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TECHNOLOGICAL ASPECTS OF APPLYING HIGH-QUALITY HARD CHROME COATING TO TITANIUM PARTS FOR THE OIL AND GAS INDUSTRY

D. V. Ardashev[1]*, A. S. Degtyareva-Kashutina[2]

South Ural State University, Chelyabinsk, Russia

ABSTRACT

Titanium parts include in deep-sea drilling and mining installations, pumps, pipelines, heat exchange equipment for various purposes and high-pressure vessels, which are used in offshore oil and gas fields. Existing methods of applying a hard chrome coating to titanium parts do not have a clear scientific justification and recommendations. The essence of author's method is the preliminary preparation of the surface of the part by etching in a bath of concentrated hydrochloric acid, followed by surface activation by passing a current in the opposite direction. The application of a hard chrome coating is performed on a rotating part when it is partially immersed in an electrolytic bath.

KEYWORDS

Titanium;
Hard chrome coating;
Electrolyte;
Chrome plating;
Electrolytic bath;
Oxide film.

Introduction

One of the materials used in aviation, missile and military equipment is titanium and its alloys. The use of this material in the aircraft industry and the space industry makes it possible to increase the carrying capacity of aircraft and reduce the operation costs. In offshore oil and gas fields, titanium and its alloys are one of the main structural materials, since it has high corrosive resistance to seawater. The use of titanium also makes it possible to reduce the weight of equipment used in oil and gas production, which increases the load capacity of oil and gas platforms.

The use of titanium alloys also has significant prospects for equipment used in offshore oil and gas fields such as deep-sea drilling and mining risers, casing pipes, water pumps, pipelines of the circulation system of technological solutions, liquid separators, heat exchange equipment, high-pressure vessels, and high-strength flexible stretchers for fixing the platform and other components [1].

Due to high friction of titanium and its alloys, a special coating, in particular hard chrome, must be applied to the outer surface of parts operating under friction. Applying a hard chrome coating to titanium parts has certain difficulties, the main one is the instant appearance of an oxide film on the titanium surface. This oxide film occurs after contact with air for a few milliseconds [2]. At temperatures of up to 200°C, the growth rate of the oxide film obeys a logarithmic dependence [3, 4]. As a result, when chrome plating titanium and its alloys, this film acts as a separating medium between the chrome coating and the base material. Thus, when chrome plating titanium parts, the coating is applied to the oxide film, and not to the titanium itself, which significantly impairs the operational capabilities of such parts.

**E-mail:* ardashevdv@susu.ru

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Problem statement

The literature on the chrome coating of titanium parts can be divided into three main groups. The first group includes studies using special methods to prepare the surface to be coated. Some authors propose carrying out preliminary preparation of the titanium surface by etching it in a mixture of hydrochloric and hydrofluoric, or nitric and hydrofluoric acid [5]. Other authors, after the procedure described above, propose additionally treating the surface to be chrome-plated with a solution containing an alkali metal or ammonium bichromate and hydrofluoric acid [6], another proposal is to introduce sodium silicate into the solution [7]. Further chrome plating occurs in two stages: first soft chrome is deposited, and then wear-resistant (hard) chrome is applied. It has also been proposed to pre-etch the surface of the titanium part in a cold 40% solution of sulfuric acid with the addition of 0.5% aluminum fluoride for 1 hour [8].

The second group includes research on developing the optimal composition of the electrolyte for applying chrome coatings to titanium alloys. Some authors propose introducing a surfactant perfluoroorganic compound into the electrolyte – a salt of alkali metals or ammonium 4-trifluoromethyl-3,6-dioxaperfluorooctanesulfonic acid [9]. Others have proposed including in the electrolyte chrome anhydride, potassium silicofluoride, strontium sulfate, metal oxide powder of groups IVB, VB, VIB, metal carbide powder of groups IVB, VB, VIB, or surfactants – chromoxane, chromine, etc. As a result, the coating has high microhardness, decorative gloss, reduced porosity and high adhesion to the surface of the part [10]. There is a study in which the chrome plating of a titanium alloy was carried out in an evacuated chamber, in a special gas environment at a temperature of 1050 °C for 4 hours. Chrome powder and carbon tetrachloride CCl_4 were used as the initial components [11].

