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Time programming of material's properties via self-irradiation phenomena

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Abstract We consider theoretically programming of ageing processes in materials over large time intervals via the introduction of small quantities of unstable nuclei in a material's structure. Incorporation of minuscule amounts of radio-active species (e.g. carbon-14, tritium) in the structure of polymers, such as polytetrafluoroethylene, can be used for presetting self-decomposition of plastic products to a certain term. Radio-decay of unstable nuclei embedded in conductive polymers and dielectrics might enable the design of electrical resistors and capacitors with time-dependent characteristics. Relaxation of internal mechanical stresses, amorphization and swelling driven by self-irradiation can be used for programming configurations of mechanical systems over large terms (from years to thousands of years). Implementations of the time-programmed materials and their possible applications are discussed.

Introduction

Structure of the majority of materials, both natural and artificial, undergoes more or less profound structural changes as time elapses. Some of these changes are rather rapid; others are hardly perceivable over a human lifespan. Ageing of artificial materials is well known to archaeologists, specialists of art, builders. Usually, it is considered as a harmful and undesirable process. Thus, crystallization of polymers and related fragilization of plastics limit the lifetime of many consumer products to few years. In certain cases, the ability of a material to change its structure with time may constitute a part of the material's functionality. This is, for example, the case of degradable environmentally friendly packaging materials, or biodegradable medical implants supposed to decompose harmlessly inside the body after completion of a therapeutic role [1]. In the most instances, structure transformations in materials are driven by thermal fluctuations, electromagnetic radiation, aggressive chemicals, or by a combined action of these factors. The rate of ageing is strongly dependent on environment conditions, like temperature, humidity, exposure to light, etc.

Structure transformations owing to self-irradiation of materials by fission products of unstable isotopes constitute a special case of ageing phenomena. Radio-decay of uranium and thorium atoms substituting zirconium atoms in the crystal lattice of zircon causes radiation damage and gradual amorphization of the mineral's structure. This process called metamictization leads to negating of birefringence, lowering of the mineral's refractive index, hardness and specific gravity [2–4]. Ageing phenomena induced by self-irradiation are well known for plutonium and its alloys [5]. The alpha-particle (an energetic helium nucleus He^{+2}) and the uranium nuclei produced by radio-decay of a plutonium nuclei generate collision cascades, which involve several thousands of atoms. An accumulation of crystal lattice defects leads eventually to decrease of the specific gravity of the material. Although the defects may cause large local internal stresses, destruction of the crystal structure along the fission products tracks leads to relaxation of macroscopic mechanical stress fields. The latter effect is also well known for construction materials in nuclear reactors. For instance, stress in a steel springs is relaxed to 10% of initial loading when structure damage caused by neutron irradiation achieves approximately 20

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displacements per atom [6]. Scission or cross-linking chemical reactions in tritiated polymers,[1] i.e. the polymers in which some hydrogen (protium) atoms are substituted by tritium ones, is an example of self-irradiation processes in soft matter materials [7]. Semiconductors doped with radio-active isotopes can have time-dependent photoluminescence spectra [8].

An interesting peculiarity of the radio-decay driven ageing phenomena is their quasi-independence from the environmental conditions. Indeed, self-irradiation can proceed in the radionuclide-modified materials at very low temperatures and in complete darkness, i.e. in circumstances when other ageing mechanisms are stopped or strongly decelerated.

In the present article, we propose and consider theoretically programming of material properties over time via introduction of unstable isotopes in the material's structure. The dependence of physico-chemical properties of artificial materials, containing radio-isotopes, is well known for aforementioned tritiated polymers and isotopically engineered semiconductors. But, in these materials, this dependence was considered as a side effect. To the best of our knowledge, engineering of materials with radio-isotopes with the purpose of programming their temporal behaviour is not yet known.

The idea of the approach is illustrated by a few examples. First, we show that introduction of tiny quantities of radio-isotopes can be used for creation of novel polymer materials, which self-destruct over large time intervals due to radiation-induced depolymerisation. Next, we argue that tailoring the time dependence of material's electric characteristics is promising for the design of electronic devices whose functioning is disabled or enabled at a well-defined date. Finally, it is shown theoretically that relaxation of internal stresses in mechanically loaded self-irradiating materials can be used for setting up slow motions and shape transformations of mechanical systems, as well as abrupt conformation changes of mechanisms at a well-defined time moments. For the numerical estimates of the self-irradiation effects, we use the known experimental data on the action of ionizing radiation on materials. Possible applications of the time-programmed materials and the safety concerns of the approach are discussed in the concluding section.

