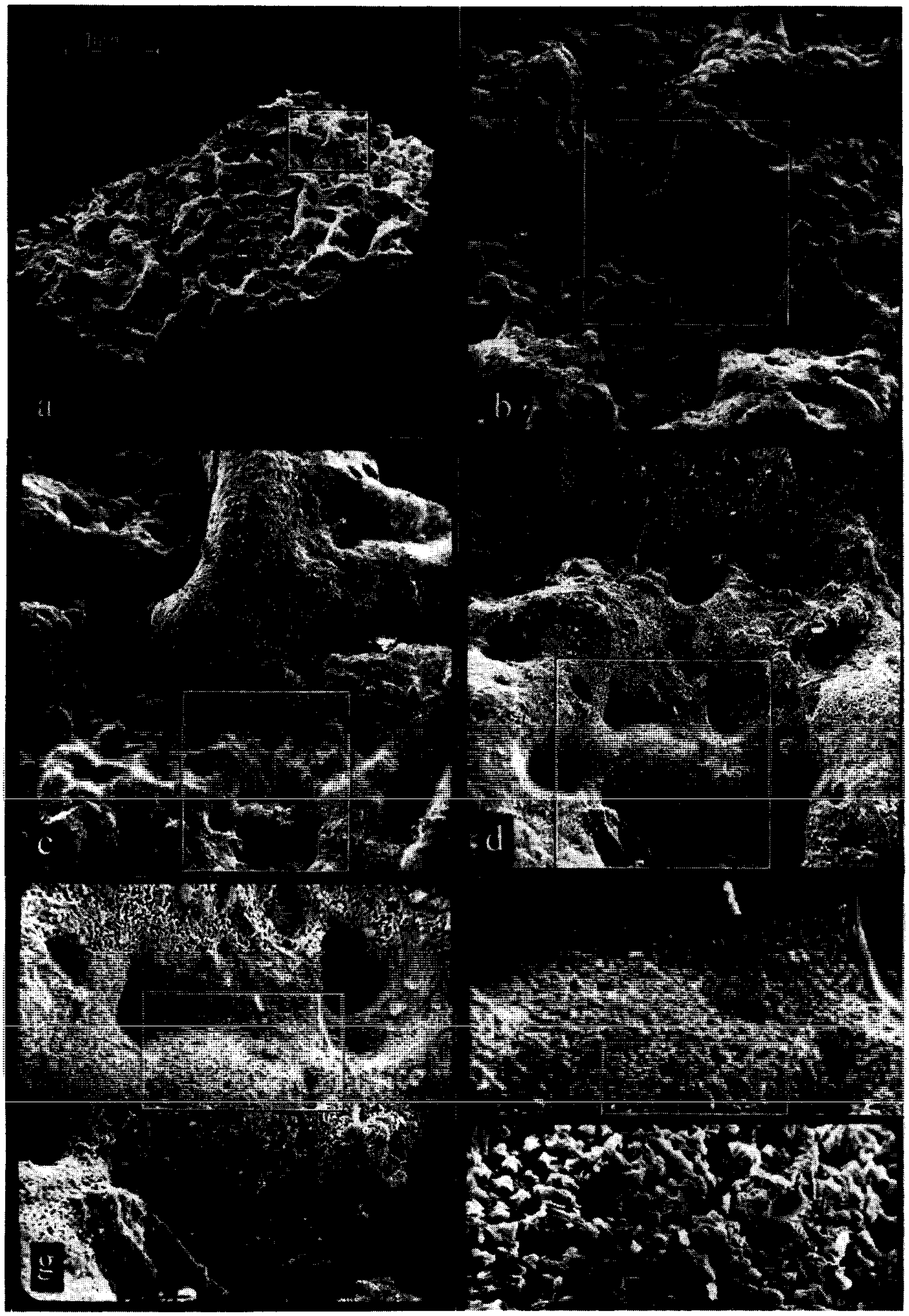

Fig. 3. Scanning electron micrographs showing the morphology of the fusion crust of the Murchison meteorite with various magnifications. The inscribed white rectangles mark the magnified section of the following micrograph.

