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Degradation of Teflon® Film Under Radiation of Protons and Electrons

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Aluminized Teflon® film (fluorinated ethylene propylene) is commonly used on exterior spacecraft surfaces for thermal control. Synergistic effects of proton and electron radiation on the Teflon film degradation were investigated in terms of ground-based simulation testing. The energy of protons and electrons was chosen in the range of a few tens of kiloelectron volts. The results showed that an absorption band from the near-ultraviolet to the visual region was formed under either proton or electron radiation. But there was no additive effect on reflective property of aluminized Teflon under synergistic radiation of protons and electrons. The effect of simultaneous radiation of protons and electrons was lower than the additive effect of these two charged particles. Under the equal fluence of radiation, the total changes in spectral reflectance were independent from the radiation sequence of protons and electrons. The structural defects induced by protons and electrons were somewhat different. The electrons preferred to activate large molecules and bombard fluorine atoms out of the main chains, forming various free radicals and carbon atoms. Under the radiation of protons, the implantation of protons played an important role in the formation of functional groups. The relation between optical properties and microdefects is discussed.

Nomenclature

a_s = solar absorptance
E_e = energy of electrons
E_p = energy of protons
e^- = electrons
J_λ = intensity of solar electromagnetic rays
$\log\Phi$ = base 10 logarithms of irradiation fluence
n = number of division along wavelength to divide the solar spectrum into equivalent parts
p^+ = protons
R_s = integration reflectance
Δa_s = change in solar absorptance
$\Delta\rho_\lambda$ = change in spectral reflectance
λ = wavelength
ρ_λ = spectral reflectance
Φ_e = irradiation fluence of electrons
Φ_p = irradiation fluence of protons
φ_e = flux of electrons
φ_p = flux of protons

Introduction

IT is known that thermal control coatings are widely used on exterior surface of spacecrafts to maintain a given thermal regime.[1] Aluminized Teflon® fluorinated ethylene-propylene (FEP) film second surface mirrors are a type of thermal control coating, which possess unique thermal emittance and high resistance to space environment irradiation.[2] Thermal control coatings on spacecrafts are subjected to damages caused by irradiation of electrons and protons in the Earth radiation belts, leading to a degradation of optical properties such as the spectral reflectance ρ_λ and solar absorptance a_s (Ref. 3). Because the degradation would destroy the thermal balance of spacecraft, it is necessary to examine the property evolution of thermal control coatings in geostationary orbit through in-flight[2,3] and ground-based simulation[4–6] experiments.

The aim of this paper is to reveal the synergistic radiation effects of protons and electrons on the aluminized Teflon FEP film degradation in optical properties in terms of ground-based simulation. The changes in spectral reflectance $\Delta\rho_\lambda$ and solar absorptance Δa_s were examined. To explore the mechanism of degradation, the formation of microdefects caused by the irradiations of protons and electrons was also investigated.

Experimental

The aluminized Teflon FEP film was used as the experimental material. The specimens were fabricated in the form of a second surface mirror consisting of Teflon FEP film with a thickness of 50 μm, an aluminum reflecting layer with a thickness of 80~100 nm, and a thin protection layer of SiO_x. The Al layer was deposited in vacuum. The specimens were adhered to the Al alloy substrate of 15 mm in diameter.

The ground simulation tests were conducted using a facility that can simulate the radiation of protons and electrons with the energy less than 200 keV, independently and simultaneously. During the tests, the temperature of specimens was maintained at 298 K using electric heating and water cooling. The energy of protons and electrons was chosen in the range of a few tens of kiloelectron volts. The proton flux was $\varphi_p = 5 \times 10^{11}$ cm^{-2}s^{-1}, and electron flux $\varphi_e = 1 \times 10^{12}$ cm^{-2}s^{-1}. The vacuum in the test chamber was 10^{-5} Pa. The spectral reflectance ρ_λ of specimens before and after the radiation in the wavelength region of 0.2~2.5 μm was in situ measured using an integration sphere. The solar absorptance a_s of the specimens was obtained according to the following equation:

$$a_s = 1 - R_s = 1 - \frac{\int_{\lambda_1}^{\lambda_2} J_\lambda \rho_\lambda \, d\lambda}{\int_{\lambda_1}^{\lambda_2} J_\lambda \, d\lambda} = 1 - \frac{\sum_{i=1}^{n} \rho_\lambda}{n} \tag{1}$$

where the n value was chosen as 24 (Ref. 7). After radiation, specimens were analyzed by means of X-ray photoelectron spectroscopy (XPS).

