Features of surface phase formation during case-hardening of iron- and titanium-based alloys

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Abstract. The article provides a detailed analysis of formation features for surface phases in technical iron and Cr20-Ni80 alloy samples that undergo case-hardening at a temperature of 850°C for 2, 4 and 6 hours of saturation in two different environments: acetylene, and molten salt consisting of sodium tetraborate and amorphous boron. We carried out an X-ray phase analysis to determine the phase structure of surface material layers that formed as a result of the case-hardening process. We discovered that after carburising it was possible to detect Fe₃C and Fe-α phases on the surface of technical iron samples, and after boriding we found Fe₅B, Fe₂B and Fe₃B phases; we noted a lack of characteristic Fe-α and Fe-γ peaks on the X-ray diffraction pattern. We detected many different phases in the Cr20-Ni80 alloy after the same type of case-hardening. Titanium oxides appeared after case-hardening of titanium in air at 800°C. We provide data on surface structure of samples subjected to vacuum carburising: over a 2 to 6 hour interval, the layer thickness is a parabolic function of time. When carrying out electrolysis-free liquid boring, increasing exposure time from 2 to 6 hours alters the thickness of the strengthened layer only slightly, so, when carrying out case-hardening, it is less efficient to increase saturation time in molten salt containing sodium tetraborate and amorphous boron.

1. Introduction
Some of the most important material properties are durability and wear resistance, since they affect potential industrial applications of these materials. Today there exist many methods to improve performance parameters of materials, for example, alloying or surface hardening. However, alloying is a very uneconomic method; moreover, certain properties of the materials to be strengthened sometimes make it unfeasible [1-3].

During operation, the surface of parts bears the main load, and, therefore, phase structure of a surface and its properties are greatly important for operability. Therefore, there is a significant interest in methods that make it possible to improve the properties of machine parts by only affecting their surface [4, 5].

There are a good number of methods dedicated to altering surface structure and properties. However, many of them have certain shortcomings, for example, they require expensive equipment. One of the most optimum methods is diffusion hardening of alloy surfaces during heat treatment [6-11].

Altering surface layer properties of parts by employing case-hardening to form diffusion layers with reinforcing phases is a promising way of manufacturing parts that are strong, with a hard surface but preserving the properties of their core material. Developing non-destructive testing methods for these processes is an urgent matter.
2. Results
In this study, we used X-ray diffractometry to perform phase analysis of surface layers of several iron-, titanium- and nickel-based alloys, subjected to different types of case-hardening. We investigated samples of various chemical compositions after carburising, boriding and oxidation.
We investigated three samples of technical iron after vacuum carburising in acetylene. Saturation time varied from 2 to 6 hours at a temperature of 850°C. Our research demonstrated that after processing, sample surface featured Fe₃C and Fe-α phases.
Analysis of X-ray data (figure 1) showed that increasing saturation time from 2 to 4 hours altered the ratio of Fe₃C to Fe-α (the amount of Fe₃C, cementite, went up); increasing saturation time up to 6 hours didn't change the phase ratio significantly. This result means that when the saturation time was 4 hours or more, the surface part of the diffusion layer at the X-ray radiation penetration depth (about 20 microns) was not significantly altered.

![Figure 1. X-ray diffraction data for technical iron samples after carburising. Case-hardening time varied from 2 to 6 hours; A- Fe-α, B- Fe₃C.](image)

We carried out electrolysis-free liquid boriding of technical iron samples in a melt of sodium tetraborate and amorphous boron at a temperature of 850°C for 2, 4 and 6 hours.
X-ray phase analysis of the sample surface showed a lack of characteristic Fe-α and Fe-γ peaks (figure 2). There are primarily iron boride lines: FeB, Fe₂B and Fe₃B.
Figure 2. X-ray diffraction data for several technical iron samples after boriding. Three samples were subjected to this type of case-hardening for 2, 4 and 6 hours respectively; C - Fe₂B, B - FeB, A - Fe₃B.

Analysis of intensity variation of characteristic boride peaks shows that increasing boriding time increases the intensity of FeB lines, while the characteristic Fe₂B peak intensity reduces. At the same time, we recorded relatively weak Fe₃B peaks for all samples.

The results obtained demonstrate that a continuous boride layer forms on the iron surface. It is over 20 microns thick, and this layer shields the iron matrix. Comparison of peak intensity for FeB and Fe₂B shows that as saturation develops, the FeB layer thickens. Metallographic analysis results confirm this.

Since relatively weak Fe₃B lines are present in the X-ray diffraction data for all saturated samples, we may assume that this phase builds up on the sample surface in the form of a thin layer or as isolated particles.

We detected several weak Fe₂O₃ lines, which may be explained by the surface oxidising lightly during boriding.

We carried out an X-ray phase analysis of the Cr20-Ni80 alloy sample after boriding (figure 3). The chemical composition of this sample is as follows: Cr – 20%, Ni – 72-78.8%, Fe – up to 1%, C – up to 0.06%, Si – 1-1.5%, Mn – up to 0.6%, Ti and Al up to 0.2%, Zn – 0.2-0.5%. After the case-hardening we discovered a variety of nickel, chrome and iron borides, as well as intermetallic compounds: Ni₂B, Fe₂B, FeB, Cr₂B, Ni₂Cr₃, Cr₂B₃.
Figure 3. X-ray diffraction data of a Cr20-Ni80 sample after boriding.

We also investigated two samples of a titanium (PT-1M) alloy. These samples were oxidized at a temperature of 800°C for 12 hours, the first one in air and the second one in graphite filling. X-ray analysis results allowed us to detect the main phase structure of these samples; when the surface oxidises, higher (TiO₂) and lower titanium dioxides are formed, which have high hardness and wear resistance (figure 4). Characteristic titanium peaks show that the oxide film thickness is small.
Figure 4. X-ray diffraction data of both PT1-M alloy samples; A - TiO, C - TiO₂, B - Ti₂O₃.

We found that the technique we applied in order to determine phase structure of thin surface layers of iron-, titanium- and nickel-based alloys has sufficient sensitivity to reliably record formation of carbides, borides, oxides and intermetallic compounds of various chemical compositions.

3. Conclusion
We analysed X-ray diffraction data of our iron- and titanium-based samples that we subjected to various types of case-hardening. As a result, we detected the presence of the following reinforcing phases:

1. We found the Fe₃C phase forming in the technical iron samples after vacuum carburising at 850 °C. When we increased case-hardening time from 2 to 4 hours, the amount of the Fe₃C phase grew significantly; a 6 hour case-hardening duration doesn't provide a significant increase in the amount of this phase as compared to a 4 hour case-hardening duration.

2. Our research revealed the presence of such phases as Fe₂B, FeB in the technical iron samples after liquid boriding at 850 °C. With an increase in processing time from 2 to 6 hours, we observed an increase in the FeB phase; when increasing case-hardening time from 4 to 6 hours, we did not find the FeB phase to grow significantly.

3. We carried out X-ray diffraction analysis of a Cr20-Ni80 sample after boriding. After case-hardening we observed a variety of phases forming: Ni₂B, Fe₃B, FeB, C₂B, Ni₂Cr₃, Cr₂B₃.

4. After oxidation in air, we located TiO₂ phases in a PT1-M alloy sample; after oxidation in graphite, we detected the TiO₂, Ti₂O₃ and TiO phases in another PT1-M alloy sample.

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