Technology

Atomic-Oxygen Tolerant Material "Siloxane Block Polyimide" for Low & Very Low Earth Orbit Satellites

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Abstract

In the low Earth orbit, Atomic Oxygen (AO) generated when oxygen molecules from the Earth's atmosphere are exposed to high-energy ultraviolet rays in the space environment collide with spacecraft such as artificial satellites flying at high speeds, causing erosion of the outer materials of the spacecraft. In space exposure tests, siloxane block polyimide resin (BSF series) used for the outer surface of spacecraft has been proven to prevent erosion and degradation caused by AO by reacting with AO to form a self-organized silicon dioxide (SiO_2) layer on the material surface after the spacecraft is ejected into the low Earth orbit. The details are described below.

1. Introduction

In recent years, there has been rapid progress in space development, with the quickly growing use of outer space for business. Space development was formerly dominated by the government but is now dominated by private companies worldwide. The space-related market size is expected to grow to 140 trillion yen by 2040.[1)] Along with the future expansion of the space market, the number of rockets and artificial satellites launched is expected to increase significantly.

Here, we focus on artificial satellites. In the orbits where artificial satellites and other spacecraft operate, the spacecraft will be exposed to a special environment different from that on the ground. Examples of environmental factors in space include cosmic radiation, strong ultraviolet rays emitted from the sun, residual atmospheric components, space debris, meteoroids, high vacuum, and widely changing temperature cycles. Since the effects of these environmental factors vary with the altitude in which the artificial satellites operate, it is necessary to select and use materials that are environmentally resistant at specific flight altitudes.

Among artificial satellites, we focus on low-Earth orbit satellites. A low-Earth orbit generally refers to an altitude of 2 000 km or less above the Earth. A satellite that operates in this orbit is called a low-earth orbit (LEO) satellite. LEO satellites mainly refer to the International Space Station, earth observation satellites, and communication satellites and are widely utilized in space. Their launches are expected to increase rapidly in the future. In the LEO, however, a high proportion of atomic oxygen (AO) is generated by residual components of the Earth's atmosphere. The AO concentration increases as the altitude decreases (**Fig. 1**). AO is produced when oxygen molecules originating from the Earth's atmosphere absorb strong ultraviolet rays emitted from the sun and dissociate into atomic oxygen. This AO is chemically very active. On top of that, when a satellite operating at a high speed of about 8 km per second collides with AO, the external materials of the satellite, especially organic materials, are subjected to strong chemical and physical oxidation. Aromatic polyimide was developed as a material with ex-

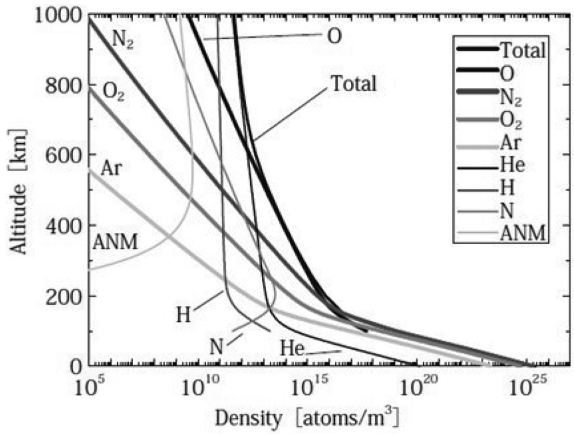

Fig. 1 Relationship between altitude and concentration of atmospherically derived elements[2)]

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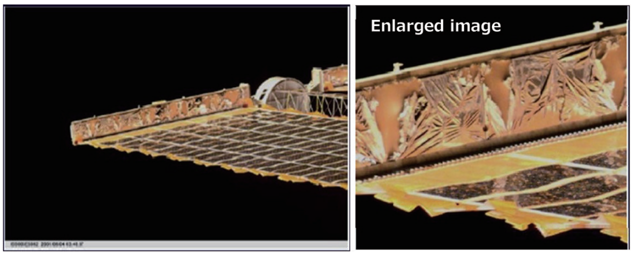


Fig. 2 Aromatic polyimide eroded by AO[3)]

tremely high chemical stability, heat resistance, heat cycle characteristics, and radiation resistance in space. However, even these materials are subject to severe erosion by AO, leaving their surfaces uneven and gouged out (**Fig. 2**). Their durability is thus an issue. In this report, we describe the mechanism by which siloxane block polyimide exhibits strong AO resistance in the LEO, as well as the exposure test results of siloxane block polyimide on the ground and in space.

