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Improving the technology of producing boron and siliconized layers and comparing their properties

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The paper presents the results of studies of single-phase boride layer formation and solid-gas siliconization on carbon structural steel. The influence of powder grain size and composition of the saturating mixture on the structure and properties of diffusion coatings is shown. The properties of the obtained surface structures are compared with those of PVD-obtained chromium nitride coatings. The possibility of obtaining thick diffusion single-phase boride and silicide layers that are not inferior in mechanical and chemical characteristics to nitride layers obtained by ion-plasma deposition was established. The presence of 75,7% FeSi, 19,6% Si_2CN_4 та 4,8% Al_5Fe phases in the silicide layer was shown, which provided high oxidation resistance at a temperature of 1000 °C.

Keywords: steel, boride layer, siliconization, metallographic studies, porosity, tool indentation, chromium nitride.

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Introduction

Modern engineering imposes increasingly stringent requirements on structural materials, particularly regarding wear resistance under extreme conditions, heat resistance, thermal strength, thermal and chemical stability. Steels maintain a strong position in this segment; however, the widespread use of alloying elements such as nickel, niobium, molybdenum, tungsten, vanadium, and cobalt is limited by economic factors. This underscores the relevance of surface modification techniques that enable the use of cost-effective base materials.

The technical feasibility of a given method is a crucial factor. Among surface engineering techniques, chemical-thermal diffusion processes are known for their relative simplicity and accessibility. This study investigates the formation of boride and silicide diffusion layers and compares their properties with those of chromium nitride coatings produced by physical vapor deposition (PVD). PVD was chosen as a benchmark method due to its ability to produce coatings with high hardness, wear resistance, and good adhesion, albeit with more complex processing requirements.

Boride layers exhibit excellent wear resistance and thermal stability up to 800°C, but tend to be brittle due to the formation of FeB on the surface [1, 2]. Silicide layers offer superior oxidation resistance at temperatures up to 1000°C and also possess high hardness and wear resistance; however, they often suffer from increased porosity. Both solid-phase and gas-phase techniques are available for producing boride and silicide layers, but they typically require prolonged exposure to high temperatures in saturating environments. This can adversely affect the base material by promoting grain growth through recrystallization processes [3–5].

Therefore, the aim of this work is to optimize diffusion saturation methods in order to minimize their drawbacks, investigate the resulting coating structures, and evaluate their performance in comparison with PVD-derived chromium nitride layers.

I. Materials and methods of research

There is a need to determine the sintering temperatures and related parameters for boron carbide-based powders [6] used in chemical heat treatment, specifically in solid-state processes. The sintering of powders complicates the boron diffusion process in steels and can lead to non-uniform diffusion layers. Several recommendations have been proposed to mitigate this effect, including the addition of inert components (e.g., corundum), reducing surface roughness, and others [7, 8]. However, these measures significantly reduce the activity of the boronizing environment, slow down the boronizing process, increase the required exposure time, broaden the range of powders used, and thereby complicate the preparation process and increase the labor intensity of part treatment.

Of both scientific and practical interest is the study of powder sintering behavior and the determination of sintering temperature thresholds for powders of various grain sizes.

The experiments were conducted on steel grade 40 (0.44% C; 0.19% Si; 0.51% Mn; 0.01% Cr; 0.01% Ni; 0.011% Cu; 0.01% Al; 0.001% S; 0.0026% P, as determined by the SPECTRO LAB LAVM11 optical emission spectrometer). The steel has a ferritic-pearlitic structure with initially fine grains.

Prior to saturation, all samples were ground using P100 and P320 grit sandpaper.

Boronizing was carried out at temperatures ranging from 850 to 950 °C for 1.5, 3, and 5 hours, using a paste composed of 60% B_4C, 15% NaF, 5% $CuCl_2$, and 10% $Al(OH)_3$, in a semi-sealed container. In selected experiments, boron carbide powders with different grain sizes were used: 160 µm, 100 µm, 80 µm, 60 µm, 50 µm, 30 µm, and a mixture of 30 + 160 µm.

Silicide coatings were produced by saturating steel with industrial silicon powder containing 5 wt% ammonium chloride and 20 wt% inert filler (merlins). The samples with the powder mixture were placed in a double crucible and held at 900 °C for 5 hours.

