

Comparative Boriding Behavior of Conventionally Manufactured and Additively Manufactured AISI 316L Stainless Steel

Polat TOPUZ

Istanbul Gedik University: T C Istanbul Gedik Universitesi

Ozan Coban

ozan.coban@gedik.edu.tr

Istanbul Gedik University: T C Istanbul Gedik Universitesi <https://orcid.org/0000-0002-1506-4619>

Ahmet KARAASLAN

Istanbul Gedik University: T C Istanbul Gedik Universitesi

İbrahim TÜTÜK

Fatih Sultan Mehmet Vakıf University: Fatih Sultan Mehmet Vakif Universitesi

Umut Can CİNGÖZ

TU Berlin: Technische Universität Berlin

Gökhan ÖZER

Fatih Sultan Mehmet Vakıf University: Fatih Sultan Mehmet Vakif Universitesi

Ebubekir KOÇ

Bogazici University: Bogazici Universitesi

Research Article

Keywords: AISI 316L, additive manufacturing (AM), Laser Powder Bed Fusion (LPBF), pack-boriding, stoichiometry, phase evolution

Posted Date: September 17th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10775307/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

This study systematically investigates and compares the high-temperature solid-state pack-boriding response of conventional wrought (CM) and laser powder bed fusion additively manufactured (AM) AISI 316L stainless steels treated at 900°C and 1100°C for 2 h. Detailed microstructural examination, X-ray diffraction, and high-resolution point-energy-dispersive X-ray spectroscopy (EDX) stoichiometry were utilized to characterize the phase evolution and diffusion kinetics. At 900°C, the boride layer in the AM specimen was thinner than in the CM counterpart due to a diffusion barrier effect caused by cell-boundary segregation of alloying elements (Chromium, Nickel, and Molybdenum). Conversely, at 1100°C, the high dislocation density and cellular boundaries of the additively manufactured matrix acted as short-circuit diffusion paths, leading to an extreme Fe₂B layer depth of $144.6 \pm 47.5 \mu\text{m}$, while the FeB layer remained restricted to $23.8 \pm 7.2 \mu\text{m}$. The extreme thermal budget of 1100°C triggered a complex, multilayered in-situ boride-carbide surface architecture in the AM steel, characterized by localized eutectic melting ($L \rightarrow \gamma + \text{Fe}_2\text{B}$), in-situ Mo₂C carbide nucleation, and grain boundary Cr₂₃C₆/Cr₇C₃ precipitates. This grain boundary sensitization subsequently induced Chromium depletion and intermetallic sigma (σ) phase nucleation. These findings provide crucial guidelines for controlling microstructural segregation and defect-driven diffusion in metal additively manufactured components during high-temperature thermochemical post-processing.

1. Introduction

Additive Manufacturing (AM) for metals is an innovative manufacturing technology that enables the layered production of complex metal parts from 3D CAD models, reducing material waste and offering design freedom compared to traditional machining or forming methods [1]. Among metal AM processes, Powder Laser Bed Fusion (LPBF) produces high-precision parts by selectively melting metal powders with a laser or electron beam. Directed Energy Deposition (DED) is used in construction or repair processes by combining material in wire or powder form with an energy source [2]. Binder Jetting provides rapid production by combining and sintering layers of powder with a binder. Furthermore, methods such as Metal Extrusion and Sheet Lamination enable the production of parts by layered bonding of composite filaments or metal sheets [3]. These methods find wide application in sectors such as aerospace, automotive, and biomedical, allowing control of microstructure and mechanical properties. However, challenges such as alloy limitations, anisotropy, residual stresses, and finishing requirements remain research topics [1]. Laser Powder Bed Fusion (LPBF) is one of the most widely used methods in metal additive manufacturing and is preferred for the production of high-precision parts with complex geometries [4]. The process begins with the deposition of a thin layer of metal powder onto the bed; then, a powerful laser beam selectively melts this powder according to the CAD model, creating layers. Once each layer is completed, the platform is lowered, and a new layer of powder is deposited, repeating the process [5]. LPBF is usually performed in an inert gas atmosphere such as argon or nitrogen; this prevents oxidation and allows for microstructure control during solidification. This method offers advantages such as the ability to produce parts with densities above 99%, design

freedom, and material efficiency; it is widely used in the aerospace, automotive, and biomedical sectors [4]. However, challenges such as optimizing process parameters, powder properties, residual stresses, and surface quality remain under investigation [6].

Boron is a metalloid element with atomic number 5, located in group IIIA of the periodic table. It does not occur freely in nature; it is usually found in the form of borate minerals (e.g., borax, kernite, ulexite) [7]. Boron is notable for its low atomic mass (10.81 g/mol), high melting point (2076°C), and chemical stability; these properties make it a strategic material for high-temperature applications, nuclear reactors, and advanced ceramics [8]. Furthermore, boron compounds have a wide range of applications, from glass and ceramic production to energy storage systems, metal surface hardening processes, and electronic applications [7].

Boriding is a thermochemical process based on the diffusion of boron atoms into metal surfaces for surface hardening purposes. As stated in the ASM Handbook's chapter titled "Boriding (Boronizing) of Metals," the process can be applied to ferrous, non-ferrous, and ceramic-metal (cermet) materials; these processes, carried out using different methods (pack, gas, plasma, electrolytic, liquid bath, and fluidized bed), form durable metal boride layers on the surface [9]. Borides such as FeB, Fe₂B, and TiB formed on the borided surface provide much higher hardness (1,200–3,000 HV) and lower friction coefficients compared to conventional nitriding and carbonitriding methods; this contributes to high wear resistance and tribological performance [10]. The thickness of the boride layer can be controlled according to the diffusion time and temperature. However, challenges such as brittleness, crack formation, and balancing mechanical properties in thick layers necessitate optimization suitable for this texture [9].

