Ground-based investigation of atomic oxygen effects on naked Ag and Ag with protective organic coatings[①]

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[Abstract] Protective behavior of organic coatings of alkyd, epoxy, urethane and siloxane applied to silver solar cell interconnects and erosion of Ag were investigated by exposure experiments to ground simulation atomic oxygen (AO). Evaluations of their protective properties were made through assessing their mass change characteristics, chemical and physical changes to AO attack. The specimens after exposure were analyzed with SEM/ EDAX and XPS. The results indicated that the silver is heavily etched, some coatings such as epoxy, alkyd, urethane are seriously degraded or removed as volatile oxides and the morphology of coatings changed. It is evident that siloxane coatings have excellent properties for anti-AO attack. The erosion product consists of silicon dioxide layer of compact texture and is left on the surface to provide adequate protection from further attack by the energetic AO.

[Key words] Ag ; atomic oxygen; irradiation; organic protective coatings

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1　INTRODUCTION

Atomic oxygen(AO) is produced due to photodissociation of diatomic oxygen molecules presented in the atmosphere by absorption of solar ultra-violent(u. v) radiation within the wavelength range 100~ 200 nm[1~ 5].

Most of the spacecraft materials are susceptible to AO erosion. The extent of degradation of materials due to AO attack clearly shows that most of the materials are unacceptable for long-duration use in low earth orbit spacecraft applications. It is necessary to apply protective mechanism, which can reduce the amount of damage. The convention methods to avoid atomic oxygen harmful effects are those various thin-film protective layers applied on the surface of spacecraft. The selection of protective mechanism candidate is primarily based on following requirements:

1) the film should be resistant to AO attack;

2) the film should be thin, light mass and adhere strongly to the base material;

3) the film should be stable in the LEO environment synergism which includes particulate radiation, u. v. radiation, micrometeoroids and orbital debris impact;

4) the film should be free from defects, pores, scratches and not alter the basic properties of the base material[6~ 9].

Silver foil of 12. 5 or 35. 0 μm thick is generally used to connect the solar cells to the electrical network. High electrical conductivity is required to maintain adequate spacecraft power. Exposure of silver interconnects on the LEO environment experiment indicated that silver is highly reactive to atomic oxygen with a strong degradation. The energetic AO reacts with silver forming oxidative compounds that are not adhere to but spall off the silver substrate[10, 11]. The highly reactive AO would limit the useful life of the solar array mainly due to its effect on silver solar cell interconnects.

The application of a thin protective coating to silver is one of the most commonly used methods of preventing AO degradation. The purpose of the coating is to provide a barrier between the base material and the AO environment or, in some case, to alter AO reactions to inhibit AO diffusion. The application and durability of different epoxy, alkyd, urethane and siloxane (SAK-9, W30-1) coatings on silver surface have been studied in the ground-base tests of atomic oxygen of Beijing Institute of Satellite Environment Engineering. Test analyses indicated that siloxane coating provide good protection to silver for resistant to AO attract, other organic coatings were highly reaction to AO with a strong degradation.

2　EXPERIMENTAL

2. 1　Sample preparation

Metal sheets of silver were used as the specimens. Each metal sheet was cut to dimension of 35 mm ×

15 mm × 1 mm. Before weighing and exposure, one specimen was polished as a blank specimen for comparison. The others were abrased with 74 μm SiC paper, washed for 10 min in ultrasonic bath containing acetone, and then dried with a hair drier and stored in desiccator over silica gel for reserving samples. Except blank specimen, the others were painted respectively with coating of epoxy, alkyd, urethane and siloxane(SAK-9, W30-1), and dried at 80 ℃ in oven, The thickness of coatings is about 50 μm. Both blank specimen and protected specimens were exposed to ground-simulation atomic oxygen facility.

2. 2 Experimental setup and conditions

Unprotected silver and coated silver have been tested at the Beijing Institute of Satellite Environment Engineering using a fast AO simulator. The facility is based upon an advanced microwave electron cyclotron resonance ion source driven by 0. 6 kW RF at 2. 45 GHz.