Metallographic analysis was performed using an IE-200 microscope. Samples were mounted in cold-curing Latacril resin, and cross-sectional grinds were prepared. Grinding was done sequentially with waterproof papers of grit sizes P100, P320, P600, P800, P1000, P1500, P2500, P3000, and P5000, followed by polishing on wet felt. Etching was conducted using a 4% nitric acid solution in ethanol.

Hardness was measured using a Rockwell PMT-3 tester, and instrumental hardness was evaluated using a Nanoscan-4D device (Berkovich indenter, 500 mN load, 15 s hold time at maximum load). X-ray diffraction analysis was conducted using DRON-3 and DRON-4 diffractometers with Cu Kα radiation and digital data acquisition.

II. Results and discussion

2.1. Investigation of samples with boride layers

To address the research objectives, preliminary boronizing experiments were conducted using boron carbide powders of various grain sizes: 160, 100, 80, 60, 50, and 30 µm. Additionally, previously used powder with a grain size of 160 µm and a mixed fraction of 30 and 160 µm were included in the study.

To ensure consistent sintering, the boronizing process was performed at 1000°C for 1.5 hours, followed by furnace cooling.

Boronized layers formed on all samples; representative microstructures are presented in Fig. 1.

Hardness measurements (Fig. 2) revealed that samples boronized with powders of 160, 50, and 30 µm grain sizes exhibited the highest hardness values. In sample 2, chipping and cracking were observed, and the hardness exceeded the upper limit of the HRA scale as defined by ISO 6508-1 Metallic materials — Rockwell hardness test — Part 1: Test method. The results presented in the bar chart were used as a basis for further investigation into the sintering mechanism.

The experiments were conducted in the temperature range of 850–950°C with varying durations: at 900°C for 3 and 5 hours, and at 950°C for 1.5 and 3 hours.

Figure 3 presents the microhardness distribution data for samples boronized under different temperature and time conditions.

The resulting boride layers ranged in thickness from 100 to 350 µm. At 850 °C, boride layer formation was negligible.

Microhardness distribution data indicate that at 950°C, boride layers with microhardness exceeding 10,000 MPa were formed, whereas at 900°C the microhardness remained below this threshold. The thickness of the hardened layer strongly depends on the duration of the boronizing process. The highest microhardness values were observed in samples treated at 950°C. Reducing the treatment time from 5 hours to 1.5 hours led to a decrease in layer thickness from 350 to 100 µm.

The microstructure shown below was analyzed using a special "color" etching technique to determine the

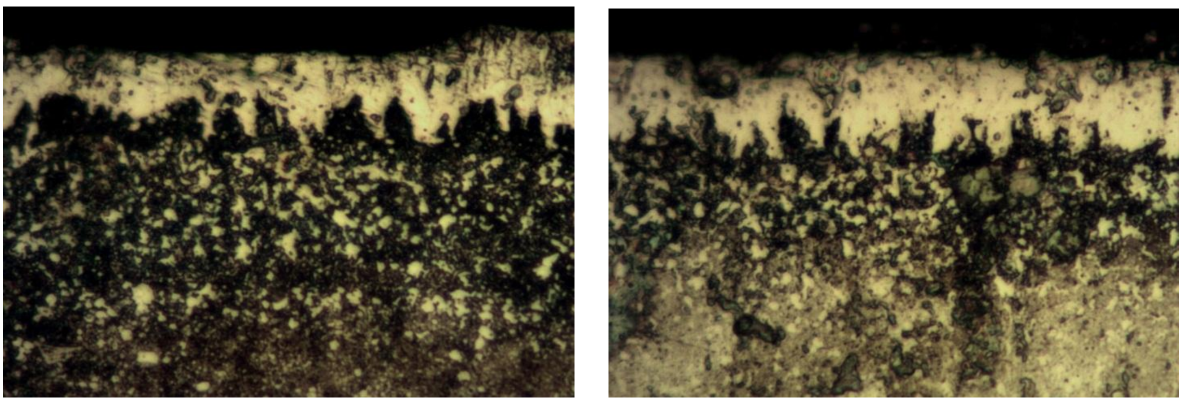

Fig. 1. Boronized layers obtained on steel with boron carbide grain size of 160 and 50 µm, respectively (x500).