2. Siloxane Block Polyimide and AO Resistance Mechanism

Siloxane block polyimide has a chemical structure in which a siloxane unit is introduced into the backbone of aromatic polyimide. When the siloxane unit is introduced into the rigid aromatic polyimide backbone, the following characteristics are realized (**Fig. 3**).

(1) The siloxane unit also has high heat resistance, which makes it possible for the siloxane block polyimide to have heat resistance (thermal decomposition temperature) close to that of the aromatic polyimide.

(2) Siloxane block polyimide has a lower glass transition temperature than that of aromatic polyimide and can be formed at temperatures lower than those of aromatic polyimide.

Siloxane block polyimide has such high heat resistance, radiation resistance, and thermal cycle resistance that it can be satisfactorily used in space. On the other hand, general aromatic polyimide has a very high softening temperature, so it is extremely difficult to use it as an adhesive. Siloxane block polyimide can be thermocompression bonded to artificial satellite components at temperatures of 200°C or less without using any adhesive. This operation means that siloxane block polyimide can be handled very easily.

Next, the AO resistance mechanism of siloxane block polyimide is described. When typical aromatic polyimide collides with AO, it is strongly oxidized, and a conical protrusion structure is formed on the surface of the collided region. The aromatic polyimide in the collided region is decomposed into carbon monoxide (CO) and carbon dioxide (CO_2) and is eroded from the surface of the film into the bulk (**Fig. 4**).[4)] On the other hand, when siloxane block polyimide collides with AO, there is little erosion on the surface of the collided region (**Fig. 5**).[5)] When siloxane block polyimide samples irradiated with AO and samples not irradiated with AO on the ground were analyzed for their chemical structure by X-ray photoelectron spectroscopy (XPS), the peaks derived from the siloxane skeletons (101.7 to 102.2 eV) were detected in the non-AO-irradiated samples. In contrast, the peaks derived from the siloxane skeleton were lost in the AO-irradiated samples, and the peaks derived from SiO_2 (103.5 to 104.2 eV) were formed instead. It was also confirmed that the conversion rate was higher in the surface layer and that the SiO_2 concentration decreased at a depth of several nanometers from the surface (**Fig. 6**). According to these results, when siloxane block polyimide is exposed to AO in space, the silicon (Si) in the polyimide skeleton is oxidized by AO, and a thin SiO_2 film with a thickness of about 10 nm is formed on the surface. This SiO_2 film functions as an AO-resistant protective film and prevents the oxidation degradation of siloxane block polyimide (**Fig. 7**). Also, when the non-AO irradiated samples and the AO-irradiated samples were analyzed for their structure from their rear side by a microscopic IR (an optical microscope combined with a Fourier Transform Infrared Spectroscopy (FT-IR) and used to analyze the chemical structure of nanomaterials), no difference was observed in the chemical structure between the non-AO-irradiated samples and the AO-irradiated samples. This finding suggests that the change of the chemical structure with the AO irradiation is limited only to the surface layer (**Fig. 8**). Furthermore, when the oxidative decomposition rate of the aromatic

