

Nitriding of chromium-nickel alloys synthesized by laser melting

O.V. Chudina^{1*} and V.A. Zorin¹

¹Moscow State Automobile and Road Technical University (MADI), Moscow, Russia

Abstract. The effect of nitriding on the structure and hardness of chromium-nickel alloy obtained by selective laser melting has been studied. It has been shown that after nitriding a weakly developed ϵ -phase nitride zone with a thickness of about 10 μm and an internal nitriding zone with a thickness of more than 300 μm are formed on the surface of the alloy, which is twice as much as that of nitrided similar alloys obtained by the conventional method. The microhardness of the nitrided layer is 3500 MPa, this is 1.5 times higher than the hardness of the core, so nitriding of powder materials produced by additive technologies can be recommended for surface hardening of parts operating under conditions of wear and cyclic loads.

1 Introduction

Currently, additive manufacturing is actively developing, the essence of which is the layer-by-layer compaction of powdered material based on a 3D model of the part. This method is an alternative to traditional mechanical methods of material processing, such as turning, milling, etc.

Additive technologies are widely enough used for both small-scale and large-scale industrial production. Parts of any complex shape with high accuracy and good surface quality are created in a few hours according to a given program and do not require additional machining [1].

The competitiveness of laser additive technologies is based on the low cost of manufacturing parts with complex geometry. The material utilization factor of the workpiece (powder) is close to 94...96%, and the remainder of the powder is used to manufacture the next product. Laser additive technologies are divided into two methods of manufacturing products [2]:

- SLM (Selective Laser Melting) is a technological process of selective laser melting (SLM) of metal powders based on creating a certain surface on which a selectively solidified layer is formed. This method is the most common method of 3D metal printing. Parts made by this method are superior to traditional production, but there are limitations in the speed of construction and the size of the "grown" parts;

- LMD (Laser Metal Deposition) is a process based on direct feeding of material in the form of powder or wire into the mold. Products produced by LMD technology have

* Corresponding author: Chudina_madi@mail.ru

limitations in terms of the complexity of the geometry and less accuracy than SLM technology.

In the process of laser melting of powders complex interrelated processes and phenomena take place. These are absorption and scattering of laser radiation by powder particles, heat transfer, mass transfer within the melt bath, phase transitions and transformations, material evaporation and ejection, and various chemical reactions.

The quality of the finished product, its mechanical and operational properties are determined by technological parameters of the process, such as laser radiation power, scanning speed, step of laser beam movement, scanning strategy (direction and sequence of laser beam movement), powder layer thickness, and physical, chemical and granulometric properties of the powder. The complexity and multifactoriality of the interacting processes require further scientific research aimed at establishing the regularities of structure formation in the process of part manufacturing by laser alloying [1, 2].

The authors of [3] studied the stress state of various alloys obtained by selective laser melting. As a rule, tensile stresses are formed in the longitudinal section of the samples, and compressive stresses are formed in the transverse section. This nature of the stress state of the alloy can lead to anisotropy of the mechanical properties of the products, which is unacceptable for most machine parts.

It is possible to eliminate the anisotropy of product properties and reduce residual stresses after laser alloying of powders by subsequent heating [4]. However, heating decreases the dislocation density achieved during laser treatment and, as a consequence, the strength of the alloy decreases.

It is known that nitriding, which is carried out at 540...570°C, allows increasing the surface hardness of the alloy due to formation of nitrides of alloying elements, and keeping the core ductile. The combination of hard surface and ductile core increases the fatigue characteristics of parts such as shafts, gears, etc.

In this regard, the purpose of this work is to study the effect of nitriding on the structure and hardness of a chromium-nickel alloy synthesized by selective laser melting in the process of manufacturing a car front axle pinion.

2 Materials and methods for the experiment

A powder consisting of Fe - base; 0,12%C; 0,8%Si; 0,84%Mn; 17,8%Cr; 10,85%Ni; 0,62%Ti; 0,013%S; 0,03%P was used as a material for production of gears by selective laser melting. The powder was obtained by gas atomization; powder particles had the shape of equiaxed crystals with a diameter of ~ 40...50 microns. The moisture content of the powder was 0.004, fluidity - 22.8 s, bulk density - 4.6.

