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Magnetron Sputtering System with Cylindrical Magnetron for Obtaining of Internal Protective Coatings for Increasing Pipe Resource

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This work presents a magnetron sputtering system with a cylindrical magnetron to can be used for protective coatings in the internal surface of pipes. The main advantage of the system is to operate in both constant and pulse current mode, to perform the preliminary surface cleaning and to form a single-layer or multi-layer coating in one technological cycle. The tantalum and chromium coatings obtained using the systems with the cylindrical magnetron have high physical and mechanical properties.

Key words: magnetron sputtering system, protective coatings, pipe internal surface, cylindrical magnetron, coating hardness.

У роботі представлено магнетронну розпорошувальну систему з циліндричним магнетроном, яка може бути застосована для нанесення захисних покриттів внутрішньої поверхні труб. Істотною перевагою нашої магнетронної системи є можливість в одному технологічному циклі проводити попереднє очищення поверхні і формування одношарового або багатоша-

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рового покриття. Одержані за допомогою системи з циліндричним магнетроном покриття танталу і хрому мають високі фізико-механічні показники.

Ключові слова: система магнетронного розпорошення, захисні покриття, внутрішня поверхня труб, циліндричний магнетрон, твердість покриттів.

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1. INTRODUCTION

Service life extension and improvement of operational reliability for pipes are a crucial problem in today industry. These elements generally undergo severe mechanical and chemical weariness due to friction of the surfaces and environment with various degree of aggressiveness, which results in physical destruction and corrosion of a material of pipes. Thus, the pipes require high mechanical, thermal and corrosion resistance as their main features [1].

Service life extension can be realized through various approaches. Of special note is that number of technologies, techniques and facilities applied for hardening the industrial products, for internal surface treatment is limited because of geometry, inaccessibility and often small parts of the products.

The most promoting and advanced techniques for hardening the internal surface of the pipes and of complex profile internal surfaces are the plasma sputtering methods [2–5] and laser facilities application.

A widely-used kind of plasma sputtering for coating is the vacuum-arc deposition technology which is popular, proven and successfully applied in industry [2]. However, because of well known disadvantages like pillar-like grain growth and dewetting which lead to degradation of coating performance, researchers and engineers keep on searching with a particular effort on other more promising methods to provide substantially better results.

Magnetron sputtering is another kind of plasma sputtering. It is one of the most widely applied approaches in plasma technologies for high-quality coating and enhancing the physical and chemical parameters of the industrial product surfaces. In particular, the magnetron sputtering demonstrates good performance in hardening the materials [6], in wear- and corrosion-resistant coating the industrial products [7, 8]. HIPIMS (High-power impulse magnetron sputtering) is being actively developed as a kind of the magnetron sputtering for protective coating where the high-power pulses are applied [9]. The distinctive feature and advantage of this technique is high density of the ionized atoms of the sputtered substance in plasma due to peak capacities or current density which result in better adhesion, lower roughness and coating hardness [10]. Leading world companies engaged in developing the technology of pipes coating focus on the cylindrical magnetron sputtering technique [11].

It is a well known fact that the most in-demand materials for hardening and protective coating are Ta, W, Nb, Mo, Ti, Cr, the alloys with these metals as the basic components in different concentrations, the CrN compound, high entropy alloys and ceramic coatings. For example, Ta is hard-melting, chemically-stable to aggressive environment and ductile; Nb and Ti have high corrosion resistance and ductile properties. Chromium nitrides are characterized by high hardness and elasticity modulus, perfect features in wear and corrosion resistance [12, 13].

It is evident from foregoing, that the issue in internal surface treatment of pipes to obtain the coating of high performance is urgent. The main difficulties, problems and tasks are related to inaccessible coatings of complex shape, limited areas and enhancement in coating quality, power and efficiency of atomizers. In this connection, the study is aimed at range of works on designing and testing a powerful system of magnetron sputtering for internal protective coating of the pipes.

2. DESIGN OF CYLINDER MAGNETRON, EXPERIMENTAL TECHNIQUE AND RESULTS

The authors from Institute of Applied Physics N.A.S. of Ukraine have developed the design documents and prepared a test model of a cylindrical magnetron with its further testing. The CM-based sputtering system used for sputtering the chemically stable and high-melting metals allows protective coatings onto internal complex profile surfaces of the pipes. This magnetron system can be applied only for the pipes with internal diameter 60 mm at least.

