REGULARITIES OF CREATION OF MODIFIED INTERLAYERS IN USING OF HIGHLY-CONCENTRATED ENERGY FLOWS

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Radiation-beam technologies applied for modifying, including those with alloying of surfaces, provide necessary topography of surface, its activation, improvement of adhesion properties, required structure and chemical composition of the surface. These characteristics are further determining in diffusion welding, brazing and deposition of coatings. In the work the low-energy high-current electron beams and high-energy plasma flows for modifying and alloying of the joined surfaces of steels and heat-resistant alloys were used. These types of surface treatment belong to the radiation-beam technologies. The treatment was carried out using low-energy high-current electron beams in vacuum 10^{-2} Pa in the installation SOLO of the Institute of High Current Electronics of the SB RAS, and also high-energy plasma flows using magnetic plasma compressor of a compact geometry of the Belarusian State University at the pressure of hydrogen and nitrogen of 3.10² Pa, and welding and brazing were performed in the installation UDSV-DT in vacuum of 10^{-2} Pa or super-high vacuum universal technological complex VVU-1D in vacuum of 10^{-5} Pa. Independently of metals being investigated the formation of sub-microcrystalline structure, presence of high density of dislocations (up to 10¹¹ cm⁻²), appearance of stresses of the 3rd kind, being the evidence of immense increase in level of energy accumulated in modified layer, are characteristic for all the modified layers. The surfaces of heat-resistant nickel alloys were alloyed by zirconium and hafnium, which are the most challenging depressants of nickel brazing alloys. For this purpose the layers of alloying element of 1-3 µm thickness was deposited on the surface using method of ion-plasma spraying and then the surface layer was remelted using low-energy high-current electron beams and high-energy plasma flows. The investigations of processes of formation of modified and alloyed surfaces showed the possibility of efficient control of structure and composition of the modified layer. Diffusion welding in a solid state and with a melting interlayer provides the high quality of joints, which can be confirmed by the structures and mechanical properties of joints. The application of radiation-beam technologies allows expanding the capabilities of joining metals and hardening the materials. 13 Ref., 6 Figures.

Keywords: surface modifying, electron beam, highpower plasma flow, diffusion welding, brazing

The operation parameters of the modern gas-turbine engines, products of the new engineering, can be increased by application of composite and dissimilar structural materials, and also technologies of formation of modified layers and coatings on their surface. For example, in manufacture of gas turbine blades the cast heat-resistant nickel alloys with corrosion-resistant and thermal barrier protective coatings are used. The serviceability of coatings, having a direct contact with the working environment, depends on strength of adhesion of alloys with a base, structure and relief of coatings. For joining of cast alloys diffusion welding is applied, including that with melting interlayers. The serviceability of joints and strength of adhesion of coatings with blades are considerably affected by activation of the surfaces being joined and coated. The challenging direction for increase of service life of parts is the modifying and alloying of their surfaces applying highly-concentrated energy pulsed sources [1–4]. In the recent years for modifying and alloying the low-power high-current electron beams (LHEB) and high-power plasma flows (HPF) are successfully used. The technologies for modifying and alloying of surfaces applying highly-concentrated sources of energy are generally called radiation-beam technologies (RBT)

15

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Figure 1. General appearance of discharge device MPCCG (*a*) and its scheme (*b*): 1 - cathode; 2 - rod anode; 3 - insulator

[1]. Due to application of RBT the change in topography of the surface, its activation, increase in adhesion capability, correction of surface defects, required chemical composition are provided, which are the decisive factors in the processes of deposition of coatings and joining of metals in the solid state using interlayers including melting ones.

The aim of the present investigations is the determination of regularities for creation of modified interlayers at the surfaces of materials applying LHEB and HPF, their influence on structure and properties of coatings, formation of joints of steels of different structural classes and heat-resistant nickel alloys.