Self-destruction of materials driven by self-irradiation phenomena

Polymers constitute probably the optimal class of materials, which can be time-programmed by radio-isotopes, because polymers are generally very sensitive to the action of ionizing radiations. Depending on the type of a polymer, either scission or cross-linking reactions can prevail in an irradiated polymer. Polytetrafluoroethylene (PTFE) is known to undergo predominantly decomposition reactions under the action of ionizing radiations at normal and low temperatures [See, e.g. 9].[2] Typical irradiation doses at which the polymer looses its mechanical integrity are of the order of 50 kGy [10]. Let us assume that the polymer is synthesized with addition of some small amount of the unstable ^{14}C isotope of carbon, which decays in the stable ^{14}N nuclei, electron and anti-neutrino: $^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + e^- + \bar{\nu}_e$. The half-life of ^{14}C is $t_{1/2} = 5{,}370$ years. The maximal energy of electrons released by the decay is 156 keV, the average energy is about $\varepsilon_{\mathrm{av}} \approx 50\ \mathrm{keV} \approx 8 \times 10^{-14}$ J [11]. It is believed that the effect of ionizing radiation on matter is quite independent on the type of particles and their energy [12]. In this assumption, one can estimate the amount of the radio-isotope, which should be introduced in the polymer in order to obtain structural effect similar to that obtained with use of electron accelerators. Let m be the initial mass of the ^{14}C nuclei in 1 kg of PTFE. The self-irradiation dose D obtained by the polymer as the time t elapses can be found as:

$$D = N_{\mathrm{A}} \frac{m}{\mu} \varepsilon_{\mathrm{av}} \left(1 - 2^{-t/t_{1/2}}\right), \qquad (1)$$

where N_{A} is the Avogadro number, and $\mu \approx 0.014$ kg/mol is the molar mass of ^{14}C. From (1), the mass of the radio-active isotope, which should be added to the material in order to provide a necessary dose of self-irradiation in a given time, is:

$$m = \frac{D\mu}{N_{\mathrm{A}} \varepsilon_{\mathrm{av}} \left(1 - 2^{-t/t_{1/2}}\right)}. \qquad (2)$$

Suppose that a product made of PTFE should decompose (loose its mechanical integrity) in 10 years. Assuming that the aforementioned irradiation dose $D = 50$ kGy is sufficient for this, one can estimate from (2) the amount of ^{14}C to be used during synthesis of 1 kg of the polymer: $m_{\mathrm{C14}} = 0.00012\ \mathrm{kg} = 120\ \mathrm{mg}$. If the decomposition should be achieved in 100 years, the amount of the necessary radio-isotope is 12 mg. If it is only required that the material self-destructs itself on the infinite time, then is might be sufficient to introduce 0.14 mg of the radio-isotope in the polymer structure. By technological reasons, it may be more convenient to introduce other radio-active species in PTFE structure. For instance, some fraction of fluorine atoms can be substituted with tritium, which has the half-life $t_{1/2} = 12.3$ years. Beta-decay of tritium to stable isotope ^{3}He

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[1] Tritiated polymers are used as radioluminescent paints in some specialized applications, such as diving watch dials.

[2] This property of the polymer is explored for the production of PTFE powders.

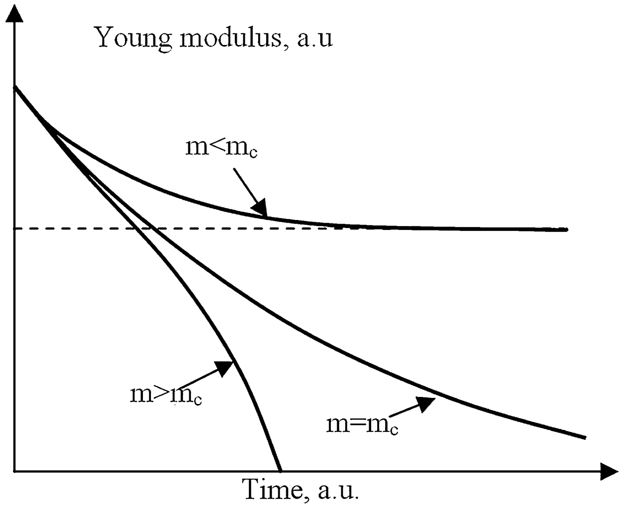

Fig. 1 Different scenarios of the dependence of material's mechanical characteristics on time, for various concentrations of the unstable isotopes in the polymer (see the text)