AISI 316 is a type of austenitic stainless steel containing molybdenum, and it is divided into various variants. This steel offers superior corrosion resistance in chloride environments thanks to its chemical composition. Molybdenum addition significantly increases pitting and crevice corrosion resistance, making this material a preferred option in aggressive environments such as the marine, chemical, and food industries [11]. The most commonly used variants of AISI 316 today are AISI 316L, which has a maximum carbon content of 0.03%, thus minimizing chromium carbide precipitation during welding and significantly increasing resistance to intergranular corrosion; AISI 316H, which mechanical strength at temperatures above 500°C is increased by raising its carbon content; and AISI 316Ti, which provides corrosion resistance even at high temperatures with the addition of Ti. Therefore, all these features make AISI 316 widely applicable in critical applications such as pressure vessels, heat exchangers, and medical devices [12–14].

Like many types of steel, stainless steel can also be borided, particularly to improve wear resistance and surface hardness. Boriding studies on AISI 316 stainless steel and variants are given in Table 1 below.

Table 1
Boriding studies on AISI 316 stainless steel and variants

Borided Material (AISI)	Boriding Method	Boriding Temp. Range (K)	Boride Layer	References
316	Plasma paste	973–1073	FeB + Fe ₂ B	[15]
316	Powder pack	1123–1273	FeB + Fe ₂ B	[16]
316	Powder pack	1073–1273	FeB + Fe ₂ B	[17]
316 L	Salt-bath (borax + SiC)	1123–1273	FeB + Fe ₂ B	[18]
316	Shot-blasted powder-pack	1123–1223	FeB + Fe ₂ B	[19]
316 L	Powder pack	1123–1223	FeB + Fe ₂ B	[20]

Many studies, like those in Table 1, have shown that boriding of austenitic stainless steels results in the formation of a double-layer composed of FeB+Fe₂B, exhibiting a columnar structure unlike other steel types [21].

Although the low-temperature (850–950°C) boriding kinetics and wear behavior of AISI 316L stainless steels produced by conventional and additive manufacturing (AM) methods have been studied in the literature, there is a significant scientific gap in the literature regarding thermochemical responses and phase evolutions under extreme thermal conditions such as 1100°C. Traditionally, high-temperature post-treatments are not preferred due to sensitization concerns; however, the rapid solidification microstructure of LPBF-produced materials, characterized by high dislocation density and cell boundary segregations, opens a completely new metallurgical window. This study is the first to systematically and comparatively investigate the extreme-temperature (1100°C) package boriding behavior of conventional (CM) and LPBF-produced (AM) AISI 316L steels and to reveal the complex, multilayered, in-situ boride-carbide surface architecture formed on the surface. This article goes beyond mere experimental thickness measurements to describe the local melting/eutectic reaction mechanism ($L \rightarrow \gamma + \text{Fe}_2\text{B}$) triggered by chromium depletion and molybdenum segregation at cell boundaries, in-situ Mo₂C carbide nucleation, and the synthesis mechanisms of the brittle sigma (σ) phase. Through high-resolution stoichiometry calculations (M/X ratios) and direct comparisons with the most current kinetic models in the literature, it provides a critical guide for controlling microstructural segregation and defect density in high-temperature thermochemical post-processing of metal additive fabricated parts.

2. Experimental

2.1. Specimen Fabrication and Initial Preparation

The additively manufactured (AM) specimens (dimensions: 50 × 50 × 20 mm) were fabricated using an EOS M290 metal-based laser powder bed fusion (LPBF) system (EOS GmbH, Germany). The system was equipped with a ytterbium fiber laser, and high-purity EOS AISI 316L stainless steel powder was utilized as the precursor material. The LPBF processing parameters were optimized based on preliminary density optimization studies to ensure a relative density exceeding 99%: 380 W laser power, a 960 mm/s scanning speed, a 110 μm scanning interval, and a 40 μm layer thickness.

For comparative evaluation, conventional wrought (CM) AISI 316L stainless steel plates were sectioned to identical dimensions (50 × 50 × 20 mm). The nominal chemical composition of the precursor AISI 316L stainless steel is summarized in Table 2.

Table 2
Nominal chemical composition (wt.%) of the precursor AISI 316L stainless steel.

Element	Fe	Cr	Ni	Mo	Mn	Si	C	P	S
wt.%	Bal.	16.0–18.0	12.0–15.0	2.0–3.0	2.0	< 1.0	< 0.03	< 0.045	< 0.03

Prior to the thermochemical treatment, the surfaces of both AM and CM specimens were ground sequentially using SiC abrasive papers down to 240 grit. This surface grinding was crucial to eliminate the typical surface ripples and partially melted satellite powder particles characteristic of the LPBF AM surfaces, thereby ensuring a uniform and flat initial surface finish for the subsequent boron diffusion process.

