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Diamond Coating Application in Surface Modification of Tire Mold

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Abstract: With the development of automobile industry, the production of tire mold increased year by year in our country. The surface integrity of tire mold, end molded equipment in tire production line, being determines tire's exterior and quality. The Teflon coating is often used for protect the surface integrity on the market today. This article introduces advantages and disadvantages of Teflon, extremely low hardness and shorter service-life and there is potential menace to the environment and body healthy. The DLC coating has exceptional hardness and environmentally friendly. But its internal stresses have very big internal stresses and poorer hydrophobicity the Teflon. Based on the analyses for property of fluorinated diamond-like(F-DLC), fluorine is helpful reduce internal stresses and improve hydrophobicity. The article produces a formulation with F-DLC used in tire mold.

Keywords: Teflon coatings; DLC coatings; F-DLC coatings

1. INTRODUCTION

Molds are widely used in various manufacturing fields [01]. Precision rubber molds are used for the vulcanization molding of high - grade rubber mold products, with tire molds being a typical example. As the terminal forming equipment in automobile tire production, the complex cavity and high - requirement surface quality of tire molds have a direct impact on various characteristics of tires [02]. China is a large - scale producer of tires and tire molds. In 2014, the national tire production reached 562 million [03]. According to the statistics of 26 key enterprises in the tire mold industry by the Machinery and Mold Branch of the China Rubber Industry Association, the tire mold production in 2014 was 29,594 sets [04].The quality of tires and the failure rate of tire molds are closely related to the surface integrity of the molds. During the tire vulcanization process, problems such as glue sticking and carbon deposition are common, which damage the surface integrity of the molds, resulting in difficult demolding and a decline in tire quality [5]. Moreover, the performance indicators of tire molds in resisting surface damage directly affect the service life of tire molds. At present, the tire production industry at home and abroad mainly improves the surface integrity of tire molds by spraying Teflon coatings on the surface of tire molds. Teflon coatings have the characteristics of low friction coefficient, low surface energy, large water contact angle, corrosion resistance, and good adhesion. However, Teflon coatings have very low hardness and extremely poor wear resistance. They are prone to failure due to scratches and wear affecting the surface finish. Moreover, the service life of Teflon coatings is short (used for 2 months per spraying / vulcanized 3,000 times), and regular dry - ice cleaning and re - spraying of the coatings are required, which takes up a large amount of production time and cost. Secondly, one of the raw materials used in the production process of Teflon, ammonium perfluorooctanoate, is considered to be potentially carcinogenic to humans, and Teflon itself may cause serious environmental pollution. In contrast, diamond - like carbon (DLC) coatings have high hardness, excellent wear resistance, low surface energy, strong hydrophobicity, and good chemical inertness [6], etc., and have more promising applications in extending the service life of tire molds, saving cleaning costs, and improving their surface smoothness, corrosion resistance, and wear resistance performance. Moreover, DLC coatings are harmless to humans and the environment. At present, there are already industrial application examples of DLC products on molds.

2. SURFACE INTERGRITY OF MOLDS

The pass rate of products and production efficiency depend on the surface quality of molds, while the surface quality of molds depends on surface integrity. Mold surface integrity mainly includes two aspects: the material properties of the surface layer, whose main indicators are residual stress, metallographic structure change, micro - hardness, and surface chemical composition; the characteristics of surface micro - geometric shapes, whose main indicators are surface roughness, micro - cracks, and three - dimensional surface micro - topography. Adhikari [07] and Esther [08]'s research on the anti - sticking of food - forming molds shows that surface integrity has a decisive influence on the working properties of molds such as anti - stickiness, wear resistance, heat - fatigue resistance, and corrosion resistance. Tire molds are usually steel molds, which are used in the tire vulcanization molding stage and are in a working environment of high temperature (about 152 °C), high pressure (about 2.7 MPa), abrasion, and chemical corrosion, and their surfaces are easily damaged. Moreover, the compounding agents and release agents used in the tire demolding process and the cleaning methods used in the mold cleaning process will cause certain damage to the tire mold surface to some extent. For precision rubber molds, surface properties are of crucial importance, and minor damage will lead to a decline in the quality of mold products and affect the service life of the mold.

