## PROPERTIES OF IRON-BASE ALLOYS FOR PLASMA POWDER HARD-FACING OF SEALING SURFACES OF FITTINGS

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The paper gives investigation results on properties of iron-base alloys designed for plasma powder hard-facing of sealing surfaces of various-purpose fittings. It is shown that deposited metal 15Kh19N9M4S5G3D features the best combination of corrosion resistance, hot hardness, score and heat resistance.

**Keywords:** plasma powder hard-facing, hard-facing consumables, properties of deposited metal, hard-facing of fittings, corrosion resistance, hot hardness

Iron-base alloys are widely applied for hard-facing of sealing surfaces of fittings used in power, petrochemical, marine and general engineering. Many CIS enterprises use manual or mechanised electric arc welding for these purposes. Depending on the service conditions of fittings, manual electric arc welding is performed by using electrodes UONI-13/NZh-2, TsN-6L, TsN-12M and TsN-24, and mechanised submerged arc welding — by using solid wires Np-20Kh14, Sv-20Kh13, Sv-10Kh17T and Sv-13Kh25T, as well as flux-cored wires PP-AN106, PP-AN133, PP-AN157 and flux-cored strip PL-AN150.

Compared to manual arc welding using stick electrodes, mechanised electric arc welding using fluxcored wires provides better quality of the deposited metal. However, it is performed at least in three layers, this leading to excessive utilisation of welding consumables and increase in time of the hard-facing process [1]. In addition, mechanised electric arc welding of small-diameter parts ( $\leq 200 \text{ mm}$ ) involves difficulties related to removal of slag crust from the previous deposited layer. In this case, when welding is performed on seats, it is necessary to use forming devices.

As proved by experience, plasma powder hard-facing provides deposited metal of a preset chemical composition even in the first layer, and is free from many drawbacks characteristic of arc hard-facing [2].

The task of this study was to investigate properties of iron-base alloys as applied to plasma powder hardfacing of sealing surfaces of different-purpose fittings.

Based on the available experience, the following materials were chosen for the investigations: chromium steel 22Kh16N2M, chrome-nickel-silicon steel 08Kh17N8S6G (corresponds to metal deposited with electrodes TsN-6L), steel 13Kh16N8M5S5G4B (corresponds to metal deposited with electrodes TsN-12M, foreign-made powders of the DS ZN12, Hoganas X-FeSP573 and C1111 grades, and flux-cored wire of the SK AF Antinit Dur500 grade [3]), experimental chrome-nickel-silicon steels 04Kh19N10M4S5GFA and 15Kh19N9M4S5G3D differing in the contents of carbon, vanadium, nitrogen and copper, and nickel alloy N77Kh16S3R3 (used as a reference).

The experimental chrome-nickel-silicon steels were alloyed with nitrogen to increase their ductility, and with copper - to improve their antifriction properties. Molybdenum in steel 22Kh16N2M provides increase in its heat resistance and hardness in the deposited state.

All of the above hard-facing consumables were used in the form of powders with a particle size of  $80-200 \ \mu\text{m}$ . They were made by nitrogen atomisation of molten metal under industrial conditions.

Plasma powder hard-facing for the investigations was carried out by using standard equipment fitted with the plasmatron with a local lateral introduction of powder into the arc, which provides stability of the hard-facing process when using ferromagnetic powders [4].

Measuring of hardness at working temperatures was performed by using the «Pomp Celtic» Instrument «Pomea» under a load of 108 N on the indenter, holding for 1 min and air pressure of 1.33 MPa in the working chamber. Hardness was measured on the hard-faced samples with a diameter of 37 mm and height of 5 mm.

Tests to general corrosion resistance were carried out in water vapour and in air at a temperature of 700 °C for 500 h, as well as in distilled water at a temperature of 300 °C and pressure of 20 MPa for 1000 h. Test specimens measuring  $40 \times 10 \times 3.5$  mm were cut out from the deposited metal after tempering at 600 °C for 2 h.

Resistance of the deposited metal to intercrystalline corrosion (ICC) was investigated by the standard AMU methods (GOST 6032–2003) [5] and electrochemical method [6]. For the latter, the test specimens measuring  $30 \times 10 \times 50$  mm were held in the NClO<sub>4</sub> + NaCl solution after provoking tempering at temperatures of 650, 730 and 850 °C for 2 h. The sensitivity to ICC was evaluated from growth of anode

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Figure 1. Appearance of rings with deposited layer for heat resistance tests

dissolution current i at a direct potential of +0.3 V within the activation region.

