SOME RADIATION-INDUCED EFFECTS IN TYPICAL CALORIMETRIC MATERIALS AND SENSORS

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Abstract

The radiation-induced effects of the electron beams (EB) generated by accelerators in typical calorimetric materials and sensors have been surveyed and investigated. These effects influence the useful lifetime of the materials and sensors at high doses of about 4,000 to 5,000 kGy.

1. INTRODUCTION

There are increasing needs to accept calorimetry as an absolute dosimetry method for radiation processing. As a result of long term development of radiation calorimetry, three materials have been found to be of practical use: water, graphite and recently also polystyrene. Problems of radiation induced heat defects in H_2O, C and $(C_8H_8)_n$ were the subject of previous paper [1].

On the other hand, there are also some radiolytic and radiation damage effects in liquid and solid state materials which can influence dosimetric responses and moreover life span of calorimetric system. Radiation can break chemical bonds in water and polystyrene and involve short term effects which usually can be estimated and taken into account. Contrary to it, atomic displacement induced by fast electrons in temperature sensors, mainly thermistors, cause long term effects gradually changing resistance/temperature characteristics of thermistors as dose increases to its critical level. Principally, thermistors which are made of semiconductor materials are more radiation sensitive in comparison to electronic conductors (graphite and metals) and radiation resistant dielectrics such as polystyrene. However, thermistors are ten times as sensitive (4 %/ ^{0}C) as thermocouples and platinum resistance thermometers.

Some calculations of the atomic displacement cross section induced by fast electrons for the quantitative estimation of the long-term changes in thermistors and typical calorimetric materials are presented in the present paper.

2. CALCULATIONS OF ATOMIC DISPLACEMENT CROSS SECTIONS IN CALORIMETRIC MATERIALS AND SENSORS INDUCED BY FAST ELECTRONS

Only several elements i.e. hydrogen, carbon, oxygen and some metals (Mn, Ni, Co, Ti) are important for estimation of radiation damage in calorimetric materials and sensors.

EB irradiation of graphite and other materials are convenient for the determination of the threshold energy for atomic displacements. Simple or primary atom displacement occurs if the energy given to the primary knock-on is between E_d and 3 E_d. Multiple (secondary) atom displacements take place if energy imparted to a primary knock-on atom exceeds three time the threshold energy. Maximum energy imparted to an atomic nucleus by fast electrons with kinetic energy of E_e and rest mass m_0 is given by Eq. (1).

$$E_{max} = \frac{2\left(E_e + 2 m_o c^2\right)}{M c^2} E_e \quad (1)$$

where, M = mass of the target atom, c = velocity of light in vacuum.

The cross section σ_d for an atomic displacement is, according to Vavilov [2], as follows:

$$\sigma_d=8\pi\sigma_o\left[\frac{1}{2}\left(\frac{1}{x_o^2}-1\right)+\pi\alpha\beta\left(\frac{1}{x_o}-1\right)+\left(\beta^2+\pi\alpha\beta\right)\ln x_o\right] \tag{2}$$

where,

$$\sigma_o=\left(\frac{2e^2}{2m_oc}\right)^2\left(\frac{1-\beta^2}{\beta^4}\right) \tag{3}$$

$$\alpha=\frac{Ze^2}{hc}=\frac{Z}{137} \tag{4}$$

$$x_o=\sqrt{\frac{E_d}{E_{\max}}} \tag{5}$$

$$\beta=\frac{V_o}{C}=\sqrt{1-\frac{m_oc^2}{\left(E_e+m_oc^2\right)}} \tag{6}$$

Z = atomic number, and h = Planck's constant.

This formula is relatively simple in comparison to very complex method of Oen's [3], which employed the Mott series with Kinchin and Pease model. Comprehensive Oen's work reports displacement cross section of 37 different elements for incident electron energies ranging from threshold to about 150 MeV (see Fig. 1).