des solaren Nebels aus Kohlenoxiden und Wasserstoff aufgebaut werden können. Sie sind also höchstwahrscheinlich nicht von lebenden Organismen erzeugt worden. Dagegen ist das Umgekehrte sehr wahrscheinlich: dass nämlich diese organischen Verbindungen die Grundlage für die Entstehung des Lebens auf der Erde (und vielleicht auch auf anderen Himmelskörpern) gelefert haben. Material wie das der kohligen Chondrite war sicherlich am Aufbau der Erde und der anderen Planeten beteiligt, so dass in einem frühen Urozean schon die ersten Bausteine des Lebens zur Verfügung standen."

Obviously the meteorites and in particular the chondrites represent a heterogeneous agglomeration of different phases. Otherwise the afore-mentioned statements could not have been possible. Among the inorganic constituents, the following minerals and phases have been found in the C-2 chondrite Murchison: quartz (SiO_2), wustite (FeO), hematite (Fe_2O_3), periclase (MgO), corundum (Al_2O_3), calcium oxide (CaO), spinel ($MgAl_2O_4$), pentlandite ($(Ni, Fe)_9S_8$), diamond (C), hibonite ($CaAl_{12}O_{19}$), perovskite ($CaTiO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), magnesite ($(Mg, Fe)CO_3$), epsomite ($MgSO_4 \cdot 7H_2O$), gypsum ($CaSO_4 2H_2O$), melilith ($((Ca,Na)_2(Al,Mg)[(Si,Al)_2O_7])$), nepheline ($KNa_3(AlSiO_4)_4$), and sodalithe ($Na_8(AlSiO_4)_6Cl_2$). As organic constituents the following compounds were observed: polymers (1.45%), carbonates (0.1–0.2%), hydrocarbons (30–60 ppm), monocarbonic acids (~330 ppm), amino acids (10–22 ppm), primary alcohols 11 ppm, aldehydes (11 ppm), ketones (16 ppm), amines (11 ppm), urea (25 ppm) and purines (1.2 ppm). Scanning micrographs of the fusion crust give evidence that not only the compositional heterogeneity but also the morphological heterogeneity is a characteristic feature (see Fig. 3). We investigated this fusion crust and the surface-near section using combined thermoanalytical tools. A comparison of the thermal decomposition between material of the fusion crust and material directly under the fusion crust reveals that the registered weight losses (see Fig. 4a) correspond to the evolution of various gases (see Fig. 4b) [11]. The thermogravimetric measurements also give evidence that

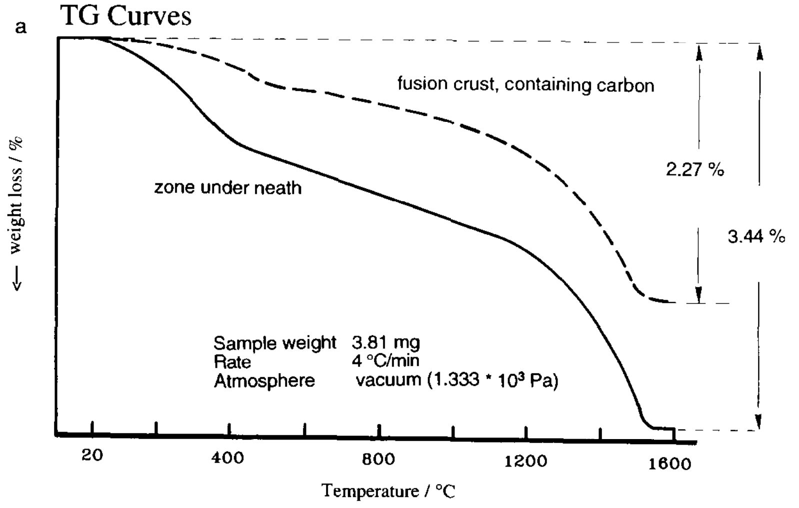

Fig. 4a.