Tests to score resistance were conducted by using a special test rig in the vapour environment under the following conditions: T = 300 °C and P = 12 MPa, T = 540 °C and P = 16 MPa, and T = 545 °C and P == 25.5 MPa. Real components of the DN150 valve gates, the sealing surfaces of which operate under conditions of the highest specific pressure, were used as test specimens. The accepted maximal quantity of openings and closings in the tests was equal to 100. The path of relative movement of the gate components under the pressure was about 32 mm per cycle. The state of the gates during the tests was monitored on a base of vapour leaks. The permissible vapour leak was about 55 g/min. The value of a specific score, i.e. the ratio of a maximal depth of scratches (in micrometres) to a total friction path (in metres) was used as an indicator of score resistance.

Tests to crack resistance under thermal cycling (heat resistance) were conducted on rings of steel 20. The rings were 130 mm in outside diameter, 18 mm wide and 25 mm high. They were subjected to onesided hard-facing on their end surfaces (Figure 1). Thickness of the deposited layer was 3.8–4.0 mm. Hard-facing was followed by tempering at a temperature of 600 °C for 2 h. The tests provided for heating of the rings in electric furnace to 300 °C and cooling in running water to room temperature. Heat resistance of the alloys investigated was evaluated from the quan-

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**Figure 2.** Temperature dependence of hardness HV of the deposited metal for hardening of sealing surfaces [6]: 1 - 08Kh17N8S6G; 2 - 04Kh19N10M4S5GFA; 3 - 22Kh16N2M; 4 - 13Kh16N8M5S5G4B; 5 - 15Kh19N9M4S5G3D; 6 - N77Kh16S3R3; 7 - Stellite No.6

tity of thermal cycles to formation of cracks in the deposited layer. The presence of cracks was detected by the fluorescent method.

Dependence of hardness of the investigated alloys on temperature is shown in Figure 2. To compare, the Figure shows hot hardness of nickel and cobalt alloys, which are characterised by the excellent performance. All types of the iron-base deposited metal, except for 08Kh17N8S6G, preserve a sufficiently high level of hardness at T = 400-600 °C. The highest value of hot hardness was exhibited by standard allov 13Kh16N8M5S5G4B and experimental deposited metal 15Kh19N9M4S5G3D. However, their hot hardness was lower than that of the nickel and cobalt alloys.

All iron-base materials oxidise in water vapour and in air much less intensively than the nickel-base alloy. All types of the investigated deposited metals are classed as «highly resistant» to corrosion in distilled water (GOST 13819–68).

As seen from potentiometric direct anode curves (Figure 3), deposited metals 22Kh16N2M and 08Kh17N8S6G are characterised by increased current i at a potential of +0.3 V, this being indicative of their sensitivity to ICC. The rest of the deposited metals feature resistance to ICC, as they have no activation region at a potential of +0.3 V.



**Figure 3.** Potentiometric direct anode curves of deposited metals in tempering at different temperatures of 650 (*a*), 730 (*b*) and 850 (*c*) °C for 2 h: 1 - 22Kh16N2M; 2 - 08Kh17N8S6G; 3 - 13Kh16N8M5S5G4B; 4 - 04Kh19N10M4S5GFA; 5 - 15Kh19N9M4S5G3D



Score and corrosion resistance test results [9]

Type of deposited metal	Hardness of deposited metal <i>HRC</i>	Specific score, μm/m	Test time, h		
			500		1000
			Water vapour	Air	Distilled water
08Kh17N8S6G	31-34	9.3	0.0135	0.0186	0.0097
13Kh16N8M5S5G4B	45-49	4.6	0.0093	0.0145	0.0061
22Kh16N2M	42-45	14.5	0.0087	0.0137	0.0081
15Kh19N9M4S5G3D	48-51	1.8	0.0075	0.0132	0.0051
04Kh19N10M4S5GFA	37-42	2.8	0.0061	0.0121	0.0041
N77Kh16S3R3	51-53	1.3	0.0991	0.0250	0.0038

When tested to ICC resistance by the AMU method, all specimens after boiling in a solution containing 160 g/dm<sup>3</sup> CuSO<sub>4</sub> and 100 g/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> for 24 h fractured in bending to 90°. The integrated tests show that ICC develops deep into the hard-faced layer in deposited metals 22Kh16N2M and 08Kh17N8S6G as a result of depletion of the boundary regions of grains in chromium.