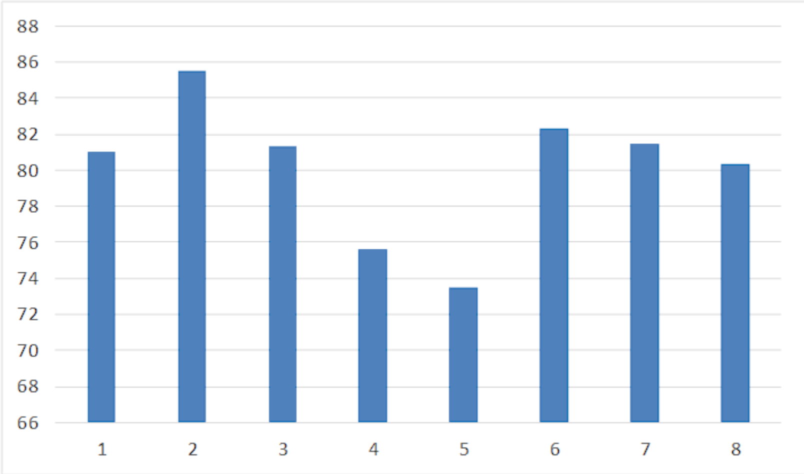

Fig. 2. Hardness level (HRA) on the boron samples: 1 – spent powder; 2 – 160 µm; 3 – 100 µm; 4 – 80 µm; 5 – 60 µm; 6 – 50 microns; 7 – 30 microns; 8 – mixture of 30 + 160 microns.

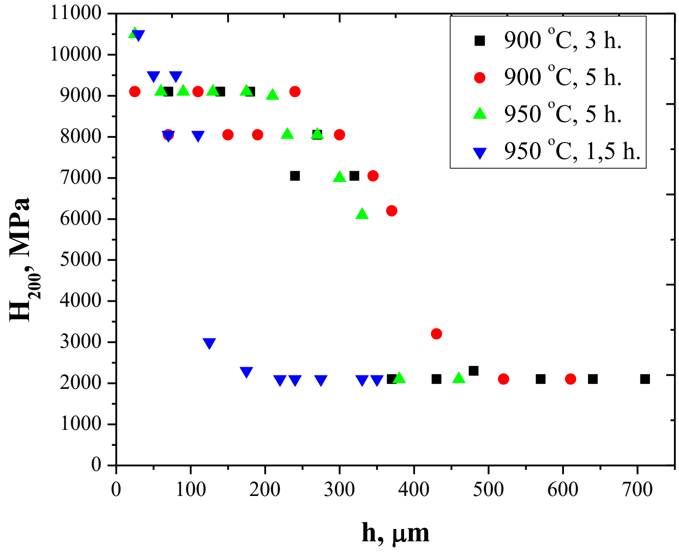

Fig. 3. Distribution of microhardness along the depth of the boron layer in different modes.

nature of the phases (Fig. 4).

As shown in the microstructure in Fig. 4, the absence of sintering enabled the formation of a high-quality, continuous boride layer with a substantial thickness of approximately 150 µm. Color etching and specific reaction characteristics caused Fe_2B to appear brown, while the solid solution needles remained light. X-ray diffraction analysis confirmed the presence of Fe_2B on the sample surfaces.

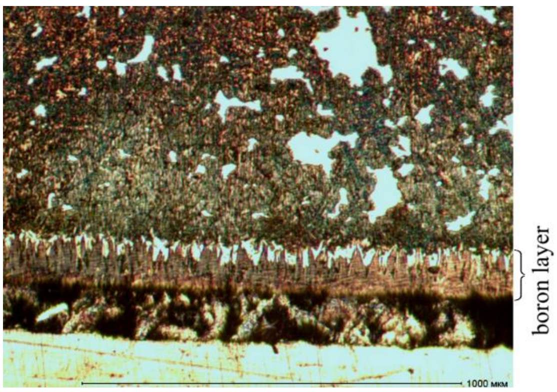

Fig. 4. Microstructure of the boron layer after color etching (x100).