the material collected underneath the fusion crust contains slightly more volatile carbon species. In order to confirm the different types of chondritic carbonaceous matter ranging from hydrocarbons to graphite, comparative thermogravimetric measurements were performed using samples of beechwood charcoal, isolated carbonaceous matter from the fusion crust of Murchison, graphite and diamond (see Fig. 4c). Further studies by electron microscopy on isolated carbonaceous matter from Murchison and Allende, another C-2 chondrite, reveal the presence of poorly ordered, amorphous carbonaceous matter in the fusion crust of the former [6] and highly ordered carbonaceous matter, so-called turbostratic graphite in the latter [5]. In summary the results support the fact that during the trajectory of meteorites or chondrites through the terrestrial atmosphere, up to 90% of the initial weight is lost by burn-off. The presence of thermally unstable carbon species con-

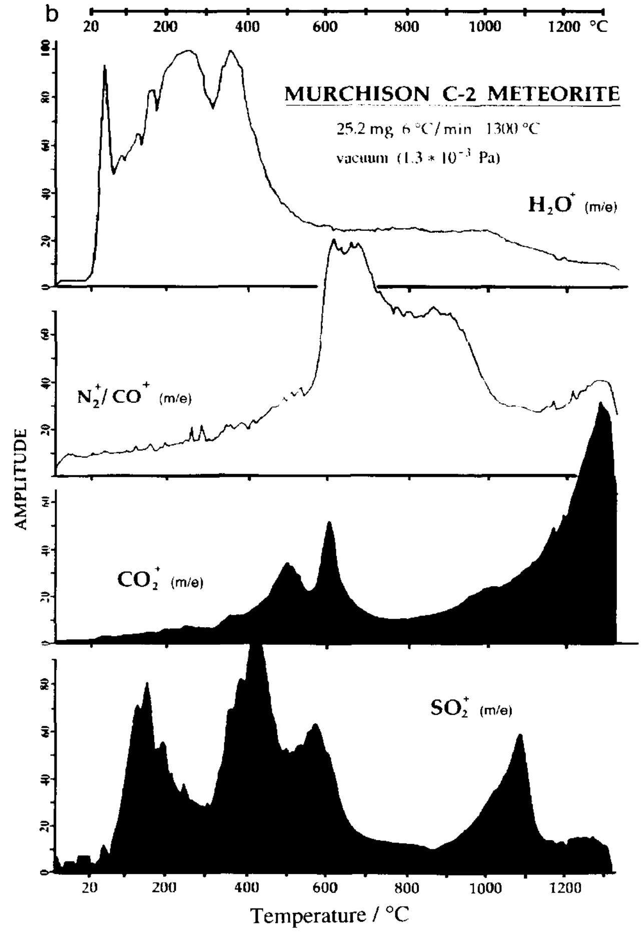

Fig. 4b.

