Complex diffusion saturation of carbon steel 1045 with boron, chromium, titanium and silicon

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Abstract. The article presents the results of studies on the formation of a diffusion layer upon saturation of steel 1045 with boron together with chromium, titanium and silicon. The results of tests of diffusion coatings on steel 1045 obtained by simultaneous diffusion saturation with boron, chromium, titanium and silicon under the action of a sulfuric acid solution under conditions of abrasive wear are presented. A comparison is made of the service life of knives for shredding lead-acid batteries made of steel HARDOX 600 and steel 1045 after diffusion saturation with boron, chromium, titanium and silicon. It was found that the simultaneous strengthening with boron, chromium, titanium and silicon made it possible to increase the operational durability of knives for shredding lead-acid batteries by 2.4 times. The possibility of highly efficient use of products made of simple carbon steel with a multicomponent (B + Cr + Ti + Si) diffusion coating instead of products made of hardened alloy steel is shown.

1. Introduction
Wear of the working surfaces of machine parts and tools is the cause of breakage in 75% of cases. The problem of increasing wear resistance is becoming increasingly important. The trend in the development of chemical-thermal treatment is due to the problem of saving alloying materials (manganese, chromium, cobalt, tungsten, vanadium, molybdenum, niobium, etc.). The use of diffusion hardening and protective coatings can significantly reduce manufacturing costs and improve the performance properties of the created products. In some cases, chemical heat treatment is the only possible means of obtaining the required performance properties not only of the surface, but also of the product as a whole.

Boriding occupies a special place among the processes of chemical thermal treatment. The increased interest in the boriding process is caused by the possibility of obtaining layers with a unique set of properties in the surface zone of the processed products. In addition, diffusion boriding can be applied to a wide range of structural and tool steels and alloys. Boron-based coatings lead the way in improving properties such as wear resistance, heat resistance and hardness. As shown [1-20], the simultaneous complex diffusion saturation with boron together with other elements makes it possible to further enhance the performance properties of boride coatings.

Our studies [15-22] on the complex saturation of steels with boron together with chromium and titanium showed a significant increase in such characteristics of the coating as wear resistance, corrosion resistance when heated and in aggressive media (for example, solutions of acids and alkalis). Leadership in durability belongs to complex diffusion coatings based on boron, chromium and titaniuim at the same time. However, the resistance of such coatings in sulfuric acid solutions is much lower than their resistance in solutions of other acids (for example, nitric or hydrochloric). The coatings obtained by siliconizing [15-16] have the maximum resistance in acidic solutions. But acid-resistant silicide coatings have high fragility, and the simultaneous diffusion saturation with silicon and boron did not solve the problem of resistance in sulfuric acid solutions. In this regard, we see it as logical to obtain diffusion coatings based on boron, chromium, titanium and silicon.

2. Methods
Experimental studies on diffusion saturation were carried out on samples of steel 1045 with dimensions of 15x25x40 mm. The saturation was carried out in a SNOL 30/13-C1 chamber furnace equipped with a PID controller. The saturation was carried out at a temperature of 950 °C, the holding time at the saturation temperature was 1.5 h. Saturating pastes of the following composition were used as saturating media:

1) paste for simultaneous hardening with boron and chromium:
   25% CrB₂ + 50% B₄C + 5% NaF + 3% Fe₂O₃ + 7% Na₂B₄O₇ + 10% graphite.
2) paste for simultaneous hardening with boron and titanium:
   25% TiB₂ + 50% B₄C + 5% NaF + 3% Fe₂O₃ + 7% Na₂B₄O₇ + 10% graphite.
3) paste for simultaneous hardening with boron, chromium and titanium:
   15% CrB₂ + 15% TiB₂ + 50% B₄C + 5% NaF + 3% NH₄Cl + 7% Na₂B₄O₇ + 5% graphite.
4) paste for simultaneous hardening with boron, chromium, titanium and silicon:
   10% CrB₂ + 10% TiB₂ + 10% Si + 50% B₄C + 5% NaF + 3% NH₄Cl + 7% Na₂B₄O₇ + 5% graphite.

Powdered saturating media of the above compositions were diluted in water to a paste state and spread on the surface of the samples with a layer of 3-4 mm. After drying, the samples were placed in a preheated oven. At the end of the high-temperature holding, the samples were removed from the oven and cooled in air. After complete cooling of the samples, they were washed in water to remove the remains of the saturating medium.