Each sample was placed in the atomic oxygen beam facility in a holder. All samples were held at a vacuum level of ~ 8×10^{-3} Pa during all tests. The atomic oxygen tests were conducted with an average flux at the target of 3.39×10^{15} atom•cm^{-2}•s^{-1}(15 cm source-to-target distance) with 5 eV energy. The test period was about 832 min and AO flux of 10^{20} atoms•cm^{-2} has been obtained. The schematic diagram of facility is shown in Fig. 1.

2. 3 Methods of analyses

Scanning electron micrographs were obtained by using model PHILPS XL30 scanning electron microscope and electron dispersion analysis of X-ray(SEM/EDAX). The surfaces of organic coatings were coated with a thin carbon film before viewing in order to prevent charging.

X-ray photoelectron spectroscope (XPS) analyses were performed with an England VG Escalab MK II

spectrometer equipped with a non-monochromatic Mg X-ray source. Survey scans of all samples were obtained using a 600 μm X-ray spot size and 150 eV pass energy. High-resolution scans of appropriate peaks of interest (C1s, O1s and Si2p) were obtained. All spectra were referenced to the C1s signal at 284. 6 eV representative of the C-C and C-H bonds.

Samples were measured using a Sartoius BP211D 200 g balance with a sensitivity of 0. 01 mg for mass change.

3 RESULTS AND DISCUSSION

3. 1 Mass loss

The results of the mass change measurements before and after exposure to AO are listed in Table 1. Exposed samples were compared with unexposed ones. The mass loss of silver is relatively little, because unprotected thin silver foil was converted to clear silver oxide (Ag_2O) that is not adherent and easily peeled off, especially to AO attack. It is obviously that there are some difference between Siloxane coating and other organic coatings. Mass loss of Siloxane coating is even less than others. It is proved that Siloxane coating would be corroded slightly by AO attack and can provide a good protection for substrates. On the contrary, other organic coatings are highly reactive to AO with a strong degradation. The degradation of organic coatings at highly levels of AO fluence is mainly due to organic polymer bond breaking and subsequent molecular fragmentation leading erosion of the organic coating, or the high-energy AO reacts with the organic coatings resulting in formation of volatile oxides on surface, which leads to mass loss.