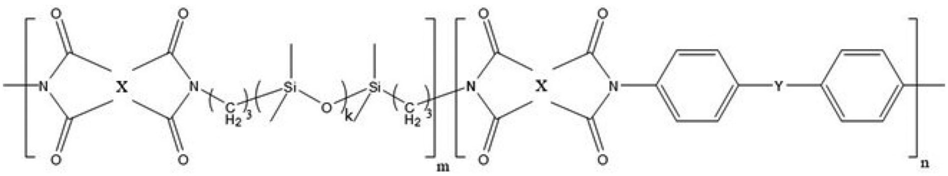
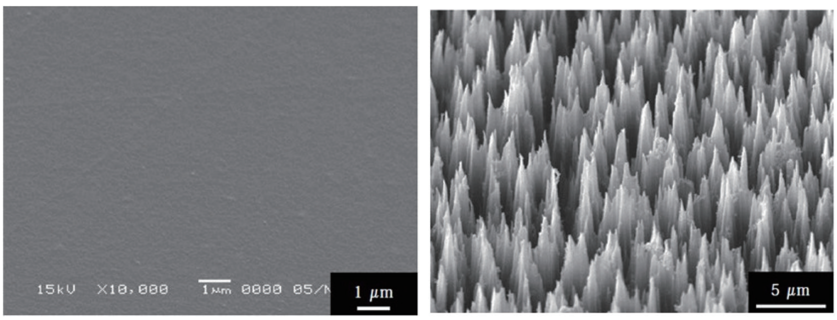
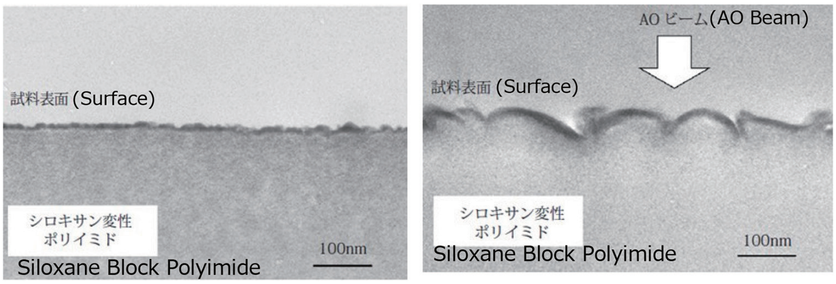


Fig. 3 Overview of the chemical structure of siloxane block polyimide



Before AO irradiation **After AO irradiation (Atomic oxygen fluence 8.5×1 020 [atoms/cm²])**

Fig. 4 Surface image of aromatic polyimide before and after AO irradiation



Before AO irradiation **After AO irradiation (Atomic oxygen fluence 2.4×1 020 [atoms/cm²])**