Surface hardness measurements yielded the following results: 933 HV at a 200 g load, 1275.8 HV (72.4 HRC) at 1 kg, and 75 HRC (approximately 514 HV) at 60 kg, where the layer began to deform. Samples subjected to boronizing followed by quenching exhibited a hardness of 1411.2 HV at 1 kg load and 77 HRA.

To minimize sintering and powder adhesion during boronizing at various temperatures, the use of specific boron carbide particle sizes is recommended: 30 µm at 870°C, 50 µm at 890°C, 60 µm at 900°C, 80 µm at 915°C, 100 µm at 930°C, and 160 µm at 950°C.

The results demonstrate that sintering negatively affects the diffusion saturation process. To avoid this, the boronizing temperature should be selected according to the powder fraction to prevent sintering. The observed variation in sintering temperatures across different powder sizes is approximately 70°C. Importantly, reducing the temperature by 70°C does not compromise diffusion activity, and the absence of sintering contributes to the formation of high-performance boride layers.

Minor diffusion of copper and aluminum also appears to play an auxiliary role, potentially enhancing boron diffusion and facilitating the regeneration of transport agents such as fluorine and chlorine, which are involved in the transfer of boron to the substrate surface.

2.2. Determination of the properties of a single-phase boride layer

To determine the mechanical characteristics of the single-phase boride layer, a series of tests were performed on samples with Fe_2B boride. Instrumental indentation was performed to determine the instrumental hardness and Young's modulus: H_I = 14.57 GPa, E = 293 GPa.

Signs of microcracks appear at a load of 360 mN and an indenter depth of 1075 nm. The approximate length of microcracks is 30 nm. These indicators indicate high crack resistance characteristics and the ability to maintain the integrity of micro-volumes when sharp, hard particles are introduced under high tension load.

The parameters of wear resistance during dry abrasive wear are determined. The results of the abrasive wear tests are the mass loss indicators. The tests were carried out in a stream of sand that was supplied under air pressure through a nozzle. The nozzle was directed normal to the surface and at an angle of 45°. For 10 hours of abrasive action, the mass loss was as follows: Δm_{90} = 0.0045 g; Δm_{45} = 0.0375 g. Thus, the high wear resistance of the Fe_2B boride layer under abrasive wear was shown.

Additionally, the data on the coefficient of thermal expansion (CTE) of Fe_2B boride were analyzed in comparison with other popular structural materials. Aluminum and its alloys have rather high CTE values: $23.1\cdot10^{-6}$ 1/K (300 °C). FeB boride has approximately the same value: $23\text{-}10^{-6}$ 1/K (600°C), which causes frequent chipping of the surface boron layer. Such materials do not work well in gaps and need to be enlarged. Iron and alloys based on it have a lower CTE: $12\cdot10^{-6}$ 1/K (800°C), but their properties are exhausted. Titanium nitride has a lower CTE: $9.35\cdot10^{-6}$ 1/K (1100°C), but its production by PVD technology requires sophisticated equipment and is not always economically viable. Titanium has an even lower CTE: $7.7\cdot10^{-6}$ 1/K - $10.4\cdot10^{-6}$ 1/K (20 - 700°C), but the problem with titanium and its alloys is easy adhesion during break-in. At the same time, Fe_2B boride has a rather low CTE: $7.65\cdot10^{-6}$ 1/K (900°C) [9].

2.3. Preparation of the silicide layer and its properties

The silicide coating was produced by saturating the surface with industrial-grade silicon containing 5 wt% ammonium chloride and 20 wt% inert filler (merlins). The samples, together with the powder mixture, were placed in a double crucible and held at 900 °C for 5 hours.

When fine silicon powder (30 µm) was used, a sintered crust formed on the surface due to the intensified silicon chloride transport reaction and the accumulation of atomic silicon. The reduced diffusion of silicon into the substrate further contributed to crust formation.

Increasing the silicon particle size to 150 µm eliminated the crusting issue; however, isolated sintered silicon grains were still observed on the surface.

Figure 5 presents the microstructure of the siliconized layer formed on steel 40.

The silicide layer is relatively dense and maintains sharp 90° transition angles without chipping, even after grinding, which indicates good adhesion strength of the coating. The layer thickness ranges from 100 to 200 µm, and the surface microhardness (H_{100}) reaches 25,185 MPa.