releases electrons with average kinetic energy $\varepsilon_{av} \approx 5.7$ keV $= 9.1 \times 10^{-15}$ J.[3] Substituting these values and the molar mass of tritium, $\mu \approx 0.003$ kg/mol in formula (2), one finds that 0.62 mg of tritium per kilogram of PTFE should be incorporated in the material's structure to achieve the polymer decomposition in 10 years; and 0.26 mg to ensure the material decomposition on the infinite term. It is obvious that such small amounts of radionuclide impurities cannot essentially change physico-chemical properties of PTFE, which is known first of all for its outstanding chemical stability, superior to that of noble metals. Other radio-isotopes can be also introduced by chemical methods in the structure of the polymer. For instance, it might be possible to incorporate in the polymer backbones or in the side groups the relatively short living isotope of silicium ^{32}Si, which has the half-life $t_{1/2} = 170$ years and β-decays with emission of electrons having the average energy close to 100 keV [13], anti-neutrino and the unstable isotope of phosphorus, ^{32}P (which β-decays in its turn to the stable isotope ^{32}S).

One can envisage three scenarios of the material behaviour (Fig. 1). If the amount of an introduced radio-nuclide is large enough, the material will loose its mechanical integrity in a finite time. If this amount is not sufficient to provide the critical self-irradiation dose, then the mechanical properties of the material will be stabilized at some level without macroscopic decomposition of the material. Finally, if the concentration of the radio-nuclides is just sufficient to provide the critical irradiation dose, the material will decompose in infinite time.

If the unstable isotopes are incorporated in the polymer backbones, as can be done for instance with use of ^{14}C, the polymer chain rupture can occur also due to the Scilard–Chalmers effect, which consists in chemical bond dissociation caused by radio-decay of an unstable nuclei participating in a chemical bond. It was found experimentally that the recoil energy obtained by the daughter ^{14}N nuclei and the electronic excitation upon the decay of the ^{14}C nuclei lead to dissociation of the (C)–(^{14}C) chemical bond in ethanol molecule with approximately 50% probability [14]. In a linear polymer, the ^{14}C nuclei is typically connected by two bonds with the neighbours, therefore, the probability of the chain break should be higher. However, this degradation mechanism seems to be negligible compared to degradation caused by high-energy β-decay events.

Programming of electronic properties of materials by self-irradiation

It is well known that ionizing radiations can significantly change the electronic properties of materials. Ion beam implantation is a well-established technology of tailoring conductivity of inorganic semiconductors. Change of electronic properties is achieved due to creation of defects (vacancies and interstitial atoms) in the crystal lattice, and doping of the material by *n*- or *p*-type, depending on the kind of the implanted ions [15]. It is recognized for a half of century that high-energy particle radiation fields, such as exist for instance in the near-Earth orbits, can cause significant changes in the optical properties (transparency, refractive index) of the scientific equipment lenses and degradation of semiconductor detectors [16]. In the last two decades, ionizing radiations are explored extensively as a tool for tailoring the electrical characteristics of conductive polymers. It was found for instance that conductivity of polyaniline and polyaniline blends can be increased by several orders of magnitude (typically, from 10^{-5} to 10^{-2}–10^{-1} S/cm) by ion or electron beam irradiation [17, 18]. The effect may be attributed either due to doping of polyaniline with hydrochloric acid released by the partner polymer in the blend [17], or formation of cross-links, which reduce the inter-chain electron hopping barrier [18]. Typical irradiation doses necessary for producing such conductivity changes are in the range of several dozens to few hundreds of kGy. Electron beam irradiation was used for local change of the refraction index of poly(methyl methacrylate) and creation of optical waveguides embedded in the matrix of the non-modified polymer [19].