At present, in the industry, Teflon coatings are sprayed on the surface of tire molds to protect the surface integrity of the molds. Due to the properties of Teflon coatings themselves, although the classic problems such as glue sticking, carbon deposition, and difficult demolding have been solved to a certain extent, new problems have been added, such as short service life of the mold and environmental pollution.

3. COMMON DIAMOND-LIKE CARBON FOR MOLD SURFACE MODIFICATION

Diamond - like carbon (DLC) coatings are collective terms for a large class of amorphous or amorphous - nanocrystalline composite carbon films with different properties, mainly composed of sp3 - hybridized carbon atoms in a diamond - like structure and sp2 - hybridized carbon atoms in a graphite - like structure mixed with each other. Their structural properties mainly depend on the ratio of sp3/sp2, and they have performance characteristics such as high hardness, abrasion resistance, corrosion resistance, low friction coefficient, good chemical inertness, low surface energy, and strong hydrophobicity. These performance characteristics can effectively improve the demolding ability of molds, significantly increase the service life of molds, and can also greatly reduce the high - cost renovation and frequent cleaning expenses of some precision molds.

For tire molds, the good chemical inertness and corrosion resistance of common diamond - like carbon can protect the molds from chemical corrosion during the high - temperature vulcanization process; abrasion resistance, high hardness, and low friction coefficient can reduce the damage to the molding surface of the molds caused by impurity particles under high pressure and ensure the vulcanization quality; low surface energy and strong hydrophobicity can reduce the adhesiveness between the molds and high - temperature rubber, which is beneficial for tire demolding. Generally speaking, common diamond - like carbon coatings help to increase the surface hardness of tire molds, reduce the damage to the molding surface, prolong the life of tire molds, improve the demolding ability, prevent release agents from contaminating products, improve product quality, ensure the surface finish of molds, and reduce tire cleaning and renovation costs.

Compared with Teflon coatings, the surface energy and hydrophobicity of Teflon coatings are slightly better than those of diamond - like carbon coatings. Through friction and wear experiments simulating the tire vulcanization process, according to the experimental data obtained, although the friction coefficient of Teflon coatings (about 0.2) is lower than that of DLC coatings (about 0.4), due to the extremely low hardness of Teflon coatings (about 65.6 MPa), their service life is extremely short, and the film peels off after a 20 - minute friction and wear experiment, while the DLC (hardness value is about 166 GPa) coating remains undamaged. However, during the experiment, the degree of glue sticking of the two coatings was similar within the same time, which indicates that the hydrophobicity and surface energy of DLC coatings can meet the requirements of tire molds for the hydrophobicity and surface energy of coatings, and the high - hardness characteristic of DLC coatings also largely compensates for its inferiority to Teflon coatings in terms of hydrophobicity and surface energy.

The cavity of tire molds is complex. In order to ensure the integrity of the coating during the coating process, it is inevitable to increase the coating time. An increase in coating time will lead to an increase in coating thickness. The thicker the coating, the greater the internal stress and the residual stress, and the smaller the film - substrate bonding force, which directly affects the service life of the coating. Moreover, although the degree of glue sticking of DLC coatings and Teflon coatings is similar within the same period of time, the starting time of glue sticking is still earlier for DLC coatings, which is closely related to the hydrophobicity of the two coatings (the water - contact angle of DLC is about 79°, and that of Teflon is about 106°).

4. CONCEPTION OF USING F - DOPED DIAMOND - LIKE CARBON FOR TIRE MOLD SURFACE MODIFICATION

By doping diamond - like carbon (DLC) with elements, the internal stress of DLC can be effectively reduced, thereby reducing the residual stress and increasing the film - substrate bonding force; doping F element into DLC can effectively improve the hydrophobicity of DLC and reduce the surface energy while reducing the internal stress and increasing the film - substrate bonding force.