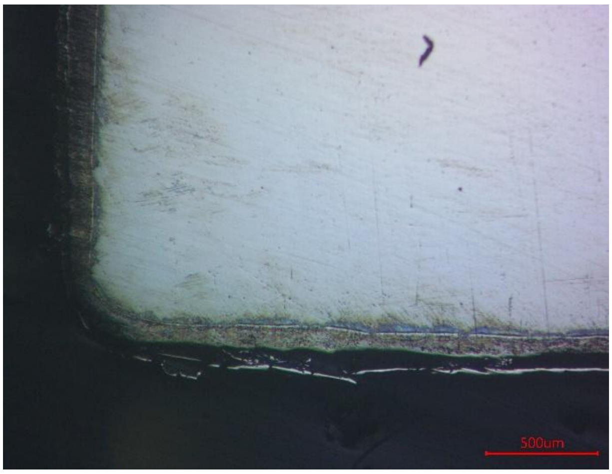

Fig. 5. A layer of silicide around the perimeter of the sample (grinding without etching) (x50).

To confirm the phase composition of the coating, X-ray diffraction (XRD) analysis was performed, and the results are shown in Fig. 6. Phase identification was carried out using the Match!4 software, which revealed that the dominant phase is iron silicide (FeSi).

Analysis of peak intensities showed that the diffusion layer consists of approximately 75.7% FeSi, 19.6% Si_2CN_4, and 4.8% Al_5Fe. The formation of Si_2CN_4 is attributed to the presence of ammonium chloride in the saturation mixture and to counter-diffusion processes occurring at the steel surface during heat treatment.

The presence of Al_5Fe is explained by the participation of aluminum, originating from the inert filler (merlins), in chemical reactions during the process. This finding indicates that at least one of the filler components is involved in both chemical interactions and the saturation mechanism.

Based on the identified phases, the elemental composition by weight is as follows: Fe – 52.5%, Si – 34.2%, N – 8.8%, Al – 2.6%, and C – 1.9%.

Silicide layers are usually characterized by high porosity [10] and a tendency to chip and delaminate, but in this case, potentially porous areas are filled with accompanying phases such as Si_2CN_4 and Al_5Fe. Thus, the fundamental possibility of obtaining silicide coatings with reduced porosity has been demonstrated.

2.4. Oxidation resistance of silicide, boride and nitride coatings

Samples with different coatings on steel substrates were tested in an oxidizing atmosphere at 1000°C for 10 hours. Prior to testing, samples of steel 40 were weighed. The silicide layer, composed primarily of FeSi, had a thickness of 100–200 µm. The boride layer consisted of Fe_2B with a thickness of 150–200 µm. For comparison, a CrN nitride layer (10 µm thick) produced by cathodic sputtering was also included. The comparative test results are presented in Fig. 7.

The lowest mass loss was observed for the siliconized samples (8.44 g/m²), where a protective SiO_2 film formed on the surface. In contrast, the boride layer