Normally, score and heat resistance of materials of the sealing surfaces is evaluated by procedures that provide for testing of small specimens cut out from the deposited metal, or 45 mm diameter hard-faced disks using special laboratory rigs simulating service conditions [7, 8].

In contrast to testing of small specimens, our experiments on real components make it possible to allow for a number of factors that may cause or accelerate formation of thermal fatigue cracks and scores, i.e. the state of structure of the deposited layer and presence of substantial stresses in it (working, welding, thermal, etc.), as well as technological defects (pores, lacks of fusion, non-metallic inclusions, etc.).

The tests show that the deposited metal of the type of chromium steel 22Kh16N2M features a good score resistance at a vapour temperature of 300 °C and pressure of 12 MPa. However, under conditions of high parameters of the working environment (545 °C and 25.5 MPa, respectively), its resistance decreases to a considerable extent (Table), although hot hardness in this case remains at a sufficiently high level (see Figure 2).

Among the chrome-nickel-silicon materials, the best score resistance was exhibited by deposited metal 15Kh19N9M4S5G3D. Both in manual welding with electrodes TsN-6L and in plasma welding by using powder as a filler, deposited metal of the 08Kh17N8S6G type was inferior in score resistance to 13Kh16N8M5S5G4B [9, 10]. As seen from the Table, all types of the iron-base deposited metals are much inferior in score resistance to nickel alloys.

Deposited metal 13Kh16N8M5S5G4B is characterised by a low heat resistance, independently of the welding method and type of a welding consumable (Figure 4). It should be noted that heat resistance of the materials under consideration decreases as a rule with increase in their hardness and score resistance, which is usually accompanied by a dramatic decrease in ductility. At the same time, the optimal level of these characteristics of the Fe–Cr–Ni–Si–Mo system deposited metals can be provided owing to rational complex alloying and modification. As seen from Figure 3, deposited metal 15Kh19N9M4S5G3D featured the optimal heat resistance. Having approximately the same hardness as nickel-base alloy of the N77Kh16S3R3 type (*HRC* 50–51), it provides approximately identical heat resistance.

Deposited metal 15Kh19N9M4S5G3D in the initial state has an austenitic-ferritic structure, the volume content of the ferrite phase being 40 %. Depending on the type of the base metal and its thermal-physical characteristics determining solidification conditions of the deposited metal, structure of the said type of the deposited metal markedly changes (Figure 5).

After welding, this metal has a comparatively high hardness (*HRC* 42–44), this indicating to the probable presence of the carbide-silicide phase in its structure. The concentration of ferritising elements (chromium, silicon, molybdenum, etc.) in the ferrite phase is known to be higher than in the austenite phase. Diffusion mobility of these elements in it is higher as well, this leading to a more intensive hardening of the ferrite component due to its ordering and decomposition processes occurring during holding within the appropriate temperature range. Tempering in a 650–



**Figure 4.** Heat resistance of deposited metal [9]: 1 - 13Kh16N8M5S5G4B; 2 - 22Kh16N2M; 3 - 15Kh19N9M4S5G3D; 4 - 04Kh20N10M4S5GFA; 5 - N77Kh16S3R3; 6 - 08Kh17N8S6G; N - quantity of thermal cycles to formation of the first crack



**Figure 5.** Microstructures ( $\times$ 500) of metal deposited with powder 15Kh19N9M4S5G3D on steel 20 (*a*, *d*), 12Kh1MF (*b*, *e*) and 08Kh18N10T (*c*, *f*) in the initial state (*a*-*c*) and after tempering at 650 °C for 2 h (*d*-*f*)

850 °C range leads to increase in hardness of this type of the deposited metal to *HRC* 46–51 and is accompanied, according to the magnetic measurement data, by a marked decrease in the amount of ferrite — the higher the ferrite content of the initial structure, the more substantial is the said decrease (see Figure 5). Probably, decomposition of ferrite under such conditions occurs by the following scheme:  $\alpha \rightarrow \gamma'' + Me_6C$  type carbides + intermetallics of the  $\sigma$ -phase type + silicides of the Cr<sub>3</sub>Ni<sub>5</sub>Si<sub>2</sub> type (where  $\alpha$  is the ferrite phase, and  $\gamma''$  is the secondary austenite).

