Some physical methods for study of irradiation effects in graphite

par

G. Mayer, M. Lecomte and R. Mattmuller

Rapport CEA n° 1122
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Quelques précedes physiques pour étudier les effets de l’irradiation du graphite.

Summary. — On décrit en détail une méthode d’étalonnage pour un appareil classique d’analyse thermique différentielle. Cette méthode permet de mesurer avec une précision relative de 5 % la libération d’énergie interne qui accompagne le « recuit » des graphites irradiés.

On déduit les constantes élastiques des graphites des fréquences des vibrations longitudinales et on décrit les procédés pour exciter et détecter ces vibrations à toutes les températures comprises entre —190° C et +1 500° C.

On discute un procédé pour obtenir une des déformations de graphites facilement mesurables après une irradiation relativement faible à l’aide de neutrons thermiques. Une application de cette méthode à l’étude du « recuit » thermique de l’allongement causée par les atomes déplacés est indiquée.

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A procedure for obtaining easily measured deformations of graphites after relatively little irradiation with thermal neutrons is discussed. An application of this method to the study of the thermal annealing of elongation caused by displaced atoms is indicated.

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SOME PHYSICAL METHODS FOR STUDY OF IRRADIATION EFFECTS IN GRAPHITE

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Abstract

A calibration method for a classical apparatus for differential thermal analysis is described in detail. This method achieves a relative precision of 5% in the measurement of the internal energy release accompanying the annealing of irradiated graphites.

Elastic constants of graphites are obtained from the frequencies of the longitudinal modes of vibration; procedures for excitation and detection of these vibrations at any temperature between −190°C and +1500°C are described.

A procedure for obtaining easily measured deformations of graphites after relatively little irradiation with thermal neutrons is discussed. An application of this method to the study of the thermal annealing of elongation caused by displaced atoms is indicated.

I wish to discuss three experimental methods utilized for studying irradiation effects on solids.

DIFFERENTIAL THERMAL ANALYSIS (D.T.A.)

Differential thermal analysis is one of these methods; we want to show how the study of some irradiated soluble materials enables us to increase and to measure the precision of our apparatus. The principle of the method is well known: a box E made of a good thermal conductor contains two identical vessels C1 and C2. An exterior heating element H permits the gradual increase in temperature of E. Thermoelectric devices measure the difference of temperature between the two vessels and the temperature of each of them. (See Figure 1.)

To make a measurement it is convenient to regulate the rate of temperature rise to obtain temperature as a linear function of time. The substance to be studied is placed in C1. In C2 is placed a similar substance without specific heat anomaly. The temperature difference ΔT between the two vessels is then recorded as a function of time.

The curve shown in Figure 2 was obtained with irradiated graphite in C1 and unirradiated graphite in C2.

Figure 1. Apparatus for differential thermal analysis

Figure 2. Differential thermal analysis of an irradiated graphite
The curve shown in Figure 3 was obtained with crystalline quartz in \( C_1 \) and fused quartz in \( C_2 \). In order to determine the total energy \( \Delta U \) involved in these phenomena, it is necessary to know, at each temperature, the thermal coupling between each vessel and the container. The simplest way to achieve this is to measure the temperature lag of the vessels when the temperature of the box rises linearly as a function of time. These measurements permit the calculation of a thermal leakage time which is a decreasing function of the temperature. This measurement has value and utility only if the leakage time is large in comparison with the time needed for temperature equalization in each crucible. Hence small crucibles and a thin envelope are needed. From the D.T.A. curves a numerical integration leads then to the total energy \( \Delta U \) involved.

How may we verify the numerical values thus obtained? If a high temperature calorimeter is available we may check a D.T.A. operation between temperatures \( T_a \) and \( T_b \) by successively measuring the quantities of heat \( U_1 \) and \( U_2 \) necessary to raise the substances \( C_1 \) and \( C_2 \) from temperature \( T_a \) to \( T_b \). The difference \( U_1 - U_2 \) must be equal to \( \Delta U \).

The very careful measurements of Moser\(^1\) on quartz \((U_1 - U_2 = 3.3 \text{ cal/g})\) have enabled us to calibrate our system in the range 550\(^\circ\) to 580\(^\circ\)C. But generally, for thermal healing phenomena, the range \( T_a - T_b \) is quite large, and the quantity \( U_1 - U_2 \) is observed as the small difference between two large energies, which makes its precise evaluation difficult.

If in the case of graphite it is decided to measure \( \Delta U \) as the difference between heats of combustion \( Q_1 \) and \( Q_2 \) of the irradiated and nonirradiated products, the same difficulty is encountered: \( \Delta U \) is small compared with \( Q \), which has a value of about 7800 cal/g. This difficulty disappears if one is interested in the stored energy resulting from the irradiation of soluble materials such as the alkali halides. In fact, their heats of solution are small and their measurement is a simple calorimetric operation. The difference between the heat of solution of irradiated and nonirradiated products allows a verification of the results of the D.T.A.

We have chosen LiF for this study: its heat of solution in \( \text{H}_2\text{O} + 18\% \text{ Al(NO}_3\text{)}_3 \) is \(-80.8 \text{ cal/g at 20}^{\circ}\). In the course of a pile irradiation the storing of energy is rapid because of the fission produced by the thermal neutron in \( ^6\text{Li}^\beta \). Figure 4 shows a curve obtained in D.T.A.