Figure 1 shows a cylindrical magnetron comprised of two magnetrons *A* and *B* identical in design. Each magnetron is equipped with an individual magnet system *1* based on permanent magnets (SmCo) with an adjusting mechanism and water-cooling (channel *2*). The main elements of the CM scheme are also the target cathodes *3*, *6* and the ring anodes *4*, *5*, *7*, *8*. The detachable target cathodes may be replaced if other materials need to be sputtered.

In the magnetron design, an economic use of the sputtering targets crucial for expensive materials is considered. For this purpose, the targets are placed at a technological minimum distance from the magnet systems. The active zone of the material sputtering may be moved with the specified speed along the whole surface of the cylindrical target due to two anodes. This allows coating of more uniform thickness. Note that the *A* and *B* magnetrons are structurally and electrically isolated from one another and may operate individually. This makes it

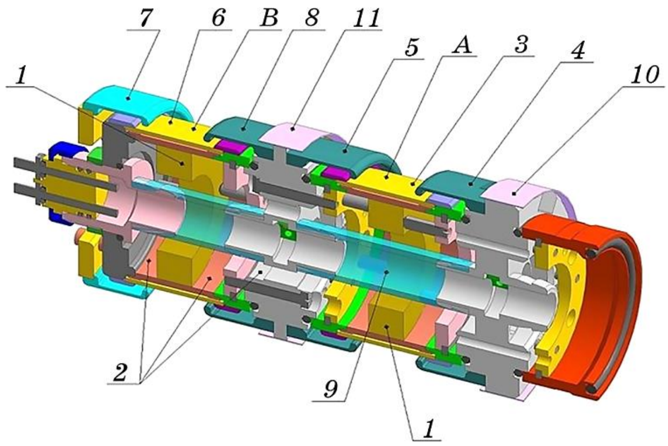

Fig. 1. Sectional head of a cylindrical magnetron: *A* is first magnetron; *B* is second magnetron; *1* are magnets (SmCo); *2*, *9* are sealed channels; *3*, *6* are target-cathodes; *4*, *5*, *7*, *8* are anodes; *10*, *11* are protective screens.

possible, in one technological cycle, with one of the magnetrons (magnetron *A*) to make preliminary cleaning of the inner surface of the pipes, and by the other (or others, in the case of three or more magnetrons), to sputtering the coating. The material of the inner surface of the tube that is deposited on the surface of the magnetron *A*, must be removed for the next experiment.

The sealed channels *2*, *9* are used for supplying the electric potentials to the target cathodes and anodes and for rejecting the excess of thermal energy from the CM magnet system. In an operating mode, after inlet of an operating gas (which is purified argon, as a rule) as the relevant potentials are supplied onto the magnetron electrodes, plasma starts burning in a target-anode gap. The main elements of the plasma here are neutral atoms and ions of the target material [15]. To accelerate the ions of the sputtered target material, potential bias is supplied between the cathode and a substrate [16].

To find the proper technological process of metal sputtering onto internal complex profile pipe surfaces, a pipe fragment (steel 0XN3MFA) equipped with the heating and temperature control systems and a steel witness sample (steel 0XN3MFA) to be coated are used (Fig. 2).

Sample surface preparation is crucial for high quality coatings. A three-stage cleaning of the surface is applied: washing in an ultrasound bath with specific detergents; heating (degasification) in vacuum before the coating; ion-plasma etching. The latter is realized with the *A* magnetron and glow discharge plasma is then generated.

The magnetron system with the cylindrical magnetron (Fig. 3) is tested at the vacuum facility VNP-350-1. The system is attached to the

a *b*

Fig. 2. A fragment of the pipe (*a*) and its witness sample (*b*).

vacuum chamber with a flange *1* and an operational sealant *2* (a fluoroplastic plug with rubber rings and other parts). The sealant ensures vacuum tightness of the moving parts when the magnetrons *3* and *4* are shifted from the position of the samples *5* to other samples along the pipe fragment *6* during the next process of ion cleaning and sputtering.