The treatment of surfaces using LHEB was carried out in the installation SOLO of the Institute of High Current Electronics of the SB RAS, the design and principle of which are described in [2]. The modifying of surfaces was carried out in vacuum of 10^{-2} Pa. The installation provides a super-rapid heating of surface of materials ($10^{6}-10^{9}$ °C/s) using electron beam of 10–30 mm diameter at the current of 20–200 A. The duration of a pulse was 50–150 µs, frequency of pulses was 1-5 s⁻¹. The acceleration of electrons was provided by electric field at the voltage of 15–20 kV.

The modifying using HPF was carried out using magnetic plasma compressor of a compact geometry (MPCCG) of the Belarusian State University [3]. In the MPCCG the acceleration of plasma was performed in the axially-symmetrical system of two electrodes and accompanied by its compression due to interaction of longitudinal component of current with its own azimuth magnetic field (Figure 1). As a result, at the output of the discharge device the compression plasma flow of 10–12 cm length and up to 20 mm diameter in the field of maximum compression is formed.

Welding and brazing of the specimens with a modified surface was carried out in the installation for arc welding UDSV-DT in vacuum of 10^{-2} Pa or in the super-high vacuum universal technological complex VVU-1D in vacuum of not worse than 10^{-5} Pa of the Admiral Makarov National Shipbuilding University.

By variation of distance from the cathode edge to the treated product from 6 to 12 cm, the power density at the constant voltage on the capacitor battery of 3 kV is changed from 15 to 21 J/cm² in one pulse. The duration of a pulse amounts to 100 μ s. Cooling rate of a melt is 10⁶–10⁹ °C/s. Depending on the material of substrate and coating the HPF modifying was performed in the nitrogen or hydrogen atmosphere at the pressure of working environment of 3·10² Pa. Before filling with gas the chamber is evacuated.

The main mechanism of surface modifying is a super rapid hardening, including also that from molten state, accompanied by amorphisation, formation of sub-microcrystaline structure, close to nanostructure, defects of crystalline lattice, stresses of the 3rd kind, change of chemical composition, etc.

Investigations of structure of the modified surface of steels and alloys showed that there is no difference between LHEB and HPF treatment as to the structure of metal. Figure 2 shows structures of base metal, modified layer of steel 10895 and also heat-resistant nickel alloy ChS88U-VI for comparison.

The analysis of results of investigations of structure and properties of modified surfaces of the investigated steels and alloys applying LHEB and HPF showed that they have a number of common regularities: formation of sub-microcrystalline structure, increase of density of dislocations, presence of treatment modes, providing smooth surface of the modified layer. High dispersion of structure (grains and subgrains), density of dislocations and stresses of the 3rd kind evidence of high level of energy, accumulated in the modified layer.

The investigated materials have also their own peculiarities influencing the results of modifying.





Figure 2. Microstructure of steel 10895 ($a - \times 160$) and modified layer ($b - \times 250$), alloy ChS88U-VI ($c - \times 50$) and fine structure of LHEB-modified layer of the same alloy ($d - \times 30,000$)

On steel 10895 (α -Fe structure) the highest hardening of the surfaced modified layer (increase of hardness by 74 %) was obtained. On steel 12Kh18N10T (γ -Fe structure) it is negligible (increase of hardness by 12 %), on the heat-resistant alloy microhardness decreased by 20 %. As far as phase composition of steels in modifying is not changed and dispersion of new structure of both steels is approximately the same, then, it is obvious that the level of hardening of these both metals is influenced by difference in energy of stacking defects, which is considerably lower for steel 12Kh18N10T (to 40 mJ/m²) than for iron, containing some hundred percents of carbon $(140-240 \text{ mJ}/\text{m}^2)$. Here it should be considered also the fact that in hardening of steel 12Kh18N10T the amount of titanium carbides. influencing the hardness and ductility of steel, is decreased.

