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Anti-icing composite fluoropolymer coatings on titanium

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Abstract. Developing anti-icing coatings is an important topic for many scientists. In this work, we describe composite coatings prepared by a combination of plasma electrolytic oxidation and deposition of polytetrafluoroethylene from suspension. The composite layers obtained had high strength and adhesion to metal, which made it possible to use them in extreme environmental conditions. The change in the adhesion strength of ice to the coating surface was considered with various methods for forming composite layers on the surface of the metal and compared with the base PEO layer. The wettability of the resulting coatings as well as the relationship between the contact angle and the ice adhesion strength were evaluated.

Keywords: titanium, anti-icing coatings, protective coatings, composite coatings, plasma electrolytic oxidation, F4-d, superdispersed polytetrafluoroethylene

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Противообледительные композиционные фторполимерные покрытия на титане

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Аннотация. Разработка способов снижения образования льда на различных конструкциях представляет большой научный и практический интерес. В данной работе рассмотрено использование композиционных покрытий, полученных комбинацией методов плазменно-электролитного оксидирования и осаждения политетрафторэтилена из суспензий. Полученные композитные слои обладают высокой прочностью и адгезией к металлу, что позволяло использовать их в экстремальных условиях. В работе рассмотрено изменение прочности сцепления льда с поверхностью покрытий при различных способах формирования композиционных слоев на поверхности металла и проведено сравнение с базовым ПЭО-слоем. Оценена смачиваемость полученных покрытий водой, а также взаимосвязь между контактным углом и прочностью сцепления льда с покрытием.

Ключевые слова: титан, антиобледенительные покрытия, защитные покрытия, композиционные покрытия, плазменное электролитное оксидирование, ультрадисперсный политетрафторэтилен

Финансирование: Формирование композиционных покрытий и исследование прочности адгезии льда с поверхностью выполнены в рамках гранта РФФИ (проект № 13020-29-19 мк). Изучение взаимосвязи смачиваемости полученных покрытий с их морфологией и составом проводились в рамках государственного задания Министерства науки и высшего образования Российской Федерации, Россия (проект № FWFN-2021-0003).

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Introduction

Ice accretion is one of the main problems that arise during operation of various equipment in the coastal regions of the Far North and in winter [1–3]. It leads to many problems that can cause the loss and destruction of equipment. Increased mass of the structure is one of the main problems for ships and aircraft, consequently increasing the consumption of fuel, and potentially leading to complete breakdown of equipment due to large quantities of ice. Furthermore, as water penetrates into cracks and surface defects, they expand, grow and violate the integrity of the structure, which can also cause breakdowns and even destruction under operating conditions.

The body of research on preventing the formation of ice on the surface of metal structures has accumulated as interest grew towards oil fields located in the Arctic Ocean. The conditions under which mining is carried out contribute to ice formation on the surface of structures. To protect ships, aircraft and mining structures, various anti-icing coatings were developed.

Most studies aimed at obtaining anti-icing coatings are associated with the formation of hydrophobic layers on the surface with high contact angles and low contact angle hysteresis [2–7]. This is ensured by the formation of a developed surface structure with the formation of micro- and nanoscale irregularities, which make it possible to achieve a superhydrophobic surface. However, at low ambient temperatures, with constant contact with a supercooled drops of water in the air, an ice can form at developed surface. That leads to damage to the structure and loss of the original superhydrophobic and anti-icing properties. At the same time, attempts to remove this ice from the surface can lead to further damage to a layer up to its detachment from the substrate.

To prevent this destructive process, it is necessary to change the principles underlying the formation of protective surfaces. Since one of the main problems observed when using protective coatings is the surface structure developing that ice can very easily adhere to, producing a flat and smooth surface which reduces the level of ice contact with the material. Fabricating smooth coatings is a more technologically simple method of forming anti-icing coatings, which also produces surfaces with high anti-corrosion properties through isolating the substrate from the environment with a strong surface layer. Nevertheless, for a better level of surface anti-icing, the protective layer had to be made of a material with strong hydrophobic properties, such as polytetrafluoroethylene [8, 9].

In this work, a protective composite coating was formed on the commercially pure titanium VT1-0 using polytetrafluoroethylene [8, 9]. To form composite layers, two types of fluoropolymer suspensions were used: commercial suspension F4-d and isopropanol suspension of superdispersed polytetrafluoroethylene (SPTFE). Changes in the adhesion strength of ice to the surface depending on the processing method and processing conditions were considered.

Materials and Methods

Commercially pure titanium VT1-0 (98.6% Ti, 1.4 % impurities) was used as the substrate material for manufacturing the samples. The dimensions of the samples were 50×50×1 mm^3. Before coating, the samples were subjected to mechanical processing with sandpaper with a decrease in abrasive grain size to 30 μm. The samples were then washed with deionized water and alcohol using an ultrasonic bath for 5 min.