Results and Discussion

Changes in Optical Properties

Figures 1a and 1b show the changes in spectral reflectance of aluminized Teflon FEP film after sequential radiation from electrons

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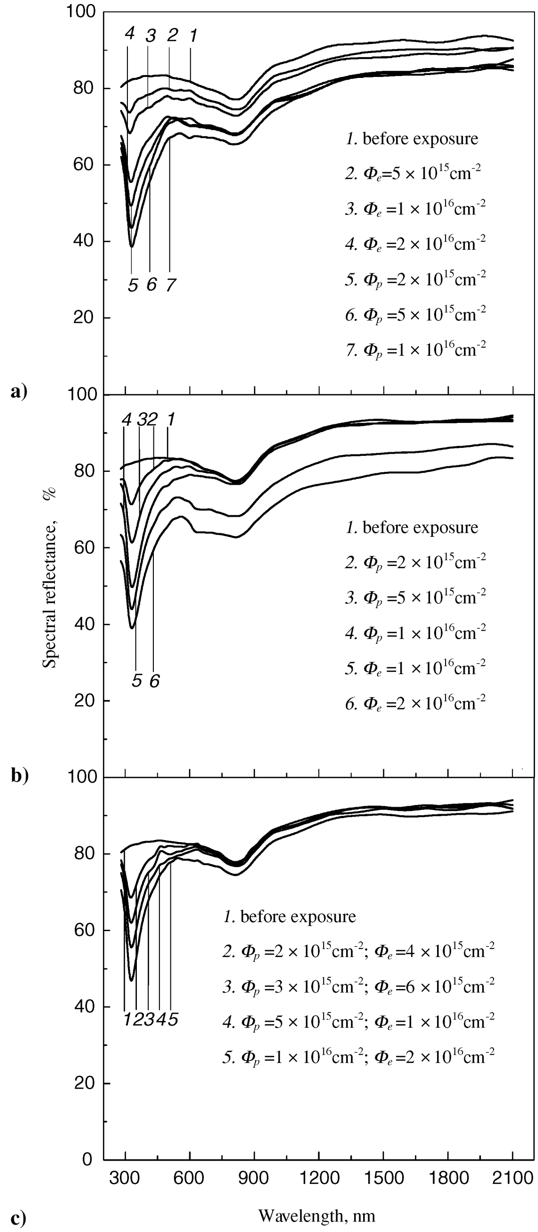

Fig. 1 Changes in reflective spectrum of aluminized Teflon FEP film after synergistic radiations ($E_e = E_p = 30$ keV, $\varphi_p = 5 \times 10^{11}$ cm^{-2}s^{-1}, $\varphi_e = 1 \times 10^{12}$ cm^{-2}s^{-1}): a) $e^- \rightarrow p^+$, sequential; b) $p^+ \rightarrow e^-$, sequential; and c) $p^+ + e^-$, simultaneous.

to protons and from protons to electrons, respectively. The change in spectral reflectance after the simultaneous radiation of protons and electrons is shown in Fig. 1c. Both the energy of electrons and protons were chosen as $E_e = E_p = 30$ keV, and the corresponding flux values were $\varphi_e = 1 \times 10^{12}$ cm^{-2}s^{-1} and $\varphi_p = 5 \times 10^{11}$ cm^{-2}s^{-1}, respectively. Before the radiation, the spectral reflectance in the wavelength region of 280~750 nm is approximately 80%, and the minimum is 77%. In the wavelength region more than 850 nm, every spectral reflectance is larger than 90% in the near-infrared region, which demonstrates that the aluminized Teflon FEP possesses an excellent reflective property before radiation. However, the reflective property decreased with the increasing of radiation fluence after the radiation of electrons and protons. As shown in Fig. 1, an absorption band appears in the 280~600-nm wavelength region, where the spectral reflectance drops suddenly. The right side of the band moves to the right with the increasing of radiation fluence, leading to the widening of the absorption band. This phenomenon might be related to an increase in the concentration of microdefects induced by electrons and protons.[8,9]

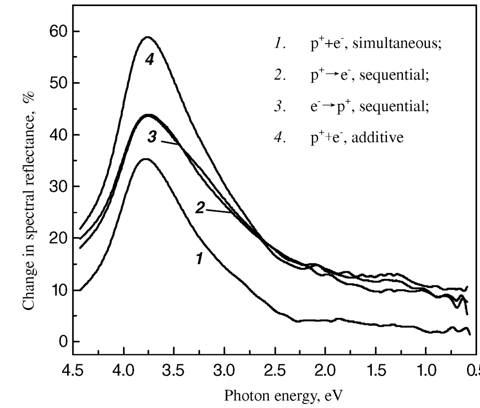

Fig. 2 Change in spectral reflectance of aluminized Teflon FEP film caused by synergistic radiations at a given fluence as a function of incident photon energy.

