Nanostructuring of the T31507 steel surface by vanadium borides under the influence electron beams in a vacuum

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Abstract: The microstructures and microhardness of boride layers formed on die steel of T31507 by electron-beam boron reduction in vacuum are investigated and compared. Formed layers have a heterogeneous structure, combining solid and plastic components, leading to a decrease in brittleness of the boride layer.

1. Introduction

The development of engineering technology largely depends on the technical level of tool production. The tool life, the number of intermediate resharpening significantly affect the cost of products. The factor for the production of high-quality and durable tool is the choice of tool material corresponding to the purpose and the loads arising during the work. This should take into account the structural, metallurgical, operational and technological factors that determine the behavior of the material during operation.

The durability of the tool depends both on the material properties determined by the manufacturing technology and volume hardening, as well as on the surface properties. Its role in ensuring the operational properties of products is constantly increasing [1].

The diffusion saturation of metals and alloys with boron is described in detail in the scientific and technical literature. Depending on the state of aggregation of the starting boron-containing substance, there are gas-phase, liquid-phase, and solid-phase boronizing methods. Each of these methods has its advantages and disadvantages. Among the common disadvantages are high temperature-time processing parameters, i.e., to obtain a diffusion layer of sufficient thickness, high boronizing temperatures and long exposures are necessary. The diffusion layers formed during boronizing consist of iron borides FeB and Fe₂B with a microhardness of 20200–21500 MPa and 14000–15000 MPa, respectively. Such a high microhardness provides high wear resistance to boronized products, but at the same time increases the brittleness of coatings [2].

The use of electronic heating can reduce brittleness and increase ductility. After electron beam boronizing, the layers are more plastic than after solid phase. In addition, the layers after electron beam boronizing have a heterogeneous structure that combines hard (brittle) and more plastic structural components [3].

T31507 tool alloyed steel is used to create measuring and cutting tools for which increased warping during quenching is unacceptable, threaded gauges, broaches, long taps, long reamers and other types of special tools, cold heading dies and punches, tooling.
The borides of transition metal possess high melting points (above 2000 °C) and hardness values, are sufficiently resistant to oxidation, and therefore are of particular interest for the formation of coatings based on them. One of the main ways to obtain borides is the interaction of metal with boron using external heating (sintering, fusing) or by initiating an external heat source followed by heating of the reagents due to the release of heat of reaction (self-spreading high-temperature synthesis).

The article discusses the features of surface hardening of T31507 steel under the influence of high-power electron beams due to quenching and the formation of layers based on vanadium borides (V\textsubscript{3}B\textsubscript{4}). The most important characteristic of borides, which determine their practical use, is their high hardness associated with the directional character and energy strength of interatomic bonds.

The mechanical properties of boride VB\textsubscript{2} are determined by the presence of structural defects, impurities, and porosity in them. During the study of single crystals revealed anisotropy of hardness on different planes.

It should be noted that high elastic and strength characteristics are observed for vanadium borides, but their order of magnitude is intermediate between borides of titanium TiB\textsubscript{2} and chromium CrB\textsubscript{2}.

2. Experimental part

2.1. Calculation method
Thermodynamic modeling was performed using the TERRA software package [4]. The program is designed to calculate arbitrary systems with chemical and phase transformations. It allows to simulate a very equilibrium state and implements method and algorithm calculations created in the N.E. Bauman Moscow State Technical University. The program is associated with an extensive database of properties of individual substances, which makes it suitable for the study of arbitrary compositions of chemical composition. The calculations were carried out in the temperature range of 273–2073 K with a step of 25 K (melting point of pure iron Fe is 1812 K) in the pressure range of 10\textsuperscript{-4}–10\textsuperscript{5} Pa for stoichiometric compositions where the formation of vanadium borides VB\textsubscript{2}, V\textsubscript{3}B\textsubscript{4} and VB was assumed.

Table 1 shows the chemical composition of the T31507 alloy steel. When modeling the interaction of the reaction coating with the substrate material, the possibility of formation of carbides and borides of dopants of the initial T31507 steel (Fe, Cr, W, Mn) was taken into account [5].

|   | C    | Si   | Mn    | Ni   | S   | P   | Cr    | W    | Cu   | Fe   |
|---|------|------|-------|------|-----|-----|-------|------|------|------|
|   | 0.9–1.05 | 0.1–0.4 | 0.8–1.1 | up to | up to | up to | 0.9–1.2 | 1.2–1.6 | up to | ~ 94 |
|   |      |      |       |      | 0.35 | 0.03 | 0.03   |      |      |      |

2.2. Experimental technique
Samples were prepared by applying a coating on a previously prepared steel surface. The coating included 1:1 by volume of a mixture of V\textsubscript{2}O\textsubscript{3} oxide, amorphous boron and carbon, and an organic binder – a solution of 1:10 BF-6 glue in acetone. Electronic heating by a continuous beam was carried out for 1–3 minutes at a specific power \( P = 5.7 \times 10^2 \) W mm\textsuperscript{-2} (electron beam diameter \( d = 1 \) mm). The residual pressure in the vacuum chamber did not exceed 2×10\textsuperscript{-5} Pa [6].

2.3. Research methods
X-ray phase analysis (XPA) was carried out on a Phaser 2D Bruker diffractometer (Cu Kb\textsubscript{1} – radiation).