Fig. 5 Surface image of siloxane block polyimide before and after AO irradiation

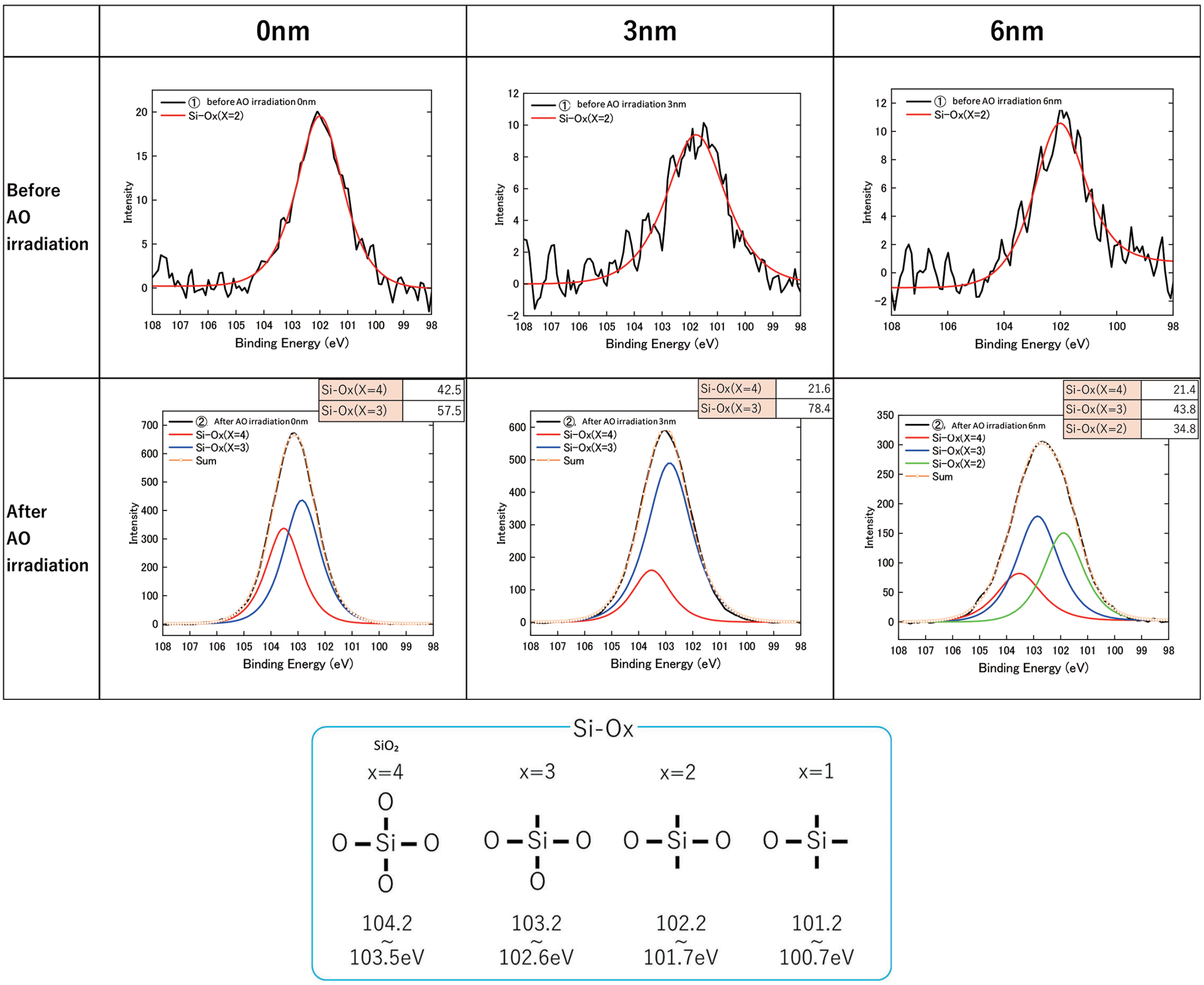


Fig. 6 XPS analysis of the surface of siloxane block polyimide before and after AO irradiation

polyimide unit and the oxidation rate of the siloxane unit are compared according to the relationship between the AO irradiation rate and the material weight loss, the oxidation rate of the siloxane unit is overwhelmingly faster than that of the aromatic polyimide unit. This result suggests the formation of a SiO_2 film on the surface of the siloxane unit. As the AO irradiation dose increases, the weight of typical aromatic polyimide films decreases significantly, but the siloxane block polyimide (BSF-30) showed almost no weight loss. This result confirms the high AO resistance of the siloxane block polyimide BSF-30 (**Fig. 9**).

Aromatic polyimide is often protected against AO by coating it on the ground with a silicon-based paint or inorganic substance such as SiO_2 or indium tin oxide (ITO). If the aromatic polyimide has defects such as pinholes, it may be eroded by AO, which may start from such defects. When protective films are attached to an artificial satellite on the ground, utmost care must be exercised to prevent defects during the assembly of the artificial satellite. Furthermore, there have been cases where the protective layers were damaged by

