EFFECT OF LASER BORONIZING ON MICROSTRUCTURE AND HARDNESS OF MARAGING STEEL PARTS MANUFACTURED BY SELECTIVE LASER MELTING

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Abstract

In the present study, surface laser boronizing technique was applied to improve wear resistance of maraging steel (MSt) parts manufactured by selective laser melting (SLM). Samples for investigation were manufactured of DIN 1.2709 steel powder using Concept Laser M3 equipment. Continuous 1 kW CO_2 laser was applied at 0.5 mm laser spot and 500–1500 mm/min laser operating speed, providing power density of 50955 $W \cdot cm^{-2}$ and heat input between 12.0 and 4.0 $J \cdot mm^{-1}$, respectively. Before laser-processing, amorphous boron paste was pre-placed on samples' surface. XPS analysis revealed increase in boron concentrations from ~3.1 wt% to ~5.7 wt% with laser speed increase from 500 mm/min to 1500 mm/min. XRD analysis revealed domination of Fe_3B type borides along with presence of FeB, Fe_2B type borides and presence of reflections attributable to austenitic and martensitic phases. The microstructure of laser-boronized layers exhibits evolution from fine dendritic boride-based eutectic plus Fe-based solid solution microstructure having ~630–780 HK0.5 hardness (at 500 and 750 mm/min laser speed) to superfine lamellar nanoeutectic (at 1000 and 1250 mm/min; ~1000–1030 HK0.2) and further to submicron-sized boride structure (at 1500 mm/min; ~1770 HK0.2). The obtained hardness is up to three times higher than that of MSt after aging (~600 HK), indicating that laser boronizing technique may be promising in term of the improve of MSt wear resistance.

Keywords: Laser boronizing, laser alloying, additive manufacturing, selective laser melting, maraging steel, hardness

1. INTRODUCTION

Selective Laser Melting (SLM) is a process utilizing high energy laser beam to selectively fuse powdered material and produce 3D parts in such a way [1]. It is one of the main processes of Additive Manufacturing (AM), which was developed for metal parts production. Fusing of powders and build-up of volume is performed "layer by layer". Using digital description of each cross-section, laser scans the pre-posited powders and melts them or leave un-melted. The thickness of each layer corresponds to the melt pool depth, which laser produces by one step. Such a technique allows producing parts with complex internal and external geometry and, therefore, it attracts growing interest in various fields of engineering, for which the components of complex geometry are typical (aircraft, aerospace, tooling) [2]. The heating and cooling of material during SLM process is very rapid; moreover, material experiences numerous reheating cycles when laser beam melts neighbouring passes or next layers. Therefore, the number of alloys suitable for SLM process is limited and carbon-free steels are usually used, which are not sensitive to thermal cracking [3]. 18-percent nickel maraging steel is suitable one.

Maraging steels (MSt) possess very high yield strength (up to ~2420 MPa) and high fracture toughness. However, the hardening is due to precipitation of intermetallics, which are not extremely hard. As a result, maraging steels have moderate hardness (~55–58 HRC max.) and, often, insufficient wear resistance.

Since 60s, when MSt were developed, thermochemical gas nitriding is known as a suitable process to improve hardness and wear resistance of MSt [4]. Such treatment results in a formation of iron nitrides and typically provides surface hardness ~900 HV. The main disatvantage of gas nitriding is long duration of process, which may reach 48 h and over to obtain the thickness of hardened layer ~100–200 μm. Laser surface alloying, metals is known as an effective technique in term of improving the metal parts surface performance, including their hardness and wear resistance. For the AM products, manufacturing process of which is based on the application of laser beam, this could be a more suitable alternative, especially, when only local hardening is required.

Laser boronizing of steels is one of the possible processes, in which the surface layer of the steel part being laser-melted and mixed together with pre-posited boron-containing layer. Boron solubility in iron is very low and, according to Fe-B phase diagram [5], iron forms with boron two types of borides – FeB (16.25 wt%) and Fe_2B (8.48 wt%), presence of which provides high hardness and wear resistance. A number of works [6-9] reports on the successful laser boronizing of steels, such as 41Cr4 steel, 100CrMnSi6-4 bearing steel, carbon steels C20, C45 and C90. To the best of authors' knowledge, at the moment, there are no data on the laser surface alloying of AM-manufactured parts produced from maraging steels. For this reason, the main objective of the present work was to determine the influence of laser boronizing process and its parameters on the microstructure, phase composition and hardness of additively manufactured MSt part surface.

