Plasma surface modification in liquid environment

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Abstract. Plasma modification of metal surfaces in liquid environment was described. Microstructure and microhardness of a hardened layer were studied. As a result of plasma impact during 0.1-1 sec, the surface is carburized and nitrated to the concentration of high-carbon steel. Microstructure and metal surface properties after plasma modification were studied. Main parameters of the modified layer were identified: the layer depth is 50-300 µm, microhardness is 6000–14000 MPa.

1. Introduction

Machine and equipment operation goes hand in hand with wearing which decreases lifetime of machines. Increasing wearing properties of high wear parts is a topical issue for modern machine building.

Currently, finishing treatment uses either highly concentrated energy sources [1] or high energy multiple impacts inducing severe plastic deformation of the surface [2]. These are laser surface processing [3], surface treatments using an electron beam [4], plasma arc [5, 6], and nanocrystal surface modification [7,8]. Hardening by these methods enables an increase in wearing properties of metal surface layers and conservation of mechanical properties of internal layers. In [9], main theoretical issues of plasma surface hardening of metals in liquid environment were studied. The work raises the possibility of thermochemical hardening by carburizing and nitriding. Later the authors focused on development of plasma methods for surface tempering of steel and cast iron [5-8].

The present research describes the results of studies of surface layer structures resulted from plasma heating in liquid environment. To carburize or nitrogenize the surface layer, the part is immersed in a liquid containing carbon (toluene, mineral oil, etc.) or nitrogen (aqueous ammonium chloride solution, etc.).

2. Materials and methods

Plasma surface modification in liquid environment was performed on steel grades 1018 and 1020 based on ASTM Specifications. The chemical composition of the material in percentage based on the ASTM Specifications is shown in the table below. In experiment, samples of 80×20×10 mm were used.
Table 1. Chemical composition of steels 1018 and 1020

|                  | 1018       | 1020       |
|------------------|------------|------------|
| Iron, Fe         | 98.81-99.26% | 99.08-99.53% |
| Carbon, C        | 0.18%      | 0.20%      |
| Manganese, Mn    | 0.6-0.9%   | 0.30-0.60% |
| Phosphorus, P (max) | 0.04%    | 0.04%      |
| Sulfur, S (max)  | 0.05%      | 0.05%      |

Figure 1 shows plasma modification in liquid environment. The part is immersed in a flow liquid (pos. 2-5). A plasmatron forms a plasma jet (pos. 1). Ammonia is added to neutralize the formed acid (pos. 6). Gas-dynamic pressure of the plasma arc forms a funnel in a liquid, and thermochemical influence of the metal surface occurs. Metal surface is modified in a semi-closed space limited by a liquid all around. When the plasma jet moves around sample surfaces heated up to structural transition temperatures, the surface is covered by a liquid which cools them.

Figure 1. Plasma surface modification of metals in liquid environment

The microstructure was studied using OLYMPUS GX51 microscopes having magnification of 100x and 500x. Electronic and microscopic analysis of metal sample surfaces was carried out with a scanning electron microscope LV-4501. Micro-hardness was measured with the HMV-2T (Shimadzu) microhardness tester under load of 2–5 N. Layer depth was taken as a distance from the sample surface to the point of base hardness.

3. Results and discussion

Studies of plasma surface modification in liquid environment identified changes in metal surface microrelief. After deep etching (Fig. 2) of a specimen in a cross section area, a white layer with microhardness of 6000-14000 MPa (under load of 2N) was observed with the microscope. Figure 2 shows the changes of microhardness by the depth of a modified layer (the first character is measurement depth in µm, the second one is microhardness value). Depending on plasma modification modes, we can obtain surface layers of different structures.

A nitrided ε-phase is formed on the surface. Under it, a supercooled γ-phase is formed. Under the supercooled γ-phase, there exists nitrous martensite. Figures show UFG strucures of carbonitriding and nitriding zones. The transition from a nitrided layer to sublayers is smooth. It is one of the main requirements to the nitrided steel microstructure. Hardened zone depth varies between 50-300 µm.
Hardened zone consists of martensite, retained austenite and carbide.

**Nitriding.** Water solution of ammonium salts of different concentrations was used as a liquid. Thermochemical treatment involves three processes: dissociation – producing an active atomic saturating element: $2\text{NH}_3 \leftrightarrow 2\text{N} + 3\text{H}_2$, etc.; absorptions – absorbing of active atoms of the saturating element by the metal surface; diffusion – moving of atoms of the saturating element deep down. The experiment showed that an increase in nitrogen concentration results in increase in nitrogen content in surface layers which causes increase in depth layer and micro-hardness. Microstructure of the layer modified in liquid environment is similar to the microstructure of the layer subjected to traditional nitriding in gas and solid environments [5] with some differences. Nitrided layer consists of two zones: a compound zone (white zone composed of submicroscopic nitrides undistinguished when analyzed using metallographic techniques) and a diffusion zone. After modification, at a minimum treatment rate of 1-3 mm/sec, there is no white layer, and the diffusion zone is more homogeneous. X-ray crystallography shows that only $\gamma'$-phase of (Fe, Me)4N type is typical for a minimum steel 1020 treatment rate, while for steel treatment at a rate of 10 mm/sec. $\gamma'$-phase of (Fe, Me)4N type and $\varepsilon$-phase of (Fe, Me)2-3N type are typical. In the first case, intensity of x-ray lines of $\alpha$-solid solution increases several fold compared to the second case and exceeds intensity of lines of $\gamma'$-phase. Hardened layer depth for steel grade 1018 and 1020 was 0.05–0.2 mm, microhardness was 8000–14000 MPa. Thus, due to changes in technological saturating factors, one can control formed layers by their structures, phase compositions, and optimize properties of nitrided parts and tools.

**Carbonitriding.** Carbonitriding is characterized by increased nitrogen and carbon concentrations. Hardened layer depth for steels grade 1018 and 1020 was 0.05–0.3 mm, microhardness was 6000–12500 MPa. Microhardness increased with rising heating rate. Lower heating rate increased the time of intensive nitrogen and carbon-containing liquid evaporation. It increased concentration of active atoms of carbon and nitrogen at the interface of saturated environment and metal surface. However increase in nitrogen and carbon concentrations on the anode spot of the plasma arc [6] caused increase in retained austenite (from 2.5 to 40 % for steel grade 1020), and it reduced microhardness. Diffusion layer depth for steel grade 1018 was 0.01–0.03 mm; microhardness was 6000–10000 MPa. Diffusion layer depth for steel grade 1020 was 0.01–0.03 mm; microhardness was 6000–11000 MPa.
Figure 2. Microstructure of the modified layer in different plasma modification modes  
a – nitriding layers;  
b, c – carbonitriding layers;

The results confirmed potential capacity of plasma surface modification in liquid carbon and nitrogen containing environments. Using this technique, skins can have traces of micro-melting without metal bath formation in the form of a thin layer. Diffusion of carbon and nitrogen into metal is accelerated. The significant parameters are liquid environment composition and metal surface heating and cooling rates.

4. Conclusion
Studies on plasma surface modification in liquid environment confirmed application benefits of the method to form modified layers with complex microstructures. Nitrided and carbonized layers with depth of 0.05-0.3 mm and microhardness of 6000-14000 MPa were formed. By controlling the composition of liquid environment, we can obtain metal surfaces with different structures and properties.

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