Complex study of the surface of adhesive functional materials

M N Savvateev, D L Zagorskiy, T I Muravyeva, O O Shcherbakova, A A Zhukov, I P Smirnov, I G Goryacheva, N N Bolotnik

1 Ishlinsky Institute for Problems in Mechanics RAS, 119526, Moscow, Russia
2 Gubkin Russian State University of Oil and Gas, 119991, Moscow, Russia
3 Moscow Aviation Institute (National Research University), 125993 Moscow, Russia

Abstract. The paper presents the results of investigation of surfaces with high adhesive ability to materials used in space technology. The object of the study was the so-called "dry" adhesive-polyimide. A method based on the use of the functionality of a scanning probe microscope was applied to estimate its adhesion properties. The method of applying polyimide to the probe of scanning probe microscope with the subsequent measurement of the force of "adhesion" by the method of force curves is developed. It is shown that the proposed "dry" adhesive has a great strength of the so-called, "adhesive strength" – 60–300 N/cm². This makes possible its practical use in the spacecraft for fixing individual parts.

1. Introduction
In the conditions of cosmos and weightlessness, the task of fixing bodies (astronauts or various objects) at a certain point in space on the details of spacecraft (SC) structures is very actual. One of the solutions to this problem can be fixation due to adhesion, adhesion of the object to the desired surface. Creation of conditions for adhesion can be achieved, for example, by applying to one of the contacting surfaces of the so-called "dry" adhesives. A. Geim et al. [1] were the first who supposed the idea of using "dry" adhesives for fixing cosmonauts inside sealed compartments under conditions of weightlessness. But, despite significant results in the field of research of adhesion interaction [2-3], the practical application of "dry" adhesives in cosmonautics has not yet been found. Therefore, the problem of creating "dry" adhesives is still relevant.

The purpose of this paper is to evaluate the adhesion properties of typical SC surfaces. To achieve this goal, it is necessary to solve three problems: to study new types of "dry" adhesives, to work out a technique for measuring adhesion strength and to evaluate adhesion to materials used in spacecraft.

2. Materials and experimental procedure
In the work, several possible types of adhesives were investigated, of which a new type of dry adhesive- polyimide- was chosen. It was necessary to study the adhesion of this material to the characteristic surfaces used in the spacecraft: the materials of the outer shell of the spacecraft (SC) - EVT1 thermal insulation and the AMG6 alloy-were used as an "adhesive" surface. These materials are widely used in assemblies and parts of space vehicles.

A new method for measuring adhesion properties at the microlevel is proposed - a "dry" adhesive was applied to the surface of a cantilever needle (tip) of a scanning probe microscope. As a part of this study, the technique of applying an adhesive of different thickness on the cantilever tip was worked out. The adhesion was characterized by interaction force of such a modified tip with the surface under study, measured by a calibrated probe microscopy method. The industrial cantilevers produced by
AIST-NT (series fpC01, fpC10 and fpN01), with force constants from 0.1 to 10 N / m [4], were used as probes for measuring adhesion. To create adhesive polyimide layers, cantilevers were coated with polyamide acid solution in dimethylformamide by the method of “irrigation” (watering). Polyimide coatings of various thicknesses were formed due to different dilutions of the initial (12-14% by weight) solution with dimethylformamide (in a ratio of 1:40 and 1:20 of the parts). Cantilevers with different coating thicknesses were obtained. The "coated" cantilevers were then heat-treated at a temperature of 80°C for 20 minutes and 150°C for 20 minutes, as a result of which thermoimidization occurred and a coating of polypyromellitimide formed [5].

A scanning probe microscope (SPM) Smart SPMM (AIST-NT) was used in the work. For surface topography investigation at the nanoscale, a tapping mode was used (resonance frequency 250 kHz). Measurement of adhesion strength was carried out by the method of force curves. The strength of adhesion in this case is defined as

\[ F = k \cdot dz, \]

where \( k \) is the force constant of the cantilever and \( dz \) is the value of the "beak" of adhesion when the cantilever is detached from the surface. (Note that EVTI was subjected to research from the outside, polymer film).

The exact value of the force constant of the cantilever was determined from the resonant frequency and cantilever geometry (length and width) according to the Sader method. The force curves (the dependence of the interaction force between the cantilever and the surface on the distance) were measured without scanning of the surface of the sample, in order to prevent the damage of the modified layer. Three or four curves were measured at three points, separated by several micrometers.

The Quanta 650 Scanning Electron Microscope (SEM) with a secondary electron detector ETD was used to study the cantilever geometry and surface topography at the micro level. To create a conductive layer, the surface of the probes was covered with a thin layer of gold.

3. Results
The results of measuring adhesion to a sample of an aluminum alloy AMG6.

Before the measurements, the surface of the sample was polished and washed in an ultrasonic bath for 10 minutes. The images of the surface are shown in figure 1.

![Figure 1. Microscopy of the surface of the AMG6 alloy: (a) – SEM image, (b) – 3D SPM image (scanning area 10x10 μm²).](image)

Adhesion tests were then carried out (measurement of “force-distance curves”) using different cantilevers. The cantilevers of the fpC01 series, having a stiffness of approximately 0.1 N / m, proved to be the most suitable for both test specimens: they gave a noticeable "beak" of adhesion, substantially exceeding the noises.
An example of the results obtained for an AMG6 alloy is shown in figure 2 (force curves were measured on smooth surfaces).