2. EXPERIMENTAL DETAILS

DIN 1.2709 maraging steel, also known as 18Ni-300 maraging steel, was investigated. This is one of the most widely used and commercially available maraging steel grade. The samples for testing were produced by SLM process using DIN 1.2709 maraging steel powder (7–30 μm). The chemical composition of powder (according to powder manufacturer) is presented in **Table 1**. Prismatic samples with the dimensions 15 mm × 15 mm × (h)10 mm were built-up using 'Concept Laser M3' SLM equipment. More detailed description of the procedure is presented in [10].

Table 1 Chemical composition of DIN 1.2079 steel powder [wt%]

Fe	**C**	**Si**	**Mn**	**Ni**	**Mo**	**Ti**	**Co**	**Al**
balance	0.03	< 0.1	< 0.1	17-19	4.8	< 0.8	8.5-9.5	< 0.1

For laser processing of the SLM samples surfaces, continuous CO_2 laser (wave length – 1064 nm) was used and the processing parameters were as follows: laser power – 1 kW; laser spot diameter – 0.5 mm (providing power density of 50955 $W\cdot cm^{-2}$); processing speeds – 500, 750, 1000, 1250 and 1500 $mm\cdot min^{-1}$ (providing heat input of 12.0, 8.0, 6.0, 4.8 and 4.0 $J\cdot mm^{-1}$). Laser processing experiments were performed on the side-on surfaces of the built-up SLM samples without any mechanical or other pre-processing. Before the laser processing, amorphous boron was pre-placed on the surface to be processed. As the reference, the specimens laser-processed at the same parameters without pre-placing amorphous boron were used.

Optical microscopy method was applied to assess geometry of laser-processed tracks. The depth and width of the melt pool were measured on samples cross-sections prepared by conventional metallographic methodology (last polishing step prepared with 0.2 μm fumed silica suspension).

Boron concentration in alloyed layers was determined by XPS spectrometry (Kratos AXIS Supra+ spectrometer with monochromatic Al Kα (1486.6 eV) X-ray radiation powered at 225 W). The measurements were carried out on tracks surface, which was slightly pre-polished before analysis with grinding paper P1000.

X-ray diffraction method was used to analyze phase composition of alloyed layers (SmartLab Rigaku); Polycapillary Focusing Optics; 9 kW rotating Cu anode; step scan size – 0.02° (in 2θ scale); counting time – 1 s per step; 2θ range – 10–75°).

For the microstructural analysis, scanning electron microscope JEOL JSM-7600F was used. For the analysis, cross-sections were etched with mixture of H_2O, CH_3COOH, HCl and HNO_3 in ratio 1:1:4:1.

Microhardness measurements were made by Knoop method using Zwick Roell ZHμ tester (0.2 kg load, 15 s indentation duration) on polished cross-sections.

3. RESULTS AND DISCUSSION

For the surface alloying process, laser is operated at the melting mode, which is provided by the appropriate processing parameters – laser power, spot size, operating speed. Laser pool geometry varies with variation of these parameters – typically, width and depth of the pool increase with the increase in laser power and decrease in operating speed. In the present study, it was determined that the depth of the melt pool, obtained after laser processing with pre-placed boron, ranged between ~85 μm and ~185 μm and was in a strong dependence on the laser operating speed, while the melt pool width did not vary (~950 μm) at laser operating speed 500–1250 mm/min and was reduced (~780 μm) at 1500 mm/min. The melt pool dimensions obtained with boron did not differ significantly from those obtained without boron (**Table 2**); however, some tendency may be pointed out that melt pools obtained with boron were slightly wider and less deep.