Microhardness was measured with a PMT-3M microhardness meter. The microhardness tester is equipped with an adapter with a digital camera and NEXSYS ImageExpert MicroHardness 2 fingerprint image processing software (GOST 9450-76).

Microstructure of transverse thin sections of the samples was examined with a METAM RV-21 metallographic microscope equipped with a VEC-335 digital camera and NEXSYS ImageExpert Pro 3.0 software for quantitative metallographic analysis.

3. Results and their discussion

3.1. Simulation of interaction of T31507 steel and reactionary coating

Initially, there was a thermodynamical investigation (the TERRA software complex (TERRA and TRIANGLE interfaces)) of the interaction of vanadium oxide with carbon and boron under equilibrium conditions at a pressure \( p \) in the range from \( 10^{-2} \) to \( 10^{-4} \) Pa, the high-temperature self-spreading synthesis (SSS) modeled under adiabatic expansion conditions) of vanadium borides [3, 4].

It was shown that the formation of \( V_3B_4 \) takes place at a temperature of 833 K through the stage of synthesis of vanadium carbide \( VC \). It is determined that the temperature of the beginning of the boride formation depends on the pressure in the system. According to thermodynamic calculations, boride \( V_3B_4 \) is rather thermally stable. For temperatures above 1600 K, ionization of \( V_3B_4^+ \) vapors is observed (figure 1).

\[
\begin{align*}
1) & \quad V_2O_3 + B + C = V_3B_4 + CO; \\
2) & \quad V_2O_3 + B_4C + C = V_3B_4 + CO; \\
3) & \quad V_2O_3 + B_2O_3 + C = V_3B_4 + CO.
\end{align*}
\]

Further, the interaction of the \( V_2O_3:B:C \) reaction mixture with the surface of T31507 carbon steel was modeled to form a composite coating to a depth of 5–150 \( \mu m \).

3.2. Synthesis of boride \( V_3B_4 \)

Simulation of boride \( V_3B_4 \) formation, taking into account the interaction of impurities and the metal base with the reaction mixture, showed that an excess of boron is necessary (figure 2).

Calculations showed that the maximum yield of boride \( V_3B_4 \) is achieved at 22 wt.% B (figure 3).

The analysis of the thermodynamic calculations allowed to determine the optimal conditions for the interaction of the \( V_2O_3:B:C \) reaction mixture with the surface of T31507 carbon steel for forming a composite coating to a depth of 5–150 \( \mu m \).
3.3. SHS and Electron Beam Welding of Vanadium Borides

Synthesis of vanadium borides was performed on the surface of the T31507 die steel. After the electron beam treatment of T31507 steel, with boron-containing applied on them, non-uniform layers are formed on the surface, 100–300 μm thick (figure 4). The formed layers have the indicated thickness almost along their entire length. Figure 4 shows that there are particles in the layer that are located inside the layer. This allows us to conclude that these particles are borides of alloying elements (tungsten, chromium, manganese, and vanadium). The layer is firmly held on a metal base.

When measuring the microhardness of vanadium borides layers with a step of 30–50 μm, its uneven distribution over the thickness was found (figure 4). However, in all studied samples, a regular distribution of microhardness was observed depending on the layer thickness. Some very rare inclusions have HV ≈ 12000 MPa and are located in the surface zones of the layer. Layers are characterized by the most complex disordered structure. The increase in the microhardness of the substrate to HV ≈ 5000 MPa is explained by the fact that it underwent quenching as a result of exposure to an electron beam. A more chaotic distribution of microhardness in thickness for boride V₃B₄ is explained by the fact that this boride is formed at a lower temperature, and accordingly there are many impurities in the layer.
Studies allow us to conclude about the use of electron-beam boronizing for hardening cutting tools, etc., experiencing heating in the process of working to high temperatures without a significant reduction in performance properties.

It is known that along with high hardness and wear resistance, boride layers also have a significant drawback – increased brittleness. Studies have shown that the use of electronic heating can reduce brittleness and improve ductility. After electron beam boronizing, the layers are more plastic than after solid phase. In addition, the layers after electron beam boronizing have a heterogeneous structure that combines hard (brittle) and more plastic structural components. This combination partly explains the absence of thermal cracks when the boride layers are heated to high temperatures.

4. Conclusion

The following conclusions can be made on the basis of the work done.

- The analysis of thermodynamic calculations, taking into account the interaction of impurities and the metal base with the reaction mixture, shows that an excess of boron is necessary. The simulation made it possible to determine the optimal conditions for the interaction of the \( V_2O_3:B:C \) reaction mixture with the surface of the T31507 carbon die-cast steel to form a composite coating to a depth of 5–150 \( \mu m \).
- As a result of electron-beam processing in vacuum, it was possible to form layers of vanadium borides on T31507 die steel. The layers of vanadium borides have a structure that is uneven in thickness, contain different phases and, as a result, a non-uniform distribution of physical and mechanical properties (for example, microhardness). Solid particles with a size of 5–7 \( \mu m \) are in plastic eutectic. The surface of the layer has maximum microhardness values.
- The study of the microhardness of the boride layers after boronizing with a continuous electron beam allows us to conclude that this method of boronizing is used to harden cutting tools, etc., which undergo heating to high temperatures during operation without significant reduction in performance properties.

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