![Figure 2](image)

**Figure 2.** Measurement of adhesion force of cantilevers to AMG6 alloy, curves: 1 – inlet, 2 – branch.

Analysis of the results allowed to estimate the adhesive forces for samples with different coating thicknesses (obtained for different concentrations of the modifier solution). The adhesion values to the surface of the alloy AMG6 are shown in table 1.

| Surface modification: | Average adhesion value, nN |
|-----------------------|---------------------------|
| in diluted solution 1:20 | 30.4                      |
| in diluted solution 1:40 | 4.3                       |
| unmodified            | 2.5                       |

It can be seen that the adhesion of modified cantilevers is higher than that of unmodified cantilevers. It is also seen that adhesion increases with increasing concentration of the modifier solution.

3.1 The results of measuring of the adhesion to the sample of screen-vacuum thermal insulation (evti)

Adhesion on the EVTI sample was measured from the film side. The image of this surface (SEM and 3D SPM) is shown in figure 3.

![Figure 3](image)

**Figure 3.** Microscopy of the EVTI surface at the film side: (a) – SEM image, (b) – 3D SPM image (scanning area 3x3 μm²).
Force curves were measured at flat areas. "Force-distance" curves, typical for this sample, are shown in figure 4.

![Figure 4](image)

**Figure 4.** Measurement of adhesion force of cantilevers to EVTI surface; curves: 1 – inlet, 2 – branch.

It can be see that the detachment of the probe from the surface is not sharp, but smoothly (a non-vertical segment at the top of the "beak"). It is possible that the probe penetrates into the surface of the film during the approach, and then (upon retraction) smoothly "falls away" from it. The results of measuring the adhesion strength are given in table 2.

| Surface modification: in diluted solution | Average adhesion value, nN |
|-----------------------------------------|---------------------------|
| 1:20                                    | 16.4                      |
| 1:40                                    | 12.2                      |

It can be seen that in this case too, the cantilever, coated with a thicker film (from a solution with a higher concentration), has better adhesive properties.

To determine the quality of the coating, the SEM images of probes coated with polyimide film with different thicknesses were obtained and the radius of the rounding (curvature) of the probes were estimated. The results are shown in figure 5.

![Figure 5](image)

**Figure 5.** SEM image of cantilevers: (a) – general view of coated cantilever, (b) – cantilever with thin coating, (c) – cantilever with thick coating.
It can be seen that the polyimide coating is continuous, without breaks. The presence of a coating leads to an increase in the radius of curvature of the tip of the cantilever: the probe with a coating of minimum thickness (dilution 1:40) has a radius of curvature of 50–55 nm, while a probe coated with a maximum thickness (dilution 1:20) has a radius of about 65 nm.

From the obtained values of the radius, it is possible to estimate the contact area – it is about $1 - 1.5 \times 10^{-14}$ m$^2$. Taking into account the obtained corresponding values of the adhesion force – from 10 to 30 nN – it is possible to evaluate the adhesive strength, which increases with increasing thickness of the coating and is 60–300 N / cm$^2$. The variation of values can be explained by the difference in the local properties of the surface and its roughness. In general, the values obtained are about an order of magnitude higher than those of existing artificial "dry" adhesives (whose adhesion strength is about 18 N / cm$^2$ [6]). Thus, the proposed adhesives and the method of their application give good results and can have practical application – for example, on the surface of a spacecraft.

4. Conclusions

- A method of surface modification providing a significant increase in its adhesion properties is proposed-the application of a "dry adhesive"- polyimide- obtained by developed “irrigation” method.
- A method of measuring the surface adhesion properties at the micro level using a probe-the cantilever (tip) of probe microscope-is proposed.
- The adhesion strength of polyimide to the most common materials of the outer covering of space vehicles (EVTI and to the AMG alloy) was estimated, using the SPM probe -the modified cantilever.
- It is shown that the adhesion strength of polyimide is very high (60-300 N / cm$^2$), which can have practical application. The obtained research results are the basis for the development of a constructive-technological version of a "dry" adhesive for space purposes.

Acknowledgments:
Preparation of samples was carried out with the support of the Grant of the RNF 14-19-00949-P. The SEM measurements were supported by the Grant of the RNF 14-19-01033-P. The work on SPM was carried out with the support of the Program of the Presidium of the Russian Academy of Sciences I.16.

5. References
[1] Geim A K et al. 2003 Nature Materials AOP vol 2
[2] Babaevsky P G et al. 2006 Practical Aspects of Nano- and Micro System Technic 9 13–20
[3] Manuilov K K 2015 Investigation of thermophysical and mechanical characteristics of composite materials of vacuum-screen thermoisolators 53 (Preprints of M.V. Keldish IPM)
[4] Bolotnik N N et al. 2016 Proc. of the 19th Int. Conf. of Climbing and Walking Robots (London)
[5] Bessonov M I et al. 1983 Poliimides – Class of Thermoresistant Polymers (L.: Nauka)
[6] Kim S and Sitti M 2006 Appl. Phys. Letters 89