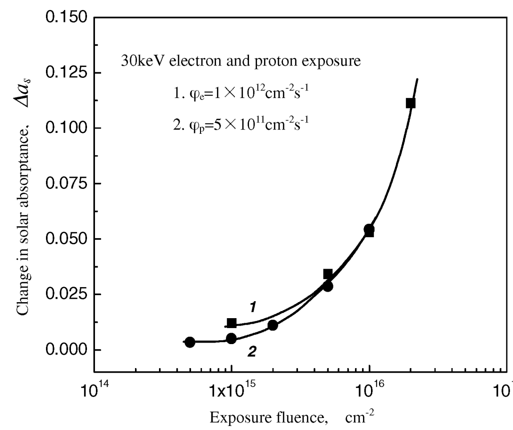

Fig. 3 Change in solar absorptance of aluminized Teflon FEP film caused by independent radiation of protons and electrons as a function of fluence.

During the sequential radiation, the effect of electrons and protons on the degradation of reflective property is different. The spectral reflectance from near-ultraviolet to visual region decreased obviously under the exposure of protons (see curves 5–7 in Fig. 1a and 2–4 in Fig. 1b), whereas the degradation resulted by the electrons almost in the whole solar spectrum (see curves 2–4 in Fig. 1a and 5 and 6 in Fig. 1b). Under the exposure of electrons, charge accumulation would occur on the Teflon FEP film. The accumulated charges could be annihilated by absorbing the incident photons of solar spectrum, thus leading to the decrease in reflective property within the region from near ultraviolet to near infrared. Under the simultaneous radiation, the degradation of reflective property is similar to that caused by proton radiation, in which an obvious absorption band only forms in the region from near-ultraviolet and visual lights (Fig. 1c). The reason for this phenomenon might be related to the annihilation of negative charges accumulated on the surface of Teflon FEP film by electron radiation and the positive charges of the incident protons.

Figure 2 shows the comparison of reflective spectrum of aluminized Teflon FEP film under different type of radiation with the same fluence of electrons and protons. Both the energy of electrons and protons were chosen as 30 keV, and the fluence of electrons and protons are $\Phi_e = 2 \times 10^{16}$ cm^{-2} and $\Phi_p = 1 \times 10^{16}$ cm^{-2}, respectively. It is indicated that under the synergistic radiation, the radiation effects due to electrons and protons do not show an additivity property. The simultaneous radiation effect is lower than the additive effect of electrons and protons. In the case of sequential radiations, the total changes in spectral reflectance are independent from the radiation sequence of electrons and protons with the same accumulation fluence.

Figure 3 shows the change in solar absorptance Δa_s of aluminized Teflon FEP film as a function of electron and proton fluence. It was

Table 1 Binding energy and area ratio of eight characteristic peaks in C_{1s} spectra after synergistic radiation

Radiation mode	Binding energy, eV, and/or area ratio, %							
	1	2	3	4	5	6	7	8
$p^+ \rightarrow e^-$	284.3(31)	285.9(10)	286.9(8)	287.9(10)	289.4(8)	290.9(9)	292.2(14)	293.7(10)
$e^- \rightarrow p^+$	284.3(40)	285.6(19)	286.5(10)	288(11)	289.9(6)	291(2.5)	292.3(8)	293.7(3.5)
$e^- + p^+$	284.4(36)	285.8(19)	286.5(7.5)	287.9(14)	289.9(7)	291(5)	292.2(5)	293.6(6.5)