3. 2 Surface morphology analyses
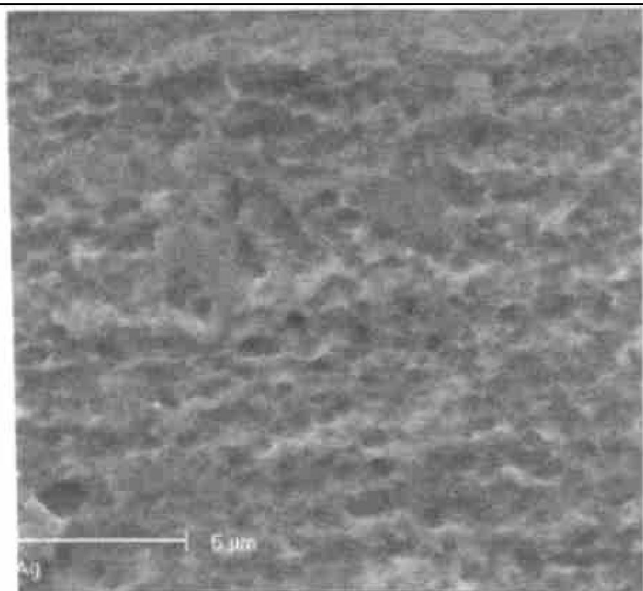
Fig. 2 gives the SEM image of silver after ex-
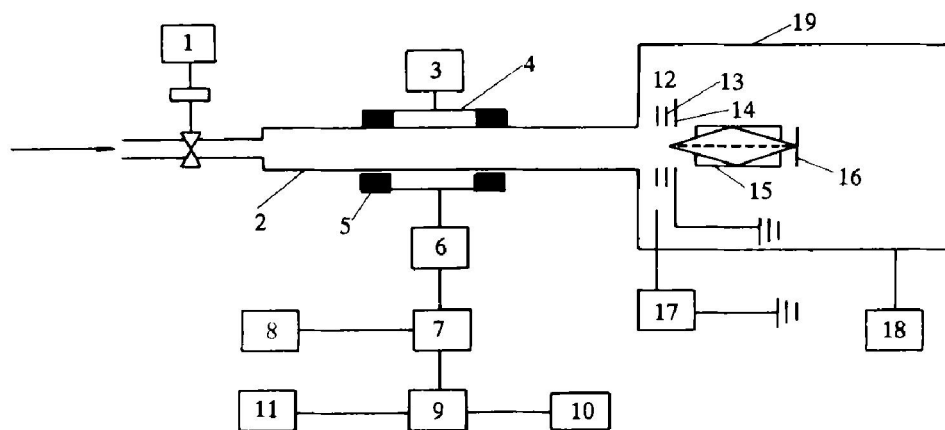
Fig. 1 Schematic diagram of ground atomic oxygen simulation facility
1 —Mass flow controller; 2 —Quartz tube; 3 —Short circuit piston; 4 —Discharge chamber; 5 —Permanent magnet;
6 —Stub tuner; 7 —Directional coupler; 8 —Power meter; 9 —Circulator; 10 —Water load; 11 —Microwave source;
12 —Source pole; 13 —Accelerate pole; 14 —Decelerate pole; 15 —Neutralizer; 16 —Sample stage;
17 —High voltage source; 18 —Vacuum pump unit; 19 —Vacuum tank
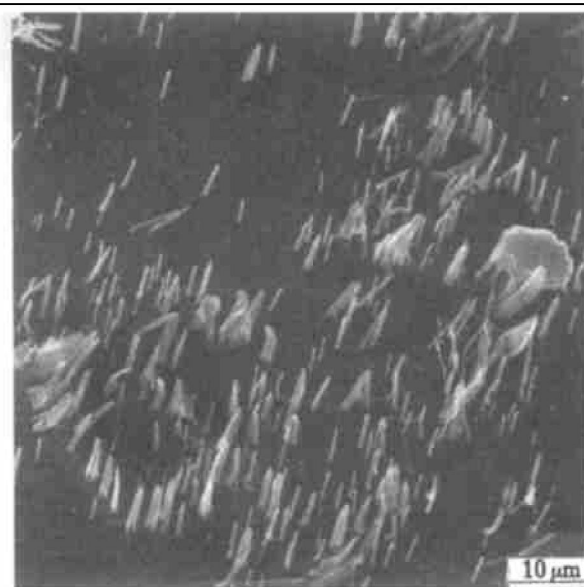
Table 1 Mass loss data of silver and organic coatings exposed to AO

Specimen	Before exposure / g	After exposure/ g	Mass loss/ mg	Exposure time/ h
Ag	1. 969 22	1. 968 65	0. 57	13. 86
Epoxy/ Ag	2. 218 43	2. 216 63	1. 80	13. 86
Alkyd/ Ag	2. 510 72	2. 508 64	2. 08	13. 86
Urethane/ Ag	2. 545 53	2. 543 65	1. 88	13. 86
SAK/ Ag	2. 306 03	2. 304 87	1. 16	13. 86
W30-1/ Ag	2. 462 57	2. 461 14	1. 43	13. 86

Fig. 2 SEM image of silver after exposure to AO

Fig. 3 SEM image of epoxy after exposure to AO

poure to AO. Before exposure, the surface structure was smooth and glossy similar to mirror. Scale and surface roughening occurred on the surface of naked silver and there the silver has been oxidized. Thick oxide formations appeared to create stress levels that produce buckling or scaling which accelerate further oxidation.