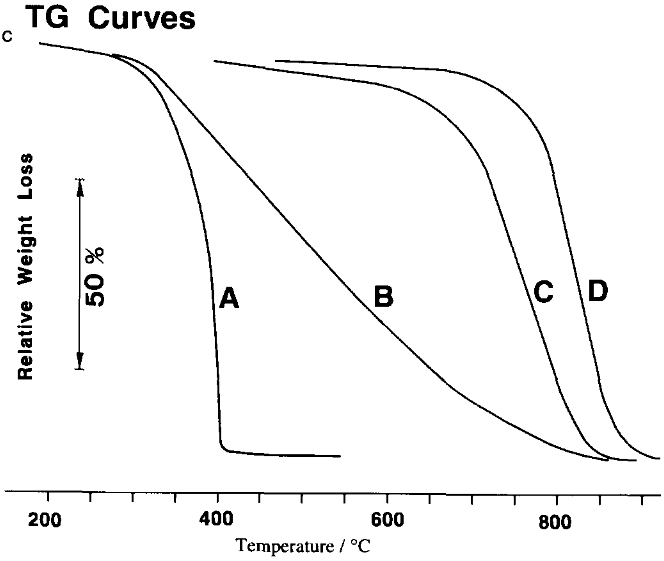

Fig. 4. Thermogravimetric measurements of the degradation of the fusion crust of the Murchison meteorite containing carbonaceous matter. Samples collected at the surface of the fusion crust prove to be slightly more stable than samples from the zone underneath the actual fusion crust (a). Mass spectrometric measurements of the fragmentary masses evolved during the heating procedure confirm the presence of carbonaceous matter as well as the presence of sulphates and water (b). The comparative thermogravimetric measurements of the decompositions of beechwood charcoal (c, curve 1), carbonaceous matter from the Allende meteorite (c, curve 2), graphite flakes from Sri Lanka (c, curve 3) and diamond powder from South Africa (c, curve 4) give evidence that meteoritic carbon is made up of many different species or modifications.

firms, however, the presence of an extreme temperature gradient between the surface, i.e. the fusion crust, and the zones underneath. On one hand this can be explained by the self-cooling caused by the endothermal burn-off processes, on the other hand these findings may also confirm the above-mentioned statements by F. Heide. Further investigations on meteorites, chondrites and interstellar grains [12] may reveal some more enigmas of the history and the phenomenology of extraterrestrial matter.

3. Transitions and decompositions of carbon modifications

3.1. Transition in the fullerene C_{60}

Fullerenes have been investigated by thermoanalytical methods shortly after its first characterizations in terms of structural and compositional features. DSC measurements brought to light that the first stable representative, C_{60}, undergoes a crystal-to-plastic-crystal transition at 256 K [9,13]. Combined thermoanalytical, structural and mechanical measurements of this phenomenon suggest that an orientational disordering takes place.