The third group combines studies devoted to forming a special conductive film on the surface of the titanium part, to which a chrome coating is applied. For this, for example, it is proposed to activate the titanium part in a solution of hydrofluoric and nitric acids in certain ratios, at a temperature of 18-25 °C, for 1.5-2.0 minutes [12, 13]. In some cases, such manipulations aimed at intentionally forming a special film on the surface of a titanium part to promote chrome adhesion require complex and expensive operations [13], for example, performing electrochemical chrome plating of titanium alloys without thermo-diffusion vacuum annealing [14], the composition of the electrolyte was experimentally determined [15], in another work the positive effect of preliminary vacuum heat treatment of the part was established [16]. As a result of these additional preparatory operations, an electrically conductive film is formed on the surface of the titanium part.

In all the studies where a hydride conductive film is formed on the surface of a chrome-plated titanium part, the process of chrome plating of titanium alloys follows the scheme: milk chrome plating, thermo-diffusion vacuum annealing, hydroblasting, the activation of milk chrome, and finally the sedimentation of wear-resistant chrome. However, this is applicable only in a very narrow range of coated grades of titanium alloys (VT-3, VT-6).

There are studies of various methods of applying chrome and other coatings to a titanium base, for example, using brush spraying [17], using arc ion spraying [18-20], followed by a study of the phase composition, the morphology of the coating and the distribution of chemical elements. However, again, this method does not exclude the formation of an oxide film on the prepared surface of the titanium part. Without preliminary preparation of the surface of the titanium part to be chrome-plated, or additional operations preceding the coating, it is not possible to form a hard chrome coating on the titanium part.

Existing studies do not contain a scientific description of the relationship between the conditions of the coating and its quality [21, 22], there is no scientific and methodological basis for the recommendations on the modes of applying hard chrome to titanium parts.

A promising and low-cost direction of titanium chrome plating and the improvement of the properties of the coating is changing current densities during chrome plating, for different times, at different initial and final current densities, and with prior preparation of the surface of the part.

The preparation of the surface includes several stages. The first is electrochemical degreasing by keeping the part in a bath of trisodium phosphate, caustic soda, and sodium carbonate at 60-80 °C for 15-20 minutes. The part is then washed in water. The next step is the activation of the surface of the parts in a bath of concentrated hydrochloric acid (ρ 1.17-1.19 g/cm^3) at 15-35 °C for 5-15 seconds.

The second stage is the transmission of a current in the opposite direction (anode polarization of the part). A thin layer of the base metal is oxidized on the surface of the part with the formation of soluble sulfates. In addition to metal removal, oxides and organic contaminants are also removed. Carbides and nitrides during anodic activation are effectively oxidized and removed from the surface of the part. This leads to the improved adhesion of the chrome as there are much fewer contaminants. Another important consequence of the anodic polarization is the very short time interval between the end of etching and the beginning of sedimentation. This interval takes less than 1 second to switch the polarity between the anode and the cathode. It is assumed that an oxide layer does not have time to form on the part, which occurs, for example, when washing the part after its activation in hydrochloric acid. This also significantly increases the adhesion strength of the coating.

The application of a hard chrome coating is carried out using an installation that provides chrome plating of cylindrical parts during their rotation and partial immersion in the electrolyte [23]. The installation scheme is shown in figure.

The installation works as follows. Part (1) rotates in the electrolytic bath (2). The electrolyte enters the bath through nozzle (3) and through the slot of the anode (4). The electrolyte level is regulated by the height of the overflow (5). From the overflow pocket, the electrolyte flows by gravity through the drainpipe (6) into a heat-resistant vessel (7), from where it is pumped into the pressure tank (9) by pump (8). The supply of electrolyte from the pressure tank to the bath is regulated by the screw clamp (10). The hoses used for draining and supplying the electrolyte are made of polyvinyl chloride. Heating of the electrolyte is carried out on the closed-type electric heater (11).

As the temperature of the electrolyte and its fluctuations during the coating process have a significant impact on the quality, a temperature of about 55 °C ± 1 °C is maintained during the electrolysis process. Automatic regulation is carried out by a thermostat (12), while the thermistor temperature sensor (13) is located in the heated vessel (7). Exhaust gases are removed through the ventilation system (14), conventionally shown in the form of an umbrella located directly above the electrolytic bath.