2.2. Thermochemical Pack-Boriding Process

The pack-boriding process was carried out in a solid-state powder pack arrangement. The pre-ground AM and CM specimens were placed together in a high-purity alumina (Al₂O₃) crucible to ensure identical thermal history and chemical exposure during the diffusion process. The crucible was filled and compacted with a commercial EKabor2 boriding powder mixture. The powder mixture had the following stoichiometric formulation, corrected for chemical consistency: 90 wt. % SiC + 5 wt. % B₄C + 5 wt. % KBF₄. Boriding agent for the boriding process. A schematic 3D cross-section view of the boriding setup is shown in Fig. 1 below.

The compacted crucible was sealed with a refractory lid using high-temperature silicate-based ceramic cement to prevent atmospheric oxygen infiltration and oxidation of the powder bed. The thermochemical treatment was performed in an electrical muffle furnace under atmospheric pressure at two distinct diffusion temperatures: low-temperature boriding: 900°C for 2 h, and high-temperature boriding: 1100°C for 2 h. The heating rate was maintained at 10°C/min. Following the completion of the isothermal holding stage, the sealed crucibles were left inside the furnace to cool slowly to room temperature (furnace cooling) to minimize thermal shock and residual stress accumulation at the boride-substrate interface.

2.3. Metallographic Preparation and Microstructural Characterization

Following the pack-boriding treatment, the specimens were sectioned perpendicular to the treated surfaces using a low-speed precision diamond saw to expose cross-sections parallel to the build direction (Z-axis) of the AM specimens. The cross-sectional specimens were mounted in a conductive phenolic hot mounting resin. The cross-sections were metallographically prepared by grinding sequentially on a semi-automatic grinding-polishing machine using water-lubricated SiC papers of 80, 240, 400, 800, and 1200 grit. Final polishing was performed on a velvet polishing cloth using a 1 μm monocrystalline diamond suspension to achieve a mirror-like finish. To reveal the boride layer morphology, the transition zone, and the matrix microstructural features, the polished surfaces were chemically etched by immersion in fresh aqua regia (3 units of HCl + 1 unit of HNO_3 by volume) for 10–15 s at room temperature, followed by rinsing with anhydrous ethanol and hot-air drying. The microstructural morphology, layer compactness, and interfacial features were examined using a Scanning Electron Microscope (SEM) operated in backscattered electron imaging (BSE) mode to highlight Z-contrast differences between the borides, carbides, and the metallic matrix. Elemental microanalysis and phase stoichiometric evaluations across the boride layers were performed using an integrated Energy Dispersive X-ray Spectroscopy (EDX) detector. To determine the dominant phases based on stoichiometry, the atomic percentages of metals ($M = \text{Fe, Cr, Ni, Mo}$) and metalloids ($X = \text{B, C}$) were computed to determine the local M/X ratios. Phase identification on the treated surfaces was conducted via X-ray Diffraction (XRD) using a diffractometer equipped with a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. The diffraction patterns were recorded in a 2θ range of 10° to 90° with a step size of 0.02° and a dwell time of 1 s per step. Phase peaks were analyzed and matched with the standard JCPDS database cards (FeB: JCPDS# 32–0463, Fe₂B: JCPDS# 36-1240).

3. Results and Discussion

The sample BSE of the matrix microstructure of the CM and AM AISI 316 L is shown in Fig. 2 below.

As shown in Fig. 2, the microstructure of conventional CM AISI 316L steel (Fig. 2a and b) exhibits a polygonal austenitic grain structure with a homogeneous distribution. In contrast, the microstructure of AISI 316L steel produced by selective laser melting (LPBF-AM) (Fig. 2c and d) displays a highly heterogeneous and oriented microstructure. Due to the rapid melting and high cooling rates in the layered fabrication process, the boundaries of the superimposed semi-elliptical molten pools are clearly defined. Within these molten pools, oriented thin cellular and columnar dendritic sub-grain structures grow parallel to the vertical thermal gradient. These significant geometric and structural differences observed between CM and AM matrix microstructures in terms of grain size and morphology directly determine the diffusion rate and reaction pathways of boron atoms.

3.1. Effect of Production Method and Temperature on Boride Layer Morphology and Kinetics

After examining the matrix microstructure of the unborided AM AISI 316L sample, microstructural analyses of the boride layers were performed on sections of the borided samples. The formation of a boride layer on the surface of CM and AM AISI 316L specimens borided using the powder-pack boriding method was observed to depend on temperature. In the case of boriding austenitic stainless steels, unlike ferritic steels, a more planar and less saw-tooth-like layer interface forms due to high alloying elements (Cr, Ni, Mo, etc.) [29, 30]. These alloying elements act as a diffusion barrier by limiting the diffusion of boron atoms in the form of inward-directed columns [14].

Figure 3 Cross-sectional microstructural SEM (BSE) images of AISI 316L stainless steels borided at 900°C for 2 hours: (a) Sample produced by conventional method (CM) and (b) sample produced by additive manufacturing (AM)

In both samples, two-phase FeB and Fe₂B boride layers were successfully synthesized on the surface. In the conventional CM sample presented in Fig. 3(a), the boride layer grew in highly homogeneous, continuous, and distinct columns. However, when the AM sample shown in Fig. 3(b) is examined, the layer morphology is disrupted in places, exhibiting a wavy and irregular thickness. The main reason for this morphological disruption is the residual micropores inherited from the layered fabrication process, melt pool boundaries, and heterogeneous microsegregation patterns of alloying elements. These defects altered the local diffusion rates, leading to the irregular growth of the boride layer. In addition, the formation of chromium- and carbon-rich dendritic transition zones between the boride layer and the austenitic matrix was observed in both samples [29, 31].