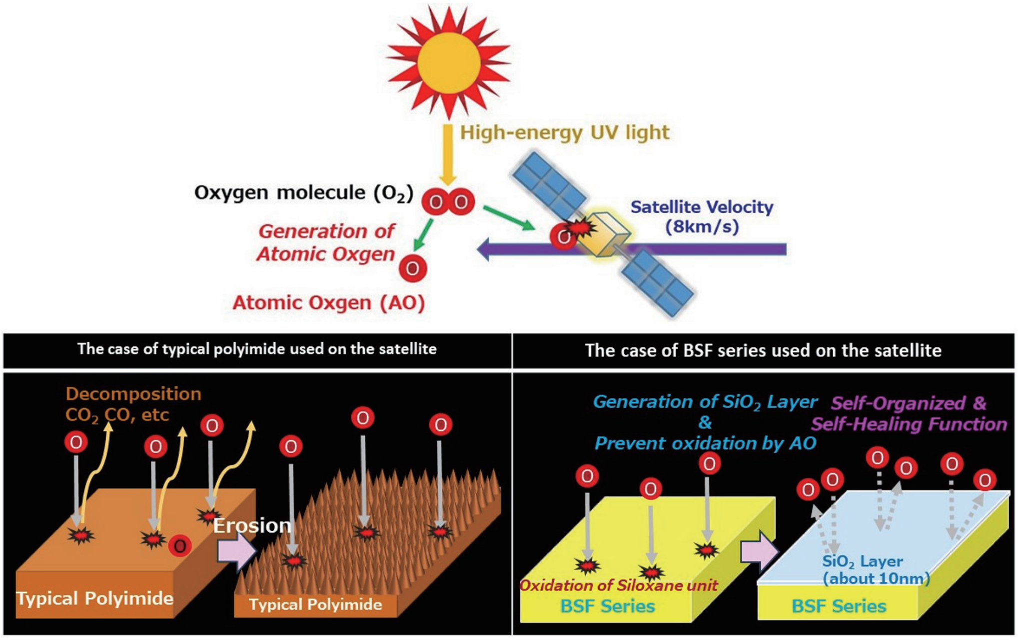


Fig. 7 Overview of the mechanism of siloxane block polyimide's AO resistance

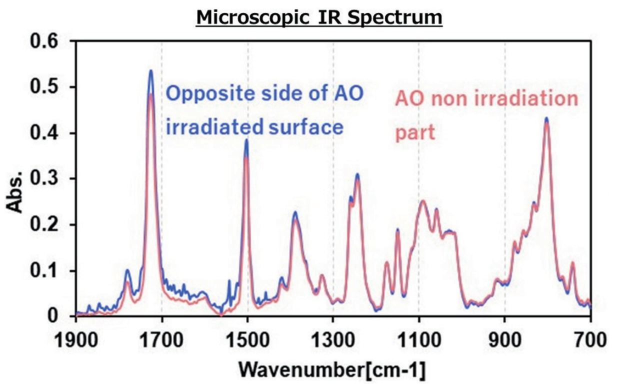


Fig. 8 Microscopic IR chart of AO irradiated/non irradiated siloxane block polyimide

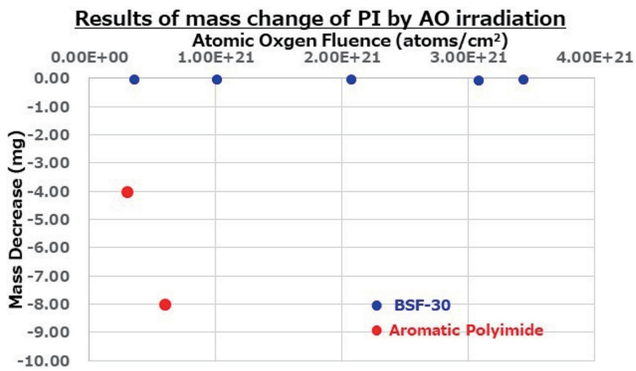


Fig. 9 Weight change behavior by AO irradiation in ground tests (provided by JAXA)

long-term exposure to AO. The protective film application technology is not yet satisfactory enough to assure the reliability of such protective films. An interesting point about siloxane block polyimide is that it self-organizedly forms an AO resistant film only when it is exposed to AO so that there is no need to apply any treatment against AO on the ground. In addition, an experiment was conducted where siloxane block polyimide was irradiated with AO, intentionally scratched to damage the SiO_2 film formed on the surface, and irradiated again with AO to see if siloxane block polyimide was degraded, starting from the scratches. The experiment confirmed that siloxane block polyimide has such a self-repairing function that a protective film was regenerated in the scratched region for protection against erosion by AO.

