Effects of Atomic and Molecular Impacts on Spacecraft

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Experimental measurements of atomic and molecular impacts on metallic surfaces are described. The measurements were collected in the upper atmosphere from satellites and in the laboratory using molecular-beam techniques at energies ranging between a few ev and several kev. Over this energy range, impacts are important in terms of surface changes they will produce, since the mean penetration depth of these particles is less than 1μ. The erosion produced by impacts in the upper atmosphere was attributed to sputtering. The maximum sputtering rate for a satellite orbiting at 400 km was found to be 50 Å/yr. For craft traveling through the solar plasma, the principle effect of the impacts will be deposition. The yields of protons and alpha particles present in the plasma are too low to produce significant sputtering. For a light metal, such as aluminum, a concentration of embedded hydrogen amounting to 6% can build up over a region extending about a thousand angstroms beneath the surface during long exposure periods.

Introduction

A VEHICLE in space is subjected to a wide range of environmental conditions. Part of this environment includes impacts of energetic ions, atoms, and molecules on its surface. A low-orbiting satellite sweeps molecules out of the upper atmosphere which impact at energies ranging up to 10 ev. In the Van Allen belts it will encounter particles mainly in the Mev range. Beyond the magnetosphere it will be irradiated by the solar plasma at energies up to several kev.[1, 2] In all these regions a vehicle will be bombarded to some degree by high-energy particles originating from the sun, and by cosmic rays.

The effects of these impacts fall into two general groupings depending on whether impacts affect the properties of the surface or the solid-state properties of a material. At energies up to several kev, impacts will affect only the surface because of the short penetration range of these particles. Impacts at higher energies will produce solid-state changes because particles at these energies will penetrate beyond the surface and become embedded in the material.

Surfaces, then, will be affected mainly by impacts in the upper atmosphere and by the irradiation effects of the solar plasma. We have been investigating these impacts in terms of their effects on metallic surfaces. The study has been motivated because of a basic interest in the effects such impacts have on surfaces and for practical reasons because these impacts will affect spacecraft. The two surface properties most affected by impacts will be absorptivity and emissivity. These will change with time because of roughening produced by sputtering[3] and by the presence of foreign particles injected into the surface by the solar plasma.

Measurements in the Upper Atmosphere

The effects of impacts in the upper atmosphere were determined from four satellite experiments. The results of the first two experiments have been previously reported.[4, 5] From one experiment, limits on the erosion rate of a gold surface of 0.2 ± 0.1 Å/day were determined. From the other, it was found that this erosion could be attributed to sputtering by molecules of the upper atmosphere.[5]

The results of the last two experiments on satellites in the upper atmosphere have now been evaluated and can be reported here. As in the first flights, the crystal-oscillator method was used in the measurements. The material to be studied is plated on a quartz crystal, and the rate at which it is eroded by impacts is determined from the change in the crystal frequency.[5]

On one satellite, measurements were made on the sputtering rate of gold for the upper atmosphere impacting at a 30° angle relative to the plane of the surface. The sputtering rate for gold was found to be 0.1 ± 0.05 Å/day.

Measurements from the other satellites were on the sputtering rate of silver for the upper atmosphere impacting at normal incidence to the plane of the surface. The sputtering rate for silver was found to be 0.15 ± 0.05 Å/day.

Sputtering

From the erosion rate for a surface, one can calculate its sputtering yield in the upper atmosphere.[5] The composition of the upper atmosphere is mainly N_2,[6] and one finds the sputtering yield μ in Au atoms ejected per incident N_2 molecule to be

$$\mu \approx 1 \times 10^{-6}\ \mathrm{Au/N_2} \tag{1}$$

This yield occurs at 9 ev, the energy of impact of N_2 on a satellite between 200 and 800 km.

The sputtering yield for gold, as measured here, is within a factor of 2 of that measured in the first experiment.[4] The experiment on this satellite was to determine the sputtering yield of gold for a surface positioned at normal incidence to the air stream. As a result of these two measurements, it

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can be concluded that there is no significant difference in the erosion of a gold surface as a function of its angle relative to the air stream.

The sputtering yield for silver in the upper atmosphere is

$$\mu \approx 2 \times 10^{-6}\ \text{atoms}/\text{N}_2 \qquad (2)$$

The higher yield for silver over that of gold is in agreement with laboratory measurements at higher energies.[7] The silver surface flown on the satellite had been exposed to the atmosphere at the launch site for several days prior to launch, and it most probably had reacted with sulfur compounds in the air to form Ag_2S. This layer of Ag_2S would have sputtered at a greater rate than Au because of the more optimum transfer of energy to Ag_2S by N_2.

