Investigation of the Structural-Phase State of Cladded Steels Treated by Pulsed Plasma Flows

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Abstract – The possibility to form nanostructured surface layers on samples by their cladding with rapidly quenched metal filler-alloys and treatment by high-temperature pulsed gas plasma flows was investigated. A technique has been improved and cladding regimes of samples from carbon- and corrosion-resistant steels of various types by rapidly quenched nickel-based filler-alloys and irradiation regimes by pulsed gas plasma flows have been developed. An X-ray structural analysis has shown that a pronounced diffuse halo is observed on cladded samples after treatment by pulsed nitrogen plasma flows ($Q = 31$ J/cm^2, $\tau_p = 20$ μs, $N = 2$). It has been found by scanning electron microscopy of a high resolution that an ordered columnar-lamellar nanostructure forms in the surface layer of the given samples. Its characteristic cross-size of plates changes in the range of 50–100 nm.

1. Introduction

The development of methods for modifying the surface layers of materials and articles is an urgent question for development of new modern technologies. Among them are the methods of surface treatment by concentrated energy flows, one of which is the use of high-temperature pulsed plasma (HTPP) flows. They are highly prospective and widely used in highly industrialized countries. The treatment by HTPP-flows is considered as an alternative method in comparison with laser radiation, high power (high current) ion and electron beams. At that, the treatment by HTPP-flows has a number of advantages not only in comparison with traditional technological processes of thermomechanical and chemicothermal treatments, but also with the action of concentrated energy flows of other types [1]. It was shown earlier [1–4] that the exposure of metal materials to the action by high-temperature pulsed plasma flows changed the microstructure and the structural-phase state of the surface layers. In particular, the treatment of steels and nickel-based alloys by HTPP-flows with a flow power density higher than 10^6 W/cm^2 results in formation of a columnar submicrocrystalline structure in the surface layers (Fig. 1). The cell cross sizes change in the range from ~ 0.1 to 1.0 μm. At that, the formed structure possesses a high heat-resistance. It does not change for austenitic steel samples under annealing up to the temperature $T = 1173$ K ($t = 1$ h).

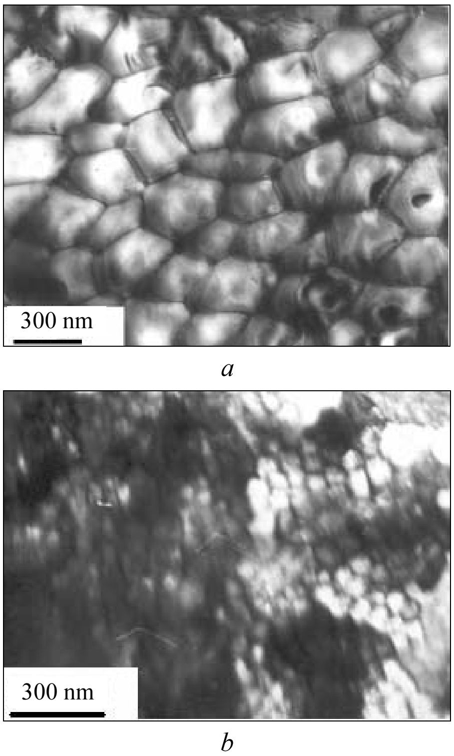


Fig. 1. Microstructure of austenitic steel after the treatment by plasma flows (*a*) and post-radiation anneal (893 K, 1 h) (*b*): *a* – $W = 5 \cdot 10^6$ W/cm^2, $N = 3$; *b* – $W = 1.5 \cdot 10^6$ W/cm^2, $N = 10$

The materials with submicrocrystalline and nanocrystalline structure has, as a rule, high operational characteristics [5]. Taking the aforesaid into account, the goal of the given work was to find the possibility of formation of nanostructured surface layers on samples made from various steels by their cladding with rapidly quenched metal filler-alloys followed by treatment with pulsed gas plasma flows.

2. Experimental technique

Plates of steels of various types, such as St3, 65G, 12Cr18Ni10Ti and 16Cr12MoSiNbVWMn, were used as substrates for samples. A thin (~ 35 μm) foil of amorphous nickel-based filler-alloys (STEMET 1311 and STEMET 1342), of which the composition is shown in Table 1, was brazed to the plates by spot-brazing.

Table 1. Composition of the type STEMET filler-alloys used in the work

Type of a filler-alloy	Content of the main elements, wt %
STEMET 1342	Ni (base) – 14% Cr – 8.5% Co – 7% Si – 6% W – 1.3% Mo – 1.2% B
STEMET 1311	Ni (base) – 16% Co – 4% Fe – 4% Si – 3.5% B – 0.4% Cr

The spot-brazing was followed by double-stage heating: at first, slow heating up to the temperature of 900 °C and holding at that temperature for 15–20 min, then rapid heating up to 1050 °C (for STEMET 1311) and 1120 °C (for STEMET 1342) and holding at those temperatures for 5 min. The plates were cooled with furnace. As a result of that, a diffusion joint of a cladding layer with the substrate was obtained.