The coating was formed by plasma electrolytic oxidation in a phosphate electrolyte containing 25 g/l sodium phosphate (Na_3PO_4). The process was carried out in two stages using a potentiodynamic mode. In the first stage, the potentiodynamic voltage changed from 80 to 300 V, at a rate of 1.83 V/s. In the second one, the voltage was decreased from 300 to 240 V, at a rate of 0.1 V/s. During the process, the electrolyte temperature was maintained at a level of about 16 °C using a ChillerSmart H150-3000 cooling unit (LabTech Group, UK). After that, the samples were washed and dried in an oven at a temperature of 105 °C.

The composite coating was formed by immersion in an industrial aqueous suspension F-4d at an angle of 15° to the horizon and holding for 60 s, followed by slow withdrawal at a rate of 60 mm/min and air drying. Then the samples were subjected to heat treatment at 365 °C for 20 min. Heat treatment was carried out after each application of the fluoropolymer to obtain a smooth uniform surface of composite coating.

The second method consisted in vertical immersion of the samples with base PEO-coating in an alcohol suspension with SPTFE concentration 15% for 10 s, after which they were removed and dried in air. Samples with deposited polymer were etched for heat treatment in an oven at 315 °C for 15 min.

Samples with composite coatings formed with both polymers were processed from 1 to 3 times.

Samples subjected to plasma electrolytic oxidation will be referred to as the Basic PEO layer. Samples with composite coatings receive the designation SS with the designations of one- (1*X*), two- (2*X*) and three-fold (3*X*) application of fluoropolymer materials and an indication of the source of the material for application: commercial suspension (F-4d), and suspension of superdispersed polytetrafluoroethylene (SPTFE).

To determine the ice adhesion to the surface the shear test was carried out. An ice column of deionized water 30 mm in diameter and 7 ml in volume was formed on the surface of the sample at a temperature of −10 °C. After that, the sample with the formed column was fixed in on a rigid frame and, under constant cooling, an increasing load was exerted on the column with a rod with a diameter of 5 mm at 1 mm from the sample surface using an AG-Xplus Universal Testing Machine (Shimadzu, Japan). At the moment of ice shear, the obtained load values were recorded and compared with those obtained for the base PEO-layer.

The wettability of the coatings was studied by the sessile drop method using a DSA-100 (Krьss, Germany). The sessile drop method measures the optical contact angle (CA) and is used to evaluate the wetting properties of a localized region of a solid surface. Distilled water was used as the test liquid. To take into account the gravitational distortions of the contour of a drop under its own weight, the Young–Laplace method was used in this work when calculating the contact angle.

Results and Discussion

The base PEO-coating formed on titanium has high hydrophilic properties, which are due to their composition (titanium dioxide) and a developed surface, on which the pores and micron size defects, due to which a capillary effect occurs, are presented. Due to this, during icing, the base PEO-layer is easily covered with a thick layer of ice. At the same time, during the formation of ice, the volume of water, that has penetrated into the pores and defects, expands, causing the formation of larger cracks, ruptures and undermining the PEO-layer. During shear, the cracked parts of the PEO-coating will finally break (Fig. 1), removing not only the ice column, but also part of the protective coating. This is the reason for such a high adhesion strength of ice to the surface, which can be observed in Table 1.