To create a 3D model of a front axle pinion of VAZ-2123 car we used a domestic 3D design system KOMPAS 3D V19. The part was made on «Concept laser m2» 3D printer. The model loaded in the program was displayed on the screen as a set of cross sections (Fig. 1).

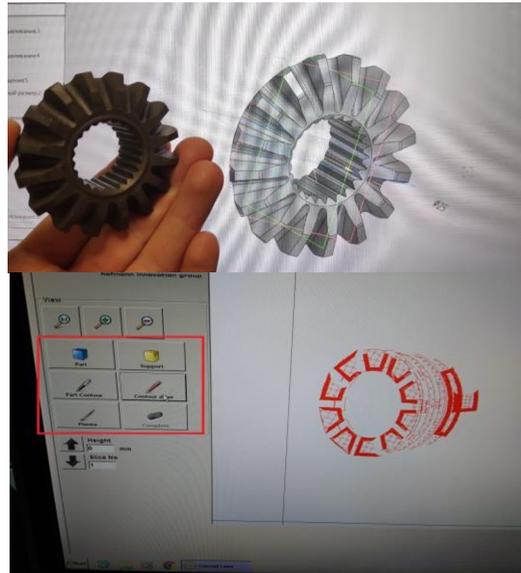


Fig. 1. Preparing the printer for printing: constructing the gear model and preparing a set of cross sections

In the process of part manufacturing, the laser beam scans each cross section according to a preset program, melting the powder particles sequentially. When creating test layers, the technological parameters of the printer were corrected, which were entered in the program. The laser melting process was conducted in a protective argon atmosphere. The finished part was ground, sandblasted and nitrided at 570°C for 6 hours in a nitrogen atmosphere.

Metallographic studies of the structure of the synthesized material were carried out on a «mvizio 221» microscope at a magnification of x100 to x1000. Keller reagent was used for etching microslides. Durometric studies were carried out on a PMT-3.

3 Research results and discussion

Analysis of the research results shows that in the austenitic alloy (Fe - base, 0.02%C, 17% Cr, 12% Ni, 2% Mo, 1% Mn, 0.7% Si), obtained by selective laser melting, a single-phase structure of alloyed austenite with microhardness of 2550 MPa is formed, which is 1.5 times higher compared with alloys of similar composition, obtained by conventional method. It is thermally stable and retains its hardness up to a temperature of 800°C. The structure of such alloy has a cellular structure (Fig. 2).

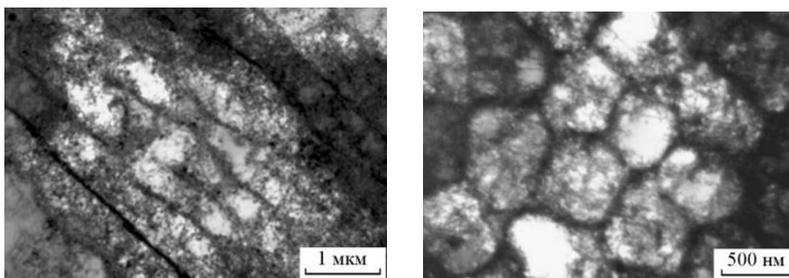


Fig. 2. Microstructure of austenitic alloy after selective laser melting

The cell boundaries are volumetric dislocation entanglements. Similar structural constructions are formed during laser surface treatment of metals, which explains the higher microhardness compared to the untreated metal.

Studies of the stress state show that in the longitudinal section there are tensile stresses of about 400 MPa, and in the cross section there are compressive stresses of about 350 MPa. The broadening of X-ray lines is caused by microdeformation of the austenitic solid solution crystal lattice and an increase in the dislocation density to 10^{12} cm^{-2} , which corresponds to the level of a strongly deformed metal.

The anisotropy of product properties can be eliminated and residual stresses after laser alloying of powders can be reduced by subsequent annealing, the temperature and duration of which depend on the chemical composition of the alloy.

The front axle pinion under study works under conditions of wear and alternating loads. To ensure the required reliability and durability, in addition to increased core strength, such parts should have a higher surface hardness. The combination of high surface hardness while maintaining a ductile core significantly increases the fatigue characteristics of the product. Traditional classical technologies of gear manufacturing imply obligatory surface hardening by methods of chemical-thermal treatment, in particular nitriding. In this regard, in this work we investigated the effect of nitriding on the structure and hardness of the alloy, the analogue of which is the classic austenitic steel 12X18H10T.