The reduction in microhardness of heat-resistant dispersion-hardening alloy after tempering from the molten state is, probably, predetermined by dissolution of the hardening γ' -phase, which is precipitated not only in the process of holding of alloy at the temperature of ageing but also during cooling of a casting. It is characteristic that on the background of the general increase of level the highest densities of dislocations are formed along the boundaries of phase precipitates inside the matrix grains. Growth of stresses in the modified surfaces is proved also by the type of microdiffraction reflections having azimuthal diffuse of reflexes.

The investigation of a thin structure of alloy ChS88U-VI showed that the same as in the base metal, the dispersion of the hardening phase in the modified layer is not similar in different areas. In the modified layer both coagulation of hardening phase as well as formation of fine-dispersed particles of the sizes of $0.1 \ \mu m$ under the effect of thermal shock are possible.

The influence of modified surfaces on the formation of joints was investigated using diffusion welding of the following specimens: specimens, where both joining surfaces were modified by LHEB and HPF treatment; specimens, where both surfaces not subjected to modifying, were cleaned before welding using fine abrasive paper, and also specimens, where surface of one of them was modified and another one was cleaned using abrasive paper.

The investigations of microstructure of metal of ChS88U-VI welded joints with both surfaces, cleaned with abrasive, showed that the depth of zone of active running of processes in joining of non-modified surfaces is small and equal to $20-45 \ \mu m$ on both sides from the butt. Along the butt the volumetric fraction of recrystallized grains amount to about 10 %. Microhardness of metal on both sides of the butt is equal on average to 3860 MPa.

In joining of specimens of alloy ChS88U-VI with modified and mechanically prepared surfaces the depth of zone of active processes of recrystallization on the side of modified surface grows to $80-120 \mu m$. The volumetric fraction of recrystallized grains along the butt on the side of modified surface amounts to 45 %, microhardness is equal to 4120-4410 MPa, size of grains is changed from 50×85 to $120 \times 350 \mu m$. The volumetric fraction of the non-modified surface amounts to 10 %, micro-



Figure 3. Microstructure of modified layer of alloy ChS88U-VI (a) and welded joint ($b - \times 500$)

hardness is 3910–4400 MPa, size of grains is changed from 20 \times 40 to 40 \times 125 $\mu m.$

The peculiarity of structure in the zone of butt of modified and non-modified surfaces is the presence of a great number of common fine grains in a butt, that are good seen at great magnifications in radiographic control of foil.

The microstructure of modified layer and metal of ChS88U-VI welded joint with both modified surfaces is presented in Figure 3. The size of grains in the butt zone is in the range from $25 \times$ \times 50 to 100 \times 180 µm, the depth of zone of intensive recrystallization is equal to 100–170 µm.

Having compared the structure of welded joints in the zone of butt of the alloy ChS88U-VI, it should be noted that recrystallization of metal is running more intensively and completely in the zone of modifying. The fracture of welded joints occurs on the base metal. The given results were obtained by diffusion welding at the temperature of 1150 °C and pressure of 20 MPa with 3 min holding, which is considerably lower than the parameters of the mode recommended for heat-resistant alloy in [5, 6]. For example, for dispersion-hardening alloy EP99 the optimally recommended are $T_w = 1150-1175$ °C, P = 40-35 MPa, $t_w = 6$ min, for austenite alloy EI602 $T_w = 1150-1175$ °C, P = 30-25 MPa, for alloy $VZh98 T_w = 1175 - 1200 °C, P = 20 - 25 MPa, t_w =$ = 30 min.

The characteristic feature of LHEB and HPF treatment of dispersion-hardening heat-resistant nickel alloys is the crack formation, the amount and sizes of which depend on power density and vary from micro- to macrosizes. This is obviously connected with a low technological strength of alloys, determining the resistance to formation of hot cracks in fusion welding. Improvement of resistance against hot cracks facilitates the decrease in energy input of welding. During decrease in energy density and increase in a number of pulses, a number of cracks is decreased, and at energy density of 15 J/cm² it is possible to succeed in avoiding them, but even at the presence of cracks after modifying they are absent in welded joint [7].

