ТЕХНОЛОГИЧЕСКАЯ МЕХАНИКА

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SURFACE ENGINEERING INNOVATIVE TECHNOLOGY FOR THE REPAIR AND PROTECTION OF SHIPS PARTS

The article describes the methods used for 30 years in the company Cosmos Metallizing Co. Ltd (South Korea) to restore parts of marine vessels. Experience has shown that the repair company should have a whole set of methods and appropriate equipment, since it is impossible to use only one or two technologies. Examples of repair and restoration of various parts of sea transport are given.

Keywords: *restoration and protection of parts, gas-thermal spraying, high-speed spraying, electric arc metallization, hypersonic metallization, wear resistance, hardness*

Introduction. Technological advance in many branches of industry is inseparably connected with surface engineering and possibility to create surfaces with new combinations of physical and mechanical properties. Nowadays, applications of the variety of surface engineering technologies and resulting coatings or surface modification let to obtain significant effects in the reliability, functionality and safety of ships and their mechanisms. Particularly, surface enhancement engineering solutions which lead to reduction of wear, friction and corrosion are particularly in the area of interesting of maritime transport.

Coatings have historically been developed to provide protection against corrosion and erosion that is to protect the material from chemical and physical interaction with its environment. Corrosion and wear problems are still of great relevance in a wide range of industrial applications and products as they result in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and in the service life of many components. Coatings can be applied by various methods, but in recent years, in all industrialized countries, methods of gas-thermal spraying are used to protect against corrosion and repair worn parts. Thermal spraying comprises a group of coating processes in which finely divided metallic or non-metallic materials are deposited in a molten or semi-molten condition to form a coating. The processes comprise: electric arc spray, plasma spray, hypersonic metallization (HM), flames wire and powder spray, high velocity oxy-fuel flames (HVOF), high velocity air-fuel flames (HVAF), detonation guns (D-gun). This article describes the methods used in the restoration and protection of parts of ships at the oldest enterprise in South Korea — Cosmos Metallizing Co. (CMC), engaged in the processes of thermal spraying.

Methods used for spraying. The enterprise CMC was organized in 1989 (January 28) and is currently located in three engineering-production buildings (Figure 1). Location: Youngsan 6 Gil, Chilwon-Eun, Haman-goon, Kyeongnam, South Korea. The technologies and equipment used are presented in Table 1. In addition to the processes listed in Table 1, the enterprise also uses detonation spraying (D-gun), gas-powder surfacing, electric arc welding.

A brief description of the most modern methods of spraying. *High Velocity Oxy-fuel Flame (HVOF) and high velocity air-fuel flame (HVAF).* These processes use significantly higher upstream pressures than flame spray processes and a de Laval nozzle; they are characterized by supersonic speeds of gas flow. The combustion of a hydrocarbon molecule (C_xH_y) either as gas or liquid (kerosene) is achieved with an oxidizer, either oxygen or air, in a chamber at pressures between 0.24 and 0.82 MPa or slightly more for high-power guns. A convergent-divergent de Laval nozzle follows the combustion chamber achieving very high gas velocities (up to 2000 m/s). The last trend is to inject nitrogen (up to 2000 slm) in the combustion chamber to