The magnetron sputters are known to require effective target and magnet cooling as they suffer a considerable thermal impact during sputtering. As a rule, they are water-cooled. In our case, CM is equipped with a cooling system operating on flow deionized water.

In an operating chamber of VNP-350.01, vacuum of about 10^{-3} Pa is maintained *via* turbomolecular pump. Pressure of inert operating gas is about 1 Pa. For operating plasma generation, a negative potential is supplied onto the target cathode, the anodes are grounded. The exper-

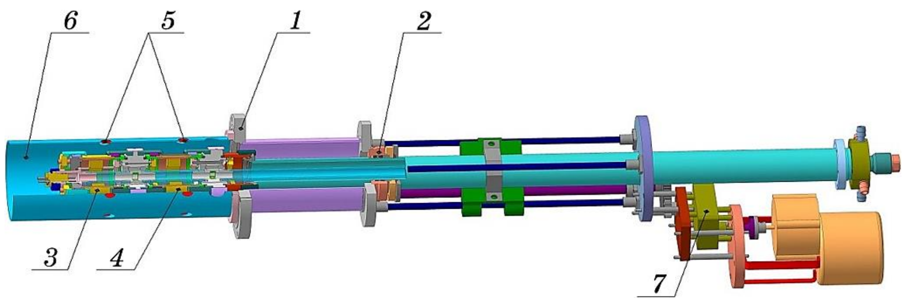

Fig. 3. The magnetron sputtering system with a cylindrical magnetron: *1* is connecting flange; *2* is a sealant; *3*, *4* are magnetrons; *5* are substrates; *6* is pipe fragment; *7* is mechanism for moving magnetrons.

iments show that the stable discharge of the magnetron is observed at discharge current of 1 A at least.

The surface cleaning with a glow discharge is a modern and the most promising technique. It allows cleaning the surfaces of various size and profile including the internal surfaces. At abnormal glow discharge, the potential can be varied in wide range at the cathode region according to gas pressure and current density at the cathode, and the energy of the ions bombarding the surface can also be varied. At ion cleaning, the internal surface of the pipe fragment is used as a cathode of glow discharge (a diode circuit etching). To test this technology, a 200 nm layer of Cu is coated onto the steel samples with our sputter. Then the obtained copper surface is cleaned. The quality of the surface treatment is visually inspected and the results are accepted as reasonable where the copper layer is completely etched.

For optimal modes and conditions of the abovementioned cleaning technology to be found, negative potential up to 900 V is supplied onto the pipe fragment and all the electrodes of the *A* and *B* magnetron are short-circuited and grounded. The surface sputtering is performed with the argon operating gas ions. The experiments show that efficient cleaning of the surface in the glow-discharge is observed at argon pressure in the range 3^{-10} Pa and at a bias voltage over 400 V. As the operating gas pressure and the bias voltage grow, quality and efficiency of cleaning increase, which is quite obvious, but there is also a possibility of the breakdowns in the chamber and arc discharge occurred. Eventually the most optimal mode for the mentioned conditions is the mode with the argon pressure in the chamber of about 3 Pa and with gradual growth of the bias voltage at the pipe fragment of up to 900 V, the ion current is about 50 mA. In this mode, the required efficiency is reached and a 200 nm copper film is completely etched.

The technology of sputtering with CM involved is elaborated with tantalum and chromium cathodes since these metals and alloys based on them ensure decent protective coatings. One of the magnetrons is grounded as another operated, the bias voltage supplied to a substrate holder (the pipe fragment) with the samples is varied. High vacuum is obtained at about 10^{-3} Pa, inlet of Ar operating gas is performed up to 1–1.5 Pa. Other technological parameters are as follows: discharge current is about 1 A, potential at the magnetron is 100–270 V, bias voltage is 100–550 V, the substrate temperature is 20–300°C.

For further information on thickness of the sputtered coatings, the additional glass samples are mounted onto the substrate holder in each experiment. The coating thickness is measured by multiple-beam interferometry (strip method) at an interferometer MII-4, the thickness is 0.5–1.5 μm.

The study of the elemental composition of the coatings is carried out using the PIXE-analysis method. For profiling, the proton beam bombarded the target at an angle of 0° relative to the normal to the sample surface. The resulting X-ray radiation is recorded using a semiconductor detector located at an angle of 45° to the direction of the beam. For profiling, the sample is irradiated with 1 MeV protons.