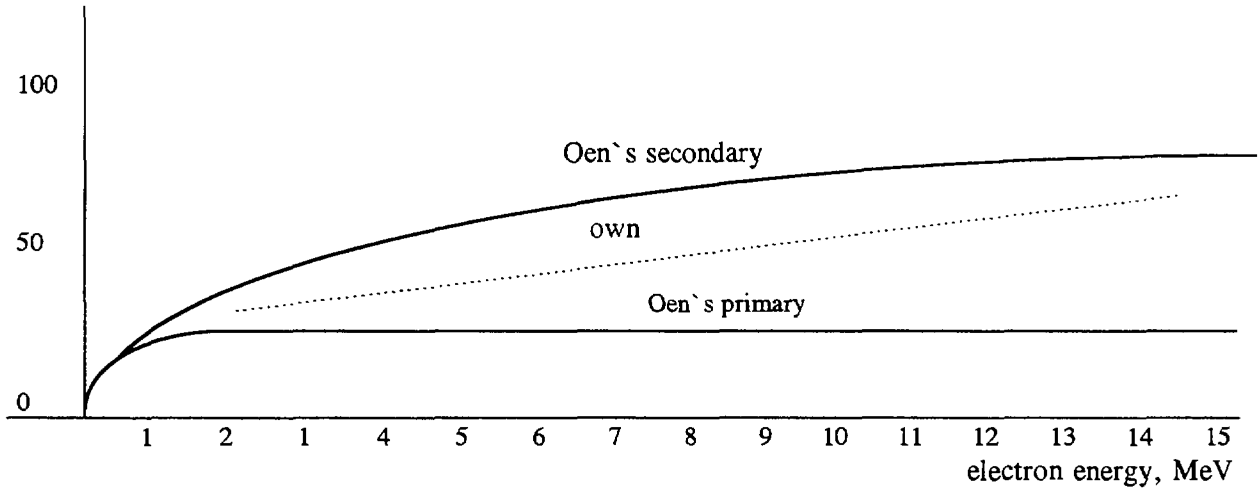

FIG. 1.Present atomic displacement cross sections of oxygen for incident electron energies in range from 2 to 13 MeV

3. EXPERIMENTAL

3.1. Materials and sensors

- Nuclear grade graphite, density of 1,670 kg/m^3, Russian production.
- Transparent polystyrene (PS) commercially available, manufactured mainly for building applications, density of 1,050 kg/m^3.
- Expandable polystyrene (EPS) foam also commercially available, produced as thermo-insulating material, density of 20 to 40 kg/m^3.
- Purified water, distilled from alkaline solution of $KMnO_4$.
- NTC - glass coated bead thermistors of Philips, VECO, Siemens and Polish production of two kinds:

  High resistance (20-40 kΩ) - low temperature (up to 200 °C)

  Low resistance (1-2 kΩ) - higher temperature (over 300°C)

3.2. Radiation sources

- UHF electron linac, type LAE 13/9, (5 -19 MeV, 9 kW average beam power, 0.5, 2.5, and 5.5 μs pulse duration),
- UHF electron linac, type UELV-10-10-70-1, (10 MeV, 10 kW average beam power, 4.5 μs pulse duration)
- HF pulsed resonant electron accelerator, type ILU-6M2, (0.7 -2 MeV, 20 kW average beam power, 400 μs pulse duration).

4. RESULTS AND DISCUSSION

4.1. Graphite

Synthetic, very pure graphite is widely used as a moderator material in nuclear reactors. Heavily irradiated nuclear graphites were tested in research and commercial reactors as early as Manhattan Project times. On the other hand, reactor grade graphites are certainly very good materials for calorimetric applications because of its excellent mechanical, thermal and radiation properties and also chemical purity. It is important to be careful during mechanical treatment of graphite because there is possibility of contamination of this very pure material.