Table 2 Dimensions of melt pool obtained after laser processing with and without pre-placed boron

Melt pool geometry parameter	**Laser operating speed, mm/min**				
	500	750	1000	1250	1500
Without boron					
Depth, μm	181±25	151±22	137±21	137±12	91±16
Width,μm	894±19	777±67	747±54	708±49	649±51
With boron					
Depth, μm	184±16	144±21	130±12	120±11	84±22
Width,μm	941±11	963±52	953±6	923±34	781±57

XPS spectrometry revealed the presence of boron in the processed layers in concentration between 3.1 wt% and 5.7 wt% with its gradual increase at rising laser operating speed, what is related with a melt pool depth decrease and, respectively, increase in boron to base metal mixing ratio during melting process. As a result, the microstructure and phase composition of the processed layers were changed. According to X-ray diffraction analysis, two phases were established to be in SLM specimen: the major one was α (Fe, Ni) type phase, having cubic crystal lattice with parameter a = 2.8681 Å, which can be identified as martensitic phase typical for low carbon maraging steels; the minor phase was identified as γ(Fe, Ni) austenite, having a = 3.5975 Å. For the laser-boronized specimens, besides α(Fe, Ni)-martensite and γ(Fe, Ni)-austenite phases, boride phases of FeB, Fe_2B and Fe_3B types were identified as well – Fe_3B(major)+FeB(minor) for laser operating speed interval 500–1250 mm/min and Fe_2B(major)+FeB(minor) for 1500 mm/min speed.

During SLM process, the part is built-up “point-by-point”; therefore specific substructure is formed with clearly seen melt pool boundaries, as shown in (**Figure 1a**). Each individual melted micro-volume has typical cellular microstructure inside it, as shown in (**Figure 1b**). The microstructure of layers laser processed without boron was similar to that of SLM (**Figure 2a**). The microstructure obtained after laser boronizing differed significantly from that of SLM part (**Figures 2b–2f**). The specimens processed at lower laser speeds (500 mm/min and 750 mm/min) and containing less boron concentrations had fine dendritic microstructure consisting of the fine primary Fe-Ni dendrites and boride-based eutectic (**Figures 2b** and **2c**). With the increase in laser speed and boron concentration, the transition to superfine nano-eutectic structure was observed (**Figures 2d** and **2e**). For the specimen processed at 1000 mm/min, besides eutectic, some amount of Fe-Ni solid solution phase may be seen as well (**Figure 2d**), indicating still hypoeutectic microstructure, while at 1250 mm/min speed, the presence of excess boride phase may be seen, typical for hypereutectic structure (**Figure 2e**). At the highest boron concentration ~5.7 wt%, submicron sized dendritic boride structure was obtained (**Figure 2f**).

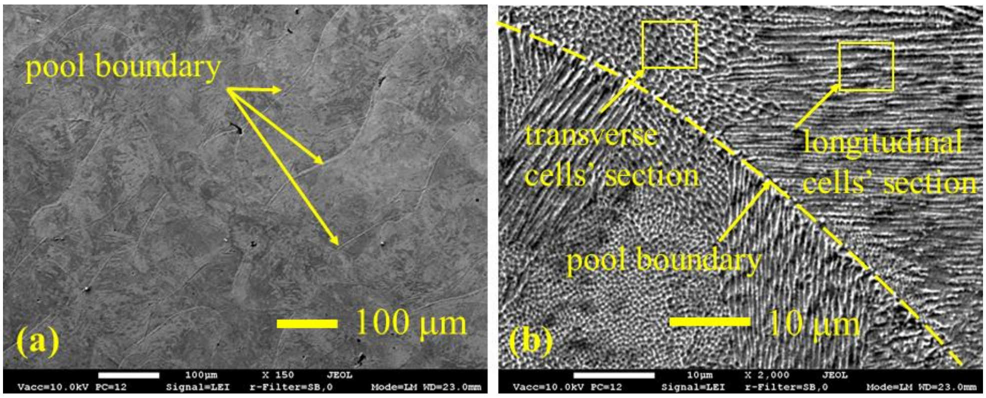

Figure 1 SEM images of SLM body microstructure: (a) overview showing substructure of SLM sample due to "point-by-point" building pattern; (b) longitudinal and transverse directions of cellular microstructure