The sputtering rate S of a surface is dependent on the yield and the number of particles the satellite sweeps out of the upper atmosphere:

$$S = \mu n v \qquad (3)$$

where n is the particle density and v is the impact velocity.

Figure 1 is a plot of S for silver as a function of altitude for a stationary atmosphere. The values of S are about the maximum one would expect for any surface in space because silver has one of the highest yields of any element.[8] The decrease in the erosion rate reflects the rapid decrease in atmospheric density with altitude. Since one atomic layer contains about 10^{15} atoms/cm^2, it is found from Fig. 1 that it would take about a year for a surface to lose an angstrom due to sputtering at 600 km.

Solar-Plasma Irradiation

The effects of the solar-plasma irradiation of a metallic surface are more complex than the low-energy impacts of molecules in the upper atmosphere. The solar plasma is composed mainly of protons and alpha particles having energies ranging up to 10 kev during periods of a quiet sun and about 20 kev during solar activity.[1, 2] At these higher energies, impacts will produce not only sputtering as experienced in the upper atmosphere but, also, radiation damage as shown by Reiffel.[9, 10] In addition, a fraction of the particle flux will become trapped or embedded in the surface in the process of displacing atoms from their lattice sites.

The mass rate of change per unit area for a thin film or target exposed to a beam of ions is

$$dm/dt = \alpha m_1 i - \beta(t) m_1 - \mu(t) m_2 i \qquad (4)$$

The absorption coefficient α is the fraction of incident particles that penetrate and become trapped in the target. The re-emission coefficient $\beta(t)$ is the number of trapped particles re-emitted as succeeding layers of target atoms are sputtered. At $t = 0$, $\beta(t) = 0$, and as t becomes large, $\beta(t) \rightarrow \alpha i$. The beam flux is i in ions/cm^2-sec. The yield $\mu(t)$ is the number of target atoms sputtered per incident ion. The mass of the bombarding ion and of a target atom are, respectively, m_1 and m_2. As can be seen from Eq. (4), once $\beta(t) = \alpha i$ the target will lose mass at a constant rate due to sputtering.

We first observed the effect given in Eq. (4) when bombarding aluminum with He^+ at 1 kev,[7] and found α to be 0.01 and μ to be 0.2. The embedding of ions in a surface has been reported by others[11–14] at higher energies purely from a scientific point of view. But now that spacecraft are being designed to travel through the solar plasma, the trapping of ions must also be considered for practical reasons, because if large numbers are trapped the surface properties of materials will be affected by the presence of foreign particles.

Analysis of Solar-Plasma Irradiation

One of the principal factors, at a given ion energy, that determines the maximum concentration of trapped particles is the sputtering yield. On impact, the incident particle will penetrate a certain number of atomic layers into a surface and become trapped. In the process of penetrating the surface, the incident particles will also sputter surface atoms. If the yield is small, the rate at which particles will be reemitted as the surface sputters will also be small and a large concentration of particles will build up.

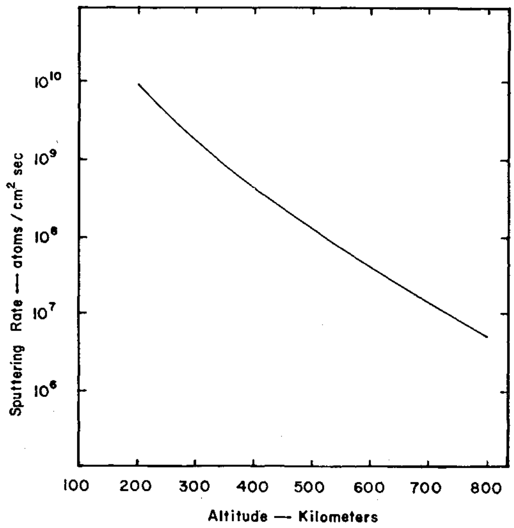

Fig. 1 **Sputtering rate of a silver surface as a function of altitude.**

The concentration of trapped particles can be derived starting with the diffusion equation and assuming the particles are being embedded in the target without sputtering taking place. In this case, the rate of change in concentration of trapped or embedded particles $c(\xi, t)$ is

$$\partial c/\partial t = D\partial^2 c/\partial\xi^2 \qquad (5)$$

where t is the time in seconds, D is the diffusion coefficient in square centimeters per second, and ξ is the distance measured from the surface of the target in centimeters.