The peculiarity of this method of the galvanomechanical sedimentation of chrome on the surface of a titanium part is that during the formation of the coating, a continuous mechanical activation of the coated surface occurs using ceramic rollers. It is proposed to combine in one bath the activation of the part, the anodic polarization of the part,

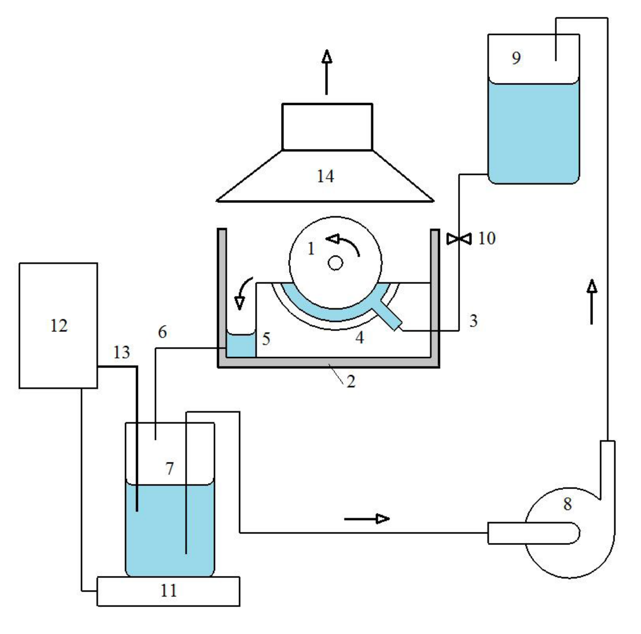

Fig. Scheme of the coating installation

and the galvanomechanical sedimentation of solid chrome. When developing chrome plating modes, options are also worked out with a change in the initial current density, its density during the coating process, and different exposure times of these densities. This will significantly increase the productivity of the electrolytic chrome build-up compared to the traditional immersion method, and improve the physical and mechanical properties of the coatings.

Conclusion

The main technological features of applying a hard chrome coating to titanium parts are shown. The analysis of existing methods for chrome plating titanium surfaces was carried out, showing three main approaches. In the first, special attention is paid to the preparation of the surface before coating by various methods of removing the oxide film. In the second, special electrolyte compositions are developed, in the third, technologies for creating a conductive film on the surface of the part are implemented.

A new approach to the application of a hard chrome coating on titanium parts is proposed: by a galvanomechanical method on a rotating part with a change in current density during sedimentation. Before applying the coating, a two-stage activation of the part is performed, including etching in concentrated hydrochloric acid and the anodic polarization of the part. These measures allow the removal of the oxide film from the surface of the part, avoid its further appearance, and improve the quality of the resulting coating. Besides it will enhance the service life of titanium products in difficult operating conditions, for example, when developing offshore oil fields.

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References

1. Shashkova, Yu. E., Smirnov, V. G. (2008). Projects, technologies and equipment made of titanium alloys for the development of oil and gas fields on the shelf. *Exhibition Oil and Gas*, 6/H(78), 8-10.
2. Karlov, A. V., Shakhov, V. P. (2001). External fixation systems and regulatory mechanisms of optimal biomechanics. *Tomsk: STT*.
3. Lazarev, E. M., Kornilova, Z. I., Fedorchuk, N. M. (1985). Oxidation of titanium alloys. *Moscow: Nauka*.
4. Aleksander, W. A., Pidgeon, L. M. (1950). Kinetics of the oxidation of titanium. *Canadian Journal of Research*, 28b, 60-72.
5. Layner, V. I. (1967) Modern electroplating. *Moscow: Metallurgy*.
6. Kazakov, V. A., Lipin, A. I., Shluger, M. A. (1962). Electrolytic coatings of light alloys. *Moscow: GOSINTI*.
7. Ryaboy, A. Ya., Solovyova, Z. A., Evdokimov, G. N., et al. (1981). A method for preparing the surface of titanium and its alloys. *Patent SU850754*.
8. Burdina, S. M., Chistov, N. M., Frumer, L. A. (1961). A method for obtaining low-stress chrome coatings on titanium or its alloys. *Patent SU141047.*
9. Plaskeev, E. V., Ovsyannikova, L. V., Kurdyukova, E. A., et al. (1984). Electrolyte for chrome plating of titanium alloys. *Patent SU1114712.*
10. Zhirnov, A. D., Ilyin, V. A, Naletov, B. P., et al. (2002). Electrolyte for chrome plating of steels, copper and titanium alloys. *Patent RU 2187587.*
11. Smokovich, I. Ya., Loskutova, T. V., Bobina, M. M., et al. (2013). Diffusion coatings based on chrome on titanium alloy VT6. *Bulletin of SEVNTU*, 137, 239-249.
12. Solodkova, L. N., Kudryavtsev, V. N. (2007). Electrolytic chrome plating. *Moscow: Globus.*
13. Yang, Z., Zhang, M. An, J., et al. (1997). Study of the process & mechanism of plating directly on titanium and its alloys. *Plating and Surface Finishing*, 84 (12), 68–71
14. Pavlenko, V. V., Gerasimenko, A. A. (1997). Chrome-plating of titanium alloys and their performance. *Zashchita Metallov*, 33 (4), 429-433.
15. Ryaboi, A. Ya., Vashentseva, S. M., Solov'eva, Z. A., et al. (1993). New method for chromium plating articles made of titanium alloys. *Zaschita Metallov*, 25 (3), 371-372.
16. Peng, X., Xia, C., Dia, X., Ma, K. (2008). Effect of vacuum heat treatment on NiCrAlY coating/ titanium alloy substrate system. *Rare Metal Materials and Engineering*, 37 (9), 1619-1623
17. Xiao, H., Clouser, S. (2011). Selective plating of metal matrix composites on titanium alloys. *Corrosion Management*, 102, 8-11.
18. Yan, W., Sun, F.-J., Liu, J.-R. (2010). Cycling thermal shock resistance of Ti-Al-Cr coating deposited on Ti60 alloy by arc ion plating. *Journal of Northeastern University*, 31(3), 411-414.
19. Yan, W., Sun, F., Wang, Q., et al. (2009). Hot corrosion behavior of arc-ion plating Ti-Al-Cr(Si, Y) coatings on Ti60 alloy. *Acta Metallurgica Sinica*, 45(10), 1171-1178
20. Yan, W., Wang, Q., Liu, J., et al. (2009). Evaluation of oxidation of Ti-Al and Ti-Al-Cr coatings arc-ion plated on Ti-60 high-temperature titanium alloy. *Journal of Materials Science and Technology*, 25 (5), 637-644

