

# Surface Alloying of Thin-Walled Tube Sections Using High Temperature Pulsed Plasma Fluxes

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**Abstract** – A technique has been improved and regimes of the liquid-phase alloying by aluminum and chromium of the surface layers of thin-walled tubes made of a 16Cr12MoWSiNbVB chromium steel using high temperature pulsed helium plasma fluxes have been developed. It has been shown that after liquid-phase alloying the surface morphology of a sample depends on the type and the thickness of an applied film, as well as the regimes of a plasma treatment. At that, the distribution of alloying elements is sufficiently uniform in the surface layer 10 ... 15  $\mu\text{m}$  thick at the thickness of an applied film of  $\sim 0.5 \mu\text{m}$ . The mean Al-content changes from 3 to 14 wt. %, and the Cr-content increases from  $\sim 11.0$  to 15.0...16.5 wt. %. The surface alloying has been found to result in a significant increase of the corrosion resistance of steel tubes in a liquid lead flow with an increased content of oxygen at 650 °C.

## 1. Introduction

One of the prospective technological directions of using the concentrated energy fluxes (laser radiation, electron and high current pulsed ion beams, pulsed plasma fluxes and others) is the surface liquid-phase alloying of materials [1, 2].

The essence of the method is to preliminarily apply a thin layer of the necessary alloying element on the surface of an article (a material) with a subsequent remelting and a mutual mixing of the applied layer's elements and the base's material under the action by concentrated energy fluxes. Previously [3] it was shown that there was a possibility to use high temperature pulsed plasma fluxes (HTPPF) for the surface liquid-phase alloying of plate and massive samples made of a type St. 3 low-carbon steel by nickel, chromium, titanium and vanadium. Surface-alloyed layers 8.5...47.5  $\mu\text{m}$  in thickness with a sufficiently uniform distribution, along their depth, of an alloying element with a concentration changing in the 0.5 ... 20 wt. % range are obtained, depending on the kind of an alloying element, the thickness of a preliminarily applied film and the regimes of a plasma treatment.

The aim of this work is to improve the technique of alloying the surface layers of thin-walled tubes using high temperature pulsed gas plasma and to study

their structure-phase state and corrosion resistance in liquid lead flow.

## 2. Technique of Surface Alloying

Sections of thin-walled (0.5 mm) tubes 10.5 mm in diameter and 50 mm in length, made of the type 16Cr12MoWSiNbVB (EP823) chromium steel were used as samples for the investigation.

The surface alloying technique included the following stages: 1. Preliminary purification of the tube surface by a weak HTPPF-action. 2. Application of thin (0.2...1.3  $\mu\text{m}$ ) uniform layers of alloying elements onto the external tube surface. 3. Intermediate vacuum annealing for a diffusion adherence of the coating with the substrate and for increasing its adhesion. 4. Liquid-phase mixing of the applied alloying element with the material of the tube surface layers under the action by pulsed plasma fluxes.

Coatings were applied by thermal evaporative precipitation in vacuum ( $\sim 10^{-3}$  Pa) of chemically pure aluminum (99.99 %), iodide chromium and a silumin-base alloy (in wt. %) Al-12%Si-0.7%Cr-0.25%Mo. At that, a boat-type evaporator with a resistance heating was used.

To form a uniformly precipitated layer of alloying elements on the tube surface during the application of coatings, the samples were rotated round the tube's axis by an electric motor. The coating thickness was calculated based on the results of weighing the samples on the type CR-202 electron analytical balance with an error of  $\pm 0.01$  mg before and after applying the coating and changed in the 0.2 ... 1.3  $\mu\text{m}$  range depending on the kind of an applied material and sputtering conditions: the quantity of a powder in the boat was 150 ... 400 mg, the current through the boat was 90 ... 110 A; the evaporation time was 30 ... 240 s.

To increase the adhesion of coatings with the substrate, diffusion anneal was carried out in vacuum for 3 h at 500 and 600 °C for samples with a coating of aluminum (silumin) and chromium, respectively.

The surface alloying by a liquid-phase mixing was carried out by the action of pulsed helium plasma fluxes on a Z-pinch installation [2]. The specific feature of the installation is a possibility to obtain magnetic pinch forming pulsed plasma fluxes directed to the chamber's axis. That makes it possible to simultaneously and thoroughly treat all the surfaces of

cylindrical articles, in particular, sections of tubes for one or several pulses with the duration about 15  $\mu\text{s}$ .