Epoxy, alkyd, urethane and siloxane (SAK-9, W30-1) coatings were evaluated in the exposure experiment. SEM examinations of each organic coating generally showed a smooth, uniform surface before AO exposure. Epoxy, alkyd and urethane coatings were affected to some degree due to exposure to AO. Visually, the exposed surface on coatings was changed from the normally smooth glossy finish to a dull one. Fig. 3 showed SEM image of the eroded surface (in direct impingement area) from the epoxy specimen. Some oxidation and erosion did occur, however, as shown by the relatively discoloration and big or small cavities spread randomly across the surface. Energy dispersive analysis of X-ray (EDAX) of these cavities shown in Fig. 3 indicated silver and oxygen only. It showed that oxygen has obviously penetrated the overcoat and oxidized the silver. Similar coatings erosion was observed for alkyd and urethane specimens. Characterization of

coatings showed that epoxy, alkyd and urethane are eroded by AO and can not be used in the LEO environment for the protection against AO attack.

Only the siloxane coating was visually unchanged after exposure. Siloxane coating appears to be quite stable in the AO environment and apparently protects the silver substrate from AO erosion. Fig. 4 showed the SEM image for one of the siloxane after expoure to AO(SAK-9) .

3. 3 Surface composition analyses

XPS measurements were also made on the surface composition of specimen. When comparing ' unexposed' with ' exposed' surface of organic coatings data (Table 2), it is interesting to note a substantial reduction in the C content and a large increase in the O content on the exposed surface. It implies that the chemical bonds on surface have been broken by AO attack. The result has explained the reason why volatile gases of CO and CO_2 could be produced[12] and AO diffused into coating surface during AO exposed tests. Note that Ag content of the polished silver specimen was reduced from 99. 99% to 72. 3%, while the oxygen content rose 27. 3% as a result of exposure. This increase in oxygen content on exposure surface is substantial, in spite of the contribution from Ag to Ag_2O. After 3 min sputtering time with 3

keV Ar^+ ions, XPS obtained depth profiling data of eroded silver. The results showed that oxygen has penetrated substrate in 3. 27% content, although it is very low concentration. In summary, these analyses to data show that diffusion of oxygen occurs beneath the scale. SAK-9 also experienced some mass loss, but with little chemical changes.
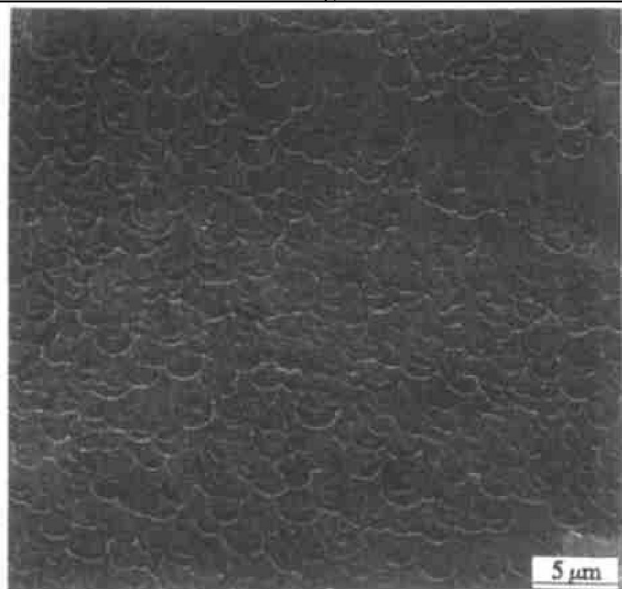
Fig. 4　SEM image of siloxane (SAK-9) after exposure to AO

Fig. 5 is the XPS spectra of unexposed and exposed surfaces of SAK-9. The change after vs before reaction is evidenced by the marked reduction in intensity of the C1s and increasing intensity of Si2p, Si2s and O1s peak.