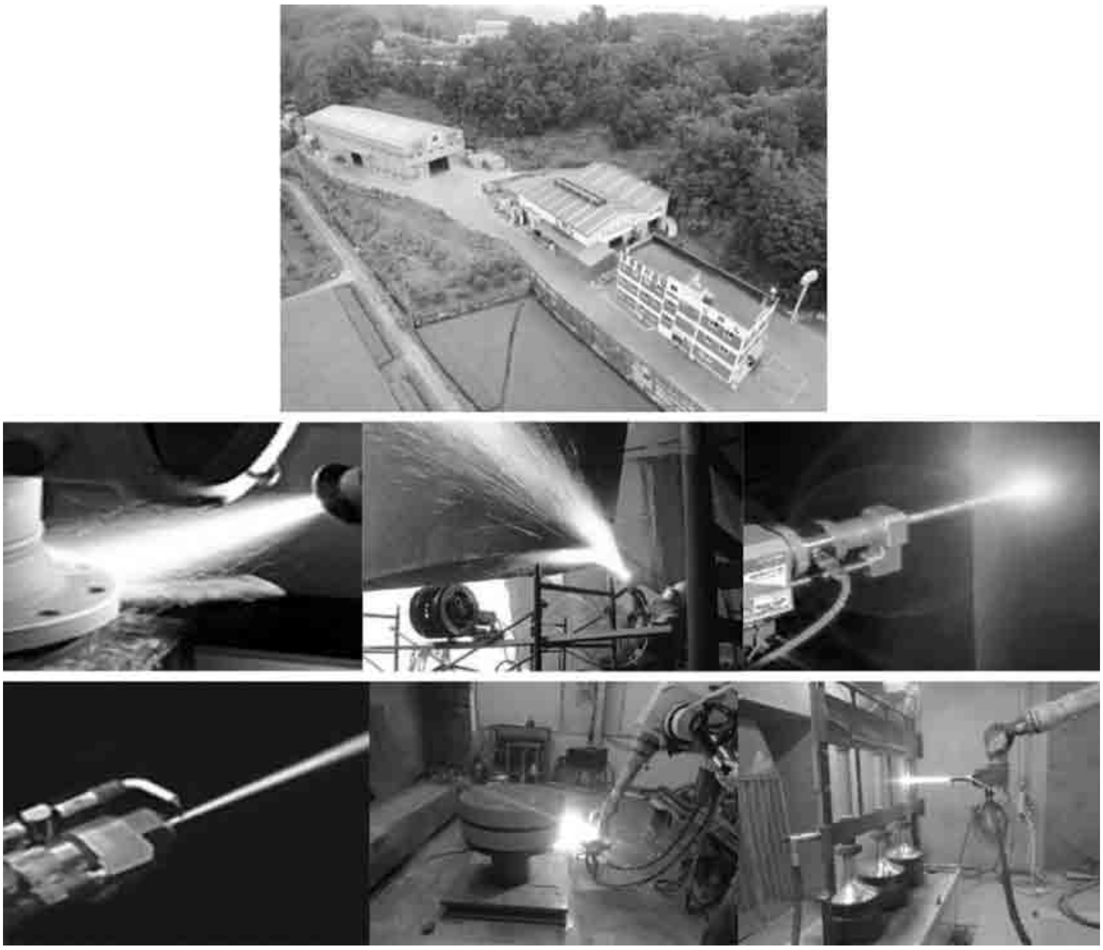

Figure 1 — The appearance of the company's buildings and some of the equipment used

Table 1 — The main processes used in the repair of ships and their technical characteristics

Items	Electric Arc Spray	Hypersonic Metallization	H.V.O.F Coating (High Velocity Oxygen Fuel)	Plasma Powder Spray	Flame Wire Spray
Coating Mat'l Type	Wire	Wire	Powder	Powder	Wire
Flame Temperature	4,100 °C	4,100 °C	3,000 °C	16,500 °C	3,100 °C
Heat Source	Electrical Arc	Arc + Gas	Oxygen + Gas	Plasma Gas	Oxygen + Gas
Particle Velocity	150 m/sec	500 m/sec	1,060 m/sec	650 m/sec	350 m/sec
Bond Strength	8,000 psi	15,000 psi	12,000 psi	10,000 psi	6,000 psi
Porosity	5~15 %	1 %	0.8 %	3 %	8 %
Coating Material	Al, Cu, Ni-Cr Inconel	Al, Ni, Ni+Cr Inconel	WC-Co, Cr_2O_3 Inconel 625	Ceramic, WC, Ni-Al	Al, Mo, Ni-Cr, Zn, St. Steel