Metallographic studies were carried out on transverse samples cut with a MICRACUT-201 precision metallographic cutting machine and pressed into a bakelite compound using a METAPRESS metallographic press. Grinding was carried out on an automatic grinding and polishing machine "DIGIPREP" using diamond wheels with a grain size of 54, 15 and 6 microns, the force on each sample was 25, 20 and 18 N, respectively, with individual clamping of the samples. Polishing was carried out on polishing cloths "ALUPOL" using monocrystalline diamond suspensions on a water basis with a grain size of 3 and 1 µm at a pressure of 15 N on the sample in the mode of individual clamping. Superfinish polishing was carried out on AQUA BLACK cloth using an acidic suspension of silica with a grain size of 0.05 µm. Metallographic analysis was performed using the "Thixomet PRO" software package and a Carl Zeiss Axio Observer Z1m optical microscope according to the methods [23–30]. To reveal the microstructure, an etchant of the following composition was used: ethyl alcohol - 95 ml, hydrochloric acid - 2 ml, selenic acid - 3 ml.

3. Results and discussion

In all cases, diffusion coatings were obtained with a morphology characteristic of boride layers. Structures and their description for complex boride coatings doped with chromium and titanium are presented in [15–22, 31–34]. The structure of the diffusion coating obtained by simultaneous saturation with boron, chromium, titanium and silicon is shown in figure 1.

The diffusion coating shown in figure 1 has an average thickness of 125 ± 2 µm and a morphology characteristic of boride layers. The microhardness measured on boride needles at a load of 100 g (0.98 N) was 2542–2776 HV₁. The microhardness of the white phase adjacent to the boride needles was 623–575 HV₁. The microhardness of the sample core is 375–385 HV₁. The light phase, is adjacent to the boride needles is morphologically similar to ferrite, however, compared to ferrite, it has a significant hardness that exceeds that of pearlite.
On closer inspection, can see dark and light concretion in this phase (figure 2).

Previous studies [17–22, 33–34] of similar concretion have shown that these are carbides, carboborides and borides with a complex composition. Also, these phases have high hardness values, reaching values of 3200–3700 HV. The average size of these secretions is 1.2–1.5 µm, the weighted average form factor according to Ferret (F2) is 0.87, which indicates that these secretions have a shape close to globular. It should be emphasized that precipitates of borides and carboborides with a high boron content are localized mainly along grain and interphase boundaries. The concretion of borides and carboborides with a high boron content inside ferrite grains is also possible and is located between the boride needles. The concretion of carbides and carboborides are located in the lower part of ferrite precipitates. Elemental analysis of the boride layer showed the following composition (wt.%): Fe - 56; B - 26; Cr - 7; Ti - 8; Si - 1.7; the rest is impurities. Elemental analysis of the ferrite phase, including concretions in it: Fe - 77; B - 8; Cr - 9; Ti - 2; Si - 2.7. Elemental analysis of the pearlite phase did not reveal any particular deviations from the natural elemental composition characteristic of this steel. The exception is in this case chromium - its content varies from 1.5-1.7 mass. % at the border with ferrite.
and gradually decreases to values of approximately 0.17 mass. % at a depth of 450–500 µm from the saturation surface.

Thus, the diffusion coating on steel 1045 obtained by simultaneous saturation with boron, chromium, titanium, and silicon contains all the introduced elements. Corrosion tests of this coating in laboratory conditions have shown a high resistance of this coating, which exceeds the resistance of coatings obtained by saturation from pastes 1–3 by 3–5 times. In addition to tests for corrosion resistance, full-scale tests were carried out in real conditions, combining the effect of a sulfuric acid solution and abrasive wear. Knives for crushing used lead–acid battery for further recycling were used as test samples. These knives were made of steel 1045 and their surface was diffusion-hardened from saturating pastes 1–4. The service life of the hardened knives was measured by the real weight of the shredded batteries. Additionally, knives made of HARDOX 600 steel, made using water-jet cutting, were used as reference knives.

The production tests carried out have confirmed the correctness of our assumptions: diffusion coatings were obtained that have high indicators of resistance to abrasion in a sulfuric acid solution. Tests of knives, hardened in various ways, made of steel 1045 for shredding lead–acid battery showed the following results:

1) simultaneous strengthening with boron and chromium - 18 tons of shredded batteries
2) simultaneous strengthening with boron and titanium - 16 tons of shredded batteries
3) simultaneous hardening with boron, chromium and titanium - 54 tons of shredded batteries
4) simultaneous strengthening with boron, chromium, titanium and silicon - 183 tons of shredded batteries.

The durability of the reference knives made of HARDOX 600 steel was 77 tons of crushed batteries. It should be especially noted that the wear of the knives was predominantly corrosive. That is, the greatest damage to all surfaces of the crushing knives occurred as a result of exposure to the sulfuric acid solution contained in the battery.

4. Conclusion

Thus, the simultaneous diffusion saturation with boron, chromium, titanium and silicon of carbon steel made it possible to increase the operational durability of knives for shredding lead–acid battery by 2.4 times. The possibility of highly efficient use of products made of simple carbon steel with a multicomponent (B + Cr + Ti + Si) diffusion coating instead of products from hardened alloy steel is shown.

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