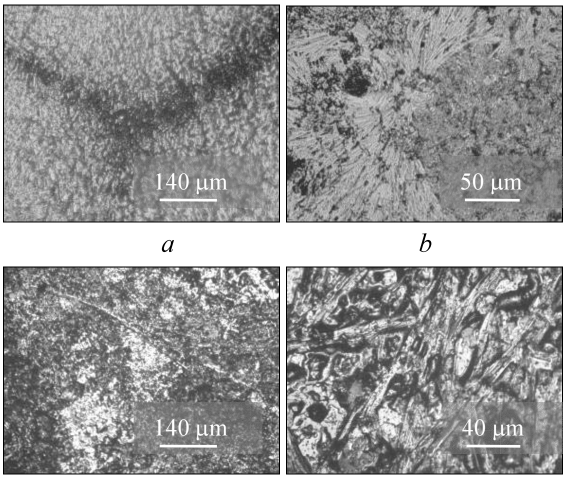
At the first stage the influence of a treatment by pulsed plasma flows on modifying the samples was studied for samples cladded by the type STEMET 1342 filler-alloy having more complex composition, then cladded by the type STEMET 1311 filler-alloy.

Irradiation of cladded samples was carried out by high-temperature pulsed nitrogen plasma flows in a *Z*-pinch type installation [1] using two regimes. At first, a relatively hard irradiation regime was used; the energy density of plasma flows was 31 J/cm^2 ($N = 2$) at a pulse duration of ~ 20 µs. This regime was chosen with the purpose to form a modified layer that would be more spread along the target depth. Besides, a milder irradiation regime was used ($Q = 22$ J/cm^2, $N = 2$).

Samples were investigated by optical and high resolution scanning electron microscopy, as well as X-ray analysis. In particular, to study the microstructure of samples, face sections from the samples of an irradiated material were made. Then they were inserted into a steel fixture and filled up with epoxy resin. After hardening the epoxy resin, the samples were exposed to grinding with emery paper of various numbers followed by diamond paste polishing. Then the samples were etched in HNO_3 (5 ml) and HCl (15 ml) at room temperature for 10–20 s and investigated in an optical microscope Neophot-30.

3. Experimental results

Investigation of the cladded samples' surface topography has shown that the character and the degree of its changes depend for the greater extent on the kind of a filler-alloy than the substrate's material. The samples cladded by STEMET 1311 have a sufficiently uniform structure with pronounced polyhedral grains. As shown in Figs. 2, *a* and *b*, the melt flew from the center of a grain to its periphery, and the grain boundaries represent junction areas of melts.



a *b*
c *d*

Fig. 2. Surface topography of St3 steel samples cladded by STEMET 1311 (*a*, *b*) and STEMET 1342 (*c*, *d*)

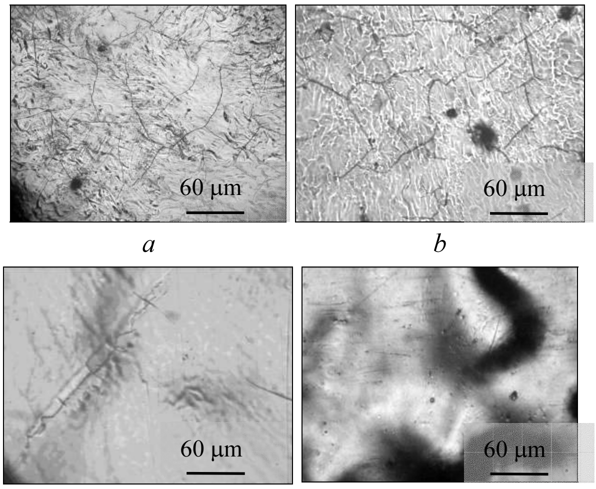
The surface structure of samples cladded by STEMET 1342 was more coarse and nonuniform. Crystallization took place predominantly through the mechanism of dendrites (Figs. 2, *c* and *d*) and pronounced grain boundaries were practically absent.