increase the gas velocity and decrease its temperature. Mostly powders are used, which are injected either axially or radially or both, depending on the gun design. Few guns have been designed to use wires or cored wires. Also, recently liquid feedstock injection (suspensions or solutions) has been developed, mainly for axial injection. Substrate and coating must be cooled during spraying. Power levels for HVOF guns working with gases is about 100—120 kW, while they can reach 300 kW for guns working with liquid. Globally this process, working mainly with metals, alloys and cermets (one of the most successful applications) has deposition efficiencies of about 70 % for powder flow rates up to 7.2 $kg.h^{-1}$ for gas-fuel guns and up to 12 $kg.h^{-1}$

for liquid-fuel guns. Resulting coating porosities are a few %, with a good adhesion to substrate (roughly 60 to 80 MPa) and low oxygen content (between 0.5 and a few %). The process is rather noisy, dusty with large quantities of explosive gases. As for detonation-gun (see below), the main applications of coatings are protection against abrasion and adhesion (friction) under low load as well as protection against corrosion.

An alternative to the HVOF process, for manufacturing cermet hard coatings, is the high velocity air fuel (HVAF) process which utilizes compressed air, instead of oxygen, for combustion and operates at lower temperatures than the HVOF process [1]. The HVAF process reduces the manufacturing cost of coatings, replacing pure oxygen by compressed air having as consequence coatings which do not show any of the oxidation or decarburization effects after spraying. WC and Cr_xC_y based thermally sprayed coatings are extensively used to decrease the friction coefficient between various sliding components and to improve corrosion resistance in many industries [1, 2]. Due to the Cr content the coatings are suitable for high-temperature applications.

Detonation gun (D-gun). The detonation is mainly generated in acetylene- or hydrogenoxygen mixtures (with some nitrogen to modify the detonation parameters) contained in a tube closed at one of its ends. The shock wave created by the combustion in the highly compressed explosive medium results in a high pressure wave (about 2 MPa) pushing particles heated by the combustion gases. Gas velocities of more than 2000 m/s are achieved. Contrary to the flame and HVOF devices where combustible gases and powders are continuously fed within the gun, combustible gases and powder are fed in cycles repeated at a frequency of 3 to 100 Hz. The resulting deposits are dense and tightly bonded to the substrate. The process is the nosiest of all the thermal spray processes (more than 150 dB). Coating porosity is low (below 1 %) and its oxygen content is between 0.1–0.5 %. The deposition efficiency is about 90 %, for powder flow rates of 1 to 2 kg.h^{-1}. The sprayed materials are mainly powders of metals, alloys and cermets; some oxides can be sprayed but with particle sizes in the 20-μm range or below. Substrate and coating must be cooled during spraying. The main applications are coatings against abrasion and adhesion (friction) under low load as well as coatings against corrosion. On-site spraying: Many applications, especially those on big parts, e. g. a bridge, require that spraying is performed on site. This is feasible with wire arc, flame and in certain cases HVOF.

Corrosion protection and corrosion resistant coatings. We give below the main factors that provide a high corrosivity of seawater.

Salinity. The salt content of seawater is higher than that of fresh water. The salt content in water directly affects the conductivity and oxygen content of water. With the increase of salt content in water, the electrical conductivity of water increases but the oxygen content decreases. Salinity in seawater is not consistent with the behavior of NaCl, which is due to the calcium and magnesium ions contained in the metal surface precipitation of calcium carbonate and magnesium hydroxide precipitation, the metal has a certain protective effect. In the estuary area, the salinity of seawater is lower than that in the sea, the content of calcium and magnesium is small, and the corrosiveness of metal increases. Chloride in seawater can destroy the oxide film on the surface of metal and form a complex with metal ions, which produce hydrogen ions during hydrolysis, so that the acidity of seawater increases, and the local corrosion of the metal is strengthened.