Since sputtering will take place as the target is irradiated, the surface will recede with a velocity $v = i\mu/k$, where k is the atomic density of the target. By introducing a coordinate system moving with the surface of the target, Kuchai and Rodin[11] found a solution applicable to the operation of an ion pump in which all the irradiating particles are assumed to penetrate a distance l below the instantaneous surface. In this case the boundary conditions are

$$c(X, t) = 0 \text{ for } X = 0 \qquad (6)$$

$$c(X, t) = 0 \text{ for } t = 0 \qquad (7)$$

$$-D[(\partial c/\partial X) - (\partial c/\partial X)] = I \qquad (8)$$

$$X = l + 0 \qquad X = l - 0$$

where i is the irradiating particle flux in ions per square centimeter-second. Since a fraction of the irradiating flux will be reflected at the surface, i is replaced by αi for our case.

The solution of Eq. (5) for the boundary conditions is

$$c(X, t) = \frac{\alpha i\, l \exp[vl(1 - X/l)/2D]}{D\pi^{1/2}} \int_0^t \left\{\exp\left[\left(\frac{vl}{2Dt}\right)^2\right] \times \left[\exp\left(-\frac{1 - X/l}{4t^2}\right) - \exp\left[-\left(\frac{1 - X/l}{2t}\right)^2\right]\right]\right\} dt \qquad X \leq l \quad (9)$$

$$c(X, t) = \frac{\alpha i\, l \exp[vl(1 - X/l)/2D]}{D\pi^{1/2}} \int_0^t \left\{\exp\left[\left(\frac{vl}{2Dt}\right)^2\right] \times \left[\exp\left[-\left(\frac{X/l - 1}{2t}\right)^2\right] - \exp\left[-\left(\frac{X/l + 1}{2t}\right)^2\right]\right]\right\} dt \qquad X \geq l \quad (10)$$

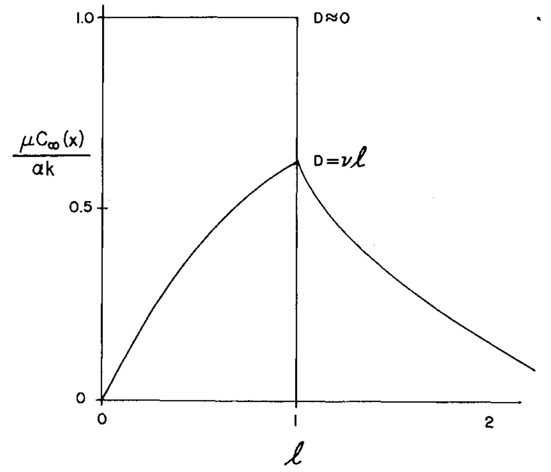

Fig. 2 Particle concentration in a target at equilibrium for different values of the diffusion coefficient.

By letting $t \to \infty$ the saturation concentration can be found:

$$C_\infty(X) = (\alpha i/v)[1 - e^{-(vX/D)}] \qquad X \leq l \qquad (11)$$

$$C_\infty(X) = \frac{\alpha i}{v}\exp\left[-\frac{vl}{2D(X/l-1)}\right] \times \left[\exp\left[+\frac{vl}{2D(X/l-1)}\right] - \exp\left[-\frac{vl}{2D(X/l+1)}\right]\right] \qquad X \geq l \qquad (12)$$

For the case that the embedded particles diffuse very slowly through the target, $D \approx 0$, and Eqs. (11) and (12) become

$$C_\infty(X) \approx \alpha i/v \qquad X \leq l \qquad (13)$$

$$\approx \alpha k/\mu \qquad X \leq l \qquad (14)$$

$$\approx 0 \qquad X \geq l \qquad (15)$$

and it can be seen that the maximum concentration of embedded particles is inversely proportional to the sputtering yield.

Figure 2 shows a plot of $C_\infty(X)$ for cases in which $D \approx 0$, and $D = lv$.

When the range of the irradiating particles is an arbitrary function, the rate of change in the concentration of trapped particles, $C(X, t)$ is

$$\partial c/\partial t = D\,\partial^2 c/\partial X^2 + v\,\partial c/\partial X + i\alpha q \qquad (16)$$

The distribution q is dependent on the relative mass of the irradiating ion and the target atom. Robinson[15] has used this relationship for the determination of ion ranges in solids. For most distribution functions, Eq. (16) becomes unwieldy and machine computations are required to determine $C(X, t)$.

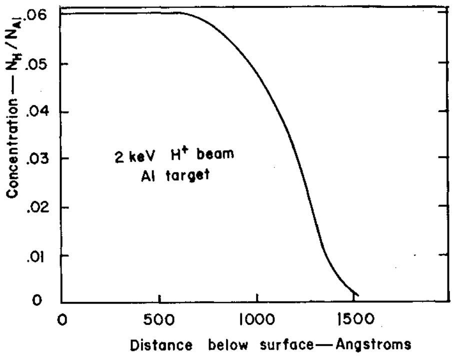

Fig. 3 Saturation concentration of hydrogen in aluminum as a function of the distance below the surface.