As seen from Figure 6, owing to a low penetration of the base metal, which is characteristic of plasma welding, the required hardness and preset chemical

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composition of the deposited metal are achieved already at a distance of 0.3–0.5 mm from the fusion surface. As a result of ageing at 600 °C for 500 and 1000 h, the ferrite decomposition processes become more completed. No substantial changes in hardness of the deposited layer take place, and no hard and brittle components form in the fusion zone, which should have a favourable effect on performance and reliability of the hard-faced fittings.

As proved by the tests conducted on iron-base alloys under the conditions that are as close as possible to the service conditions of power fittings, the best combination of corrosion resistance, hot hardness, score and heat resistance was exhibited by deposited



**Figure 6.** Distribution of hardness in height of deposited layer 15Kh19N9M4S5G3D: a - base metal steel 20; b - base metal steel 12Kh1MF; c - base metal steel 08Kh18N10T in the initial state (1), after tempering (2), and after tempering and ageing at T = 600 °C for 500 (3) and 1000 (4) h, respectively



metal 15Kh19N9M4S5G3D. This material is not inferior in heat resistance at dramatic thermal cycles and in score resistance to known chrome-nickel alloys containing boron and silicon, and is much superior to metal 13Kh16N8M5S5G4B (hard-facing with electrodes TsN-12M and their analogues). As to a number of service properties and price, chromium steel 22Kh16N2M is fully acceptable for hard-facing of sealing surfaces of components of general-engineering fittings, which are used at a temperature of up to 400 °C and pressure of 16 MPa.

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## PARTICLE DISPERSITY AND MANGANESE VALENCE IN WELDING AEROSOL

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Method of X-ray photoelectron spectroscopy was used to establish the valent state of manganese compounds in the welding aerosol. Valent state of manganese compounds ( $Mn^{+4}$ ) was found in welding with basic electrodes. Analysis of dispersity of welding aerosol solid compound was performed using the method of laser granulometry.

**Keywords:** arc welding, coated electrodes, solid component of welding aerosol, particle dispersity, bimodal distribution, agglomerates, manganese valence

In welding of carbon low-alloyed steels, manganese compounds are the most hazardous components of the solid component of welding aerosol (SCWA) [1, 2]. Toxicity of these compounds, in its turn, depends on manganese valence and increases with the increase of its oxidation level. Threshold limit values (TLV) of manganese and its compounds in the welding aerosol (WA) in the working zone air are equal to 0.6/0.2and  $0.3/0.1 \text{ mg/m}^3$  (numerator shows the maximum one time, and the denominator - shift average TLV) at its content in WA below 20 % and from 20 up to 30 %, respectively [3]. Modern norms of manganese TLV in WA and recommendations do not separate manganese compounds by valence and establish one TLV norm equal to 0.2 mg/m<sup>3</sup> [4, 5]. Manganese in WA belongs to the second hazard class [3].

A number of investigations devoted to study of SCWA composition [1, 6–9] showed that the most probable manganese state is  $Mn^{2+}$ ,  $Mn^{3+}$ .

Staff members of the E.O. Paton Electric Welding Institute and I.M. Frantsevich Institute of Problems of Materials Science studied the valent state of manganese in aerosols formed in welding with electrodes with coating of rutile and basic types. Investigations were performed using X-ray photoelectronic spectrometer ES-2401.

Investigations were performed using SCWA forming in welding with test electrodes with coating of rutile (electrode index E4) and basic types (electrode index PSh4 and PSh5). Here, SCWA for analysis were selected by deposition on a filter, mechanical removal from the filter and placing into a brass weighing bottle with subsequent filling of the latter by argon to prevent final oxidation of samples at contact with ambient oxygen. Spectra were excited by non-monochromatized radiation of Mg $K_{\alpha}$ -lines. SCWA were rubbed into the copper plate surface, which was first ground and etched by nitric acid. Studied samples completely covered the copper plate, so that lines corresponding to copper atoms were not observed in the plain spectra. Mn2p- and Mn2p-spectra were filmed in the plain mode and optimum mode of Mn2p-spectra measurement was selected for investigations. By the results of obtained Mn3p-spectra (Figure 1, a) it was established that manganese in SCWA of electrodes with basic type coating (PSh4, PSh5) is present in valent state +4 (peak I), and in SCWA of electrodes with a

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