According to our experiments and literature data the bulk nuclear graphite samples showed very high radiation resistance, without any property changes even above 10,000 kGy. It is enough for ensuring the long-term life time of the calorimetric body.

On the other hand, powdered graphite samples, irradiated in contact with air exhibited some physiochemical effects (wettability with water, insignificant oxidation) at about 800-1000 kGy. Assuming a threshold energy, E_d, of carbon atom in elastic collision with fast electron as equal to 24.7 eV, we calculated cross section of displacement of about 17 b at 10 MeV [4]. Several Japanese authors [5-6] report displacement damage in local electronic structure of graphite lattice irradiated using high voltage electron microscopy with energy > 0.12 MeV. At this incident energy, the cross section of carbon atom displacement is one order of magnitude smaller than for 10-MeV electrons. The stored energy of atomic displacement in crystalline lattice of graphite can be released only at dose level of 10^6 kGy (so called Wigner effect, observable in nuclear reactors).

4.2. Polystyrene

The bulk polystyrene (PS) appears to have a considerable resistance to ionizing radiation because of the radiation protection effect of the benzene ring. Also, some styrene copolymers (for example with acrylonitrile) are highly resistant to radiation, having a small G-value for cross-linking [G(C) = 0.77] and chain scission [G(S) =0.055] [7]. The energy dissipated per cross-link in polystyrene is 1400 to 1800 eV, about thirty times the 45 to 60 eV per cross-link in polyethylene [8].

We used commercially available transparent PS as a possible pure polymer without dyes. As well known, the mechanical properties of polystyrene are changed very little by irradiation. The tensile strength elongation at break of unmodified polystyrene is reduced by only 5 to 10% by exposure of 50,000 kGy. High-impact polystyrene, which contains modifiers, show greater susceptibility to radiation damage. The samples of transparent polystyrene were irradiated on a conveyor belt by 10 MeV electrons analogically as during sterilization procedure of medical supplies. After several sterilisation doses (25 - 35 kGy) the yellowish colour was observed. Also, polystyrene disks in PS calorimeters show the change of colour, without worsening of mechanical properties at very high dose of 5,000 kGy.

4.3. Water

Water has been used nearly as extensively as graphite as a moderator in nuclear reactors. Radiation effects on water are complex and have been investigated extensively since fifties [4]. The primary effect of radiation on water is probably excitation and ionization of the molecules and to a lesser extent dissociation into free radicals, hydrogen atoms and hydrogen peroxide.

The value of water as a calorimetric body is due to its stability toward radiation. Our experiments with irradiation of distilled water encapsulated inside sealed glass vessels show that the G-value of formation of gaseous hydrogen is equal to 0.4. This value agrees very well with the literature data [9,10]. Also, water calorimeters containing water inside glued Petri dishes show weight losses of about 1-2% after dose close to 2,000 kGy. This result depends on the purity of the used polystyrene vessel.

4.4. Thermistors

Negative temperature-coefficient (NTC) bead thermistors are manufactured mainly from the metallic oxide semiconductor materials sintered on platinum-iridium thin lead wires. A glass coating applied to these beads provides them with an effective hermetic seal against conductive, corrosive and other hostile environment. Most of the commercially available thermistor beads are made from transition metal oxides with spinel structure, sintered at temperature close to 1300 ^{0}C.

It is often assumed that the activation energy, B of thermistor material is constant, and the plot of lnR vs. 1/T, where R is thermistor resistance in ohms at the temperature T in Kelvin, is approximately linear, and is described by Eq. (7):

$$R = A \bullet e^{B/T} \tag{7}$$

Radiation tolerance of the thermistors used in calorimeters depend on chemical composition, structure and manufacturing technology. We statistically observed some stages of thermistor radiation damage on absorption of high doses from fast electrons:

- several percent resistance rise (at about 1,000 kGy)
- characteristic drift of resistance readout (at about 3,000 - 4,000 kGy), see Fig. 2.
- lack of resistance readout, caused by break of electrical circuit of thermistor.