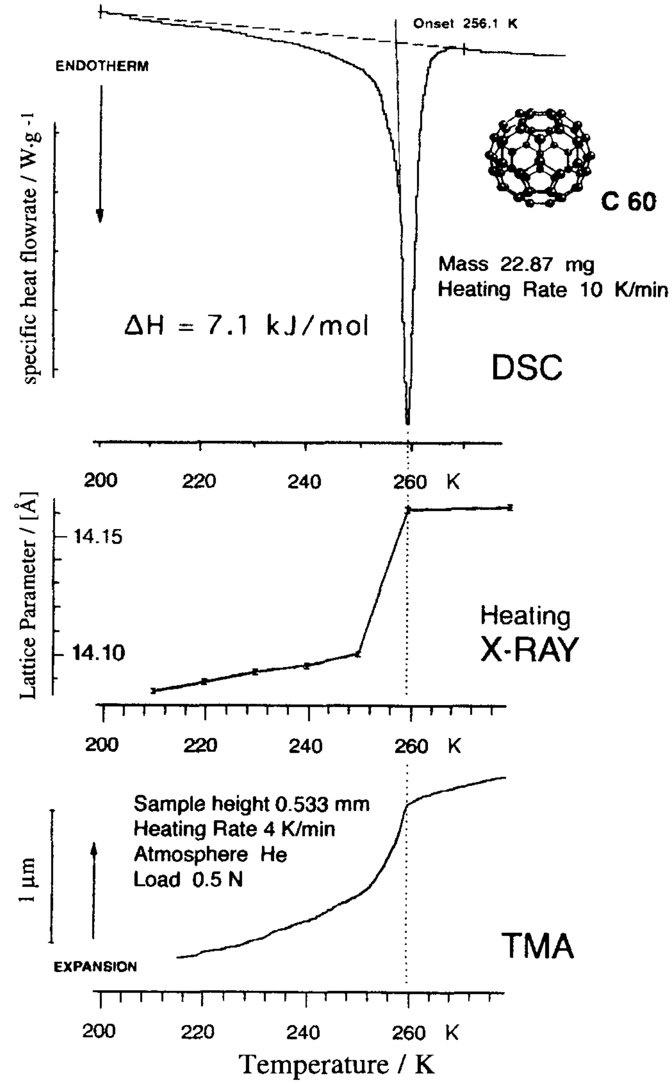

Fig. 5. Comparative studies on the crystal-to-plastic-crystal transition of C_{60} at 256.1 K characterized by DSC (top), temperature dependent X-ray diffraction (middle) and thermomechanical analysis (bottom).

This is accompanied by an increase of the entropy of ~27.3 J K^{-1} mol^{-1} (see Fig. 5a). Temperature dependent X-ray diffraction confirms that in the same temperature interval an increase of the lattice parameters, i.e. of the unit cell volume, is observed (see Fig. 5b). This volume increase is confirmed by thermomechanical studies (see Fig. 5c) measured by using a special sensor (see Fig. 6). The comparison between the microscopic increase of the unit cell volume and the macroscopic expansion registered by thermome-

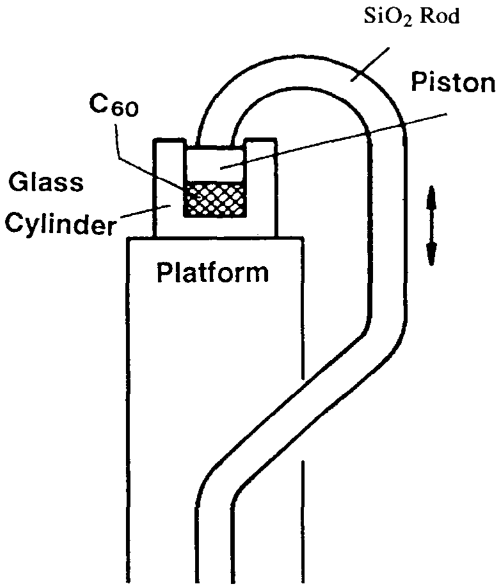

Fig. 6. Experimental set-up, i.e. sensor for the determination of thermomechanical properties.

chanical methods will be discussed elsewhere. Such combined experiments confirm that the phenomenological changes in the transition of C_{60} represent the basic data for a better understanding of the relationship between atomic structure and microscopic or macroscopic properties. Considering the fact that meanwhile there exist many more fullerenes and derivatives of fullerenes exhibiting interesting physical and chemical properties, the correlation of results obtained from thermoanalytical methods with data achieved by complementary techniques is indispensable for the detailed characterization of this new class of materials.

3.2. Thermochemical reactivity of diamond

Even the purest natural diamonds contain gases, which often cause colour effects. Early investigations on the thermochemical reactivity of diamonds under various atmospheres and pressures are reported in the literature [14]. It is suggested that under vacuum conditions above 1500°C these gas inclusions are desorbed and simultaneously, any trace of oxygen is readily absorbed. At higher temperatures the degradation is observed. In order to further specify these high-temperature processes, thermogravimetric studies under vacuum conditions were carried out using “gas-free” diamonds. At ~1500°C a weight gain is observed. This corresponds to the uptake of traces of oxygen, i.e. under the given conditions, diamond is an extremely active in the uptake of oxygen (see Fig. 7). By keeping the sample at 1500°C for 30 min this oxygen uptake is compensated by vaporization and decomposition of the nuclei layers of graphite formed, a process which can be