It is evident that similar changes in the electronic properties of a material can be induced by radio-decay of unstable isotopes embedded in the chemical structure of a material, with such a difference that these changes can take

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[3] The spectrum of electron energies in the tritium β-decay is available at, e.g. http://www.tpub.com/content/doe2/hdbk113299/hdbk1132990108.htm.

place over extended time intervals. Let us consider for instance a resistor made of polyaniline in which a part of hydrogen atoms is substituted by tritium. According to the reference [17], the conductivity of polyaniline-base/chloral (100/30) blend increases from approximately 10^{-10}–10^{-4} S/cm after receiving the 100 kGy irradiation dose. Using the formula (2), one can estimate the mass of ^{3}H, which should be added per kilogram of the blend to have similar effect on the conductivity of the polymer in one year: $m \approx 9.7$ mg. A resistor with a programmed conductivity can be used for instance as an element of electronic schemes, which should be disabled after a certain time interval. Let us consider an electronic relay (Fig. 2) consisting of a transistor T whose states "off" and "on" are controlled by the electrical potential on the gate electrode, and the consecutive connection of two resistors, with the conductivity of one of the resistors being time-programmed and increasing by the low $R(t)$. The potential on the gate electrode depends on time as $U(t) = U_0 R(t)/(R_0 + R(t))$. The relay is turned "off", when the potential on the gate electrode drops below the critical value U_c at the moment:

$$t_c = R^{-1}[U_c R_0/(U_0 - U_c)]. \tag{3}$$

Here, R^{-1} designates the inverse function for $R(t)$. The switching of the relay can disable an electronic device (or, in contrary, enable a device functioning) at a prescribed moment t_c. From the numerical estimated given above for the PTFE self-irradiation doses follows that the programming of the relay can be made over the time intervals varying from years to dozens of years with minimal inclusion of a radio-active substance (e.g. tritium). It is implied of cause that the material of the resistor is well protected against the action of the environmental factors (moisture etc.) by encapsulating it in a chemically stable shell (e.g. PTFE).

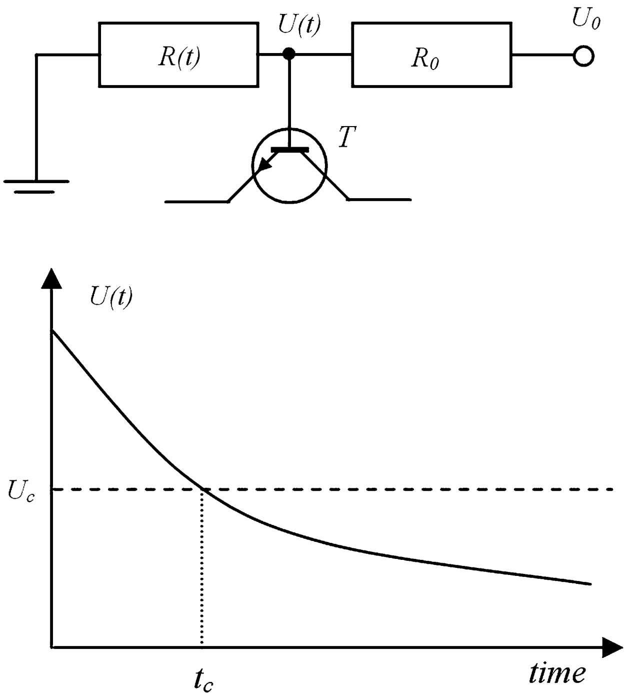

Fig. 2 The use of a time-programmed resistor in a simple electronic scheme (*top*), and the potential on the gate electrode of the transistor as function of time (*bottom*). The transistor turns in the "off" state when the potential drops below the critical value U_c in the time moment t_c

An electrical capacitor also can be time-programmed by the use of self-irradiating dielectrics for a capacitor's fabrication. The time-dependent capacity can be exploited for programming the resonant frequency $\omega = 1/\sqrt{LC}$ of an oscillating electrical circuit. Assuming the linear dependence of a capacitor on the electric permittivity ε, one obtains the approximate relation for the shift of the resonance frequency with time:

$$\Delta\omega(t) \approx -\frac{1}{2}\frac{\Delta\varepsilon(t)}{\varepsilon}\omega_0 \tag{4}$$

where ε and ω_0 are the initial permittivity and the resonance frequency of the contour. Since the change of the permittivity is relatively small, the quality factor Q of the contour should be sufficiently high for the shift to be well measurable.