The part was manufactured by 3D-printing technology on the printer "Concept laser m2" in accordance with the production process cycle, which includes annealing of the finished product at a temperature of 250°C for 6 hours in an argon atmosphere. In our case, the annealing was performed at 570°C in an atmosphere containing nitrogen.

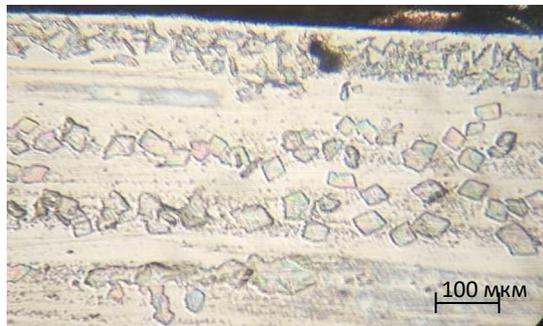


Fig.3. Microstructure of Fe-base alloy; 0.12%C; 0.8%Si; 0.84%Mn; 17.8%Cr; 10.85%Ni; 0.62% Ti; 0.013%S; 0.03%P after nitriding at 570°C for 6 hours

The microphotograph (Fig. 3), taken at 100x magnification, shows the crystallographic orientation of the texture. Usually, in simple-shaped parts, the grains are oriented mostly parallel to the growing direction. In complex-shaped parts, such as gears, the orientation of the grains and the nature of pore distribution in the synthesized material depend on the heat transfer in the melt zone. There are spherical pores in the structure, which are gas bubbles preserved after solidification of the powder containing gas impurities. The flat pores located perpendicular to the direction of laser beam scanning are apparently the result of incomplete melting of the powder layer, when in some areas the molten particles did not "merge" with the previously treated layer.

Initial etching of the thin sections with Keller reagent revealed the hardened layer structure typical of nitrided alloys (Fig. 3). An underdeveloped ϵ -phase nitride zone with a thickness of about 10 microns is formed on the product surface, which is a nitrogen solid solution based

on the chemical compound $(Fe,Cr,Ti)_{2-3}N$ with a nitrogen content, as a rule, of no more than 11%.

The main part of the nitrated layer - the zone of internal nitriding consists of doped γ' -phase and is the result of the decomposition of nitrogenous austenite upon cooling. Deeper etching has revealed the nature of the distribution of nitride phases. Fig. 4 shows the microstructure of the nitrated layer and the graph of microhardness variation along the thickness of the diffusion layer.

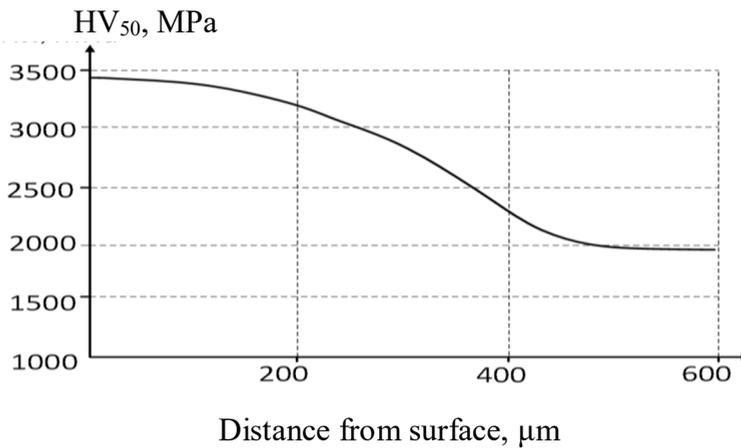
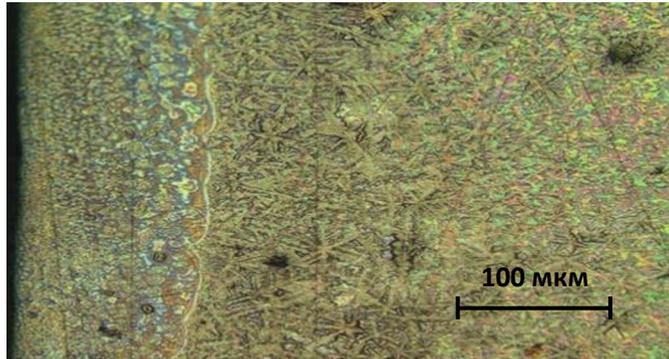


