

Electro-Explosive Alloying of Metals: Surface Morphology, Phase Structure and Defective Substructure

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Abstract – Methods of scanning and diffraction electronic microscopy of thin foils have been used in surveying the surface relief structure and phase structure conditions of electro-explosive iron aluminizing and boroaluminizing zone, as well as iron and nickel coppering and borocoppering. It has been established that owing to overheating and subsequent boiling up of melt on the external surface of the alloying zone pores arise. Mechanical interaction of the condensed particles of jet with the melt causes occurrence of advanced relief morphology sites on the surface. It has been shown that content of alloying elements and the synthesized phases are decreasing with depth. This is better manifested during coppering, than during aluminizing. At binary alloying the gradient of phase structure conditions on depth is higher, than at single-component alloying. Features of three typical layers have been considered. These are a thin surface layer of the synthesized phases with nanocrystalline or quasia-morphous structure, an intermediate layer with cellular crystallization structure and a frontier layer at the bottom of an alloying zone with high degree of plastic deformation. In some cases on basement border a thin layer of nanocrystalline structure and low alloying degree appeared. Structural changes affect a thermal impact zone also, in which the high scalar density of dispositions is observed.

1. Introduction

One of the new ways of hardening of metals and alloys is processing of their surface by the heterogeneous plasma jets generated from products of electrical explosion of conductors. Electro-explosive alloying (EEA) essentially reduces time of processing in comparison with traditional ways of thermo-chemical treatment of surface, combining its local melting and saturation with alloying elements with the subsequent self-hardening. Material of exploding conductor sets the chemical compound of plasma jet at processing. Expanding technological opportunities of the method and a range of its practical application, one place powder weighting of any substance in explosion area. It allows to carry out two and multi-component alloying.

Practical use of the EEA is now restrained by low understanding of its typical interrelated thermal, power, hydrodynamic and physical-chemical proc-

esses impact on irradiated surface at various kinds of processing which determine its structure-phase conditions and properties. The aim of the present work was to reveal the laws of structure formation, phase structure and defective substructure of the surface layers of model materials of iron and nickel after four kinds of the EEA – iron aluminizing and boroaluminizing, as well as iron and nickel surface coppering and boro-coppering.

2. Materials and technique of research

At choosing the kind of the EEA the results of traditional thermo-chemical treatment of metals were taken into consideration. Processed were the plates of the model material – technically pure iron of 3–5 mm thickness and plates of technically pure nickel of ~2 mm thickness. As exploding conductors aluminum or copper foils of 20 or 15 mm weighting 40 and 100 mg accordingly were used. At boroaluminizing and boro-coppering in explosion area the powder weighting of amorphous boron weighting 60 mg was introduced.

The heterogeneous plasma jets formed at discharge of energy through the coaxial-to-front-end system of electrodes of the capacity store serve as a tool of impact on surface at the EEA. They consist of purely plasma high-speed head part continuously transferring into service element with gradually increasing content of explosion products condensed particles in it. As a result of plasma thermalization during braking the sample surface is heated up and, at certain parameter values of processing, melts. The service element of jet interacts with already fused metal on its surface and forms the relief.

Processing was carried out in highly intensive mode at which there was the remarkable radial current of melt under jet pressure upon surface from center to periphery of the plasma impact. Effective value of processing time was believed to be equal 100 μ s. The absorbed density of capacity on jet axis has been appreciated equal to 6,0 GW/m², and pressure in a dispatch-compressed layer, formed near to irradiated surface has been equaled to 14,2 MPa.

Researches of surface relief after processing was carried out using methods of scanning electronic microscopy. The subsequent analysis of structure-phase conditions of plasma impact zone was carried out using methods of transmission electronic diffraction microscopy of thin foils. Investigated was the surface of samples, as well as the layers located on various depths. For this purpose foils were prepared by electrolytic thinned down of the plates, which had been cut out using electro-spark erosion of simultaneously processing surface from intermediate area of alloying zone at the distance of 10–15 mm from the center where its thickness reached 20–25 μm .