Devices based on radiation-induced internal stress relaxation and swelling

From the practice of storage of uranium and plutonium, and exploitation of nuclear reactors it is well known that self-irradiation of materials or their external irradiation leads to gradual relaxation of mechanical stresses. Structure of materials is constantly "shaken" at the atomic level by the energetic particles. This leads to erasing of initial structural information on stress fields. For instance, the isotopes of plutonium release 4.9–5.5 MeV per radio-decay event in form of the kinetic energy of the decay products (daughter uranium atom and alpha-particle (or electron, for ^{241}Pu). This energy is dissipated via the electronic excitations and knocking out the ions along the tracks of the decay products from their equilibrium positions in the crystal lattice. The decay of an isotope of Pu causes in average 2,500 displacements per decay event [5].The total rate of the structure damage, described usually in terms of average displacements-per-atom (dpa) constitutes for typical isotopic composition of weapon-grade plutonium approximately 0.1 dpa/year [5]. In other words, in average every atom is knocked out of its position in the crystal lattice every 10 years. The atomic displacements cascades eventually lead to relaxation of any macroscopic stress fields existing in the material at some starting time point.

Alongside with the stress relaxation, the material undergoes the reduction of specific gravity (swelling) caused by accumulation of the lattice defects and, at long terms, formation of helium micro-bubbles inside the metal. Neutron irradiation causes stress relaxation and creep of construction elements of nuclear reactors [6].

Radiation-driven stress relaxation can be explored for programming motions of mechanical systems over extended time intervals. Let us consider a system of two springs S_1 and S_2 connected to each other and attached by one end to immobile foundations (Fig. 3). The springs mutually elongate each other by the reaction forces. Suppose that a small fraction of a radio-active isotope is added to the material of the spring S_1, while the spring S_2 is made of a normal material not containing radio-active species. It is easy to predict the behaviour of such a system on the qualitative level. Self-irradiation will constantly relax the mechanical stress in the spring S_1, and therefore reduce the reaction force produced by the spring. To restore the mechanical equilibrium, the spring S_1 has to be elongated. This is equivalent to the increase of the spring S_1 length in the unloaded state. Thus, the point of the spring's connection, which can be marked by a bead, will have to move from left to right, until the spring S_2 acquires its equilibrium length.

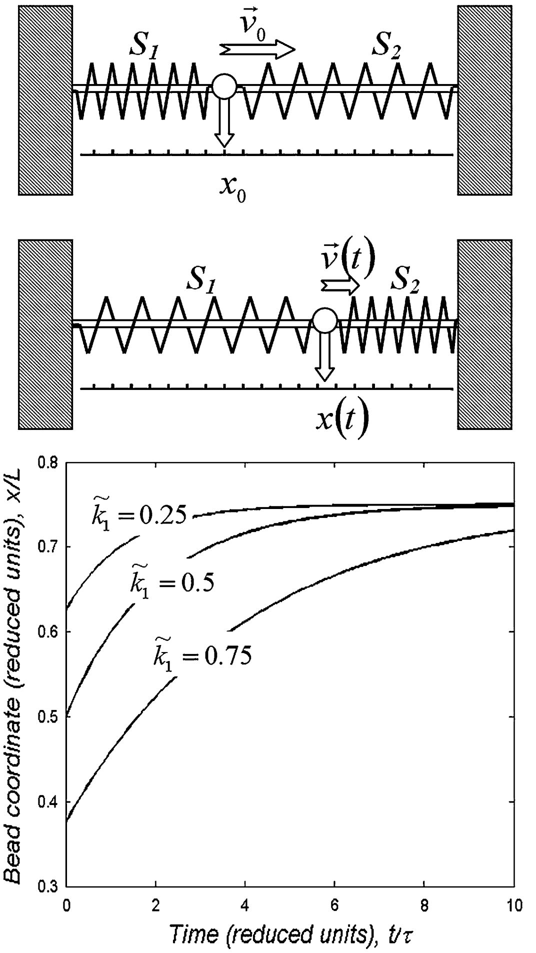

Fig. 3 A two-spring mechanism driven by self-irradiation stress relaxation in one of the springs. *Left:* the configuration of the mechanism at the initial (*top*) at an arbitrary (*bottom*) moments. The stress is gradually relaxed in the material of the spring S_1. *Right:* the coordinate of the bead at the connection of the two springs, as the function of time, for different relative stiffness of the spring S_1