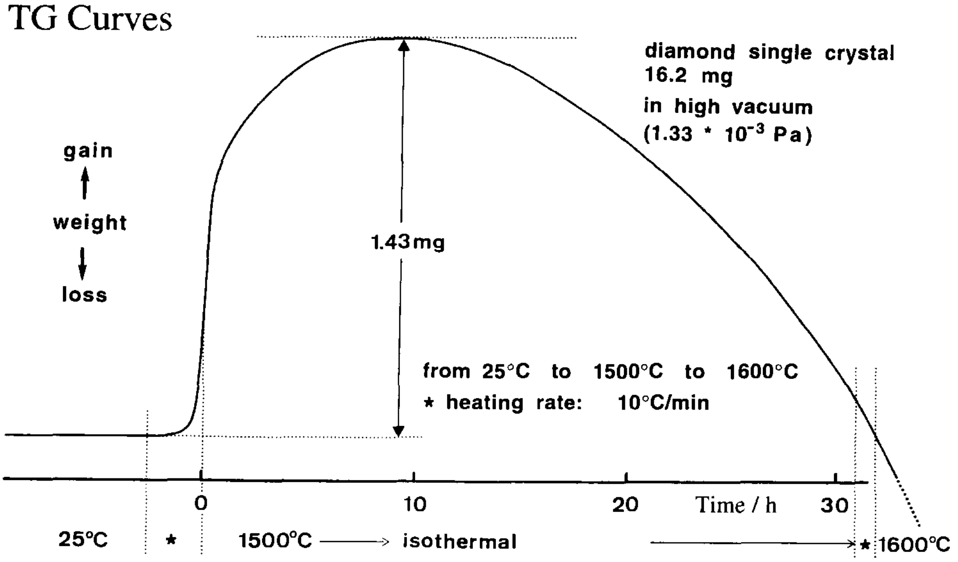

Fig. 7. Thermogravimetric measurement of the initial oxygen uptake and simultaneous/subsequent graphitization/degradation of single-crystalline, gas-free diamond powder.

monitored by electron microscopy (see Fig. 8). This behaviour is analogous to that of diamonds with high gas content. The formation of graphite nuclei (see Fig. 8a) appears at the weight maximum of the adsorption/desorption curve. As HREM investigations reveal, graphite layers are formed shortly after an initial weight loss of ~1% (see Fig. 8b). By increasing the temperature to 1600°C full graphitization is reached (see Fig. 8c). Concomitantly, an overall weight loss of >10% is measured. Nuclei and extended layers of the graphite product phase are highly orientated, i.e. the mechanism of the degradation of diamond to graphite is governed by the structural features of the parent phase diamond and by the relationship between the structural frameworks of graphite and diamond. These findings are confirmed by HREM and selected area electron diffraction studies on the first steps of graphitization (see Fig. 8d); at the surface of single-crystalline diamond domains highly orientated layers of graphite can be observed.

3.3. Oxidation of diamond and graphite

The burning profile of diamond in air clearly shows that the temperature onset is higher than that for graphite (see Fig. 4c). The detailed mechanism of the oxidation of diamond has not yet been determined. For the oxidation of graphite, a set up of thermobalance, light microscope and video equipment has been constructed. With this instrumentation, the course of the oxidation of graphite flakes in air has been monitored. It can be seen that the oxidation proceeds parallel to the layers, again indicating a mechanism governed by the structural features of the parent phase (see Fig. 9). This instrumentation