Increasing the temperature to 1100°C exponentially increased the boron diffusion coefficient and chemical reaction activity. Figure 4 shows microstructural cross-sectional SEM images of CM and AM AISI 316L samples borided at 1100°C for 2 hours.

As seen in Fig. 4(a), in the conventional CM sample, a very thick and distinct columnar biphasic (FeB+Fe₂B) boride layer was obtained in parallel with the increasing diffusion rate. In contrast, the situation in the AM sample in Fig. 4(b) took on a completely different dimension. In the AM sample, instead of a classic columnar biphasic layer, a multilayered, extremely heterogeneous and complex boride-carbide surface architecture was formed on the surface. This situation is due to the high dislocation density, microsegregation boundaries, and pores in the AM matrix at a high thermal budget of 1100°C, which excessively accelerates the diffusion of alloying elements (especially Cr, Mo, and C) into and out of the layer. This situation dramatically altered the boron diffusion kinetics and phase stability, leading to localized melting, eutectic reactions, and dense carbide precipitation [25, 29].

Detailed thickness analyses performed on micro-images obtained from cross-sectional SEM examinations quantitatively revealed the effects of boriding temperature and production method on layer

growth rate and mechanism. Figure 5 shows a comparative analysis of the average thickness measurements of FeB, Fe₂B, and transition zone layers formed after a 2-hour boriding process at 900°C and 1100°C for both conventional CM and layered AM AISI 316L steels.

At 900°C, the FeB layer thickness in the CM sample was $16.2 \pm 3.4 \mu\text{m}$, the Fe₂B thickness was $11.4 \pm 3.1 \mu\text{m}$, and the transition zone thickness was $12.9 \pm 5.6 \mu\text{m}$. Increasing the temperature to 1100°C, these layers reached thicknesses of $37.8 \pm 10.1 \mu\text{m}$, $23.9 \pm 5.2 \mu\text{m}$, and $47.1 \pm 14.5 \mu\text{m}$, respectively, due to the increasing diffusion rates of boron and carbon.

In the AM sample, at 900°C, the FeB layer was measured at $6.4 \pm 2.5 \mu\text{m}$, the Fe₂B layer at $12.1 \pm 1.8 \mu\text{m}$, and the transition zone at $30.5 \pm 6.4 \mu\text{m}$. Remarkably, at 1100°C, the boride layer structure in the AM sample deviated completely from the conventional one, with the Fe₂B layer depth reaching a high average of $144.6 \pm 47.5 \mu\text{m}$, while the FeB thickness was measured as $23.8 \pm 7.2 \mu\text{m}$. At 900°C, the layer thicknesses of the AM sample remained lower than those of the conventional CM sample due to the barrier effect created by microsegregation of alloying elements (Cr, Ni, Mo) at the grain boundaries. However, the excessive Fe₂B thickness of $144.6 \pm 47.5 \mu\text{m}$ observed in the AM sample at 1100°C is unique in demonstrating the character of high-temperature reactions in additively manufactured parts. At a high thermal budget of 1100°C, the high dislocation density and sub-grain (cellular) boundaries inherited from rapid melting/cooling acted as "short-circuit diffusion paths" for boron atoms. The boron diffusion front penetrated very deep into the matrix using these channels, triggering liquefaction/eutectic reactions ($\gamma + \text{Fe}_2\text{B}$ eutectic formation) and causing localized displacement of the layer. The high standard deviation value ($\pm 47.5 \mu\text{m}$) of the Fe₂B layer in the AM sample also microstructurally demonstrates this uncontrolled, channeled, and heterogeneous diffusion depth.

3.2. XRD Phase Analysis and Boride Formation Mechanism

Figure 6 XRD diffraction patterns taken from the surface of AISI 316L steels borided at 1100°C for 2 hours: (a) Sample (CM) produced by the conventional method and (b) Sample (AM) produced by layered manufacturing

As shown in Fig. 6, strong diffraction peaks belonging to the tetragonal Fe₂B (tetragonal, JCPDS# 36-1240) and orthorhombic FeB (orthorhombic, JCPDS# 32-0463) phases, which are the main components of the boride layer on the surface, were detected in the diffraction patterns of both (a) CM and (b) AM AISI 316L steels. In addition to iron borides, orthorhombic CrB, tetragonal Cr₂B, and Ni₃B alloy borides, formed by the reaction of chromium and nickel elements present in the high-alloy steel with boron, were also identified. As reported in the literature, the main peak positions of alloy borides tend to overlap with the peaks of iron borides [21, 29]. High boron diffusion at 1100°C facilitated the boron concentration reaching the FeB stable phase boundary (16.23% wt. B) on the surface, resulting in a significant increase in FeB peak densities. The fluctuations and slight shifts observed in peak intensities in the AM sample compared to the CM sample indicate lattice deformations resulting from high internal stress levels and diffusion anisotropy in the layered fabrication microstructure [1, 29].

3.3. EDX Point Chemical Analysis and Stoichiometric Phase Determination

To verify the phases formed in the boride layer and at the interface at the microscopic scale, point EDX analyses were performed along the cross-section of layered fabrication (AM) samples borided at 900°C and 1100°C. The obtained atomic percentage data were converted according to metal/metalloid (M/X; where M = Fe, Cr, Ni, Mo and X = B, C) atomic ratios and subjected to stoichiometric analysis to identify the dominant phases. The analysis results are summarized in Table 3.