Solar-Plasma Irradiation Effects on Aluminum

As an example of the effect the solar plasma will have on a surface, let us take aluminum, which is commonly used in the construction of spacecraft. The plasma flux for a quiet sun at 1 a.u. is approximately 2×10^8 particles/cm^2-sec as measured from Mariner II.[2] The main constituents of the plasma are protons and alpha particles.[16] The intensities of these two components are approximately 1×10^8 protons/cm^2-sec, having an average energy of 2 kev and 3×10^7 alphas/cm^2-sec, having an average energy of 8 kev. Once the protons penetrate the surface, little will diffuse out because of the affinity of aluminum for hydrogen,[12] and $D \approx 0$. Any alpha particles that penetrate the surface will readily diffuse out because of the inert nature of helium.[12] The principle effect of alpha irradiation will be that of sputtering the surface.[10]

To determine the saturation concentration for protons in a surface, the distribution function q from Nielsen[17] can be used:

$$q = i(4\pi R)^{-1/2}\exp(-x^2/4R) \qquad (17)$$

The distribution is for the case $m_1 < m_2$. It has a maximum near the surface because of large angle scattering that occurs for the case in which the incident particle mass m_1 is less than the target atom mass m_2. The distribution has the value $\frac{1}{2}$ at a distance R from the surface.

The mean penetration depth R_m of the particles needed to scale the distribution function can be found from the ρ-ϵ relationship of Lindhard and Scharff,[18] which relates the range-energy of particles in solids:

$$\rho = R_m\left(1 + \frac{A_2}{3A_1}\right)\frac{166}{(Z_1^{2/3} + Z_2^{2/3})}\frac{A_1}{(A_1 + A_2)^2} \qquad (18)$$

$$\epsilon = \frac{33}{Z_1 Z_2 (Z_1^{2/3} + Z_2^{2/3})^{1/2}}\frac{A_2}{A_1 + A_2}E_1 \qquad (19)$$

where the subscripts 1 and 2 refer to the incident ion and the target atom, and E_1 is the energy of impact in kev.

Davie's group has shown that the ρ-ϵ relationship is accurate to about 20% for $\epsilon < 10$. Values for ρ, knowing ϵ, have been plotted by them for $0 < \epsilon < 10$ and $0 < \rho < 100$.[12, 19]

The absorption coefficient α was found, experimentally, to be about 0.01.

The velocity v at which the surface is sputtered was calculated using a yield, for Al in H$^+$ (protons) at 2 kev, of 0.02 as determined from the measurements of KenKnight and Wehner.[20] It was assumed that the yield of Al in He$^+$ is the same as that for He^{++} (alpha particles). Experimentally, the yield for He$^+$ at 8 kev was found to be 0.3.[7] The average erosion velocity of Al using these yields for H$^+$ and He^{++} is $v \approx 1$ Å/yr. By assuming that $D \approx 0$, the saturation concentration of trapped hydrogen in aluminum was found by an integration of Eq. (16).

The saturation distribution of hydrogen in aluminum, in hydrogen atoms per aluminum atom N_H/N_{Al}, is shown in Fig. 3. The exposure time necessary to reach saturation is approximately 1000 years at the earth's distance from the sun. It should be noted that for materials such as plastics, which are composed of large amounts of hydrogen, most of the plasma will be absorbed.[17] For such materials, concentrations as shown in Fig. 3 would be reached in about 10 years.

Over the region in which the protons and alpha particles have penetrated there will be many displaced surface atoms. It takes about 25 ev to displace an atom from its lattice point.[21] In a year the plasma will produce about 10^{17} atomic displacements. For metallic surfaces there should be no lasting effects because the defects will tend to anneal out in the heat of the sun. It should be pointed out, though, that in insulators the displacements can produce discoloration through the creation of color centers as described by Reiffel.[9]

Discussion

The effects of particle impacts do not present any significant problem to exposed metallic surfaces on spacecraft in the vicinity of the earth. Molecular impacts in the upper atmosphere will produce some sputtering but, even at low altitudes of 400 km, a satellite will lose only 50 Å from its surface over a period of the year.

Also, the effect of the solar plasma on a vehicle at the earth's distance from the sun will not be great. This is true not because the impacts will not affect a surface, but because the plasma density at this distance from the sun is too low to produce measureable effects during the useful life of a vehicle. The effects will have to be taken into account, though, for probes that venture close to the sun.