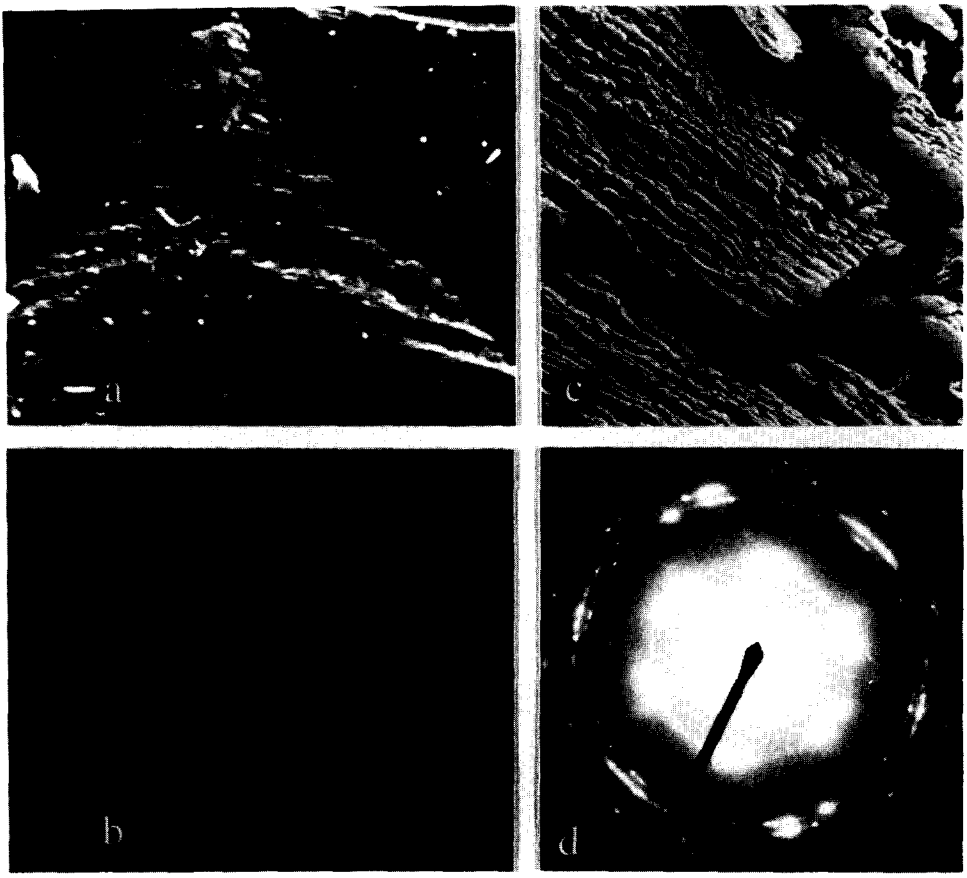

Fig. 8. Scanning electron micrograph showing a graphite nucleus on a diamond surface (a), high-resolution micrograph and the corresponding selected area electron diffraction pattern of a by-phasic domain showing some layers of graphite on parent diamond (b) and scanning electron micrograph showing a section of fully graphitized diamond (c).

allows the determination of the kinetics of the oxidation of isolated graphite flakes as follows: the temperature-dependent advancement of the "oxidation zone", i.e. the boundary prismatic faces, can be determined as direction-dependent velocity. These data can be evaluated in terms of carbon atoms being oxidized along a given crystallographic direction as functions of time, temperature and atmosphere. Thus kinetic data are available which contain information on the actual structural mechanism, i.e. the anisotropic reaction behaviour of graphite can be quantified. Similar approaches have been established for the highly topotactic decomposition of solid coordination compounds [15].

The investigations elucidate the relationship between structure and microscopic oxidation mechanism. They are complementary to the mechanistic investigations performed on a nanoscopic level using sophisticated techniques such as atomic force microscopy [16].