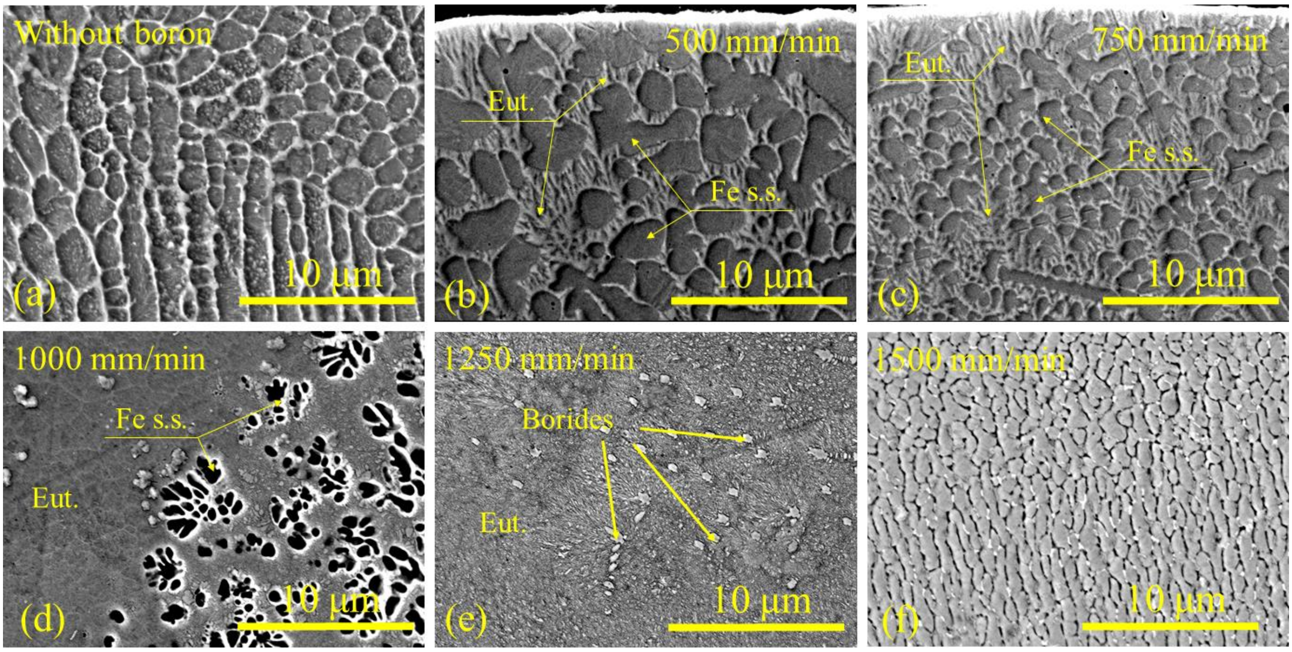

Figure 2 Microstructure SEM images of surfaces laser processing without (a) and with (b–f) boron

With the increase in laser operating speed and respective increase in boron concentration, not only evolution of microstructure was established, but a significant increase in hardness as well, as shown in (**Figure 3**). The hardness of as-manufactured 18Ni-300 maraging steel SLM part is ~385 HK0.2 and it reaches ~600 HK0.2 after appropriate aging. The microhardness of laser-boronized layers ranged between ~630 HK0.2 and ~1770 HK0.2. Accordingly, all the applied laser boronizing parameters provided hardness higher than that after aging. Hardness increase with an increase of laser operation speed is related with two factors – growing boron concentration, resulting in an increase of hard boride phase amount, and increased cooling rates, resulting in a formation of finer microstructure. From the point of wear resistance improvement, 1000 mm/min and 1250 mm/min laser operating speeds, providing hardening effect comparable with nitriding one, and 1500 mm/min speed, providing hardness comparable with that of thermochemically borided parts, may be considered as promising.