Table 3
Stoichiometric analysis results of the borided samples

Spectrum	Stoichiometry	Dominant	Spectrum	Stoichiometry	Dominant
1100°C	(M/X)	phase	900°C	(M/X)	phase
1	0.66	FeB	1	0.93	FeB
2	1.06	FeB	2	0.87	FeB
3	1.46	Fe ₂ B	3	1.04	FeB
4	0.98	Fe ₂ B + Mo ₂ C	4	1.55	Fe ₂ B
5	2.15	γ + Fe ₂ B Eutectic	5	1.82	Fe ₂ B
6	1.51	Mo ₂ C	6	2.16	Fe ₂ B (alloyed)
7	2.25	Fe ₂ B	7	2.38	Cr ₇ C ₃
8	2.24	Fe ₂ B (Cr-rich)	8	2.21	Cr ₇ C ₃
9	1.02	FeB	9	4.04	Cr ₇ C ₃ / Matrix
10	1.44	Mo ₂ C	10	3.56	Cr ₂₃ C ₆ / Matrix
11	1.83	Cr ₇ C ₃	11	3.88	Cr ₂₃ C ₆ / Matrix
12	3.24	Cr ₂₃ C ₆	12	7.61	Matrix (γ)
13	7.60	Matrix (γ)	13	8.02	Matrix (γ)

Figure 7 Point EDX measurement locations subjected to stoichiometric analysis as shown in Table 3 on the cross-sectional SEM (BEI) image of the AM AISI 316L stainless steel sample borided at 900°C for 2 hours

At 900°C, the diffusion depth is relatively limited, and a classical boride layer structure is observed, consistent with the literature [16, 29]. Analyses performed at positions 1, 2, and 3 of the spectrum

confirm that the FeB phase with high boron concentration dominates in the region closest to the surface, as the M/X ratios are 0.93, 0.87, and 1.04, respectively. In the lighter contrast regions 4, 5, and 6 immediately below, the M/X ratios were measured as 1.55, 1.82, and 2.16, and it was determined that these regions consist of the Fe₂B phase. It was determined that the M/X ratios at points 7, 8, and 9, located at the layer-matrix interface, varied between 2.38 and 4.04. This proved that in this transition region, carbon, pushed out of the matrix by the diffusion of boron, combines with chromium to form dendritic Cr₇C₃ carbides. While Cr₂₃C₆-type carbide precipitates were observed at points 10 and 11 near the matrix boundary, the M/X ratios at points 12 and 13, which were 7.61 and 8.02, respectively, confirmed the presence of the main austenite matrix structure.

Increasing the temperature to 1100°C resulted in much more dynamic elemental displacement and phase separation within the sample. Figure 8 shows a cross-sectional SEM image of the AM sample borided at 1100°C and the EDX analysis positions on it.

In the evaluation made together with Table 3, it is seen that Spectrum 1, 2, and 9 points just below the surface (M/X ratios 0.66, 1.06, and 1.02) correspond to the FeB phase. At the same time, Spectrum 3, 7, and 8 positions consist of the Fe₂B phase (Spectrum 8 is a chromium-rich alloyed Fe₂B). The most striking findings at this temperature were obtained at Spectrum 4, 5, 6, and 10 positions. At Spectrum 4, the M/X ratio was found to be 0.98, and it was determined that this region consists of a mixture of Fe₂B and molybdenum carbide (Mo₂C) phase developing within the Fe₂B layer. The M/X ratio of 2.15 at Spectrum 5 confirms the gamma + Fe₂B eutectic mixture formed as a result of eutectic reactions occurring with high-temperature liquid-phase boron welding or during solidification. The M/X ratios of 1.51 and 1.44 at points 6 and 10 of the spectrum, respectively, indicate that Mo₂C phase precipitated directly as a result of peaking Mo segregation in these regions. Spectrum 11 represents Cr₇C₃ carbide at the interface; Spectrum 12 represents Cr₂₃C₆ carbide precipitates accumulating at grain boundaries and forming a necklace structure. Spectrum 13 (M/X = 7.60) shows the main austenite matrix partially depleted of alloying elements [17, 29].

In samples produced by the additive manufacturing (AM) method, phase evolutions, diffusion, and segregation mechanisms occurring at extremely high boriding temperatures such as 1100°C revealed a highly unique "microstructure architecture" along the cross-section. Figure 9 details the sub-regions, phase boundaries, and precipitation patterns of this complex structure in high-resolution SEM images.

At 1100°C, the diffusion coefficient of boron increases dramatically, and it penetrates deeply into the matrix using high-speed diffusion pathways along the cellular grain boundaries of AM steel [5, 29]. Unlike Fe₂B, it appears darker in the BSE mode due to its higher boron content and lower capacity to combine chromium and molybdenum [24].