The beam current is chosen taking into account the dead time of the ADC and the duration of the required charge accumulation, which is 10 μs. In the experiment, the beam current is in the range from 35 to 55 nA. Under these conditions, the dead time did not exceed 9%. The research results are shown in Table 1.

Physical and mechanical features of the coatings are studied at Frantsevich Institute for Problems in Material Sciences N.A.S. of Ukraine. Microhardness and the elasticity modulus are presented in accordance with the International Standard ISO 14577-1:2002. These measurements are performed with the Berkovich pyramid (angle of 65°) with load of 200–300 g at the 'Mikron-Gamma' appliance [17] with load accuracy of 10^{-3} N, and depth penetration of an indenter of 2.5 nm.

There are a number of methods for determining adhesion that can be classified according to the prevailing normal or shear test loads at the interface with the substrate. The most common methods for determining of adhesion are methods of indentation with various indenters, detaching a film of material from the substrate, as well as the method of sclerometry (scratching) [16].

The sclerometry (scratch) is the best method for determining adhesion characteristics. When determining adhesion by the scratching method, the film breaks through until the substrate is exposed and the coating peels off. To research adhesion it is necessary to measure precision magnitude of the maximum load leading to the breaks of the film [17].

The parameter of adhesion, characterized by the parameter of the maximum load when scraping the coating. All this do technological processes of sputtered coatings better, in such parameters as the modes of their deposition, the method of preparing the substrate surface, *etc.* and evaluate their quality.

Parameters of coating adhesion are found by a sharp indentor im-

TABLE 1. Elemental composition of coatings determined using PIXE analysis.

Cr electroplated	Cr 95.74	Fe 2.90	Mn 0.43	Mo 0.30	Cu 0.18	Ni 0.11			Impurity 0.34
Ta magnetron sputtering	Ta 97.83	Fe 1.40	Cr 0.30	Ni 0.19					Impurity 0.28
Steel (substrate)	Fe 92.92	Ni 3.00	Cr 1.30	P 0.65	Mo 0.44	Mn 0.3	Cu 0.28	V 0.12	Impurity 0.99

TABLE 2. Physical and mechanical parameters of the coatings.

Material	H_{IT}, GPa	f	F_a, cN	$I_{lin}\cdot 10^{-7}$	d, μm
Cr electroplated	13.0	0.053	11	0.33	0.90
Ta magnetron sputtering	5.5	0.265	21	0.34	0.65
Cr magnetron sputtering	11.5	0.060	27	0.49	0.75
Steel (substrate)	3.3	0.198	28	2.87	–

H_{IT} is hardness at autoidentation; f is friction coefficient; I_{lin} is a parameter of linear wear; F_a is load whereby the cracks occur in the coating; d is coating thickness.

mersed into the coating surface and moved at constantly growing mechanical load. The main physical and chemical parameters of the coatings made by the cylindrical magnetron system and features of the electroplated chromium coating are tabulated in Table 2.

The measurements showed that the cracks in the Ta coatings occur only when the load is over 21 cN. It is particularly remarkable that the electroplated coating of Cr made by PJC ‘Sumy Frunze Machine-Building Science and Production Association’ the cracks are observed even at a two times less load (about 11 cN) and the coating is rather brittle. Among all studied samples, the Cr coating made by the magnetron sputtering also had the highest adhesion of 27 cN. It may be deduced from the data in Table 2 that the parameters of linear wear for the samples obtained by electroplated coating and magnetron sputtering differ little from each other and are 6–9 times less than those of the steel samples (the substrates).

3. CONCLUSIONS

The magnetron sputtering system with a cylindrical magnetron for thin protective coating of internal surface of pipes has been developed, designed and constructed. This system allows elaboration of technology of sputtering a single-layer or multi-layer coating required for various industrial products.

Basing on physical and chemical parameters it can be concluded that the Ta and Cr coatings obtained with this sputtering system in relevant operating modes are highly competitive with the chromium coatings in hardness and are also advantageous in elasticity modulus which is close to that of steels. This benefit may be used for protective coating of internal surface of pipes. It is also important to note that the magnetron sputtering system is environmental friendly and safe for human [18] in contrast to electroplating.