Fig. 4. Microstructure and microhardness distribution over the thickness of the nitrated layer of Fe-base alloy; 0.12%C; 0.8%Si; 0.84%Mn; 17.8%Cr; 10.85%Ni; 0.62% Ti after nitriding at 570°C for 6 hours

The character of the microhardness distribution shows that the thickness of the diffusion sublayer is more than 300 μm , which is twice as much as for similar steels obtained by conventional methods. It is known that austenitic steels are nitrated worse than ferritic ones, and the higher the degree of alloying of steel, the more difficult is the process of nitrogen diffusion. After nitriding of the austenitic 12Cr18Ni10T-type steel at 570 ° C for 50 ... 60 hours, the thickness of the hardened layer does not exceed 250 ... 260 μm and the maximum surface hardness 8000 MPa.

Analysis of the experimental results shows that after nitriding the austenitic alloy obtained by selective laser melting, a diffusion sublayer of greater thickness but less microhardness is formed compared with steels obtained by the conventional method. This is explained by the specific structure of the synthesized alloy, which, as noted above, has a cellular structure (Fig. 2), and the cell boundaries are dislocation structures with a high dislocation density up

to 10^{12} cm^{-2} . According to classical concepts of nitrogen diffusion in metals and alloys, during nitriding nitrogen diffusion along intergranular boundaries occurs at a higher rate than in the grain volume. At the boundary, the nitrogen concentration rapidly increases, a concentration gradient between the boundary and the grain volume is created, and, when the saturation limit is reached, the nitrogen diffusion flux in the grain volume is realized. An intergrain boundary is generally a two-dimensional crystalline structure defect whose size is 5...7 periods of the crystal lattice. In our case, intergrain boundaries are clusters of dislocations along which nitrogen diffusion deep into the metal is further accelerated, forming a diffusion layer of greater thickness than in conventional alloys. The low hardness of the nitrided layer as compared to conventional alloys, apparently due to the accumulation of nitrogen atoms at the grain boundaries and the insufficient rate of diffusion into the grain volume, which complicates the formation of the main strengthening phases - nitrides of alloying elements.

Thus, the diffusion processes occurring during nitriding of powder alloys produced by selective laser melting depend largely on the nature and transparency of the intercrystalline boundaries for the diffusing element. The morphology of the cellular structures and other strengthening phases of the diffusion layer, can be regulated by selecting the optimal technological solutions for the processes of laser alloying of powders and subsequent chemical-thermal treatment.

4 Conclusions

1. The effect of nitriding on the structure and hardness of chromium-nickel alloy obtained by selective laser melting has been studied.
2. It has been shown that after nitriding a weakly developed ϵ -phase nitride zone with a thickness of about $10 \mu\text{m}$ is formed on the surface of the alloy, which is a nitrogen solid solution based on the chemical compound $(\text{Fe,Cr,Ti})_{2-3}\text{N}$. The main part of the nitrided layer - the internal nitriding zone consists of the alloyed γ' -phase, its thickness exceeding $300 \mu\text{m}$, which is two times greater than that of analogous nitrided alloys produced by conventional methods.
3. The microhardness of the nitrided layer is 1.5 times higher than the hardness of the core, so nitriding of powder materials obtained by additive technologies may be recommended for surface hardening of parts operating under conditions of wear and cyclic loads.

5 Acknowledgements

The study was supported by Grant No. 22-29-00986 of the Russian Science Foundation.

References

1. N. Li, S. Huang, G. Zhang, et al., *J. Mater. Sci. Technol.* **35(2)**, 242–269 (2019)
2. D. Herzog, V. Seyda, E. Wycisk, C. Emmelmann, *Acta Mater.* **117**, 371–392 (2016)
3. Z.C. Fang, Z.L. Wu, C.G. Huang, C.W. Wu, *Opt. Laser Technol.* **129**, 106283 (2020)
4. E.V. Borisov, K.A. Starikov, A. Kim, V.A. Popovich, A.A. Popovich, *Heat Treatment Effect on the Structure Formation of Directionally Solidified Nickel Alloy after SLM* Proceedings 30th Anniversary International Conference on Metallurgy and Materials, P. 927-931. (2021)