In the course of investigations of influence of HPF treatment of surfaces on the preliminary deposited plasma surfaces, it was established that for modifying of corrosion-resistant sublayer (SDP-8) the energy density of 15–21 J/cm² can be recommended, and for thermal barrier (ZrO₂ stabilized by Y_2O_3) it should be not more than 15 J/cm². Here the smoothing of relief (Figure 4) and packing of a thin, up to 10 µm, surfaced layer are observed, thus contributing to increase of erosion resistance of coating in the process of service.

The investigations of composition of modified layer using X-ray spectral analysis from the surface showed that its chemical composition is close to the composition of base metal. HPF treatment of thermal barrier coatings in H_2 environment results in formation of a glittering surface layer, and in the environment of N_2 — in formation of nitrides.

The surfaces of alloy ChS88U-VI were alloyed with elements decreasing the temperature of melting of the surface layer. It is known [8–11] that brazing alloys with zirconium and hafnium at comparatively low concentrations do not negatively influence the properties of heat-resistant



Figure 4. Microstructure of thermal barrier plasma coating before (a) and after (b) HPF treatment





Figure 5. Microstructure $(a - \times 500)$ of Zr-alloyed surface layer of alloy ChS88U-VI, and distribution of zirconium concentration (b) at different modes of HPF treatment (1-4)

nickel alloys and provide high mechanical properties to the joints. In the alloys of ChS70 type zirconium negligibly decreases and hafnium increases the resistance against high-temperature salt corrosion.

Investigations of modified surfaces showed that formation of fused layer depends, in the first turn, on thickness of sprayed layer of the alloying element, energy density, number of pulses. Microstructure of the modified layer and distribution of the alloying element in the layer at different modes of treatment are shown in Figure 5.

At one and the same thickness of the sprayed alloying element and growth in number of pulses, the uniformity of distribution of zirconium and hafnium is increased, but their concentration at the surface of layer is decreased. As is seen from Figure 5, concentration of zirconium near the surface is close to eutectics one only for curves 1 and 2. At the same time it is known [8, 12] that in nickel alloys the eutectic concentration of hafnium is somewhat decreased as compared to the Ni–Hf system. At high rates of cooling (10^{4} – 10^{5} °C/s) the equivalent concentration of hafnium is widened and temperature of melting is decreased to 1178 °C. Besides, it is established that melts filling interdendritic capillaries of super-strength nickel alloys even at 16 wt.% Hf represent eutectics Ni_{all}–Ni₅Hf [13]. The similar effect can be also present in the system Ni_{all}–Zr. In any case at 1200 °C the liquid in a butt is sufficient even to form fillets.

At the compression pressure of 10-15 MPa in joint of alloys ChS88U-VI the butt is not revealed in the microstructure (Figure 6, *a*). Distribution of microhardness in the joint area is shown in Fi-



Figure 6. Microstructure of joint with Zr-alloyed surfaces of alloy ChS88U-VI in brazing under pressure $(a - \times 500)$, integral distribution of microhardness (b), microstructure of joints with after heat treatment, Hf- $(c - \times 150)$ and Zr-alloyed $(d - \times 300)$ surfaces

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gure 6, b, and the structure of welded joints with surfaces alloved with hafnium and zirconium after heat treatment - in Figure 6, c, d.

Investigations of structure of joints of alloy ChS88U-VI showed that in the butt zone the structure is formed similar to the structure of base metal. Mechanical tests confirmed the high quality of joints both at modified and also at alloyed surfaces. The tensile strength of joints at 900 °C is not lower than 90 % of base metal.

Similar results were obtained also in joining with alloyed surfaces of alloy Inconel 718. The tensile strength of the joints at the test temperature of 550 °C exceeded 900 MPa, which is 90 % higher than the strength of base metal, and in fatigue test at 785 °C, standard stresses and duration, the welded specimens were released without fracture.

Therefore, LHEB and HPF treatment of materials surface provides formation of a necessary topography, structural, chemical and phase composition of surface layers, being the main factors for formation of quality joints in arc welding and deposition of coatings.