Conductivity. Seawater has not only high salt content, and almost all of which is in the ionization state of the salt, which makes the sea water as a good conductivity of the electrolyte. This determines the process of seawater corrosion, not only micro-battery corrosion activity, while the macro battery activity is also large. The results show that with the increase of conductivity, microcrystalline corrosion and macroscopic cell corrosion will accelerate.

Dissolved oxygen. The more the dissolved oxygen content of the sea, the higher the electrode potential of the metal in the sea, the faster the corrosion rate of the metal. But for aluminum and stainless steel a class of metal, when it is oxidized, the surface to form a thin layer of oxide film to protect the metal is no longer corroded, that is, to maintain a passive state. In addition, in the absence of dissolved oxygen in the sea, copper and iron have almost no corrosion.

pH. In general, the pH of the sea water is conducive to the inhibition of seawater corrosion of steel. However, the pH of the seawater is far from the effect of oxygen content on the corrosion. Although the surface seawater pH is higher than that of the deep seawater, the corrosion of the surface seawater is far higher due to the photosynthesis of the seawater in the surface Stronger than deep seawater, which is consistent with the actual experimental conclusion.

Marine environments are some of the most demanding for coatings. Corrosion resistant coatings protect metal components against degradation due to moisture, salt spray, oxidation or exposure to a variety of environmental or industrial chemicals. Anti-corrosion coating allows for added protection of metal surfaces and acts as a barrier to inhibit the contact between chemical compounds or corrosive materials. In addition to corrosion prevention, many of the coatings listed below also provide a bonus of abrasion resistance, non-stick performance and chemical protection. Metal Coatings provides both corrosion resistant bolt coating services and rust protection fastener coating services to prevent rust and wear.

Corrosion protection coatings on CMC are formed using spraying techniques wire materials (aluminum, zinc, various non-ferrous alloys). This is due to the fact that wire materials are much cheaper than powders, and wire spraying methods (arc metallization) are

Table 2 — Examples of deposition of corrosion-resistant coatings by arc metallization

Customer	Project Name	Part	Area
Hyundai Heavy Industries Co., Ltd.	Phillips Bayu-Undan Gas Recycle Project	Cellar Deck & Piping	11,280 m^2
Daewoo Shipbuilding & Marine Engineering Co., Ltd.	Exxon Mobile Pipe Repair TSA coating	Piping	600 m^2
Il-sung Co. Ltd.	Odoptu FSP	Vessel	620 m^2
	Chayvo Ope Expansion	Vessel	890 m^2
	Ruwats 4th NGL	Vessel	1,740 m^2
National Oilwell Varco Co., Ltd.	Main Boom & Knuckle Boom	Boom	910 m^2
Daewoo Shipbuilding & Marine Engineering Co., Ltd.	P6049 Flare Tower	Flare Tower	649 m^2
	P6052(Wheastone)	Flare Boom	3,449 m^2
	P6054(Inpex)	Flare Boom	2,507 m^2
	P6056(Mariner) / P6058(Gina Krog)	Flare Tower	3,386 m^2
	Yamal LNG Heating Coil T.S.A Coating	Heating Coil	2,418~
			2,430 m^2
Wooyang HC Co., Ltd.	Toyo / Brazil P74	Vessel	296 m^2
Doosan Heavy Industries Co., Ltd.	Integrated Refinery Expansion	Vessel	1,110 m^2
	Longford Gas Conditioning Plant	Vessel	1,584 m^2
Hanjoo Machine Industrial Co., Ltd.	Nsrp Complex	Vessel	150 m^2
CCI Korea Co., Ltd.	Statoil Gina Krog	Valve	472 m^2
Sebo Tech Co., Ltd.	DSME – 6054	Sub-Structure	859 m^2
	DSME – 6056	Sub-Structure	650 m^2
Korea zinc Co., Ltd.	Hwang-san 1st Line Converter	In-Converter	200 m^2
Samsung Heavy Industry Co., Ltd.	SN2090-2091 Johan Sverdrup T.S.A Coating	Cellar Deck Under	24,370 m^2
	7115 Martin PJT T.S.A Coating	Flare Tower	2,050 m^2

rather high-performance. The spraying capacity in this case is an important factor, since the surface areas that are covered are very large (Table 2).