To find the equation of motion of the junction point of the springs, we assume that the stress relaxation rate in a self-irradiating material is proportional to the stress tensor itself [5, 20]:

$$\frac{d\sigma_{ik}}{dt} = -\frac{1}{\tau}\sigma_{ik}. \tag{5}$$

Here, τ is the characteristic relaxation time, which depends on the mass fraction of the radio-isotope in the material, the energies and the masses of the fission products, the half-life of the isotope and the structure of the material. The rate of annealing of the defects produced by energetic particles depends also on the temperature. Since the reaction force is linearly proportional to the stress, one can write the differential equation for the reaction force F_1:

$$\frac{dF_1}{dt} = -\frac{1}{\tau}F_1. \tag{6}$$

Suppose that the bead at the junction point shifts every time when the misbalance between the forces F_1 and F_2 exceeds some small static friction force δF between the bead and the rod on which the bead is planted. Let k_i be the rigidity and l_i the length in the not-stretched state of the ith spring, $l_{1,0}$ the initial not-stretched length of the first spring, and x the coordinate of the bead measured from the left foundation. Neglecting the effect of the material swelling on the spring constants and aspiring δF to zero, it is easy to derive the equations of motion of the bead:

$$\begin{aligned} x(t) &= \tilde{k}_1 l_1(t) + \tilde{k}_2(L - l_2) \\ &= \tilde{k}_1\left\{l_{1,0}e^{-\tilde{k}_2 t/\tau} + \left(1 - e^{-\tilde{k}_2 t/\tau}\right)(L - l_2)\right\} \\ &\quad + \tilde{k}_2(L - l_2), \end{aligned} \tag{7}$$

$$v(t) = \dot{x}(t) = \tau^{-1}\tilde{k}_1\tilde{k}_2\left(L - l_{1,0} - l_2\right)e^{-\tilde{k}_2 t/\tau}, \tag{8}$$

where $\tilde{k}_i = k_i/(k_1 + k_2)$. The dependence of the bead coordinate on time is shown in Fig. 3 for a particular case $l_{1,0} = l_2 = L/4$ for a few values of the dimensionless parameters $\tilde{k}_1$ and $\tilde{k}_2$ (note that $\tilde{k}_2 = 1 - \tilde{k}_1$ by definition). Above, we assumed that τ is constant during the whole duration of the experiment. In fact, this parameter may itself depend on time due to the gradual decomposition of the radio-active isotope and the change of structure of the material. This should lead to more complex dependencies of the system configuration on time.

Not only slow motions of mechanisms, but also sharp switching of a mechanism configuration at a remote time moment can be programmed by the internal stress relaxation. Let us consider the two-spring system introduced above with the bead connected to a bistable switch (Fig. 4). The switch changes its state from “on” to “off” (or vice versa) upon application of a finite critical force δF. This change is activated when the misbalance between the reaction forces F_1 and F_2, $\Delta F = F_2 - F_1$ reaches the critical value $\Delta F_c = \delta F$. The moment when it happens can be found as:

$$t_c = -\tau \ln(1 - \delta F / F_0), \tag{9}$$

where $F_0 = \frac{k_1 k_2}{k_1 + k_2}\left(L - l_{1,0} - l_2\right)$ is the initial reaction force generated by each of the springs. If $\delta \mathrm{F} \ll \mathrm{F}_0$, then $t_c \approx \tau \delta F / F_0$. Switching can denote the activation or deactivation of a device at a definite time moment. Thus, the system can function as a mechanical time relay.