Sometimes a single thermistor can be damaged on absorption of several sterilization doses. However, average radiation tolerance is worse in the case of high resistance and lower permissible temperature and is better for low resistance and higher permissible temperature of thermistor.

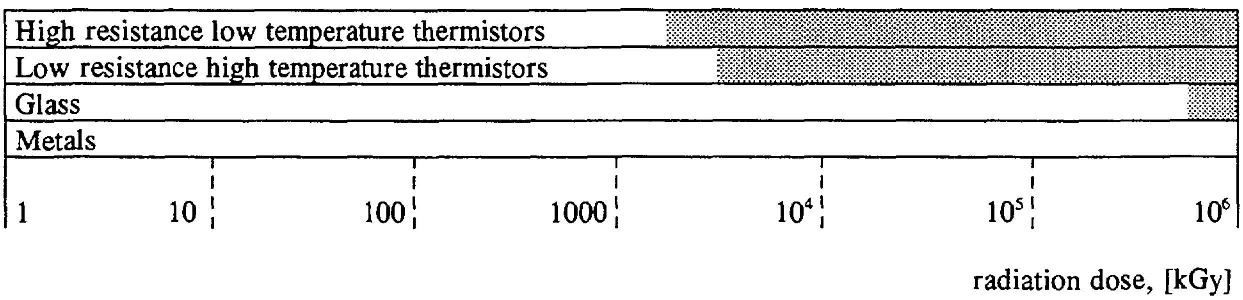

FIG. 2. Approximate tolerance of calorimetric materials to EB irradiation

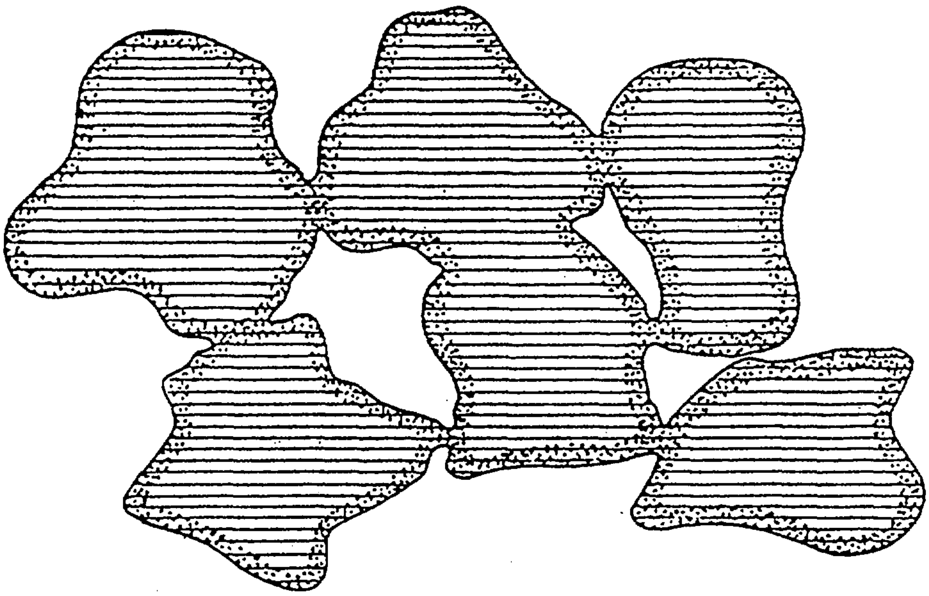

FIG 3. Cross section of a sintered sample

On the other hand, we also observed long term degradation of thermistor parameters without any irradiation. Some thermistor manufacturers state that their products are stable over period of about 10^8s (roundly 3 years). A small sample of ten thermistors was stored in dark, at room temperature during over twenty years. All thermistors of this sample were out of order [11].