Basing on the successful experimental tests and studies of the test model of the cylindrical magnetron and the coated films, the construction of a facility for protective coating in internal surface of pipes for various industries becomes real.

REFERENCES

1. A. V. Krutikov and M. S. Devyat'yarov, *Collection of Reports of the International Forum 'Welding and Diagnostics' (Nov. 25–27, 2014)* (Ekaterinburg: UrFU: 2015), p. 75 (in Russian).
2. V. N. Nadtoka, R. V. Pankov, L. N. Deyneko, and N. V. Maslyanyy, *Artilleriyskoe i Strelkovoe Vooruzhenie*, No. 1: 54 (2009) (in Russian).
3. V. I. Perekrestov, S. N. Kravchenko, Yu. A. Kosminskaya, and I. N. Kononenko, *Metallofiz. Noveishie Tekhnol.*, **33**, No. 2: 211 (2011) (in Russian).
4. V. I. Perekrestov, *Selektyvni Procesy pry Znyzhenyh Koeficijentah Kondensacii'* [Selective Processes at Reduced Condensation Rates] (Thesis of Disser. for Dr. Tech. Sci.) (Kharkiv: 2006) (in Ukrainian).
5. E. A. Anan'eva, *Razrabotka Tekhnologii Naneseniya Plazmennykh Teplozashchitnyh Pokrytiy na Malorazmernye Vnutrennie Slozhnoprofil'nye Poverkhnosti Detaley Goryachego Trakta GTD* [Development of a Technology for Obtainig Plasma Heat-Shielding Coatings on Small-Sized Internal Complex-Profile Surfaces of Gas Turbine Engine Parts] (Thesis of Disser. for Cand. Tech. Sci.) (Samara: 2007) (in Russian).
6. O. B. Hasiy, *Naukovyy Visnyk NLTU Ukrayiny*, **28**, No. 10: 85 (2018) (in Ukrainian).
7. A. N. Bebenin, V. I. Rudyy, V. N. Litovchenko, R. A. Vorob'ev, I. A. Yankitova, and T. G. Karnavskaya, *Trudy Nizhegorodskogo Gosudarstvennogo Tekhnicheskogo Universiteta im. R. E. Alekseeva*, **107**, No. 5: 143 (2014) (in Russian).
8. G. V. Moskvitin, E. M. Birger, A. N. Polyakov, and G. N. Polyakova, *Metalloobrabotka*, **85**, No. 1: 44 (2015) (in Russian).
9. G. V. Lepesh and E. S. Ivanova, *Tekhniko-Tekhnologicheskie Problemy Servisa*, **36**, No.2: 7 (2016) (in Russian).
10. J. Alami, P. Eklund, J. M. Andersson, M. Lattemann, E. Wallin, J. Bohlmark, P. Persson, and U. Helmersson, *Thin Solid Films*, **515**: 3434 (2007).
11. F. Yee, M. Wotzak, M. L. Cipollo, and K. Traszkowska, *Fall News Bulletin SVC*, **2004**: 28 (2004).
12. I. Ahmad, *Gun Propulsion Technology. Progress in Astronautics and Aeronautics*, **109** (1988).
13. S. L. Lee, R. Wei, J. Lin, R. Chistyakov, D. Schmidt, M. Cipollo, F. Yee, and M. Todaro, *Techn. Report ARWSB-TR-12007*, April (2012).
14. V. N. Nadtoka, R. V. Pankov, and L. N. Deyneko, *Stroitel'stvo. Materialovedenie. Mashinostroenie. Ser. Starodubovskie Chteniya*, No. 58: 471 (2011) (in Russian).
15. M. M. Nikitin, *Fizika i Khimiya Obrabotki Materialov*, No. 2: 27 (2011) (in Russian).
16. L. Mayssel and R. Gleng, *Tekhnologiya Tonkikh Plenok: Spravochnik* [Thin Film Technology: A Guide] (Moscow: Sovetskoe Radio: 1977) (in Russian).
17. S. R. Ignatovich and I. M. Zakiev, *Zavodskaya Laboratoriya*, **77**, No. 1: 61

(2011) (in Russian).
18. G. Brauer, B. Szyszka, M. Vergohl, and R. Bandorf, *Vacuum*, **84**: 12: 1354 (2010).