Numerical estimates

Let us estimate the characteristic times over which the devices shown in Figs. 3 and 4 can be programmed. Suppose that the spring S_1 is produced from an alloy of ^{241}Am (the isotope of americium used in home smoke detectors) having the half-life $t_{1/2} = 423$ years, and ^{238}U, which has the half-life 4.468 billion years and can be considered here as practically stable.[4] We assume here that the effect of the ^{241}Am decay on the structure of Am/U alloy is similar to the self-irradiation of plutonium, taking into account that the masses and the energies of the fission products, as well as the molar masses of the metals are close for the both decay processes. This assumption allows us to estimate the rate of the structure damage rate Q (measured in the units of dpa/year) in our hypothetical spring using the literature data on the structural damage rate for plutonium [5]. In frames of this assumption, one has $Q_{\mathrm{Pu}} = A \sum_k f_k \Big/ \left(t_{1/2}\right)_k$, where f_k is the mass fraction of a k-th Pu isotope, $(t_{1/2})_k$ the half-life of the k-th isotope, and A the coefficient of proportionality, which we assume to be the same for the Pu and the Am/U systems. From Table II of reference [5], we estimate it as $A \approx 1.77 \times 10^3$ dpa. Now, the radiation damage rate for the Am/U system can be estimated as $Q_{\mathrm{Am/U}} = A f_{\mathrm{Am}} \Big/ \left(t_{1/2}\right)_{\mathrm{Am}} \approx 4.09 f_{\mathrm{Am}}$ dpa/year. Unfortunately, the stress relaxation times for Pu and its alloys are absent in the open literature. We assume that the relative stress in a stretched Am/U spring diminishes in e times at the same degree of the structure damage, D, as in the neutron-irradiated Inconel X750 springs [6]. From Fig. 18 of reference [6], it can be estimated as $D \approx 7.1$ dpa. Thus, the characteristic stress relaxation time τ for the Am/U spring can be estimated as $\tau = D / Q_{\mathrm{Am/U}} \approx (0.24 / f_{\mathrm{Am}})$ years. From the last formula, the relaxation time of the spring equals to 1 year when ^{241}Am constitutes approximately 1/4 of the spring’s material. When the mass fraction of ^{241}Am is 1%, the relaxation time is 24 years, etc. Let us calculate now to what time intervals can be programmed a “time relay” based on the self-irradiation induced stress relaxation. As follows from the formulas above, the relay changes its state at the moment $t_c = (\delta F / F_0) \cdot (0.24 / f_{\mathrm{Am}})$ years. The fraction of

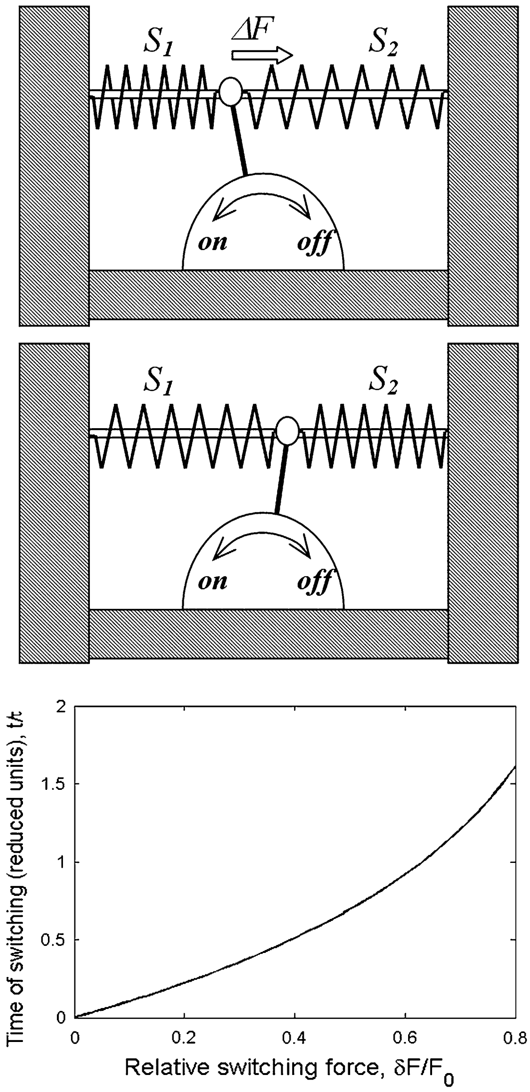

Fig. 4 A principal scheme of operation of a time relay based on the radiation-induced stress relaxation in a two-spring system. The stress in the spring S_1 is gradually reduced due to self-irradiation of the material of the spring. The switch occurs when the misbalance of forces acting on the switch exceeds a certain critical value δF. The time of switching can be preset by regulating the critical switching force, δF, or by adjusting the initial reaction forces of the springs, F_0 (*bottom*)

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[4] This naturally abundant isotope of uranium is broadly used in different branches of civil and military technologies. For instance, it was used as colorants in uranium glass.

