Nitriding of martensitic steel after laser melting deposition

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Abstract. In this study martensitic steel Fe-13% Cr-2% Ni-0.25% C in three initial state was nitrided. The steel in the initial state was made by laser melting deposition (LMD), LMD and tempering and quenching. The structure of steel after LMD was martensitic and sorbit after LMD and tempering and quenching. The result of research showed that the nitrided layer of steel after LMD is 160 μm, which exceeds the thickness of the nitrided layer of the steel after quenching and tempering by approximately 2 times. In steel after LMD and tempering, the thickness of the nitrided layer is 140 μm.

1. Introduction
In recent years, additive technology has been widely used for the synthesis of parts of different composition and mechanical properties. In a number of cases, the properties of the surface layer of the part must differ substantially from the properties of the core. In this regard, there is a need for the development of complex technologies that include recrystallization of the material with additive technology followed by heat or mechanical treatment of a part.

In this paper, a complex technology involving laser melting deposition (LMD) followed by chemical-thermal treatment, namely, nitriding, was studied. LMD is one of the methods of additive technologies. In this method the powder material fed with a shielding gas jet coaxially with the laser radiation onto the metal substrate. The laser beam forms a molten pool on the substrate, into which the powder enters. The laser beam is moved along the surface in accordance with the desired section of the part, then the next section is formed, and so until the part is completely formed [1, 2]. The main advantages of this method is the ability to build surfaces in different directions, change the composition of the powder to produce gradient materials; the dimensions of the part obtained by this method are limited only by the capabilities of the displacement system.

During the recrystallization of the powder, due to the intensive heat removal, the cooling rates reach about 10⁵-10⁶ °/s. Such cooling rates correspond to the quenching of alloys from the liquid state, therefore, for metallic parts obtained by additive technologies, in particular LMD, the formation of a nonequilibrium state [3, 4], a large number of crystal structure defects [5], and a high level of residual stresses are characteristic [6, 7]. It is known that a nonequilibrium structure and defects of crystal structure affect the rate of diffusion processes in a solid. From this point of view, the study of the effect of laser melting deposition on the nitriding process has great practical and fundamental importance.

2. Materials and methods
The object of the study was a highly alloyed corrosion-resistant martensitic grade steel Fe-13% Cr-2% Ni-0.25% C, the composition of which is presented in Table 1. This steel is used for parts with increased ductility subjected to impact loads. The samples of steel were subjected to nitriding in three different structural states: after LMD, after LMD, followed by high tempering at 700 °C for 5 h and after quenching at 1050 °C in air and tempering at 700 °C for 5 hours. The chemical composition of steel Fe-13% Cr-2% Ni-0.25% C according to GOST is presented in Table 1.
Table 1. Chemical composition of steel Fe-13% Cr-2% Ni-0.25% C in accordance with GOST and samples after LMD.

| Chemical element, % mass. | C | Si | Mn | Ni | S | P | Cr | Ti | Cu |
|---------------------------|---|----|----|----|---|---|----|----|----|
| GOST 5632-72              | 0.2-0.3 | до 0.5 | 0.8-1.2 | 1.5-2 | 0.15-0.25 | 0.08-0.15 | 12-14 | до 0.2 | до 0.3 |
| LMD                       | 0.23 | 0.57 | 0.07 | 2.32 | 0.01 | 0.01 | 11.39 | 0.01 | 0.05 |

LMD was carried out with the following parameters: laser power 800 W, laser scanning speed 500 mm/min, powder consumption 3 g/min, nozzle diameter 1 mm. The powder was obtained by the method of gas atomization and its dispersion was 80-140 μm. The grown samples had a size of 10 × 10 × 30 mm, their chemical composition is also shown in Table 1. Samples in a different structural state were subjected to nitriding in a glow discharge at a temperature of 540 °C for 24 hours (3 times for 8 hours) at a pressure of 500 Pa. Nitriding was performed in an ION-251 ion-plasma nitriding unit in a working gas of 5% H2 + N2.

The parameters of the nitrided layer were investigated by metallographic analysis and microhardness measuring. Microhardness was determined at a load of 100 g; the error of determination was 5%. The phase-structure state of steel in the initial states and after nitriding was determined by the X-ray diffraction analysis in Co Kα radiation on a diffractometer Bruker D8 Advance.

3. Results and discussion

Figure 1 shows the microstructure of the samples in the initial state, and Table 2 shows its microhardness. After LMD, the steel has a needle structure and microhardness of 520 HV 0.1, which means that the structure of steel is martensite. In the structure, the boundaries of large (more than 100 μm) crystals, apparently, of the original austenite, are etched. Their size in the longitudinal section is approximately 2 or 3 times greater than in the transverse section (Figure 1a, 1b). The microstructure of the steel after LMD and high tempering is a directional sorbit of tempering (Figure 1c, 1d), which is also confirmed by the value of microhardness (300 HV 0.1). The microstructure of Fe-13% Cr-2% Ni-0.25% C steel after the improvement is also sorbit of tempering (Figure 1e) with a microhardness of 300 HV 0.1.

Table 2. Microhardness of the samples

| Structural state | LMD | LMD and tempering | Quenching and tempering |
|------------------|-----|-------------------|-------------------------|
| Microhardness HV 0.1 | 520 | 300 | 300 |

X-ray phase analysis of steel after LMD, followed by tempering and after quenching and tempering, fixes reflections only from the α-solid solution (Figure 2b). After LMD, in addition to reflections from the α phase, the most intense reflection of residual austenite are observed; The quantity of austenite is about 10%, it was calculated from the intensity of the diffraction peaks (Figure 2 a). The diffractograms obtained from the
longitudinal and the transverse sections of the samples practically do not differ, which indicates that there is no texture in the objects.