3. Results of research and their discussion

During the surface relief study at ~ 100 – 400 times magnification on after the EEA the sites with highly developed relief were found out on rather plane surface of samples. After iron aluminizing their share was less than a half, and after iron and nickel coppering of the share of the surfaces occupied with the both types of structure, were approximately equal. In threefold systems Fe-Al-B, Fe-Cu-B and Ni-Cu-B their ratio was 1,5 : 1, 1 : 5 and 1 : 8 accordingly. At the same time the average sizes of areas with rather smooth relief in a number of systems Fe-Al, Fe-Al-B, Fe-Cu, Ni-Cu, Fe-Cu-B, Ni-Cu-B decreased and totaled to ~ 1000 , 400, 350, 250, 150 and 100 μm accordingly.

At ~ 1000 – 3000 times magnification in areas with a highly developed surface relief morphologically distinguished were 2 types of structure: thin extended formations and particles of spherical or globular forms changing sizes from 10 to 0,3 μm .

It is possible to assume, that islands of developed relief on the surface appeared after its interaction with drops of the various sizes formed during foil explosion, or with the particles emerged during interaction of these drops with powder of boron particles. The maximal size of particles depending on foil thickness, could reach several tens of micrometers. Moving in back part of the jet, they collided with already melted surface. Not having time to dissolve completely in melt, the deformed particles left traces of islands with an advanced relief on surface. The peculiarities observable at mesoscale level, represented separate streams, breaking up in fine droplets in their ends.

Beside this, the cracks were found out on surface. On smooth relief sites their length reached 40–50 μm , and on advanced relief sites – about 1 μm . There were practically no cracks on the surface of Fe-Al system, their were small amount of them in case of Fe-Cu-B and Ni-Cu-B systems and a little bit more in case of Ni-Cu, Fe-Cu and Fe-Al-B systems.

One more element of the meso- and micro-scale levels were traces of open pore shapes (fig. 1). They

were mostly manifested on the surface of Fe-A-B system. At ~ 6000 – 10000 times magnification well distinguished were micropores with the sizes of 2,5 to 0,15 μm . Most brightly microporosity was shown on the surface of Ni-Cu and Fe-Al systems. Explaining the reason of pores formation it is necessary to consider the fact, that in high pressure conditions in dispatch-compressed layer which is formed at surface during processing, metal of the basis is heated above temperature of boiling at normal pressure conditions. Therefore after the ending of pulse of impact when pressure recession took place, overheated top layers melt boil [1]. From this point of view pores are the traces bubble boiling.

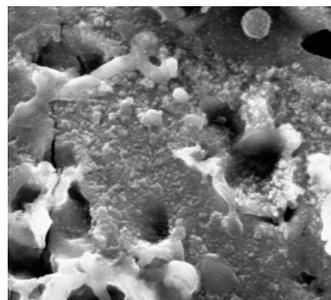


Fig. 1. Pores on iron surface after boroaluminizing. $\times 3500$

TEM study of thin foils has shown, that the EEA leads to formation of four characteristic layers which regularly replace each other traveling from surface into depth. There are: 1) thin near-surface layer of the synthesized phases; 2) intermediate layer with structure of cellular crystallization; 3) the frontier layer adjoining to the zone of thermal influence; 4) thin sub-layer with nanocrystalline structure dividing them.

The near-surface layer as a layer basically formed of new compounds crystallites with participation of alloying elements, at single-component alloying was almost not found out. However, after two-component alloying such layer with nanocrystalline structure of ~ 1 μm thickness was present in all cases. It was basically formed with borides, oxides, oxiborides of iron, nickel and copper. For example, after boroaluminizing on the surface of iron the layer was formed, in which it was possible to distinguish two classes of crystallites with the average sizes of ~ 30 – 35 nm and ~ 4 – 5 nm. They could belong to iron oxide of FeO structure, aluminum boride of $-\text{AlB}_{12}$ structure and iron alu-moboride of AlFe_2B_2 structure, and also to compounds of Fe_3B and AlB_2 . From the interior of synthesized phases layer the sizes of crystallites had two characteristic values – about 30 and 50 nm. The most probable compound of smaller crystallites corresponds to AlFe , and larger crystallites are iron oxides of FeO compound.

Formation of oxygen containing phases in alloying zone could be caused by uncontrollable interaction of residual air atmosphere oxygen with melt in

technological chamber. Besides, oxygen could get in melt together with particles of the collapsed foil containing oxides. Using boron powder adsorbed oxygen could be transferred to irradiated surface by these particles also. Presence of carbon in alloying zone could emerge due to erosion of dielectric lining between electrodes of the plasma accelerator.