The coating internal stress is one of the main sources of the coating residual stress, and its magnitude depends on the kinetic energy of each atom hitting the film surface during the deposition process. In diamond - like carbon, the residual stress is manifested as high - energy carbon ions embedding into the substrate or coating and being unable to move and diffuse. Subsequently, the deposited ions form bonds with adjacent atoms, forming an extremely complex and highly cross - linked three - dimensional network structure. At this time, the sp3 bonds in the coating will be distorted due to structural factors, the deformation degree in the film increases, and the residual stress is formed [9]. When F element is doped into diamond - like carbon, the ratio of sp3/sp2 decreases, the content of sp3 bonds directly related to the residual stress relatively decreases, the value of the residual stress decreases, and, analyzed from the entire macroscopic carbon film network, the carbon film is separated by F atoms, the stress is released, the coating internal stress is reduced, and the film - substrate bonding force is enhanced.

Doping F element into DLC coatings can effectively improve the hydrophobicity of DLC. Some data show [10] that the water contact angle of F - DLC can reach 115°. One of the reasons why the tire mold industry chooses Teflon coatings as the final treatment for the tire mold surface is that Teflon coatings have high hydrophobicity and can effectively solve the problems of glue sticking and difficult demolding during the tire vulcanization process. The chemical structure formula of Teflon is -[-CF2 = CF2 -]n-, which is mainly composed of the highly hydrophobic group CF2. F - DLC has a similar structure to Teflon and also contains CF2, and the F element mainly exists in the form of the hydrophobic group CFx in the DLC coating, which makes the hydrophobicity of F - DLC similar to that of Teflon.

Compared with ordinary DLC, with the doping of F element, the content of H element in DLC coating relatively decreases. At the molecular level, it can be understood that the content of hydrogen bonds formed after contact with water will decrease, the water solubility will decrease, and the hydrophobicity will increase. Inside the coating, the interaction force between F atoms is small. An increase in the F content per unit volume

will cause the "migration" of F atoms. In this way, F atoms will easily gather on the coating surface, reducing the surface energy of the coating [11], thereby improving the hydrophobicity of the F - DLC coating surface. The strength of the C - F bond is greater than that of the C - C and C - H bonds, and the radius of the F atom is larger than that of C. The existence of F atoms will play a certain protective role for the C - C bonds in the DLC coating, ensuring some original properties of the DLC coating; at the same time, according to the properties of the F element, the surface energy, internal stress, and film - substrate bonding force of the entire coating system will be improved.

On the basis of the above research, if a DLC coating doped with a certain amount of F can be prepared on the surface of tire molds by plasma surface modification technology, the entire coating system will be more suitable for the tire mold industry in terms of performance and environmental protection to replace Teflon.

5. SUMMARY AND OUTLOOK

At present, the output of tire molds in China is increasing year by year, and the market has increasingly higher requirements for tire molds. Research on mold surface properties has always been in a dominant position. Teflon, with characteristics such as corrosion resistance, small friction coefficient, excellent hydrophobicity, and good film - substrate bonding force, is very suitable for the surface modification of tire molds. Therefore, spraying Teflon is still the mainstream method currently used by enterprises for tire mold surface modification. However, enterprises have also found that Teflon has extremely low hardness and poor wear resistance during the tire vulcanization process, thus greatly shortening its service life and increasing the production costs and production time of enterprises. Moreover, among the raw materials for preparing Teflon, ammonium perfluorooctanoate poses a great threat to human health; Teflon will decompose significantly at a certain high temperature, releasing toxic gases; at room temperature, Teflon itself also causes great controversy regarding environmental pollution and threats to human health. In contrast, the DLC series is pollution - free, has high hardness, good wear resistance, and a long service life. Moreover, its performance can be improved by doping elements to better meet the needs of enterprises. Compared with Teflon, F - DLC has high hardness, good wear resistance, and is pollution - free, and they have similar hydrophobicity; compared with ordinary DLC, it has small internal stress, high film - substrate bonding force, and good hydrophobicity. Overall, F - DLC is more suitable for tire mold surface modification.

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