The main variable parameters under the irradiation were the energy density of a plasma flux  $Q$  and the number of irradiation pulses  $N$ . The total  $Q$ -value changed in the 150...1470  $\text{J}/\text{cm}^2$  range and  $N$  from 3 to 21, depending on the type and the thickness of an applied coating.

The surface topography, structure-phase state and element composition of alloyed samples, as well as their corrosion resistance after dynamic isothermal tests in liquid lead with an increased ((5...8)  $10^{-5}$  wt.%) controlled oxygen content were investigated. The lead flow velocity  $V_{\text{pb}}$  was equal to  $1.0 \pm 0.1$  m/s. The samples were tested at 650  $^{\circ}\text{C}$  for 1680 h. These tests were carried out in the State Russian Scientific Center - Institute of Physics and Power Engineering (FSUE SSC IPPE, Obninsk) on the installation TsU-1.

### 3. Experimental Results and Discussion

Investigations by optical and scanning electron microscopy have shown that the surface morphology of samples after the liquid-phase alloying depends on the type and the thickness of an applied film and the regimes of a plasma treatment. The typical pictures of the tube surface after the pulsed plasma treatment are shown in Fig. 1.

An analysis of the pictures obtained has shown that the surface-alloyed samples' topography with a preapplied coating of Al and an Al-12%Si-base alloy under similar conditions of mixing is practically the same. Depending on the coating thickness and the plasma treatment regimes, drops of the coating mate-

rial (Fig. 1, *a*) are observed or a net-like structure of irregular long "islands" of the applied coating's hardened melt forms (Fig. 1, *b*). The height of these "islands" can exceed the applied film thickness by several times. The sizes of forming microdrops can change in the 0.6...5.4  $\mu\text{m}$  range with the most probable diameter of  $\sim 1.8 \mu\text{m}$  at the density of  $\sim 2.5 \cdot 10^5 \text{ cm}^{-2}$ . At that, it is possible to choose the optimal treatment regime and obtain a sufficiently smooth surface of tubes. Similar structures were observed under the liquid-phase mixing of the "Al-film – sodium-silicate substrate" system, depending on treatment conditions by high power ion beams [4].

The surface of chromium-coated samples had a more pronounced relief. Drop-like formations are also observed on their surface. The formation of microcracks on the surface of samples was found in a numbers of cases for sufficiently thick ( $> 0.5 \mu\text{m}$ ) films and "hard" regimes of a plasma treatment (Fig. 1, *c*). The last is undesirable with the viewpoint to preserve the service (strength) characteristics of tubes. At the same time, as it is seen in the picture of the end microstructure (Fig. 2, *c*), the cracks are perpendicular to the surface and localized close to it.

The surface chemical composition and the distribution of elements along the depth of surface-alloyed tubes were investigated by the X-ray spectral microanalysis using the "WDX-3PC" (Microspec) wave spectrometer.

As it is seen from Fig. 1, *a* and *b*, the alloying element distribution (in particular, aluminum) along the surface after the HTPPF-treatment is not uniform; drop-like precipitates (black points) with an increased aluminum content (Table 1) form.

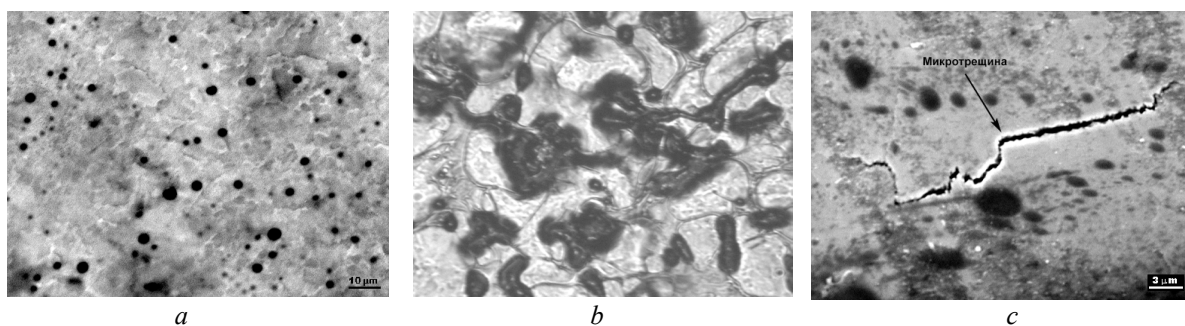


Fig. 1. Topography of surface-alloyed tubes: *a*, *b* – initial silumin-base coating; *c* – chromium coating