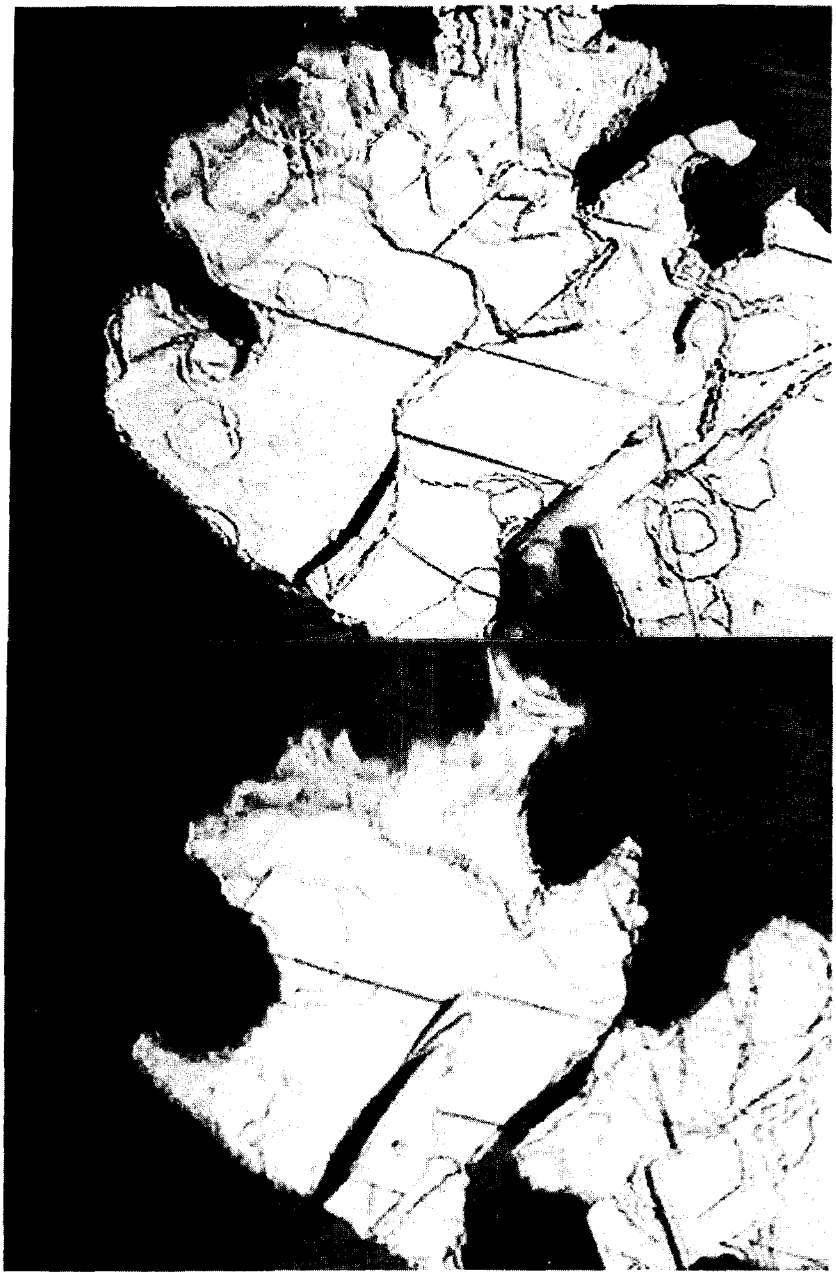

Fig. 9. Light microscopic images documenting the course of the oxidation of a graphite flake. Two stages observed during the isothermal heat treatment of an isolated flake at 800°C in air are shown: after 15 min oxidation (top) and after 45 min oxidation.

4. Conclusions

Thermoanalytical methods have proved to be very useful tools for characterizing and distinguishing the formation pathways, transformation and degradation processes of the known three carbon modifications. The combination of the said methods with com plementary techniques elucidating compositional and structural speciation or visualization of processes allows far-reaching interpretations on the relationship between "Realstruktur" on one side and physical properties, mechanism, kinetics and energetics of the various transformations on the other side. However, the results obtained so far are of a preliminary nature and further investigations have to be carried out in order to achieve a broad knowledge on the phenomenology of this crucial element carbon in all its apparent or still disguised forms. All findings are not only of fundamental interest but represent the basis for any technological or industrial applications.

Acknowledgements

The authors would like to thank E.K. Gibson and S.M. Johnson (NASA, Houston) for the mass spectrometric measurements of the Murchison meteorite samples and H. Werner (Fritz-Haber-Inst., Berlin) for the temperature-dependent X-ray diffraction measurements of the fullerene sample, and H. Kollmann (University of Frankfurt) for the graphite measurement.

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