In the uppermost part of the surface layer, large, angular, and block-like tetragonal M₂B (mainly Fe₂B) crystals, commonly encountered in high-temperature boriding of austenitic stainless steels, are observed. The bright contrast of these crystals in BSE mode is explained by the presence of high-atomic-

number chromium (Cr) and molybdenum (Mo) elements dissolved in them. Between these primary boride crystals, distinct lamellar eutectic regions are observed, formed as a result of local liquefaction or eutectic reaction occurring in the presence of high boron below the melting point of the matrix [17]. Immediately below the eutectic region, there is a dark-colored FeB layer growing in columnar form with high boron activity. The FeB phase has a highly brittle structure due to the internal stresses caused by its orthorhombic crystal structure, and tends to contain micropores and microcracks under high-temperature stresses [20, 21]. Immediately below the FeB layer and at the main matrix boundary, there is a dendritic Cr₇C₃ transition zone formed by the reaction of carbon atoms accumulating in front of the boron diffusion front with chromium. In addition, continuous Cr₂₃C₆ carbide precipitates, called "necklace-structured," extending along the grain boundaries of the austenitic matrix have been detected. High temperatures such as 1100°C cause severe grain boundary sensitization in AISI 316L steels. Carbon diffuses towards the grain boundaries and combines with Cr there [25, 26]. These Cr depletion (chromium depletion) regions formed at the grain boundaries, combined with Mo segregation in the matrix, triggered the nucleation and growth of the thermodynamically brittle and undesirable intermetallic sigma phase. Furthermore, multilayered, bright-looking Mo₂C carbide grains were identified, nucleated in situ as a result of molybdenum reaching its insolubility and segregation limits in the immediate vicinity of the FeB and Fe₂B phase boundaries. This situation proves that the 1100°C boriding temperature in high-alloy additive fabricated parts causes not only a boriding reaction but also deep microstructural phase breakdowns and carbide synthesis reactions within the matrix [29, 26, 27].

When our findings are compared with similar boriding studies in the literature, it is seen that the additive manufacturing (AM) microstructure plays a bidirectional role in boron diffusion mechanisms. On the one hand, the high dislocation density and dense cellular grain boundaries in the AM structure contribute to the rapid infiltration of boron atoms via diffusion [17, 29]. On the other hand, dense chromium, nickel, molybdenum, and silica segregations occurring at the cellular boundaries create a strong chemical and mechanical resistance (diffusion barrier) against the inflow of boron. This explains why the growth rate and layer thickness of the boride layer in additive manufacturing samples are lower than in conventional CM samples. In the kinetic study carried out on SLM 316L by Demirci and Tünçay [29], it was determined that the diffusion activation energy of boron in the AM structure ($Q_{\text{FeB}} = 256.56 \text{ kJ/mol}$, $Q_{\text{Fe}_2\text{B}} = 161.61 \text{ kJ/mol}$) is higher than in conventional CM 316L steels. This high activation energy requirement is directly related to the segregation boundaries of the alloying elements blocking and delaying the boron atoms. Furthermore, in boriding processes carried out at high temperatures such as 1100°C, dislocation accumulations at the grain boundaries of the AM sample accelerated the diffusion of carbon atoms, resulting in the synthesis of much more stable and dense Cr₂₃C₆, Cr₇C₃ and Mo₂C carbide networks at the interface compared to CM steels [15, 26, 35]. This situation once again highlights the importance of controlling microstructural segregation and initial defect density in high-temperature thermochemical processes of additive manufacturing parts [25–28].

4. Conclusion

Based on the experimental findings, microstructural characterizations, and kinetic analysis of wrought (CM) and additively manufactured (AM) AISI 316L stainless steels borided at 900°C and 1100°C for 2 h, the following main conclusions are drawn:

- Highly dense and metallurgically bonded dual-phase iron boride coatings, primarily consisting of tetragonal Fe₂B and orthorhombic FeB phases, were successfully synthesized on both conventional CM and additively manufactured AM AISI 316L stainless steels. Additionally, alloying borides such as CrB and Cr₂B were detected, which overlapped with the main iron boride peaks under X-ray diffraction (XRD).
- At a lower boriding temperature of 900°C, the boride layer in the AM specimen was significantly thinner (FeB = 6.4 ± 2.5 µm, Fe₂B = 12.1 ± 1.8 µm) than that in the CM counterpart (FeB = 16.2 ± 3.4 µm, Fe₂B = 11.4 ± 3.1 µm). This is attributed to the strong chemical and mechanical diffusion barrier (blocking effect) created by the microsegregation of alloying elements (Cr, Ni, Mo) along the cell boundaries of the LPBF-AM starting microstructure.
- Increasing the temperature to 1100°C completely altered the diffusion kinetics in the AM steel. The defect-rich matrix of the additively manufactured (AM) steel, characterized by high dislocation densities and cellular boundaries, acted as highly active short-circuit diffusion pathways. This facilitated extreme boron penetration, resulting in an exceptional average Fe₂B layer depth of 144.6 ± 47.5 µm, while the outer FeB thickness remained restricted to 23.8 ± 7.2 µm.
- High-temperature boriding of AM AISI 316L at 1100°C triggered a highly complex, multilayered in-situ surface architecture. High-resolution point-EDX stoichiometry (M/X ratios) confirmed localized eutectic melting (L → γ + Fe₂B) at the surface [23], in-situ nucleation of Mo₂C carbides, and continuous grain boundary sensitization via continuous Cr₂₃C₆ and Cr₇C₃ ("necklace-structured") networks. The resulting local Chromium depletion subsequently triggered the nucleation of the brittle intermetallic sigma (σ) phase.

Declarations

Conflict of Interest

No conflict of interest exists in the submission of this manuscript, and manuscript is approved by all authors for publication. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Funding

Not applicable.