3. Space Exposure Experiments and Results

In July 2009, the siloxane block polyimide BSF-30 was mounted for the first time in the Space Environment Exposure Test (JEM/MPAC & SEED Experiment) conducted by the Japan Aerospace Exploration Agency (JAXA) on the Japanese experiment module "Kibo" in the International Space Station (ISS). The siloxane block polyimide BSF-30 was exposed to space for the next 8.5 months (**Fig. 10**). The weight of the siloxane block polyimide samples was 15.300 mg before the flight and 15.289 mg after the flight. The weight change was only 0.11 mg. The formation of a thin SiO_2 film was confirmed on the surface to verify that the AO resistance of siloxane block polyimide was developed by the same mechanism as that observed in the AO irradiation test on the ground (**Fig. 11**).[6]

After that, siloxane block polyimide was space exposure tested in the small demonstration satellite 4 (SDS-4) project in 2012, in the material degradation monitor 2 (MDM2) mounted on the ISS "Kibo" exposure module in 2015, and in the material degradation monitor (MDM) mounted on the super low altitude test satellite (SLATS) in December 2017. These tests verified the effectiveness of siloxane block polyimide against atomic oxygen (**Fig. 12**). In particular, the SLATS represented an AO exposure test in an orbit with a higher AO concentration and demonstrated that siloxane block polyimide develops AO resistance in a harsher environment.

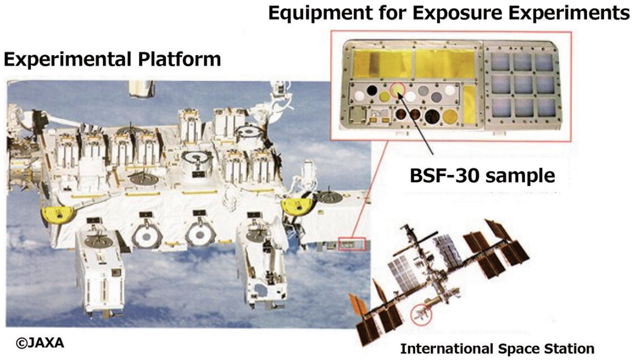


Fig. 10 Space environment exposure test on the International Space Station in 2009 (provided by JAXA)

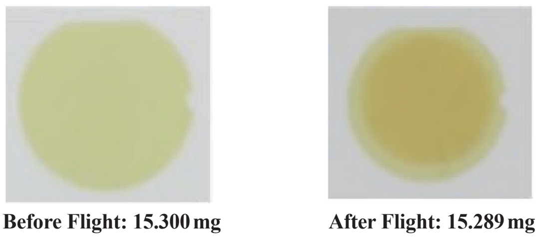


Fig. 11 Image of siloxane block polyimide before and after space environment exposure test in 2009 (provided by JAXA)