Peculiarity of iron aluminizing and boroaluminizing zone was difficulty in distinguishing intermediate and frontier layers from each other in both cases, therefore for these systems we shall consider those layers as a whole. After aluminizing the basic phase of the given layer appeared to be the α -phase of firm solution of aluminum in BCC crystal lattice of iron. The sizes of grains in it varied from units up to tens of micrometers. In grains the reticular dislocation sub-structure, or chaotic dislocation substructure was observed. The scalar density of dislocation totaled to $5,4 \cdot 10^{10} \text{ cm}^{-2}$.

Alongside with the α -phase, the boroaluminizing layer contained inclusions of the second phase – particles of aluminum, aluminides and iron alumo-carbide. Aluminum in alloying layer was found in two morphological versions: as plates of various sizes and as particles of round form of 25–35 nm size located in α -phase grains. Occasionally the plates of aluminum divided by layers a of α -phase, formed small colonies located in joints of ferrite grains. Iron aluminides also had some morphological versions. Namely, iron aluminide of AlFe structure was found as formations of grain type; FeAl_6 , Fe_2Al_5 , Fe_3Al aluminides – as the plates located in grains of ferrite, or forming small colonies, similarly to aluminum. FeAl_6 aluminide was also found as the particles of 3–5 nm size located in dispositions in ferrite grains. $(\text{Fe}, \text{Al})_3\text{C}$ iron alumo-carbide was found in grains of ferrite as nanodimensional particles (3–5 nm) of round form, and also along the inter-phase borders dividing α -iron and aluminum.

It is necessary to point out one more feature of iron aluminizing zone. In the intermediate layer there was not found structures of concentration stratification cells which was formed during other systems crystallization. It may be caused by effective hashing of al-loying element in basis melt which is mentioned above.

On the contrary, after boroaluminizing moving from surface of sample processing 1–1,5 μm in depth of alloying zone led to detection of layer of cellular crystallization of melt. And in this case it was the basic on volume. The sizes of crystallites in its top part changed within the limits of 150–200 nm. Thickness of layers made $\sim 50 \text{ nm}$. According to the microelectronic diffraction patterns cells of crystallization here have been generated by $\gamma\text{-Al}_2\text{O}_3$ aluminum oxide, and the layers dividing cells of crystallization by $\gamma\text{-Fe}_2\text{O}_3$ iron oxide.

The analysis of iron boroaluminizing layer at 20–25 μm depth, i.e. near the lower border of alloying zone, has shown, that its structure also was submitted by cells of crystallization (fig. 2) which had been generated by α -iron, the layers dividing them were formed with AlB_{10} aluminum boride, or AlFe iron aluminide. In the first case cells of crystallization appeared to be nanodimensional ($\sim 10\text{--}20 \text{ nm}$) particles. According to the microelectronic diffraction patterns of the given site of the foil, given particles were Fe_3B iron boride.

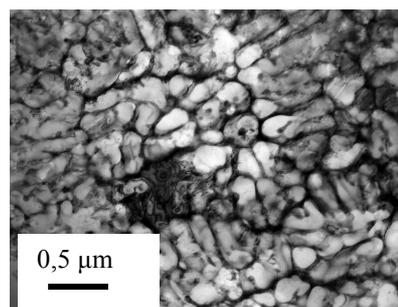


Fig. 2. Electron microscopy image of cellular crystallization layer structure near the border of iron boro-aluminizing zone

After iron coppering and borocoppering the intermediate layer with cellular crystallization structure in samples of these two systems had sufficient differences [2]. In the first case near-surface and intermediate layers in this system had small thickness making together $\sim 1\text{--}1,5 \mu\text{m}$. In the given system the basic (on volume) was the frontier layer which basically was represented α -phase (Fig. 3). On the contrary, in Fe-Cu-B system sample basic layer, extending to border of the thermal impact zone was the layer of cellular crystallization. It is necessary to note change with depth of structure of crystallization cells and the layers dividing them, caused by essential reduce of copper and oxygen concentration to the depth.