Metallographic investigations of the surface of irradiated samples have shown (Fig. 3) that the result of action by pulsed plasma flows is determined by the composition of a cladding alloy and the regime of plasma treatment. At that, the following effects were observed for the given irradiation conditions:

– intensive melting of the surface layers and formation of melt waves after hardening;

– partial surface oxidation;

– intensive surface cracking owing to formation of thermal stress fields in samples.



a *b*
c *d*

Fig. 3. Surface topography of 16Cr12MoSiNbVWMn steel samples, cladded by STEMET 1342 (*a*, *b*) and STEMET 1311 (*c*, *d*), after treatment by nitrogen plasma flows: *a*, *c* – $Q = 31$; *b*, *d* – 22 J/cm^2

Taking intensive cracking of the surface layers of steels cladded by STEMET 1342, which took place under plasma treatment with an energy density of flows $Q = 31$ J/cm^2, into account, irradiation under "milder" conditions was carried out ($Q = 22$ J/cm^2). However, in case of using relatively mild irradiation conditions, too, the surface topography of samples cladded by STEMET 1342 has practically the same character, independently of a substrate material: intergranular cracking and local surface meltings are observed. At that, an analysis of the photographs obtained has shown that the development degree of the surface relief, as well as the surface cracking degree decrease with the energy density of plasma flows (and the power density of an incident flow).

It has been found that at the same irradiation conditions, the cracking degree changes in dependence on the king of substrate steel. In particular, less cracks are observed on samples in case of using St3 and 65G carbon steels as a substrate material than on samples with the use of steels of more complex composition as a substrate material. The most formation of cracks took place on the surface of samples with a substrate of 16Cr12MoSiNbVWMn-type steel.

As an intensive surface cracking was observed after the treatment of samples (which were cladded by STEMET 1342) by plasma flows for both hard and milder regimes, the type STEMET 1311 filler-alloy was used as a cladding material. This alloy was selected because of using a smaller number of alloying components and a higher content of the base material (nickel) (Table 1).

After irradiation by pulsed plasma flows, a more uniform surface structure is formed on the samples cladded by STEMET 1311 than that on the initial samples. Pronounced melting waves (Fig. 3, *d*) were formed on the surface of samples as a result of melting and subsequent hardening. In comparison with the behavior of samples cladded by STEMET 1342, the surface of which intensively cracked at the same irradiation conditions ($Q = 31$ J/cm^2), formation of a slight quantity of cracks was found predominantly on the borders of samples. However, separate microcracks were also observed in the centre of samples.

It should be pointed out that for samples cladded by STEMET 1311 and treated by HTPP-flows, the same regularity, which was found in case of using STEMET 1342, was observed: more uniform surfaces with less number of damages and microcracks are formed for samples with substrates made of low-alloy steels (St3, 65G) than for substrates made from high-alloy steels.

On account of formation of separate cracks predominantly on the borders of samples cladded by STEMET 1311 after the action by nitrogen plasma flows at $Q = 31$ J/cm^2, samples were treated under milder regimes ($Q = 22$ J/cm^2, $N = 2$). As shown in Fig. 3, *d*, the surface damage (formation of cracks) was not practically observed under the given irradiation conditions of cladded samples independently of the type of a substrate used. However, as to samples with a 16Cr12MoSiNbVWMn steel substrate, there is formation of a more relief surface in comparison with that of other samples, as well as there are local damages in the form of pores. Formation of local microcracks is observed close to the pores.

More detail investigation of the surface microstructure of samples after plasma treatment was carried out using a high resolution scanning electron microscope HITACHI S-4800. Figure 4 shows a picture of a 65G steel sample cladded by STEMET 1311 and treated by high-temperature pulsed nitrogen plasma flows ($Q = 31$ J/cm^2, $N = 2$).

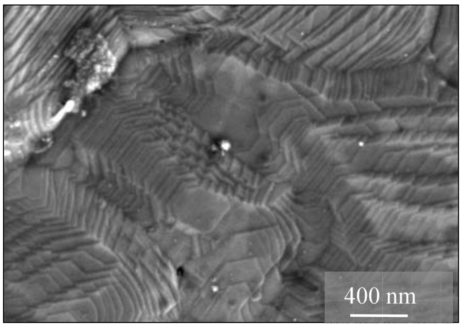


Fig. 4. Surface topography of a 65G steel sample, cladded by STEMET 1311, after plasma treatment

As seen from Fig. 4, there is formation of an ordered columnar-lamellar nanostructure with typical cross sizes of plates changing in the 50–100 nm range in the surface layers as a result of the action by plasma flows. The orientation of the forming plates depends on the crystallographic orientation of the initial grains of a sample.

In studies of the surface of cladded samples with a 65G steel substrate after the action by nitrogen plasma flows at $Q = 22$ J/cm^2, formation of a columnar nanostructure was also found in a scanning electron microscope ZEISS EVO 50. The mean grain size was from 50 to 150 nm.

Investigation of the cross structure of samples treated by HTPP-flows has shown that there is formation of a multi-layer structure in their surface layers (Fig. 5): a white unetched layer; a layer of the filler-alloy without treatment (the zone of thermal action); a transition layer between the filler-alloy and the substrate; an initial substrate.