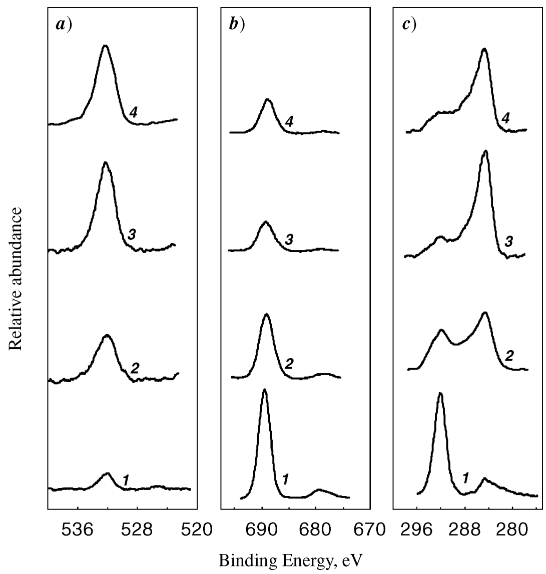

Fig. 4 Changes in XPS spectra of Teflon FEP film caused by synergistic radiation for energy bands of a) O_{1s}, b) F_{1s}, and c) C_{1s} ($E_e = E_p = 30$ keV, $\varphi_e = 1 \times 10^{12}$ $cm^{-2}s^{-1}$, $\varphi_p = 5 \times 10^{11}$ $cm^{-2}s^{-1}$, $\Phi_e = 2 \times 10^{16}$ cm^{-2}, and $\Phi_p = 1 \times 10^{16}$ cm^{-2}): 1, before exposure; 2, $p^+ \rightarrow e^-$, sequential; 3, $e^- \rightarrow p^+$, sequential; and 4, $p^+ + e^-$, simultaneous.

found that, although the effect of independent radiation of electrons and protons on the degradation of reflective property was different, almost the same changing tendency appeared in the relation of Δa_s vs $\log\Phi$ after the electron and proton radiation with the same energy. Thus, if the products of radiation fluence and energy are equal almost the same Δa_s values could be gotten after the various types of radiation. This result is in agreement with Refs. 8 and 9.

Changes in the XPS Spectrum

The changes in the XPS spectrum of Teflon FEP film after the synergistic radiation of electrons and protons are shown as Fig. 4, in which curve 1 stands for that before radiation, curve 2 for the sequential radiation from protons to electrons, curve 3 for the radiation from electrons to protons, and curve 4 for the simultaneous radiation of protons and electrons. Figure 4 shows the spectra of O_{1s}, F_{1s}, and C_{1s} energy bands before and after radiation, respectively. It is shown that the energy band spectra of O_{1s}, F_{1s}, and C_{1s} before the radiation are typical for the Teflon FEP film, and a small amount of oxygen was detected on the film surface. After the synergistic radiation, the XPS spectra changed obviously. In the C_{1s} energy band spectra (Fig. 4c), the peak of the binding energy at 292.2 eV, which characterizes the basic chain unit of CF_2 for the fluorinated ethylene, dropped remarkably, while the peak of the energy less than 285 eV rose noticeably. Figure 4b demonstrates that the fluorine content reduces by the radiation. Figure 4a shows that the oxygen content increases after the radiation. It was found that the effect of the sequence radiation of protons and electrons on the XPS spectra was different. The C_{1s} spectrum after the simultaneous radiation of protons and electrons was similar to that obtained by the proton radiation only and by the sequential radiation from electrons to protons, as shown by curves 4 and 3 in Fig. 4c. In both cases, the peak of binding energy at approximately 292.2 eV dropped remarkably, while the peak of binding energy less than 285 eV rose evidently. The C_{1s} spectra after the radiation can be characterized by eight characteristic peaks, as shown in Table 1. For example, Fig. 5 shows the eight peaks for the characterization of the C_{1s} spectrum after the simultaneous radiation of protons and electrons, in which the serrated line shows the experimental curve and the dotted one is given by imitation of the eight characteristic peaks.

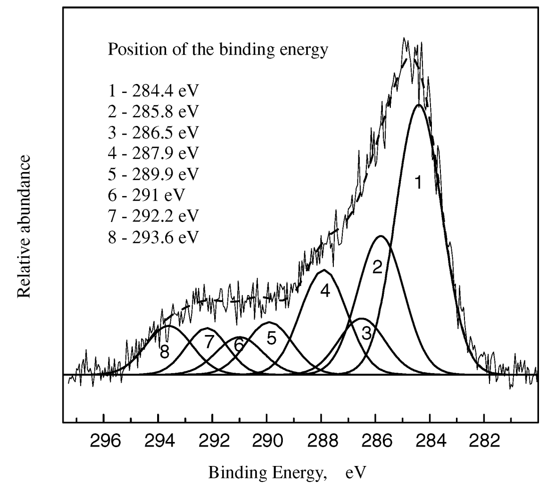

Fig. 5 XPS spectral resolution of Teflon FEP film caused by synergistic radiation for energy bands of C_{1s} ($E_p = 30$ keV, $\varphi_p = 5 \times 10^{11}$ $cm^{-2}s^{-1}$, $\Phi_p = 1 \times 10^{16}$ cm^{-2}; $E_e = 30$ keV, $\varphi_e = 1 \times 10^{12}$ $cm^{-2}s^{-1}$, and $\Phi_e = 2 \times 10^{16}$ cm^{-2}).