The Si2p and O1s spectra in Fig. 6 shows that the decrease in intensity of the Si-R peak at 102. 3 eV is accompanied by major increases intensity at 103. 1 eV, and the decrease in intensity of the O1s of siloxane peak at 532. 2 eV is accompanied by major increases intensity at 532. 6 eV. The peak of silicon is intensified and shifted to high energy, and the same change occurred with the O1s peak. The higher binding energy from silicon, probably SiO_2[13], is dominant in SAK - 9 sample and is indicative of
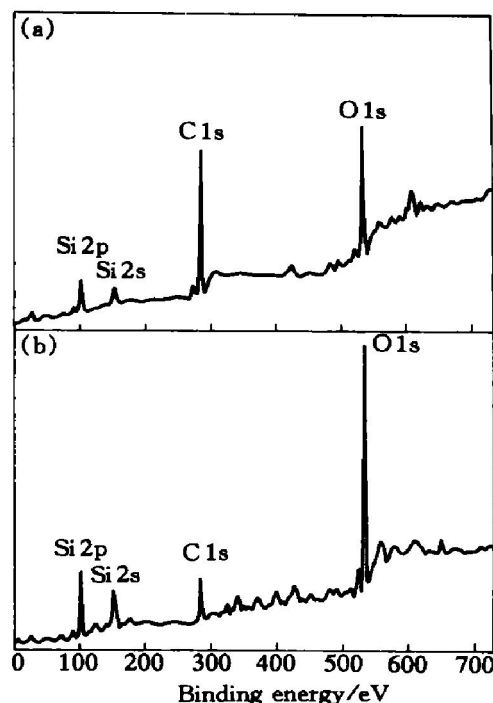
Fig. 5　Survey-scan spectra from surface of siloxane (SAK) coating before (a) and after (b) exposure to AO

complete oxidation of the siloxane.

The XPS data on composition of these residual oxidized layer lead to the conclusion that the initial or primary interaction of organic coating surfaces with atomic oxygen of partially oxidized intermediate state, which may undergo volatilization or subsequent further oxidation leading to the formulation of SiO_2 found the XPS spectroscopy.

4　CONCLUSIONS

(1) The silver is highly sensitive to AO irradiation, so it must be protected.

(2) The applied epoxy, alkyd and urethane are inadequate for protecting silver under conditions of AO. Once the AO diffuses through these coating to the silver, the oxidation of the silver is initiated. Some intermetallic diffusion may accompany this process to accelerate the reaction.

Table 2　Compositions of specimen surface from XPS analyzing data (mole fraction, %)

Specimen	Unexposed sample composition				Exposed sample composition			
	C	O	Si	Ag	C	O	Si	Ag
Ag				99. 99		27. 70		72. 30
SAK/ Ag	39. 03	3. 22	57. 75		26. 86	42. 80	30. 35	
W30-1/ Ag	57. 15	23. 45	19. 40		11. 26	76. 87	11. 87	
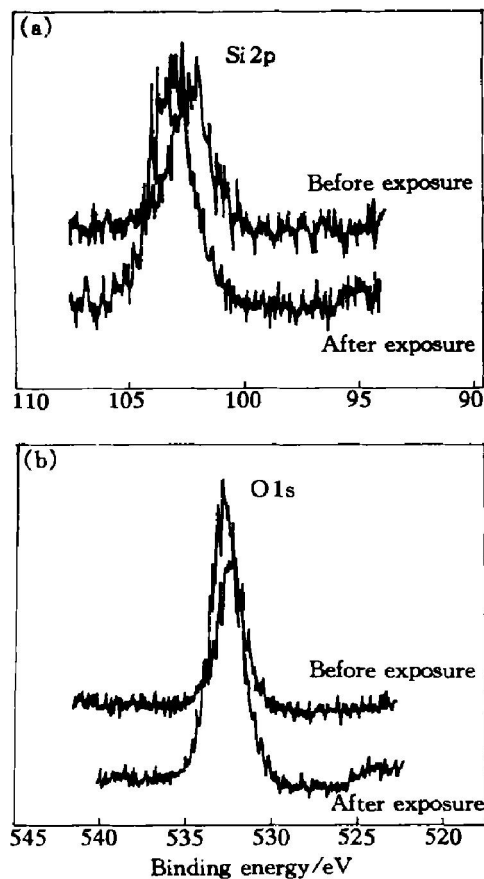
Fig. 6　XPS spectra for siloxane (SAK)
coating surface before and after exposure to AO
(a) —Energy spectra of Si2p electron;
(b) —Energy spectra of O1s electron

(3) Siloxane coatings have previously been shown to provide substrate protection from AO. The use of a thin siloxane overcoat shows promise of providing a protective barrier to AO attack without altering the base properties of the material.

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