Aluminum was used widely in many sectors such as chemical plant, manufacturing lines, and marine industries. The advantage of using aluminum is due to their excellent corrosion resistance property and thus it becomes a priority in materials selections in most industries [3]. Aluminum coatings were applied to the hulls of ships, tanks, installation structures, bridges, masts, towers, fences, port facilities (Table 3). Spray parameters used for the coating production: wire diameter 1.8–2.3 mm; wire feed rate 98.7 g/min; spray distance 95 mm; increment step 15 mm; traverse speed 0.5 m/s; nominal thickness 200–300 μm.

Use of aluminum alloys in seawater is of continuous interest because of the need for light-weight structural materials. As long as galvanic contact with more noble metals is avoided, most structural alloys, such as those in the AA1000 (commercially pure), 3000 (AlMn), 5000 (AlMg), and 6000 (AlMgSi) series, are resistant to corrosion in seawater, especially the so-called seawater-resistant alloys in the 5000-series. Under stagnant and low flow-rate conditions, uniform corrosion rate lies below 1 μm/y [3]. Crevice corrosion is normally not a problem for aluminum alloys. However, it is observed in joints and it is basically a design problem like galvanic corrosion. Pitting, flow-dependent corrosion, and erosion–corrosion are the basic corrosion problems for aluminum alloys in seawater.

The coating was characterized by SEM. The top surface had many defects which is a well-known feature for such coatings. The melted metal particles continuously impinged on the base metals and formed layer upon layer of plate-like microstructures. With the high velocity deposition of the coating and after rapid cooling at room temperature, the air diffused from the coating surface resulted in the formation of a splashed zone or pores/defects on the coating surface. These splash zones contributed to getting moisture and other aggressive ions from the atmosphere. A chemical analysis of the coating is shown in the EDS spectra.

Table 3 — Examples of the protection of steel structures from the effects of seawater by arc metallization of aluminum (99.5%)

Customer	Work performed	
Daewoo Shipbuilding & Marine Engineering, Sebo Tech	Inpex (P6054) Project Helideck Sub-Structure Mariner Project (P6056) Helideck Sub-Structure	
	 Area — 859 m^2	 Area — 650 m^2
Doosan Construction Co., Ltd.	Integrated Refinery Expansion: Vessel Longford Gas Conditioning Plant: Vessel	
	 Area — 1,110 m^2	 Area — 1,584 m^2

On the surface of coating, 2.20 wt.% oxygen was present; this oxygen might have come during the spraying of the coating at high temperature and in-flight particles oxidation from the atmosphere.

We have investigated the corrosion protection of Al coating before and after anodic oxidation with the test for immersion in seawater. The mechanisms of corrosion resistance of Al and anodic oxide layers in seawater were also investigated. The results show that the thickness of Al coating is about 300 μm by arc spraying, the sample surfaces become loose after seawater immersion corrosion and Cl- and O_2-penetrate into the substrate from the cracks, destroying the binding properties of coating–substrate, and the coating fails. After anodic oxidation, the oxide layer is formed in the surface of Al coating with the thickness of about 30 μm; the corrosion products are mainly composed of $Al(OH)_3$, which barraged the holes caused by seawater corrosion. The corrosion cracks are formed during the corrosion, while the number and depth of cracks decrease obviously after anodic oxidation treatment. The corrosion of Al coating becomes the local corrosion after anodic oxidation treatment, and the grains are smaller, which are easily nucleated to form a new corrosion resistance layer [4].