The layers modified using LHEB and HPF are characterized by a high density of dislocations (to 10^{11} cm^{-2}), increased level of stresses of the 3rd kind and also high level of intergranular energy, that positively effects the formation of joints in arc welding and deposition of plasma coatings. Smoothing of surface and packing of structure of the HPF-modified layer of thermal barrier coatings facilitates the improvement of their erosion resistance in the process of operation.

The application of HPF is the challenging trend in development of diffusion welding, brazing and deposition of coatings.

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- 1. Gribkov, V.G., Grigoriev, F.I., Kalin, B.A. et al. (2001) Advanced radiation-beam technologies for treatment of materials: Manual. Ed. by B.A. Kalin.
- Moscow: Krugly God. 2. Kvasnitskii, V.V., Kuznetsov, V.D., Koval, N.N. et al. (2009) A high-current electron beam application for the surface modification of iron. Stainless steel and heat resistant alloys. Surface Eng. and Applied
- *Electrochem.*, (**45**)3, 180–185. 3. Kvasnitsky, V.F., Kvasnitsky, V.V., Cherenda, N.N. et al. (2011) Effect of surface modification using concentrated energy beams on formation of solid phase joints. In: Proc. of 9th Int. Conf. on Interaction of Emissions with Solid (Minsk, 20 Aug.-2 Sept., 2011), 228-230. Minsk: Tsentr BGU.
- 4. Belov, A.B., Britsenko, O.A., Krajnikov, A.V. et al. (2012) High-current pulsed electron beams for aero-
- nautical engine engineering. Moscow: DIPAK. 5. Musin, R.A., Antsiferov, V.N., Kvasnitsky, V.F. (1979) Diffusion welding of heat-resistant alloys. Moscow: Metallurgiya. 6. Ermolaev, G.V., Zhitnikov, N.P., Zabolotsky, V.M. et
- al. (1988) Vacuum diffusion welding of dispersion-hardened heat-resistant alloys with inserts. Sudostroit. Promyshlennost, Series Welding, Issue 6, 13–23. 7. Cherenda, N.N., Uglov, V.V., Kvasnitsky, V.F. et al.
- (2014) Elemental composition of surface layer of heat-resistant nickel alloy alloyed with zirconium atoms under action of compression plasma flows. Poverkhnost. Rentgen., Sinkhron. i Nejtron. Issledov., 2, 74-79.
- 8. Khorunov, V.F., Ivanchenko, V.G., Kvasnitsky, V.V. (1999) Structure and phase composition of Ni-Cr-Zr and Ni-Cr-Hf alloys applied as braze filler materials. Avtomatich. Svarka, 11, 14-21.
- 9. Kvasnitsky, V.F., Kostin, A.M., Kvasnitsky, V.V. (2002) Effect of elements-depressants on properties of nickel braze materials and heat-resistant alloys. Adgeziya Rasplavov i Pajka Materialov, 35, 129–139.
- 10. Lugscheider, E., Bushke, I., Daichend, D.M. et al. (1998) Evaluiring des Eizatzpotential und rostfreien Edelstahlen. In: Vortrage und Posterbeitrage des 5. Kolloquium in der Hart- und Hochtemperaturloten und Diffusionsschweissen (Aachen, 16-18 June, 1998), 192, 242-245. Duesseldorf: DVS.
- 11. Zeng Yun-Rong, Ca Yu-Lin, Ruan Zong-Ci et al. (2006) Investigation of effect mechanism of hafnium and zirconium in high temperature materials. J. Aero*naut. Mat.*, 26(**3**), 25–34. 12. Sircars, S., Mazumder, J. (1989) Microstructure evo-
- lution and nonequilibrium phase diagram Ni-Hf binary alloy produced by laser cladding. Acta Metallurgi-ca, 37(1), 1167–1176.
 13. Zehg, Y., Ruan, Z. (1990) Microstructure and perfor-mance of Ni–Hf brazing filler alloy. Acta Metall. Si-
- nica, 10, 335–340.

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