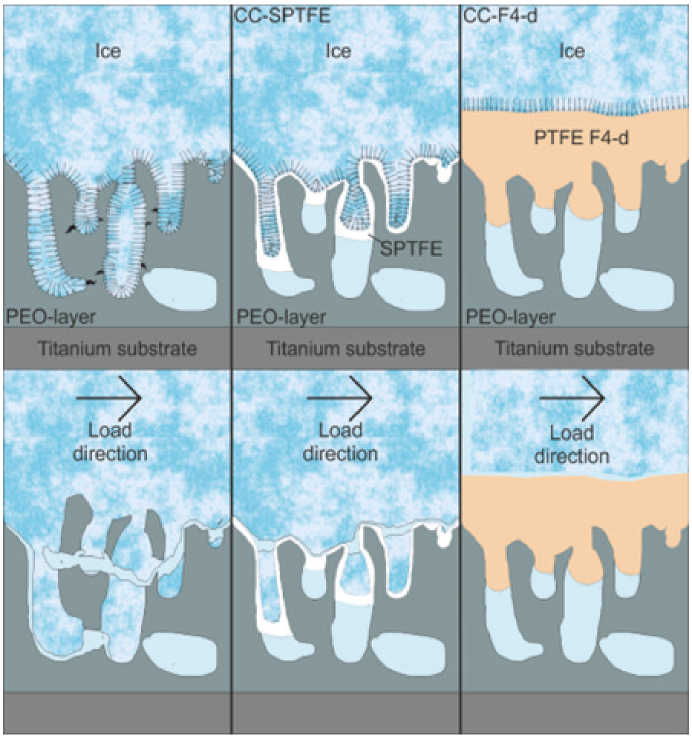

Fig. 1. Schematic representation of ice adhesion to various types of coatings

Comparing the adhesion strength of the ice to the base PEO-layer and composite coatings of the two types, we can trace noticeable changes even after a single application. Thus, for composite coatings obtained using SPTFE, the ice adhesion strength to the coating decreased by more than 4 times compared the sample with base PEO-coating. This was due to the change in the level of interaction between water and the surface. Due to the hydrophobicity of PTFE, fewer spots are available for the ice formation, which reduces the ice adhesion to the coating. However, the adhesion strength is still high due to presence of open pores and defects in the coating, forming cavities and irregularities to which the ice can still adhere (Fig. 1). The processing of composite coatings with SPTFE affects the change in the adhesion force of ice to the surface. Triple application of polytetrafluoroethylene on the base PEO-coating reduces the ice adhesion strength to the surface by 6 times. This is due to penetration of PTFE into the pores and defects of the coating. This decrease is the result of obtaining smooth surface with small amount of defects compared to the PEO-coating or composite coatings obtained with single and double treatment with SPFTE (Table 1).

Table 1

Strength of ice adhesion to the surface of samples for different processing methods

Coating	Ice adhesion strength (kPa)
Base PEO-layer	653
CC-1X–F-4d	27
CC-2X–F-4d	17
CC-3X–F-4d	5
CC-1X–SPTFE	157
CC-2X–SPTFE	111
CC-3X–SPTFE	107

Table 2

Changes in contact angle depending on processing

Processing type	Contact angle (º)
Base PEO-layer	72.2
CC-1X–F-4d	115.7
CC-2X–F-4d	114.6
CC-3X–F-4d	111.3
CC-1X–SPTFE	98.2
CC-2X–SPTFE	141.2
CC-3X–SPTFE	137.1

At the same time, composite coatings formed using the commercial suspension F-4d have an even lower ice adhesion strength between to the surface. This is caused by the formation of a more uniform and smoother fluoropolymer film on the surface, which closes pores and defects, and evens out most of the irregularities on the coating surface providing fewer contact points. This reduces the ice adhesion strength to the coating by more than 20 times. Further observation and evaluation of the adhesion strength of the coating to the surface showed that a single application does not provide the most uniform distribution of the polymer over the surface. There are still some defects that the ice can catch on. Further processing of the composite coating makes it possible to obtain a more uniform distribution of the polymer over the coating, which reduces the adhesion force of ice to the surface by more than two orders of magnitude in comparison with base PEO-layer.

The wettability of the obtained coatings is an important indicator of ice adhesion probability since they are in close contact with water. Depending on wettability, the composite coatings have a certain chance to prevent ice growth. However, as can be seen from the values in Table 2, the ice adhesion in the event of ice formation also depends on which contact angle provides the coating.

Analyzing the wettability of the PEO-layer, we established that the coating possesses hydrophilic properties (Table 2). Because of this, water actively interacts with the coating and penetrates into the pores of the layer. In the process of water freezing and ice is formed, the ice is locked and fixed on the surface due to a large number of pores and defects, which leads to the high of ice adhesion.

However, it should be noted that there is no direct correlation between the wettability of the composite coatings and the ice adhesion to their surface (Table 2). Thus, the wettability of composite coatings obtained using the F-4d suspension is higher than that of the layers formed using the SPTFE suspension (Table 2). However, the latter's adhesion to the surface is much higher (Table 1). This is explained by the difference in the structure of the composite layer. Therefore, F-4d can be used to form a smooth and thick polymer film on the surface, which exhibits low hydrophobic properties. Hydrophobicity also decreases with increasing multiplicity of treatment due to increasing surface continuity. At the same time, SPTFE envelops the already existing PEO-layer surface relief, retaining most of the protrusions and irregularities that crystallizing ice can catch on during formation, which provide high wetting angles of the coating, but the presence of a fluoropolymer on the surface reduces the adhesion force of ice to the treated surface.

Thus, it can be concluded that a more important parameter in the formation of anti-icing coatings is to obtain a smooth surface with a minimum number of defects, and not to achieve high hydrophobicity or superhydrophobicity of the surface. However, low wettability as such is still an important factor in the case of a decrease in the ice adhesion to the surface of the material.

Conclusion

In the course of the work, composite coatings were obtained on commercially pure titanium VT1-0 using a 15 % alcohol suspension of SPTFE, and commercial suspension F-4d. Studies have been carried out on ice adhesion to the surface of coatings, which showed a strong decrease (by 6 times) in the ice adhesion strength to the surface for the surface layers obtained using SPTFE, and by two orders of magnitude for composite structures formed with using the commercial suspension, compared to the base PEO-layer. The wettability of the obtained surfaces was also studied to identify the main causes affecting the ice adhesion to the surface. The resulting smooth films have the lowest strength of ice adhesion to the surface due to the small interaction between the ice and the surface, as well as the absence of any large number of surface irregularities that crystallizing ice can catch onto.

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