the ^{241}Am isotope, which should be added to program the relay activation at the moment t_c is $f_{Am} = 0.24(\delta F/F_0) \cdot (t_c/\text{year})^{-1}$. Suppose that the switch changes its state when misbalance of the forces exerted by the springs S_1 and S_2 achieves 10% of the spring initial reaction forces, that is $\delta F/F = 0.1$. The relay is activated in 1 year, if the mass fraction of ^{241}Am is 2.4%. To program the relay switch to, say, 10 years, one should diminish the fraction of the ^{241}Am to 0.24%, etc. The moment of the relay activation can be in principle postponed to hundreds and even thousands of years, if the isotope ^{243}Am with the half-live 7,370 years is used in the alloy instead of the relatively short living ^{241}Am. At the mass fraction of ^{243}Am equal to 0.1%, the relay activation time is $t_c = 982$ years; if, at the same mass fraction of the isotope, the relative switch force is increased to $\delta F/F = 0.2$, then $t_c = 1{,}965$ years. Analogously, one can use the isotopes of plutonium, for instance, ^{239}Pu (the half-life 24,100 years), as the source of the self-irradiation of the alloy, and increase the switch times even further. There exist plenty of other possibilities, exploiting other chemical elements and their isotopes, to manufacture the devices driven by self-irradiation induced internal stress relaxation. Programming the mechanical time relays over large terms may be more reliable if noble metals (e.g. gold or iridium) are used as the main material of the mechanical system, in order to provide the system necessary chemical stability.

Swelling of self-irradiating metals and minerals can be also exploited for programming of material's shape transformations. Consider, for instance, a bilayer stripe, with one of the layers made of a self-irradiating material. If initially the bilayer is flat, swelling of the self-irradiating layer will eventually cause curling of the stripe. It is obvious that complex shape transformations and motions of mechanisms can be programmed by exploiting both the internal stress relaxation and swelling in self-irradiating materials.

Possible applications of time-programmed materials and radiation safety concerns

Use of radioactive substances limits the potential applications of the proposed materials to the fields where the radio-activity safety is not a primary concern. Nevertheless, ongoing miniaturization of electronic circuits will constantly decrease the amount of the isotopes needed for the time programming of the electronic elements and can eventually make the technology sufficiently safe. It is worth to note that functioning of a large class of home smoke detectors is based on the ionizing radiation of ^{241}Am. Each detector contains approximately 0.2 mg of the radio-active metal that is much greater than the mass of elements of modern electronic circuits. Another example of publically accepted radio-nuclide technology is the production of radioluminescent paints on the base of tritiated polymers, which may contain up to 20% of hydrogen sites occupied by tritium [21]. Our numerical estimates show that much smaller amounts of radio-nuclides are sufficient for programming electronic characteristics of conductive polymers and self-destruction processes in PTFE. Time-programmed materials can be useful for the design of devices that should be disabled after a certain period for the safety or security reasons, but may become hardly accessible (e.g. high-tech warfare). Programmed self-destruction of PTFE may, to some extent, resolve the problem of the "orbital garbage" in the space industry, where this polymer is broadly used. Lost fishing nets, which self-destruct after a certain term, may reduce the danger to marine fauna. On the other hand, mechanical devices and time relays based on the relaxation of internal stresses can be in principle programmed over time intervals extending to thousands of years. Although applications of such devices are not evident, the principal possibility to program the functioning of mechanisms in remote future is intriguing. One can envisage such an exotic application as the backup mechanisms for the deployment of photovoltaic panels to a certain date for the future interstellar space probes.

Isotopes, which are potentially suitable for material time-programming, should have the lifetimes sufficient for a production cycle, which means, several dozens of days at least. On the other hand, the isotopes with very large half-lives are also not practical because of their low activity. Some of the isotopes may be particular interesting for the approach in view of an element rich chemistry (^{3}H, ^{14}C, ^{32}Si, ^{55}Fe, ^{68}Ge), or chemical stability (^{194m2}Ir, ^{195}Au, ^{194}Os, ^{192m2}Ir)**,** or widespread use of an isotope (^{60}Co, ^{241}Am).

In summary, we have considered an application of radio-isotopes to programming mechanical and electric properties of materials over extended time intervals. A few implementations of time-programmed materials are suggested. It is shown that it is possible to program self-decomposition of PTFE plastics by means of incorporation of radio-nuclides (^{14}C, ^{3}H) in the polymer structure. We have argued that conductivity of conjugated polymers such as polyaniline can be set up to change in time by adding a small quantity of a radio-isotope to the polymer formulation. Refraction index of a dielectric can be time-programmed by addition of unstable nuclei to the material. Time-dependent electrical resistors and capacitors are interesting for the design of electronic circuits that can be disabled or enabled at a certain date. Swelling and mechanical stress relaxation induced in self-irradiated materials can be used for setting up slow motions and configuration changes of mechanical systems. Both electronic and mechanical time relay systems can be created on the base of isotope modified materials. Our conclusions are supported by numerical estimates based on the literature data concerning the radiation effects on matter.

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