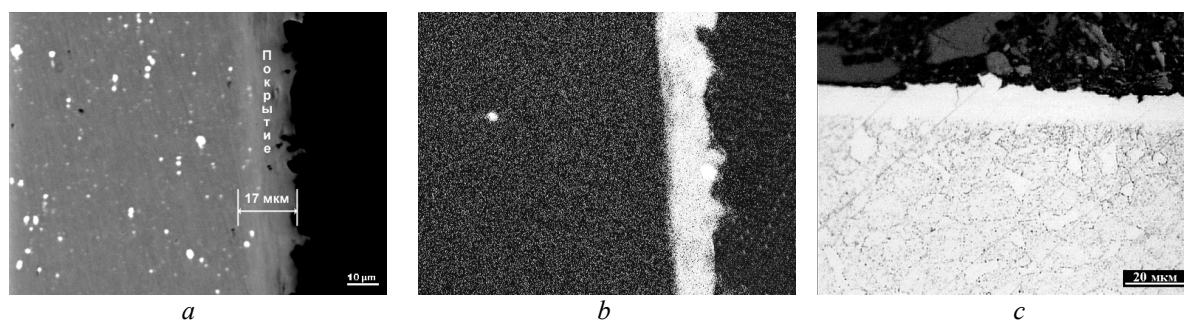


Fig. 2. Structure of the tube cross-section after the surface-alloying by silumin (*a*, *b*) and chromium (*c*): *a*, *c* – in reflected electrons; *b* – at aluminum radiation

Table 1. Element composition of surface-alloyed tubes\*)

No.	Main elements, wt. %						
	Cr	Si	Mo	W	V	Nb	Al
1	11.2	1.0	0.6	0.6	0.4	0.3	0.0
2	10.5	0.6	0.6	0.4	0.4	0.3	13.0
3	4.9	0.2	0.5	0.1	0.3	0.1	73.5
4	12.4	1.5	0.7	–	0.4	–	2.3
5	7.9	0.9	0.2	–	0.3	–	42.2
6	15.7	0.9	0.6	0.3	0.4	0.2	0.0

\*) 1 – EP823 (base); 2 – Al,  $Z = 0.9 \mu\text{m}$ ; 3 – Al,  $Z = 0.9 \mu\text{m}$  (drops); 4 – Silumin,  $Z = 0.4 \mu\text{m}$ ; 5 – Silumin,  $Z = 0.4 \mu\text{m}$  (drops); 6 – Cr,  $Z = 0.3 \mu\text{m}$ .

From the other side, it has been found (Figs. 2 and 3) that there is a sufficiently uniform distribution of the alloying elements in the surface layer with a thickness by order of magnitude greater than that of the preliminary applied coating. In particular, aluminum at the coating thickness of the order of  $0.4 \mu\text{m}$  is found in the surface layer up to  $\sim 15 \mu\text{m}$  in depth, and its mean concentration is about 3 wt. % (Fig. 3).

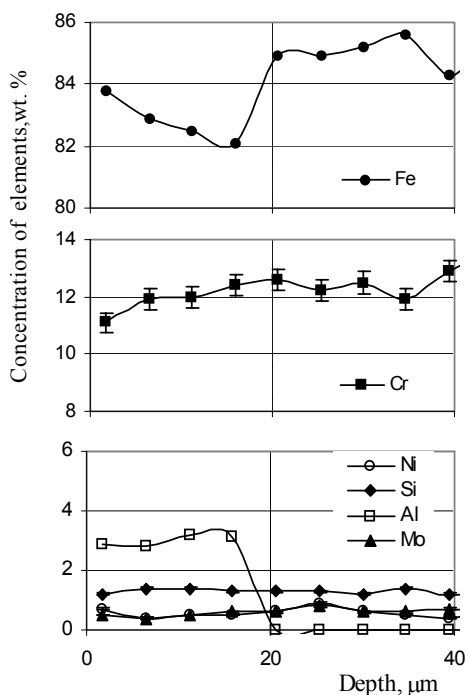


Fig. 3. Distribution of elements depending on the target thickness alloyed by silumin ( $z = 0.4 \mu\text{m}$ )

It should be pointed out that the use of silumin-base alloy thin layers as a material of coatings did not result in a significant change of the silicon content in Table 1. Element composition of surface-alloyed tubes\*) the surface layer after plasma treatment in comparison with that of the base. That testifies to a selective evaporation of aluminum during the thermal evaporation in vacuum.

The chromium distribution in the surface layer of alloyed tubes is more uniform and its content attains 15.0...16.5 wt. % at the volume concentration of

11 wt. % (Table 1). An increased content of chromium is found in the surface layers up to  $\sim 10 \mu\text{m}$  in depth for the thickness of a preliminary applied layer of  $\sim 0.3 \mu\text{m}$ .