Figure 2 — General view of the offshore oil platform, which used steel piles with aluminum coatings

Good adhesion is important for preventing blistering of TSA (thermally sprayed aluminium) in immersed conditions. This is especially true for coatings applied to underwater elements of offshore oil platforms (Figure 2). Blistering is the separation of the coating from the substrate, and is a common and wellstudied phenomenon in organic coatings. It does, however, also occur in TSA coatings as well. Blistering tends to become more extensive with increasing temperatures, and so the quality of the coating must be high, if used at high temperatures. The life time of a TSA coating is normally determined by the dissolution rate of the coating [5]. However, if blistering occurs in TSA the lifetime of the coating is strongly reduced. The porosity in the coating might effect the blistering properties of the coating, where high porosity leads to a higher probability of blistering. This is because corrosion products accumulate in pores and at the substrate-coating interface, which might occur if the coating is permeable. This creates internal stresses in the coating and may lead to blistering.

Wear resistant and thermal barrier coatings. More than 60% of the parts that come to us for restoration

Table 4 — Examples of applying heat-resistant and wear-resistant coatings

Customer	Part	Coating
GS Caltex	Tube sheet	H.V.O.F
	Tower (Shell/Column)	Arc + HVOF
S-Oil	Tube sheet	H.V.O.F
	Tower (Shell/Column)	Arc + HVOF
SK energy	Tube sheet	H.V.O.F
Hyundai Oilbank	Tube sheet	H.V.O.F
Domestic Power Plant	Blade (Bucket/LSB)	H.V.O.F
	Rotor/Cover	HVOF/Arc
POSCO	Boiler Tube	Cladding

are sprayed by the HVOF method. HVOF-coatings increase surface hardness resulting in a substantial increase in material life. Normal carbon steel hardness is 22 HRC by coating with WC–Co the hardness is increased to 64 HRC, almost three times the hardness of the original material.

Table 4 presents data on the application of wear-resistant coatings (Cr_3C_2, Inconel 625) only in 2018. Table 5 presents some typical ship parts with wear-resistant coatings.

If for the application of wear-resistant coatings we mainly use tungsten carbide — cobalt, chromium carbide, and inconel, then the formation of heat-resistant coatings requires the use of multi-component compounds. Thermal barrier coatings (TBC) are widely used to increase the efficiency and protection of metallic components that suffer degradation due to corrosion, oxidation, or excessive heat load during service in thermally drastic environments. Some of its main applications are on gas turbines engines and also in aerospace and aircraft applications. The most common TBC-systems consist of a nickel-base super alloy as substrate, a MCrAlY layer (M: Ni, Co, Fe, or combination of these elements) as bond coat. MCrAlYs are one of the most important protective coating materials applied to gas turbine parts. MCrAlY coatings protect the components against high temperature oxidation and hot corrosion attack, typically deposited by Vacuum Plasma Spray (VPS) or Low-Pressure Plasma Spray (LPPS), by Air Plasma Spray (APS), and recently by HVOF.

MCrAlY systems provide some benefits of Ni and Co base superalloys. In particular CoNiCrAlY alloy provides protection against high temperature oxidation, while CoNiCrAlY alloy provides excellent protection against molten salt corrosion. Due to the combination of Ni + Co the MCrAlY system it now widely used as an option for application that requires protection against oxidation at high temperatures (hot corrosion), and where the thermal insulation it's not a primary requirement.

The aluminum effect at a MCrAlY system it's to provide an oxide layer that can be regenerated constantly to prevent the aggressive attack of chemical species, such as Cl- and sulfides, which can be harmful to the coating and the base metal, while chromium helps stability of total oxide layer to maintain its protective features. However, excessive content of Cr affects the stability. Finally, yttrium helps maintain adherence of the oxide layer on the surface of the substrate.