It is believed from the preceding characteristic binding energy in Table 1 that peaks 1 and 7 originate from the ethylene chain segments and the tetrafluoro-ethylene chain segments in Teflon FEP film, respectively. The binding energy at 285.6 and 285.9 eV related to peak 2 originates from the two ethylene units near the tetrafluoro ethylene and the ethylene units in the $–CFH–CH_2–$ chain segments, respectively, and peak 3 originates from the base of C–O or the ethylene units in the $–CF_2–CH_2–$ segments. Peak 4 can be caused by carbonyl groups ($C=O$), for its energy (287.9 eV) is very near to the latter. The binding energy of 289.9 and 289.4 eV related to peak 5 might originate from the base of $=CF–$ in the hexafluoro propylene and the $–CFH–$ in the $–CF_2–CFH–$ chain segments, respectively. Peak 6 originates from the tetrafluoro ethylene units in the $–CF_2–CH_2–$ segments, and peak 8 is from the fluorinated methyl bases $–CF_3$ in the molecular chains.

The preceding analyses indicated that under the synergistic radiation of protons and electrons complex changes in the structure of Teflon FEP film occurred. Because the fluorine atoms and the fluorinated methyl bases are much larger than carbon atoms in the molecular main-chains of Teflon FEP copolymer, the chain backbones of carbon atoms could be closely encased to form a stable structure. During the radiation, the charged particles would preferentially interact with the fluorine atoms and fluorinated methyl bases in the external layer of molecular chains. When electrons radiated Teflon FEP film, the incident electrons were caught preferentially by fluorine atoms because of their strong electronegativity. The fluorine atoms were bombarded out of the molecular chain segments, leading to form active radicals such as $–C^*F_2$, $–C^*F–$, $–C^*=$, $–C^{**}–$ and free carbon atoms. In the case of proton radiation, except for the preceding defects, the following functional groups could also be formed by the implanting effect of protons (H^*): $-CF_2H-$, $-CFH_2-$, $-CFH-$, $-CH_3$, $-CH_2-$, and $=CH-$, as well as free radicals on basis of the preceding functional groups. For instance, peak 4 of C_{1s} binding energy at 287.9 eV related with carbonyl groups in Table 1 might result from the product formed by the combination of $-C^{**}-$ with oxygen.

The structural defects induced by the radiation of electrons and protons could be related to the changes in optical properties. Both the active radicals induced by electrons and the functional groups produced by protons might contribute to forming the absorption band in the regions from near-ultraviolet to visual light, by interaction with the incident photons. As just mentioned, the accumulated charges on the surface of Teflon FEP film caused by the radiation of electrons would be annihilated through absorbing the incident photons and lead to the decrease in spectral reflectance with fluence of electrons in the near-infrared range (Figs. 1a and b). Generally, the degradation of reflective property in the near-infrared range is easier to recover.[6,9] In addition to the formation of functional groups, the protons can also interact with the fluorinated methyl bases in the molecular segments of Teflon FEP to form CF_3^* ion fragments. Such ion fragments readily escape from the surface and result in changes both in the density of surface layer and the external roughness. Therefore, under the exposure of protons, except for the formation of structural defects, changes of the surface layer density and the surficial roughness might also contribute to the reflective property degradation of the Teflon FEP film.

Conclusions

The radiation of 30-keV protons with the flux 5×10^{11} $cm^{-2}s^{-1}$ results in the formation of an absorption band in the regions of near-ultraviolet to visual light in aluminized Teflon FEP film. Under the electron exposure with the flux 1×10^{12} $cm^{-2}s^{-1}$, except for the formation of absorption band, the spectral reflectance decreases with fluence in the near-infrared region. There is no additive effect on reflective property of aluminized Teflon under synergistic radiation of protons and electrons. The effect of simultaneous radiation of protons and electrons is lower than the addition effect of independent ones. Under an equal fluence of radiation, the change in spectral reflectance is independent from the radiation sequence of protons and electrons.

The structural defects induced by protons and electrons are somewhat different. Under the electron exposure, the fluorine atoms could be bombarded out of the main chains to form free radicals such as $-C^*F-$, $-C^*=$, and $-C^{**}-$, as well as free carbon atoms. Under the radiation of protons, except for the preceding defects, the functional groups of $-CF_2H-$, $-CFH_2-$, $-CFH-$, $-CH_3$, $-CH_2-$, and $=CH-$ could be induced as a result of the implantation of the incident protons.

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