Figure 1. Microstructure of the longitudinal (a, c) and cross sections (b, d) of Fe-13% Cr-2% Ni-0.25% C steel specimens in different structural states: after LMD (a, b); after LMD and tempering (c, d); after quenching and tempering (e)
Figure 2. Diffractograms of the cross section of samples of steel Fe-13% Cr-2% Ni-0.25% C after LMD (a), LMD and high tempering (b)

Figure 3 shows the profiles of the X-ray reflection line (211) of the α-phase. It is known that from the integral broadening of the x-ray line $\beta$, one can indirectly judge the number of crystal structure defects in the phase [8]. It can be seen from the figure that in the steel after LMD the x-ray line broadening ($\beta = 1.21^\circ$) is the widest and there is no splitting into the doublet $K\alpha_1$ and $K\alpha_2$. The considerable broadening of the x-ray line can be explained by the formation of a supersaturated solid solution - martensite with a high concentration...
of defects in the crystal structure. A high tempering leads to a reduction of defects, and a narrowing of the diffraction line ($\beta = 0.77^\circ$). In the sample obtained by the quenching and tempering, the line is split into a doublet and its integral width is 0.45 $^\circ$. It should be noted that the integral broadening of the X-ray peaks correlates well with the microhardness. But the microhardness of the samples after LMD with tempering and after quenching and tempering is the same (300 HV0.1) and their integral broadenings differ 1.7 times.

Figure 3. Profile of the x-ray line (211) of the $\alpha$-phase: 1 - quenching and tempering; 2-LMD and tempering; 3 – LMD

Figure 4 shows the microstructure of the diffusion layer of samples after nitriding. The results of metallographic analysis of nitrided layers showed that in the sample after LMD, which in the initial state had a martensite structure with the greatest number of crystal structure defects, the thickness of the diffusion layer is the largest and amounts to 160 $\mu$m. In the reference sample after the quenching and tempering, the total thickness of the nitrided layer of steel is half as much and is about 80 $\mu$m. Steel obtained by LMD followed by high tempering, compared to steel after quenching and tempering, has an increased thickness of the nitrided layer of 140 $\mu$m, which is only slightly less than the layer observed in the sample after the LMD. A significant increase in the thickness of the nitrided layer in the sample obtained by the LMD is presumably associated with an increased concentration of crystal structure defects that accelerate diffusion processes. However, judging by the value of the microhardness and the decrease in the integral broadening of the X-ray peak, subsequent tempering led to a significant decrease in the defect concentration, while the thickness of the nitrided layer changed insignificantly.
Dependences of the microhardness on the depth of the nitrided layer for samples in a different structural state are shown in Figure 5. It can be seen from the figure that the microhardness of the nitrided layer of the sample after the LMD is 900 HV 0.1. The microhardness retains its value to a depth of 120 μm from the surface, then its decrease, taking the value of microhardness, characteristic for steel before hardening, at a depth of 160 microns. A higher value of microhardness of 1000 HV 0.1 was recorded in the sample after LMD and high tempering. The microhardness begins to decrease smoothly at a depth of 100 μm, reaching a value of initial state at the depth 140 μm.

On the sample after the quenching and tempering, the hardened zone with microhardness HV 0.1 1000 is 60 μm, at a depth of 80 μm the microhardness already corresponds to the initial state. Perhaps a somewhat smaller value of the microhardness of the nitrided surface in the sample after LMD can be explained by the retention of residual austenite in the structure. In all samples, the same microhardness dependence was observed for the thickness in the longitudinal and cross sections. It is important to note that the drop in microhardness over the thickness of the nitrided layer of steel obtained by direct laser growth occurs more smoothly than that of steel after quenching and tempering, and the thickness of its transition zone is 80 μm versus 20 μm in steel after quenching and tempering. A sharp decrease in microhardness can lead to peeling of the hardened zone, which can occur on nitrided specimens. The probability of peeling on samples after LMD is less, since the transition zone is four times larger than on the sample after quenching and tempering.
Figure 6 shows the diffractogram of the nitrided surface of the sample after the LMD. In addition to the $\alpha$-phase, reflections from nitrides Fe$_4$N and CrN are seen. The phase composition of the nitrided layer is independent of the initial state of the sample, and the phase composition of the longitudinal and transverse cross sections of the samples after nitriding also coincides.

![Diffractogram of the sample cross section after LMD and nitriding](image)

**4. Conclusions**

1. In the initial state Fe-13% Cr-2% Ni-0.25% C steel after LMD has a martensite structure with a microhardness of HV 0.1 500. The subsequent high tempering of the steel results in a decrease of the microhardness to HV 0.1 300 and the decay of martensite into the sorbit of the tempering.

2. The nitrided layer of steel after LMD is 160 $\mu$m, which exceeds the thickness of the nitrided layer of the steel after quenching and tempering by approximately 2 times. In steel after LMD and high tempering, the thickness of the nitrided layer is 140 $\mu$m.

3. The microhardness of nitrided layers is HV 0.1 900-1000 due to the formation of Fe$_4$N and CrN nitrides.

4. The drop in microhardness over the thickness of the nitrided layer of steel after LMD occurs more smoothly than that of steel after quenching and tempering, and the thickness of its transition zone is 80 $\mu$m in steel after quenching and tempering.

5. Chemical-thermal treatment of alloys, in particular, nitriding, is a low-productivity process. From this point of view, nitriding of alloys after LMD can be considered as a way to increase the productivity of the process.

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