The hardness of thermal barrier coatings is very sensitive to technological spraying modes, for example,

Table 5 — Typical ship parts with wear-resistant coatings

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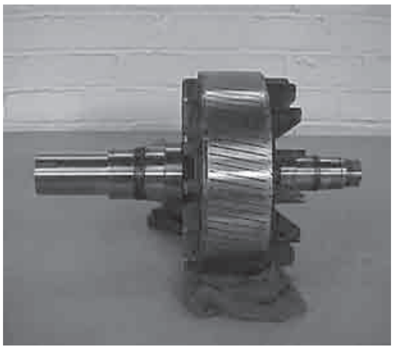
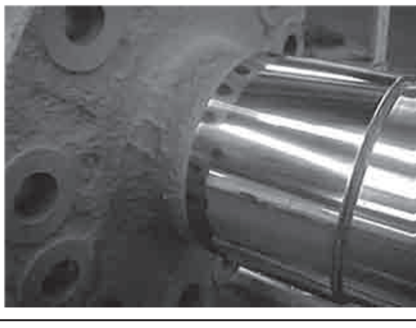
bearing area repaired with HVOF applied WC-Co / NI

Main propulsion shafts installed in strut bearings after repair</td><td> </td></tr>
<tr><td>Seal repaired with HVOF applied WC-Co / Ni

The process of repairing marine engine valves (HVOF)</td><td> </td></tr>
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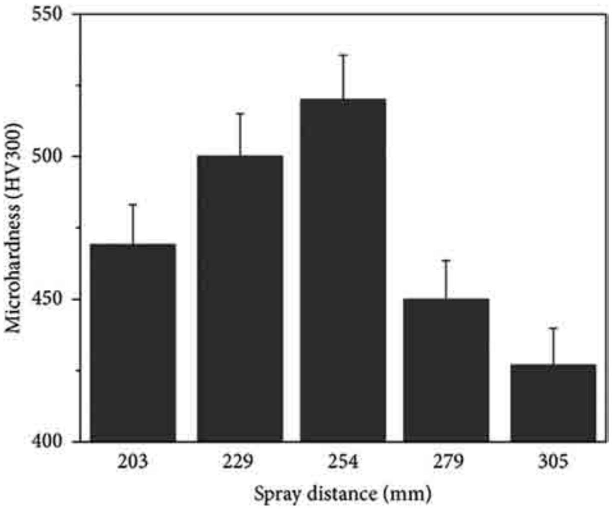

Figure 3 — Microhardness Co32Ni21Cr8Al0.5Y coating to different spray distances employed

to the spraying distance. Figure 3 shows the microhardness results of the five spray distances used.

It can be seen that the sample sprayed from a distance of 254 mm is the one with a higher hardness, followed by the sample that was sprayed at 229 mm.

Conclusion. Based on 30 years of experience in restoring and hardening parts of sea vessels, the following conclusions can be drawn:

- the repair company should have a whole set of methods and appropriate equipment, since it is impossible to use only one or two technologies (there is no one cure for all ills);
- the most effective methods for applying corrosion-resistant coatings are the methods of metallization — electric arc metallization and hypersonic metallization;
- for the application of wear-resistant coatings with a hardness of more than 55 HRC it is advisable to use HVOF-method, but it depends on the cost of the part;
- for coatings with a hardness of 40–52 HRC, it is rational to use the spraying of steel wires, for example, by the method of hypersonic metallization;
- when applying thermal barrier coatings, one should always consider their dependence on the spraying distance, which is due to the large number of components in the sprayed material.

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ИННОВАЦИОННЫЕ ТЕХНОЛОГИИ ИНЖЕНЕРИИ ПОВЕРХНОСТИ ПРИ РЕМОНТЕ И ЗАЩИТЕ ДЕТАЛЕЙ МОРСКИХ СУДОВ

В статье описаны методы, применяемые в течение 30 лет в компании Cosmos Metallizing Co. Ltd (Южная Корея) для восстановления деталей морских судов. Опыт показал, что ремонтная компания должна иметь целый комплекс методов и соответствующее оборудование в связи с невозможностью использования только одной или двух технологий. Приведены примеры ремонта и восстановления различных частей морского транспорта.

Ключевые слова: *восстановление и защита деталей, газотермическое напыление, высокоскоростное напыление, электродуговая металлизация, гиперзвуковая металлизация, износостойкость, твердость*