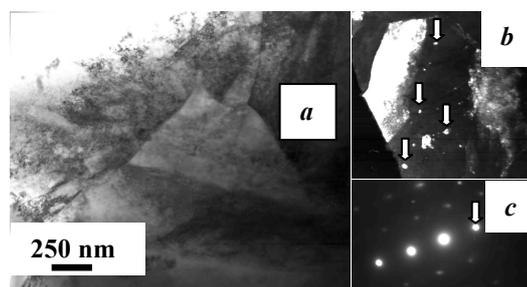


Fig. 3. Electron microscopy image of structure of the layer formed at the bottom of bath melt of iron being alloyed by copper: a – light field; b – dark field received in reflexes $[110]\alpha\text{-Fe} + [002]\text{FeO}$; c – the microelectronic diffraction patterns. Specified by arrows are: (b) particles of iron oxides, (c) reflexes of dark field

Such strong difference in thickness and morphological features of cellular crystallization layers in the investigated volumes of iron coppering and borocoppering zones testified the following. Even in conditions of high-energy impact on surface for which intensive convective intermix of melt is typical, in alloying zone essential local heterogeneity of chemical and phase structure can be observed. It is possible, that the reason of dissimilarity is that copper badly mixes up with iron. In this case it is possible to assume, that pouring boron in melt promotes their better hashing.

After nickel coppering the volume of cells was formed by firm solution of copper in nickel. Crystallization cells of the average size of 50 nm were divided by layers oxide phases of NiO or Cu₂O. At distance from processing surface cell degenerated in structure, typical for high-speed dendrite crystallization of solutions. It in turn was passing in grain type structure, the sizes of grains in which changed within the limit of 0,5 to 5 μm.

After nickel borocoppering the layer of cellular crystallization was the basic in alloying a zone volume, therefore with deepening its phase structure, morphology, crystallites sizes and defective substructure changed appreciably. On depth of 2 μm the multiphase structure consisted of crystallites of the spherical form, divided by wide layers was observed. Cells have been formed by firm solution of atoms of copper and boron in crystal lattice of nickel. Layers dividing them were generated with nickel borides of the crystallites size of 30–35 nm. With increase of depth cells got irregular globular form with developed borders. Thus the cross-section sizes of layers decreased, their continuity was broken.

It is known, that structures of cellular crystallization are formed at high-speed cooling of melts of the multicomponent systems, processed by concentrated streams of energy, for example by laser radiation, electronic and ionic beams. We found out similar structures in the modified superficial layers of iron and nickel after electro-explosive carbonizing and carboboronizing earlier [1].

Moving off the top layers formed during melt crystallization after iron aluminizing, allowed to reveal nanocrystalline sublayer settled down along border of alloying zone with the basis being generated by γ- and α-iron crystallites. The average sizes of crystallites in

it totaled to 45–50 nm. On borders of iron crystallites Al₆Fe iron aluminide and aluminum crystallites of 3–5 nm were found out. Similar sublayer with nanocrystalline structure was also found out after boroaluminizing. The size of crystallites in it changed within the limits of 35–40 nm and 2,5–3 nm. According to the microelectronic diffraction patterns of this site of foil, crystallites of the first dimensional level were formed by α-iron, crystallites of the second dimensional level were preferably Fe₃B iron boride.

In zone of thermal impact of iron in which transformations occurred in firm phase, ~30–35 μm deep in iron grains volume dislocational substructure of various degree of perfection was observed. Its formation was determined by action of thermal and phase pressure caused by pulse character of plasma impact on surface during the EEA. Depending on grains orientation in relation to working pressures, formation of dislocation chaos, reticular, cellular-reticular and fragmented substructures in them is observed.

After nickel processing in both cases the relaxation of thermal and phase pressure in cellular crystallization layer, frontier layer of alloying zone, together with zone of thermal impact was accompanied by formation of dislocation structures in grains of firm solution. Its type and size of scalar density of dispositions were determined by level of working pressures and their orientation to grains of nickel. Thus in crystallites which sizes did not exceed 500 nm, the dislocation structure was not observed. In zone of thermal impact deepening from border of alloying zone dislocation substructure changed from cellular to cellularreticular, then to reticular and chaotic. The scalar density of dispositions changed accordingly from $4,2 \cdot 10^{10}$ to $1,2 \cdot 10^{10} \text{ sm}^{-2}$. Borders of grains had been curved and contained the big number of ledges. It testified the development of recrystallization processes in layer.

References

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