CRediT Authorship Contribution Statement

Conceptualization: Ozan Çoban, Polat Topuz. **Methodology:** Polat Topuz, Ozan Çoban, Ahmet Karaaslan. **Formal analysis:** Polat Topuz, Umut Can Cingöz, Gökhan Özer. Investigation: Polat Topuz, Gökhan Özer, İbrahim Tütük. **Resources:** Ozan Çoban, İbrahim Tütük, Ebubekir Koç. **Data curation:** Polat Topuz, Gökhan Özer. **Writing - original draft preparation:** Polat Topuz, Ozan Çoban. **Writing - review and editing:** Ozan Çoban, Ahmet Karaaslan, Umut Can Cingöz, Ebubekir Koç, Gökhan Özer, İbrahim Tütük, Polat Topuz. **Supervision:** Ozan Çoban, Ahmet Karaaslan. **Project administration:** Ozan Çoban.

References

1. Badoniya P, Srivastava M, Jain PK et al (2024) A state of the art review on metal additive manufacturing: Milestones, trends, challenges and perspectives. J Braz Soc Mech Sci Eng 46:339. <https://doi.org/10.1007/s40430-024-04917->
2. Booyesen TWJ, Jamiru T, Adegbola TA (2023) Classification of metal additive manufacturing technologies. R&D J 39:35–43
3. Tebianian M, Aghaie S, Razavi Jafari NS, Elmi Hosseini SR, Pereira AB, Fernandes FAO, Farbakhti M, Chen C, Huo Y (2023) A review of the metal additive manufacturing processes. Materials 16:7514. <https://doi.org/10.3390/ma1624751>
4. Ali MH, Sabyrov N, Shehab E (2022) Powder bed fusion-laser melting (PBF-LM) process: Latest review of materials, process parameter optimization, application, and up-to-date innovative technologies. Prog Addit Manuf 7:1395–1422. <https://doi.org/10.1007/s40964-022-00311->
5. AMPOWER (2023) Laser beam powder bed fusion. AMPOWER Report. <https://www.ampower.eu/report/laser-beam-powder-bed-fusio>
6. Dejene ND, Lemu HG (2023) Current status and challenges of powder bed fusion-based metal additive manufacturing: Literature review. Metals 13:424. <https://doi.org/10.3390/met1302042>
7. Greenwood NN, Earnshaw A (2012) Chemistry of the elements, 2nd edn. Butterworth-Heinemann, Oxford
8. Callister WD Jr, Rethwisch DG (2021) Materials science and engineering: An introduction, 10th edn. Wiley, Hoboken
9. Zimmerman C (2013) Boriding (boronizing) of metals. In: Steel heat treating fundamentals and processes, ASM Handbook, vol 4A, pp 709–724. ASM International, Materials Park. <https://doi.org/10.31399/asm.hb.v04a.a000577>
10. Casteletti LC, Lombardi AN, Totten GE (2007) Boriding. Encyclopedia of tribology. Springer, New York, pp 249–255. https://doi.org/10.1007/978-0-387-92897-5_72
11. Sun YT, Tan X, Lei LL, Li J, Jiang YM (2021) Revisiting the effect of molybdenum on pitting resistance of stainless steels. Tungsten 3:209–217. <https://doi.org/10.1007/s42864-021-00099->
12. Davis JR (1994) Stainless steels. ASM International, Materials Park
13. Sedriks AJ (1996) Corrosion of stainless steels, 2nd edn. Wiley-Interscience, New York

14. Lippold JC, Kotecki DJ (2005) *Welding metallurgy and weldability of stainless steels*. Wiley-Interscience, Hoboken
15. Keddarn M, Chegroune R, Kulka M, Makuch N, Panfil D, Siwak P, Taktak S (2018) Characterization, tribological and mechanical properties of plasma paste borided AISI 316 steel. *Trans Indian Inst Met* 71:79–90. <https://doi.org/10.1007/s12666-017-1142-6>
16. Campos-Silva I, Ortiz-Domínguez M, Bravo-Bárcenas O, Doñu-Ruiz MA, Bravo-Bárcenas D, Tapia-Quintero C, Jiménez-Reyes MY (2010) Formation and kinetics of FeB/Fe₂B layers and diffusion zone at the surface of AISI 316 borided steels. *Surf Coat Technol* 205:403–412. <https://doi.org/10.1016/j.surfcoat.2010.06.068>
17. Aydın Ö, Topuz P, Aydoğmuş T (2020) Kinetic characterization of boride layers formed on AISI 316 stainless steel. *Mater Test* 62:652–656. <https://doi.org/10.3139/120.111530>
18. Khater MA, Arroussi C, Yahiaoui M, Abid M (2025) Sliding wear behavior of AISI 316L stainless steel treated by boriding in molten salts. *Int J Adv Manuf Technol* 140:6397–6412. <https://doi.org/10.1007/s00170-025-16668-4>
19. Ayvaz Sİ, Aydın İ, Bahçepınar Aİ (2023) Effect of shot blasting on the boriding kinetics of AISI 316L stainless steel. *Prot Met Phys Chem Surf* 59:671–678. <https://doi.org/10.1134/S2070205123700624>
20. Hernández-Sánchez E et al (2019) Tribological behavior of borided AISI 316L steel with reduced friction coefficient and enhanced wear resistance. *Mater Trans* 60:156–164. <https://doi.org/10.2320/matertrans.M2018282>
21. Keddarn M, Topuz P, Aydın Ö (2021) Simulation of boronizing kinetics of AISI 316 steel with an integral diffusion model. *Mater Test* 63:906–912. <https://doi.org/10.1515/mt-2021-0023>
22. Keddarn M, Ortiz-Domínguez M, Elias-Espinosa M, Zuno-Silva J (2014) Characterization and kinetics of the boride layers formed on AISI 316L steel. *Appl Surf Sci* 305:666–672. <https://doi.org/10.1016/j.apsusc.2014.03.159>
23. Dybkov VI (2015) Boride coatings of Fe-Cr alloys and chromium steels. *Int J Mater Chem Phys* 1:43–66
24. Brakman CM, Gommers AWJ, Mittemeijer EJ (1989) Boriding of Fe-Cr-Ni alloys. *Surf Eng* 5:37–49. <https://doi.org/10.1179/sur.1989.5.1.37>
25. Kokawa H, Koyanagawa T, Shimada M, Sato YS, Kuwana T (2000) Dependence of carbide precipitation on grain boundary structure in sensitized austenitic stainless steel. *Properties of complex inorganic solids 2*. Springer, pp 15–26
26. Wasnik DN, Dey GK, Kain V (2003) Precipitation stages in a 316L austenitic stainless steel. *Scr Mater* 49:135–141. [https://doi.org/10.1016/S1359-6462\(03\)00220-3](https://doi.org/10.1016/S1359-6462(03)00220-3)
27. Hu J, Pei Y, Liu Y, Yang X, Li H, Xu H, Guo N (2020) Microstructure and properties of Cr-Fe₂B composite coatings prepared by pack-preboronizing combined with electro brush-plating. *Coatings* 10:519