The results of a qualitative X-ray phase analysis performed have shown that no noticeable lines were observed in the surface-alloyed samples which would correspond to Fe–Al intermetallic phases. The main difference at alloying by various elements (Al or Cr) consists in the value of the crystal lattice spacing, which testifies to the formation of a solid solution in the surface layers. The lattice parameter of the sample alloyed by aluminum was equal to 0.2866 nm, for the sample alloyed by chromium, 0.2856 nm (the experimental error was less than 0.0001 nm).

The plasma treatment significantly changes the surface layer structure, which is revealed in an essential X-ray line broadening. At that, increasing the number of pulses and the total energy density of plasma fluxes, for example in case of the surface alloying by aluminum, doesn't only increase the structure defect character of the main phase, but also results in an essential increase of the crystal lattice spacing.

The growth of the unit cell's parameter can be due to an increase of the aluminum content that has a high diameter of a metal ion ( $d_{\text{Al}}/2 = 1.46 \text{ \AA}$ ,  $d_{\text{Fe}}/2 = 1.239 \text{ \AA}$ ) in  $\alpha$ -phase.

The surface alloying technique using HTPPF has been improved with the aim to reveal the possibility of using the given method to increase the corrosion resistance of tubes in liquid lead flow.

Metallographic investigations of the end microstructures of samples after dynamic corrosion tests in lead made it possible to find a significant inhomogeneity of the forming oxide film thickness, both on initial samples and on samples preliminarily alloyed under the action by pulsed plasma fluxes. The observed inhomogeneity in the growth of a forming oxide film, as well as its relatively small thickness make it difficult to determine the extent of the absolute surface alloying influence on the steel corrosion resistance. The corrosion data of tubes under various states are shown in Table 2.

The experimental results obtained have shown that the preliminary HTPPF-treatment and the surface alloying of tubes result in a change of their oxidation extent when they are endured in a liquid lead flow. In doing so, as a rule, a decrease of the oxide film thickness is observed that is determined by the conditions of a pulsed plasma flux treatment and the type of an alloying element. Corrosion tests at  $T = 650 \text{ }^\circ\text{C}$  for  $\tau = 1680 \text{ h}$  have shown that under definite regimes of the surface-alloying of tubes it is possible to significantly decrease the oxide film thickness up to full suppression of oxidation.

An analysis of the surface state, the element composition and the microstructure of tubes after their endurance in a liquid lead flow makes it possible to

conclude that the content of aluminum in the surface layers must be of the order and higher than 13...14 wt.% to suppress the oxidation of the EP823 steel in lead with an increased oxygen content.

Table 2. Corrosion of surface-alloyed tubes in a lead flow ( $T = 650\text{ }^{\circ}\text{C}$ ,  $\tau = 1680\text{ h}$ )

Coating		Condition of plasma treatment		Oxide film thickness, $\mu\text{m}$		
Material	Thick-ness, $\mu\text{m}$	$Q\Sigma_2$ , $\text{J}/\text{cm}^2$	N, unit	min	max	<d>
EP823 initial		–		9	18	12
EP823 initial		Purification by plasma		6	10	8
EP823 initial		423	7	3	8	5
Aluminum	1.5	–		6	13	8
	0.4	240	5	0	1	1
	0.5	449	8	1	5	3
Silumin	1.3	1368	21	0	5	2
	0.5	183	3	2	6	5
	1.1	1473	21	3	9	5
Chromium	0.4	150	8	1	8	4
	0.6	292	4	3	6	5
	0.6	246	5	2	6	3
	0.3	330	6	3	6	5
	0.9	475	7	5	8	6

#### 4. Conclusion

The technique and regimes have been developed for the liquid-phase mixing of aluminum, silumin and chromium films, 0.2...1.3  $\mu\text{m}$  in thickness, applied on

the surface of steel tubes under the action by helium pulsed plasma fluxes.

It has been found that at the applied film thickness of  $\sim 0.5\text{ }\mu\text{m}$ , the distribution of alloying elements in the surface layer 10...15  $\mu\text{m}$  thick is sufficiently uniform. At that, the mean aluminum concentration changes from 3 to 14 wt. %, and the chromium content increases from  $\sim 11.0$  to  $15.0\text{...}16.5\text{ wt. \%}$ .

An analysis of the surface state of tubes and the microstructure of end sections after endurance in a lead flow at  $650\text{ }^{\circ}\text{C}$  give grounds to conclude that the technique of surface-alloying using the pulsed plasma treatment is prospective for increasing the corrosion resistance of a chromium steel in a lead flow.

#### References

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