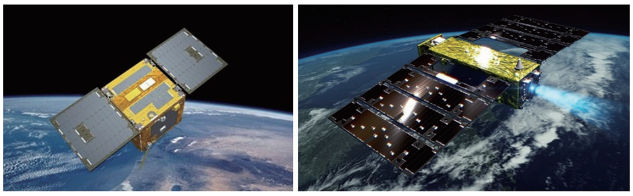


Fig. 12 Exposure test examples (Left) SDS-4, (Right) SLATS ©JAXA

4. Conclusions

Siloxane block polyimide is expected to contribute to the longevity of LEO satellites because it is expected to fully display AO resistance over a long period of time. When existing materials are used in LEOs, they must be used in greater thicknesses if they are not resistant to AO or they must be pretreated with an AO-resistant coating on the ground. However, conventional materials are not satisfactorily reliable in the space environment and increase the weight of artificial satellites and their launching costs. Also, when an AO-resistant coating is used, the utmost care must be taken when the artificial satellite is assembled. Siloxane block polyimide obviates that need and is expected to facilitate the assembling of artificial satellites significantly. Components in satellites where siloxane block polyimide is expected to be used are multilayer insulators (MLIs). MLIs are used on the surfaces of many satellites for thermal control. Aromatic polyimide is often used as MLI material from the perspective of heat resistance and radiation resistance. If aromatic polyimide MLIs are oxidized and degraded, their thermal balance changes, making it difficult to control the satellite. The mechanical strength of the aromatic polyimide itself is also reduced. MLIs are studied as an appropriate application for siloxane block polyimide. Siloxane block polyimide has also been studied as a substrate material for solar cell paddles installed on artificial satellites.

On the other hand, siloxane block polyimide has recently been focused on as a material for reducing the generation of space debris in LEOs. Space debris is mainly produced by the fragmentation of spacecraft that have completed their missions and small mission-related objects. These fragments float in space and are particularly concentrated in the LEOs that account for the majority of human space activities. As human space development becomes more active, the quantity of space debris has been increasing rapidly in recent years. Some 23 000 pieces over 10 cm in size, 500 000 to 700 000 pieces over 1 cm in size, and over 100 million pieces over 1 mm in size[7] are flying around the Earth. These space debris pieces make it difficult for spacecraft activities in orbit without measures to control them. Space debris flies very fast and generates even more space debris when it collides with other spacecraft. The space debris thus represents a serious problem in the space environment. Siloxane block polyimide can contribute to this problem in two ways. One is the covering of carbon fiber reinforced plastics (CFRPs), for example, with siloxane block polyimide to prevent the CRFPs from being destroyed by AO and released into space as further space debris. The other is the drag sail technology that prevents satellites that have completed their missions from becoming space debris (**Fig. 13**). When an artificial satellite completes its mission, it deploys drag sails in space, captures with the drag sails the slight resistance in the orbit, accelerates the re-entry into the atmosphere, and burns itself without remaining in the orbit for a long period of time. The drag sail technology is being investigated mainly in Japan, Europe, and the United States as a means to solve the space debris problem.

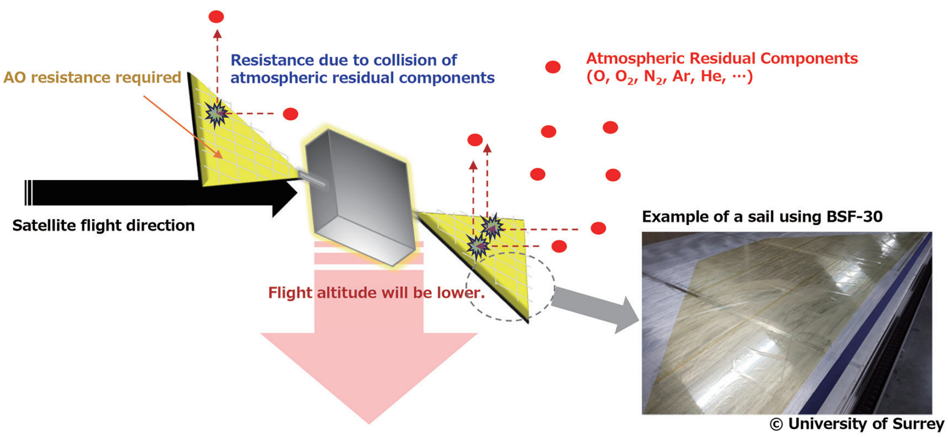


Fig. 13 Drag Sail

The drag sails pass through an orbit with a high AO concentration and must be made of materials with high AO resistance. Siloxane block polyimide is evaluated as a material for the drag sails.

Contributions to space development lead to contributions to the global environment and social development, which are the management philosophy of Nippon Steel Chemical & Material Co., Ltd. We will endeavor to make the most of the technologies that Nippon Steel Chemical & Material possesses for space development.

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