![Figure 3. Differential thermal analysis of \( \alpha-\beta \) transformation in quartz](image)

![Figure 4. Differential thermal analysis of lithium fluoride irradiated at \( 5 \times 10^{17} \text{n/cm}^2 \)](image)
This salt, employed after different stages of irradiation and then of healing, served for both the calorimetric and the D.T.A. measurements and allowed the apparatus to be calibrated in the range 100° to 500°C. The accuracy obtained is better than 5%. The minimum amount of heat detectable is 0.01 cal/g, provided this quantity of heat is released in less than 10 min. One can present the thermal healing study of LiF as a by-product of the calibration of the D.T.A., or vice versa, depending on the nature of the meeting at which one is speaking.

ELASTIC CONSTANTS

It is also equally interesting to study the effect of radiation on the elastic constants. In the majority of single crystals the relative variations of the elastic constants are an order of magnitude greater than the variations of length for a given irradiation. In irradiated polycrystalline graphite, Young's modulus can be increased by a factor of 2.5 before the relative elongation has increased by $10^{-3}$.

For these studies we have constructed an apparatus to measure the elastic constants. During the measurements, the sample is in a furnace which permits the continuous observation of the elastic constants of an irradiated body during the thermal healing.

Figure 5 is a sketch of the apparatus. In $E$ is the ultrasonic emitter. This is a simple platinum wire. If it is supplied with several watts of high frequency current (~20 megacycles) a luminous discharge is produced at its extremity. If, by means of a variable frequency generator a modulating frequency, $f$, is superimposed on the high frequency current, sound waves of the same frequency are produced in the luminous zone surrounding the wire.

When one asks those physicists who are specialists in the questions of electric discharges in gases why the sound waves are produced, their answer is always "why not." This phenomenon takes place equally well in air as in inert gases like He and Ar up to frequencies greater than 600 kc. The ultrasonic waves emitted in $E$ traverse the tube $T$. The sample to be measured, $S$, a cylinder, is placed on two fine metal wires. When the frequency of the acoustic waves approaches one of the proper frequencies of longitudinal vibration of the sample, the latter resonates and the alternating motion of its extremities is considerably amplified.

These movements are detected as follows: a point $P$ of graphite or of germanium is lightly pressed on a face of the sample, supposedly a conductor of electricity. The electrical resistance of such a contact depends on
the pressure of the point on the face. A circuit is made consisting of a battery, the primary of a transformer, and the point of contact in series. The secondary current is fed into an oscilloscope. When the sample resonates, the contact resistance is modulated and a signal appears from the transformer secondary. Periodic elongation of the sample of the order of $10^{-10}$ cm can thus be detected. Once the frequencies of two successive harmonics have been measured, the elasticity equations enable the Young's modulus and the Poisson's ratio to be calculated relative to the direction of the axis of the cylindrical sample. Besides this, the measurement of the width of the resonance band about a proper frequency gives a measurement of the internal friction. We have employed this method in the range $-190^\circ$ to $+1200^\circ$C and the apparatus is such that this range could be extended.

**RADIATION EFFECTS ON DENSITY**

Finally, I would like to describe a method which we have used to obtain rapid qualitative data on elongation under radiation. The sample to be studied is made up in the form of a thin sheet, $L$, relatively long and as thin as possible (Figure 6). A layer $C$ several hundredths of a millimeter thick of a compound of boron or lithium is deposited on one face; the sample is then put in the pile. The Li$^6$ or B$^{10}$ nuclei undergo reaction with the thermal neutrons, the ions formed having sufficient energy to travel about 20 $\mu$ and to displace atoms all along their path. A fraction of the ions thus formed in the layer penetrates the sample and produces alterations in the lattice similar to those produced by fast neutrons.

If the effect of these displacements is a lengthening for example, the sample will take up a curved form, the arc of a circle with the irradiated surface turned outwards. If $\Delta_0$ is the relative elongation of the most irradiated part of the sample, assuming it is completely separated from the rest, and if $e$ is the depth irradiated and $d$ the thickness of the sample, then the radius of curvature $R$ will be given by the expression

$$\frac{l}{R} = \frac{6\Delta_0 e}{d^2}.$$

If one extremity of such a sample is fixed (Figure 6) the other end will be displaced by an amount $x = l^2/2R$. This is an example:

$$l = 7 \text{ cm}; e = 2 \times 10^{-3} \text{ cm};$$
$$d = 4 \times 10^{-2} \text{ cm}; \Delta_0 = 10^{-3}.$$

For a silica plate covered with boron carbide, this deflection of 2 mm is obtained with a dose of $2 \times 10^{17}$ thermal neutrons. Reheating leads to restoration of the original plane form.

This system provides then a very convenient experimental method for studying the thermal healing of elongation due to radiation.

In concluding I would like to emphasize that these indirect methods have the distinct advantage of enabling the beginning of a study of density changes without the necessity of waiting for the long period of irradiation often necessary to reach high doses of fast neutrons.

**REFERENCES**