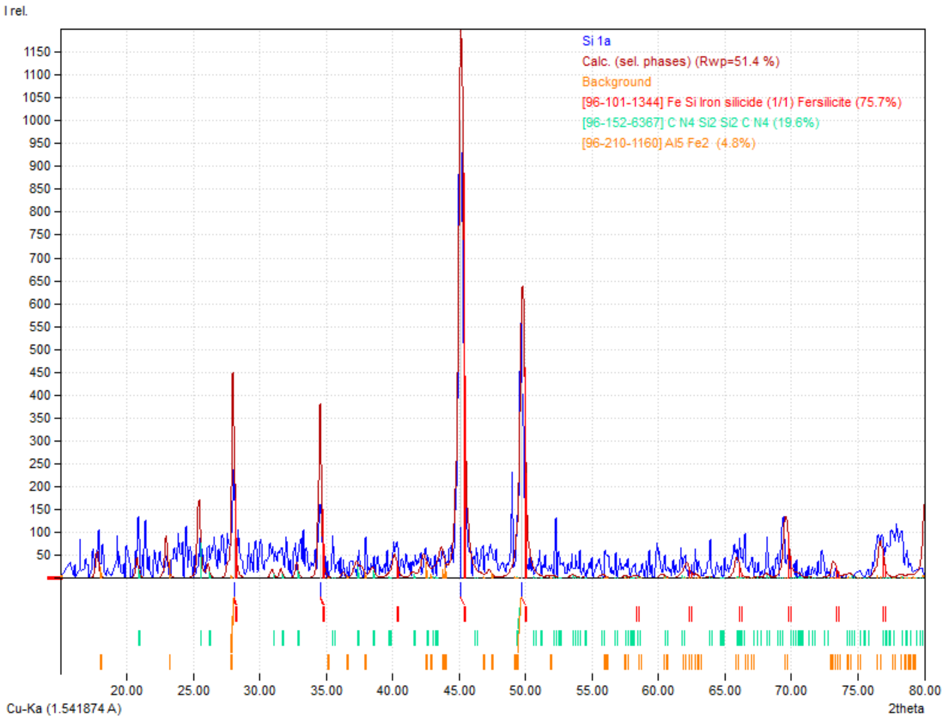

Fig. 6. Diffractogram of a silicide layer with a leveled background and a dashed diagram of candidate phases.

exhibited significantly higher mass loss – 42.21 g/m² – due to the formation of a less stable oxide layer of B_2O_3.

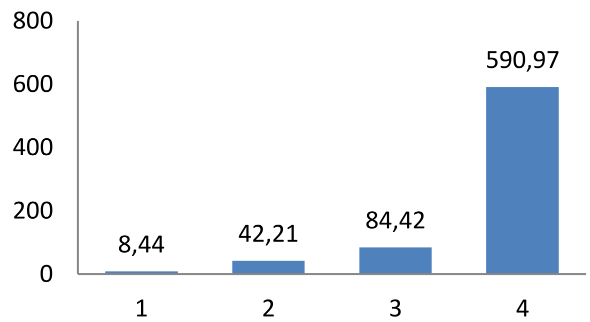

Fig. 7. Mass gain index (g/m2) of samples at 1000 °C for 10 hours (±0.01 g): 1 - silicide layer; 2 - Fe2B boride layer; 3 - CrN (PVD) layer is shown for comparison; 4 - steel 40.

The CrN coating demonstrated a mass gain index of 84.42 g/m², which is approximately twice lower than that of the boride layer. However, the thickness of the CrN layer is 15–20 times smaller than that of the boride coating. In certain applications, particularly those requiring minimal dimensional changes to the part, the thinness of the CrN layer can be a decisive factor in selecting a protective coating technology. Nevertheless, the complexity and high cost of the equipment required for physical vapor deposition (PVD) significantly limit its practical appeal.

Conclusions.

Single-phase boride layers with a thickness of 150–200 µm can be obtained within 1.5 hours at 950–1000°C. The saturation temperature can be lowered by selecting an appropriate boron carbide particle size and by applying combined saturation with boron, copper, and aluminum, resulting in relatively thick diffusion layers.

Fe_2B layers exhibit high hardness, elastic modulus, coating thickness, abrasive wear resistance, and oxidation resistance.

Siliconized layers of adequate quality can be formed by heating at a temperature of 900 °C for 5 hours.

The phase composition of the siliconized layer was identified as 75.7% FeSi, 19.6% Si_2CN_4, and 4.8% Al_5Fe. This composition provides superior oxidation resistance compared to both boronized and PVD CrN-coated samples, with a mass loss of only 8.44 g/m².

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Вдосконалення технології отримання борованих і силіцьованих шарів та порівняння їх властивостей

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В статті представлені результати досліджень отримання однофазного боридного шару та твердо-газофазного силіціювання на вуглецевій конструкційній сталі. Показано вплив зернистості порошків і складу насичуючої суміші на структуру та властивості дифузійних покриттів. Порівняно властивості отриманих поверхневих структур з покриттями нітриду хрому, отриманого методом PVD. Встановлено можливість отримання товстих дифузійних однофазних боридних та силіцидних шарів, що за рівнем механічних і хімічних характеристик не поступаються нітридним, отриманим іонно-плазмовим осадженням. Показано наявність у силіцидному шарі 75,7% FeSi, 19,6% Si_2CN_4 та 4,8% Al_5Fe фаз, що забезпечило високі показники стійкості до окислення при температурі 1000 ˚С.

Ключові слова: сталь, боридний шар, силіціювання, металографічні дослідження, пористість, інструментальне індентування, нітрид хрому.