21. Klots, M. U. (1982). Experience of chemical and electrochemical processing of titanium alloy parts. *Leningrad: LDNTP.*

22. Davydov, V. M. (2009) The materialology of the coating of titanium alloys by the methods of physico-chemistry and electric spark alloying. Part 1. Coatings by the methods of physicochemistry. *Khabarovsk: TOGU Publishing House.*

23. Ardashev, D. V., Diakonov, A. A., Zherebtsov, D. A., et al. (2019). Installation for electroplating. *Patent RU 186265.*

Технологические аспекты нанесения высококачественного твердохромового покрытия на титановые детали для нефтегазовой промышленности

Д. В. Ардашев[1], А. С. Дегтярева-Кашутина[2]

Южно-Уральский государственный университет, Челябинск, Россия

Реферат

Титановые детали используются в составе глубоководных буровых и горнодобывающих установок, насосов, трубопроводов, теплообменного оборудования различного назначения, а также сосудов высокого давления, которые применяются на морских нефтяных и газовых месторождениях. Существующие методы нанесения твердохромового покрытия на титановые детали не имеют четкого научного обоснования и рекомендаций. Суть авторского метода заключается в предварительной подготовке поверхности детали путем травления в ванне с концентрированной соляной кислотой с последующей активацией поверхности за счет пропускания тока в обратном направлении. Нанесение твердого хромового покрытия выполняется на вращающуюся деталь, при ее частичном погружении в электролитическую ванну.

Ключевые слова: титан; твердое хромовое покрытие; электролит; хромирование; электролитическая ванна; оксидная пленка.

Neft və qaz sənayesində istifadə olunan titan hissələrinə yüksək keyfiyyətli sərt xrom örtüyünün çəkilməsinin texnoloji aspektləri

D. V. Ardaşev[1], A. S. Deqtyareva-Kaşutina[2]

Cənubi Ural Dövlət Universiteti, Çelyabinsk, Rusiya

Xülasə

Titan hissələrindən dərin dəniz qazıma və dağ-mədən hasilatı qurğularında, nasoslarda, boru kəmərlərində, müxtəlif təyinatlı istilik mübadiləsi avadanlıqlarında, eləcə də dəniz neft və qaz yataqlarında istifadə olunan yüksək təzyiq tutumlarında istifadə olunur. Titan hissələrinin üzərinə sərt xrom örtüklərinin çəkilməsi ilə bağlı mövcud üsulların dəqiq elmi əsaslandırması və tövsiyələri yoxdur. Müəllif metodunun mahiyyəti hissənin səthinin əvvəlcə konsentratlaşdırılmış xlor turşusu olan vannada aşındırılaraq hazırlanmasından, sonradan cərəyanın əks istiqamətdə buraxılması hesabına səthin aktivləşdirilməsindən ibarətdir. Sərt xrom örtüyünün çəkilməsi fırlanan hissəyə onun elektrolitik vannaya qismən batırılması ilə həyata keçirilir.

Açar sözlər: titan; sərt xrom örtük; elektrolit; xromlama; elektrolitik vanna; oksid təbəqə.