In the light of these experiments we try to interpret some important aspects of complex mechanism of irradiation damage of NTC bead thermistors. On the one hand, semiconductor sintered material of beads have some tendency to long term recrystallization, which reduces its starting electrical conductivity. In effect, constant B (so called material constant) rises slowly with the absorbed dose. Just 2% change of B involves about 5% rise of resistance at the same temperature. The bead material is prepared by sintering the microcrystalline powder of metallic oxides mixtures. The individual microcrystallites have dimension of the order 10^{-3}-10^{-4} cm.

A schematic magnified cross section of sintered powder specimen is show in Fig.3. There are clearly seen sprinkling of voids and mutual contacts of individual microcrystallites grains.

On the other hand, radiation worsens the quality of the electrical contacts of bead sintered microcrystallites with thin platinum-iridium lead wires. Pulsating EB induces thermal microstrain cracks, which cause fatigue of surface contact of sintered material with wires. There is an additional possibility that the oxygen atoms of the oxides knocked on by fast electrons can generate some volatile platinum oxides which reduce conductivity of contacts. The old model of radiation induced “thermal spikes” suggested in fifties by Seitz becomes an argument for possibility of surface oxidation of Pt-Ir wires.

5. CONCLUSION

Transient and delayed radiation effects in calorimetric materials and sensors have been surveyed and interpreted.

Commercially available nuclear grade graphite and polystyrene and also re-distilled water can be used as durable materials of calorimeters for doses of 4,000 to 5,000 kGy without observable damage.

Carefully selected NTC bead thermistors with resistance of 1 to 2 kΩ (at 25 ^{0}C) and permissible work temperature above 300 ^{0}C exhibit average radiation tolerance at the similar dose range.

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REFERENCES

[1]. PANTA P.P., ZAGÓRSKI Z.P., GLUSZEWSKI W.J., Thermal defects of water, graphite and polystyrene affecting calorimetric response, IAEA TECDOC-1023, IAEA Viena (1998), 499-509
[2]. VAVILOV V.S., Destviye izlucheniy na poluprovodniki, Atomizdat, Moskwa, 1963, 264 pp
[3]. OEN O.S., Cross sections for atomic displacements in solids by fast electrons, ORNL - 4897, Oak-Ridge (1973), 207 pp.
[4]. ETHERINGTON M., Nuclear Engineering Handbook, Mc Graw Hill, New York 1958, 10.099 - 10.101 pp.
[5]. MUTO S., TANABE T., Damage process in electron irradiation graphite studied by transmission electron microscopy., I, High resolution observation of highly graphitized carbon fibres, Philos. Mag.A., **76**, 679 (1997)
[6]. TAKEUCHI M., MUTO S., TANABE T., ARAI S. AND KUROYANAGI T., Damage process in electron irradiation graphite studied by transmission electron microscopy., II, Analysis of extended energy-loss fine structure of highly oriented pyrolytic graphite, Philos. Mag.A., **76**, 691 (1997)
[7]. T.Q. NGUYEN, H.H. KAUSCH., Protective effect of the phenyl group in γ- irradiated compatible blends of Poly(methyl methacrylate) and poly(styrene-Co-acrylonitrile), Journal of Applied Polymer Science, Vol. **29**, 455-460 (1984)
[8]. BOLT R.Q., CARROLL J.G., Radiation effects on organic materials, Academic Press, New York - London 1963, 576 pp
[9]. SPINKS. J.W.T., Wood R.J., Introduction to radiation chemistry, J.Wiley New York 1976, p. 258
[10]. BUGAENKO. V.L., BYAKOV. V.M., Quantitative model for the radiolisis of liquid water and dilute aqueous solutions of hydrogen, oxygen , and hydrogen peroxide: I. Statement of the model, High Energy Chemistry, **32**, 411 (1998), (In Russian: Journal „Khimiya Vysokikh Energii)
[11]. P.PANTA., unpublished results, Warsaw 1996