Since the effects of the solar plasma take years to build up, it is interesting to consider the effect it has had on natural bodies in the solar system. Bodies that would be affected are those that have no atmosphere and lack a magnetic field. For example, the surface of the moon has been irradiated by the plasma for about 10^9 years. During a significant part of this time, the energy of the particles in the plasma has exceeded 10 kev because of periodic solar storms. As a result of this irradiation, its original surface material is saturated with hydrogen down to a depth of several thousand angstroms. Since the surface of the moon is now saturated, it is presently losing mass at a constant rate as a result of sputtering, as described by Wehner et al.[22, 23]

References

[1] Freeman, J. W., Van Allen, J. A., and Cahill, L. J., "Explorer 12 observations of the magnetospheric boundary and the associated solar plasma on Sept. 13, 1961," J. Geophys. Res. **68,** 2121–2130 (1963).

[2] Neugebauer, M. and Snyder, C. W., "The solar plasma experiment," Science **138,** 1095–1097 (1962).

[3] Anderson, D. L. "Ion bombardment and its effects on the optical properties of metals," *Transactions of the 10th National Vacuum Symposium* (The Macmillan Co., New York, 1963), pp. 37–41.

[4] McKeown, D., Fox, M. G., and Schmidt, J. J., "Measurement of surface erosion from Discoverer 26," ARS J. **32,** 954–955 (1962).

[5] McKeown, D., "Surface erosion in space," *Rarefied Gas Dynamics,* edited by J. A. Laurmann (Academic Press, New York, 1963), pp. 315–326.

[6] *U. S. Standard Atmosphere* (U. S. Government Printing Office, Washington 25, D. C., 1962), p. 81.

[7] McKeown, D., Cabezas, A. Y., and Adelson, H. E., "Low energy sputtering studies," Bull. Am. Phys. Soc. **6,** 359 (1961).

[8] Laegreid, N. and Wehner, G. K., "Sputtering yields of metals for Ar^+ and Ne^+ ions with energies from 50 to 600 eV," J. Appl. Phys. **32,** 356–368 (1961).

[9] Reiffel, L., "Structural damage and other effects of the solar plasma," ARS J. **30,** 258–262 (1960).

[10] Reiffel, L., "Structural effects and particle content of interplanetary space," ARS J. **30,** 654, 655 (1960).

[11] Kuchai, S. A. and Rodin, A. M., "Electric absorption of a gas by a metal with a vaporizing surface," Soviet J. At. Energy **4,** 277–282 (1958).

[12] Bergström, I., Brow, F., Davies, J. A., Geiger, J. S., Graham, R. L., and Kelly, R., "On the electromagnetic separation method of preparing radioactive sources for precision β-spectroscopy," Nucl. Instr. Methods **21,** 249–276 (1963).

[13] Almen, O. and Bruce, G., "Collection and sputtering experiments with noble gas ions," Nucl. Instr. Methods **11,** 275–278 (1961).

[14] Power, D. and Whaling, W., "Ranges of heavy ions in solids," Phys. Rev. **126,** 61–69 (1962).

[15] Robinson, M. T., "Deduction of ion ranges in solids for collection experiments," Appl. Phys. Letters **1,** 49–50 (1962).

[16] Goldberg, E. A., Müller, E. A., and Allen, L. H., "The abundance of the elements in the solar plasma," Astrophys. J. Suppl. **45,** 135 (1961).

[17] Nielsen, K. O., "The ranges of atomic particles with energies about 50 keV," *Electromagnetically Enriched Isotopes and Mass Spectrometry* (Academic Press, New York, 1956), pp. 68–81.

[18] Lindhard, J. and Scharff, "Energy dissipation by ions in the keV region," Phys. Rev. **124,** 128–130 (1961).

[19] Davies, J. A., McIntyre, J. D., and Sims, G., "The range of C_s 137 ions of keV energies in germanium," Can. J. Chem. **40,** 1605–1610 (1962).

[20] KenKnight, C. E. and Wehner, G. K., "Sputtering of metals by hydrogen ions," J. Appl. Phys. **35,** 322–326 (1964).

[21] Seitz, F. and Koehler, J. S., "Displacement of atoms during irradiation," *Solid State Physics* (Academic Press, New York, 1956), pp. 307–448.

[22] Wehner, G. K., "Sputtering effects on the moon's surface," ARS J. **31,** 438–439 (1961).

[23] Wehner, G. K., KenKnight, C. E., and Rosenburg, D. L., "Sputtering rates under solar-wind bombardment," Planetary Space Sci. **11,** 885–895 (1963).