The mean thickness of a modified layer is equal to (12 ± 2) μm. The error in determination of a modified layer's thickness is conditioned by a nonuniform surface treatment. Nonequal boundaries between the first two layers can be explained by partial crystallization (which takes place in the filler-alloy under hardening) after the treatment of a sample by high-temperature plasma.

Investigation of the element composition of cladded samples before and after the treatment by HTPP-flows was carried out by X-ray spectrum microanalysis (XRSMA) using a wave spectrometer WDX–3PC. The element composition was determined both over the surface and in depth of samples.

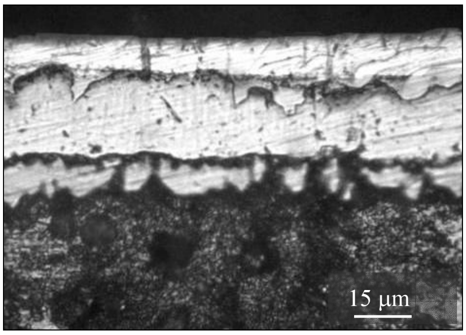


Fig. 5. Cross structure of a St3 steel sample, cladded by STEMET 1311, after irradiation by HTPP-flows ($Q = 31$ J/cm^2, $N = 2$)

The XRSMA-results have shown that the distribution of the main elements both in initial cladded samples and in samples treated by HTPP-flows is relatively uniform over the surface. It has been found that the irradiation of samples by pulsed plasma flows, which were preliminarily cladded by STEMET 1311, does not practically result in changing the element composition of their surfaces. This points to the fact that the selective evaporation of the filler-alloy's components for such small irradiation times (~ 20 μs) is absent. At that, it has been revealed that under a modified layer at 12–20 μm depth, there is an increase of the silicon concentration and a decrease of the relative content of iron and cobalt.

X-ray investigations have shown that the spectra of initial samples are very similar in appearance and practically do not depend on the material of a substrate. A qualitative X-ray phase analysis has shown that the main lines correspond to nickel silicide of a $Ni_{31}Si_{12}$ type and Ni. Besides, there are some lines possessed by indefinite phases. It was impossible to determine their composition owing to their small quantity and complex composition.

The kind of the spectra significantly changed after the treatment by HTPP-flows at $Q = 31$ J/cm^2. A pronounced diffusion halo is observed for all the samples which is typical for amorphous or X-ray amorphous, i.e., very fine crystalline, materials. At that, there are additional peaks in the spectra of samples with substrates from steels of complex composition. These peaks correspond to release of a small part of a crystalline phase. Individual differences in these spectra can be connected to both some dispersion in the treatment parameters and a various cooling rate of claddings that can depend on the type of the substrate steel.

The spectra view of samples irradiated under milder regimes ($Q = 22$ J/cm^2, $N = 2$) significantly differs from that obtained for samples treated under hard regimes. The character of these spectra more resembles the character of spectra obtained for the initial samples: the lines of $Ni_{31}Si_{12}$ (nickel silicide, sometimes it is identified as Ni_5Si_2) and Ni were identified. Besides, there are also some lines possessed by indefinite phases. At that, the lines of nickel silicide are significantly broadened, which can point to a high dispersion of that phase.

4. Conclusion

A technique has been developed and the regimes of cladding the samples of various steels by rapidly quenched STEMET 1311 and STEMET 1342 filler-alloys have been determined, including brazing of a thin (~ 35 μm) rapidly quenched foil to steel plate-type substrates, a subsequent thermal treatment for diffusion joining of a filler-alloy with the substrate, and irradiation by high-temperature pulsed gas plasma flows.

It has been found that the distribution of the main elements in cladded samples both initial and treated by HTPP-flows is practically uniform over their surface and the treatment by plasma flows does not result in a significant change in the element composition of their surface layers.

It has been revealed that the treatment of steel samples, cladded by a STEMET 1342 filler-alloy of complex composition, by pulsed plasma flows with an energy density $Q = 22–31$ J/cm^2 results in surface cracking, which testifies formation of high-level thermal stresses in the surface layer. The cracking extent of the cladded samples has been shown to depend on the composition of substrate steel.

Local formation of microcracks is also observed in irradiation of samples, cladded by a STEMET 1311 filler-alloy, in a hard regime ($Q \sim 31$ J/cm^2). But cracks were not observed in a relatively soft irradiation regime ($Q \sim 22$ J/cm^2).

It has been found by X-ray structural analysis that after the treatment by pulsed nitrogen plasma flows ($Q = 31$ J/cm^2, $N = 2$) a pronounced diffusion halo (which is typical for X-ray amorphous, i.e., fine crystalline, materials) is observed for samples cladded by STEMET 1311. It has been shown by scanning electron microscopy of a high-resolution that in the surface layer of samples there is formation of an ordered columnar-lamellar nanostructure with typical cross sizes of plates changing from 50 to 100 nm.

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