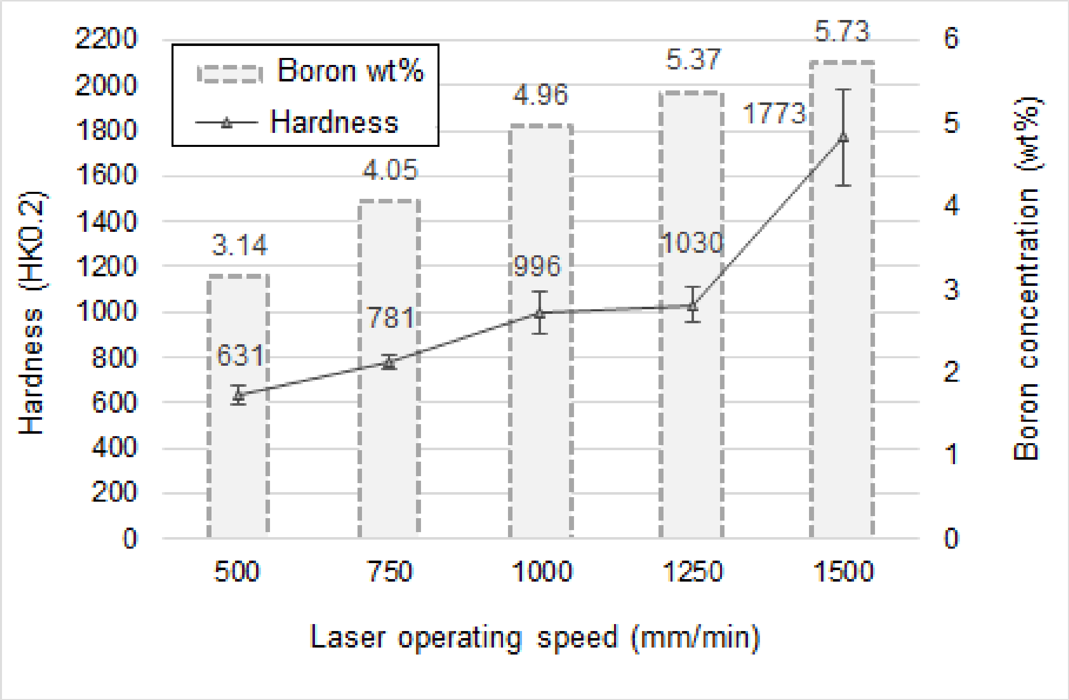

Figure 3 Boron concentration in laser alloyed layers (by XPS) and their hardness in dependence on laser operating speed

4. CONCLUSION

In the present study, the laser surface boronizing was applied for the 18Ni-300 maraging steel parts manufactured by SLM process. The following main conclusions were drawn from the results of the phase and microstructural analyses along with microhardness measurements.

1) The application of 1 kW CO_2 laser for the surface processing of maraging steel parts at the parameters as 0.5 mm laser spot diameter and 500–1500 mm/min laser operating speed provided the process in a melting mode with a melt pool depth between ~85 μm and ~185 μm and width – ~650–960 μm.
2) According to XPS analysis results, boron concentration in processed layers ranged between 3.1 wt% and 5.7 wt% and was in a strong dependence on the laser operating speed, which predetermined the melt pool depth.
3) XRD analysis revealed presence of two phases in SLM sample – martensite and austenite. For the samples laser-boronized at 500 mm/min, 750 mm/min, 1000 mm/min and 1250 mm/min laser operating speeds, the prevailing of Fe_3B type borides and presence of some amount of FeB type borides, martensite and austenite were established. In a sample laser-boronized at 1500 mm/min laser operating speed, Fe_2B type borides replaced those of Fe_3B type.
4) The microstructure of surface layers laser-processed without boron did not differ from that of SLM sample and showed typical cellular solidification. Boron addition resulted in a formation of different microstructure: for the samples containing ~3.1 wt% B and ~4.1 wt% B it was fine dendritic hypoeutectic microstructure, consisting of primary dendrites of Fe-based solid solution and boride-based eutectic regions between them; for the samples containing ~5.0 wt% B and ~5.4 wt% B – mainly superfine boride-based nanoeutectic; for 5.7 wt% B – submicron sized dendritic boride structure.
5) The hardness of laser-boronized layers ranged from ~630 HK0.2 to ~1770 HK0.2 and this is up to ~3 times higher hardness than that of maraging steel part after appropriate aging, what allows assuming that laser boronizing of maraging steels is promising way in terms of their wear resistance improvement.

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