28. Göl Y, Kılınç B (2025) Effect of boron concentration in Fe–Cr–Mo–(B,C) hardfacing alloys on microstructure and mechanical properties. *J Mater Eng Perform* 34:14325–14336
29. Demirci S, Tünçay MM (2025) Growth kinetics of borided 316L stainless steel obtained by selective laser melting. *J Cent South Univ* 32:332–349. <https://doi.org/10.1007/s11771-024-5733-1>
30. Sabuz EH, Noor-A-Alam M, Haider W, Shabib I (2023) Improving the mechanical and electrochemical performance of additively manufactured 8620 low alloy steel via boriding. *Corros Mater Degrad* 4:623–643. <https://doi.org/10.3390/cmd4040032>
31. Balhara H, Yelkarasi C, Erdemir A, Bukkapatnam STS (2024) Spatial characteristics of ultra hard coating on directed energy deposition (DED)-printed 316L with a novel ultra-fast boriding. *J Manuf Process* 121:92–99. <https://doi.org/10.1016/j.jmapro.2024.03.044>

Figures

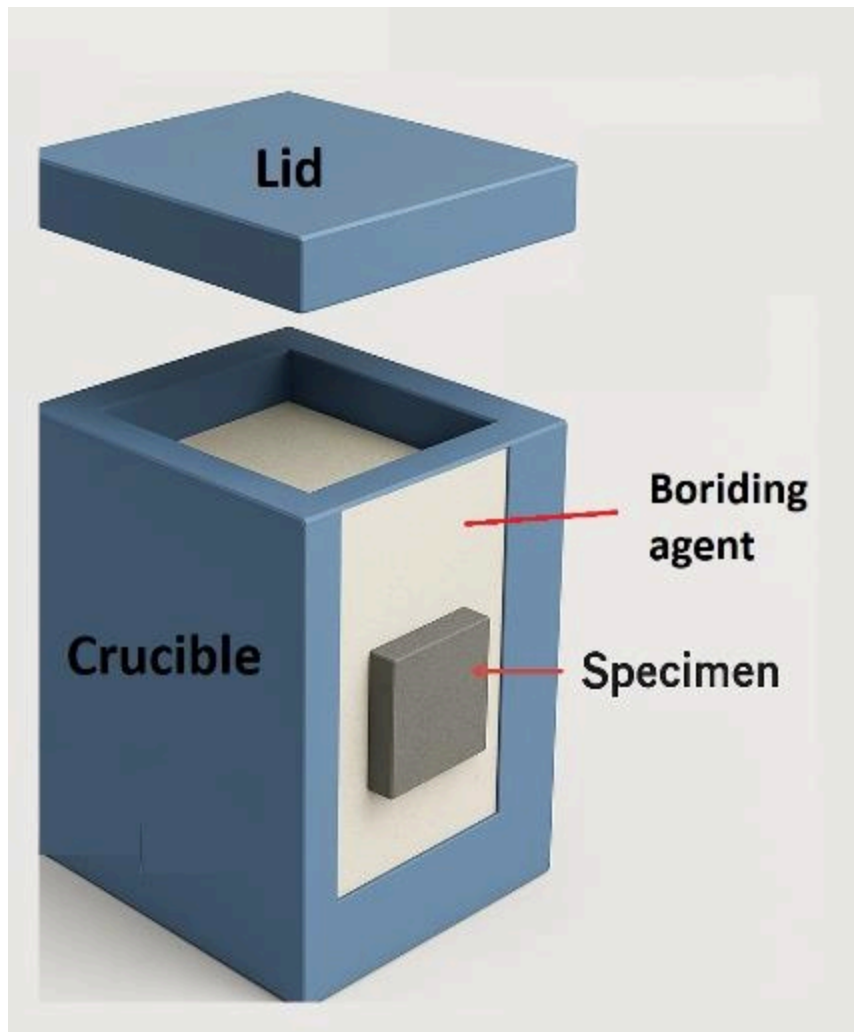


Figure 1

Schematic 3D cross-section view of the boriding setup

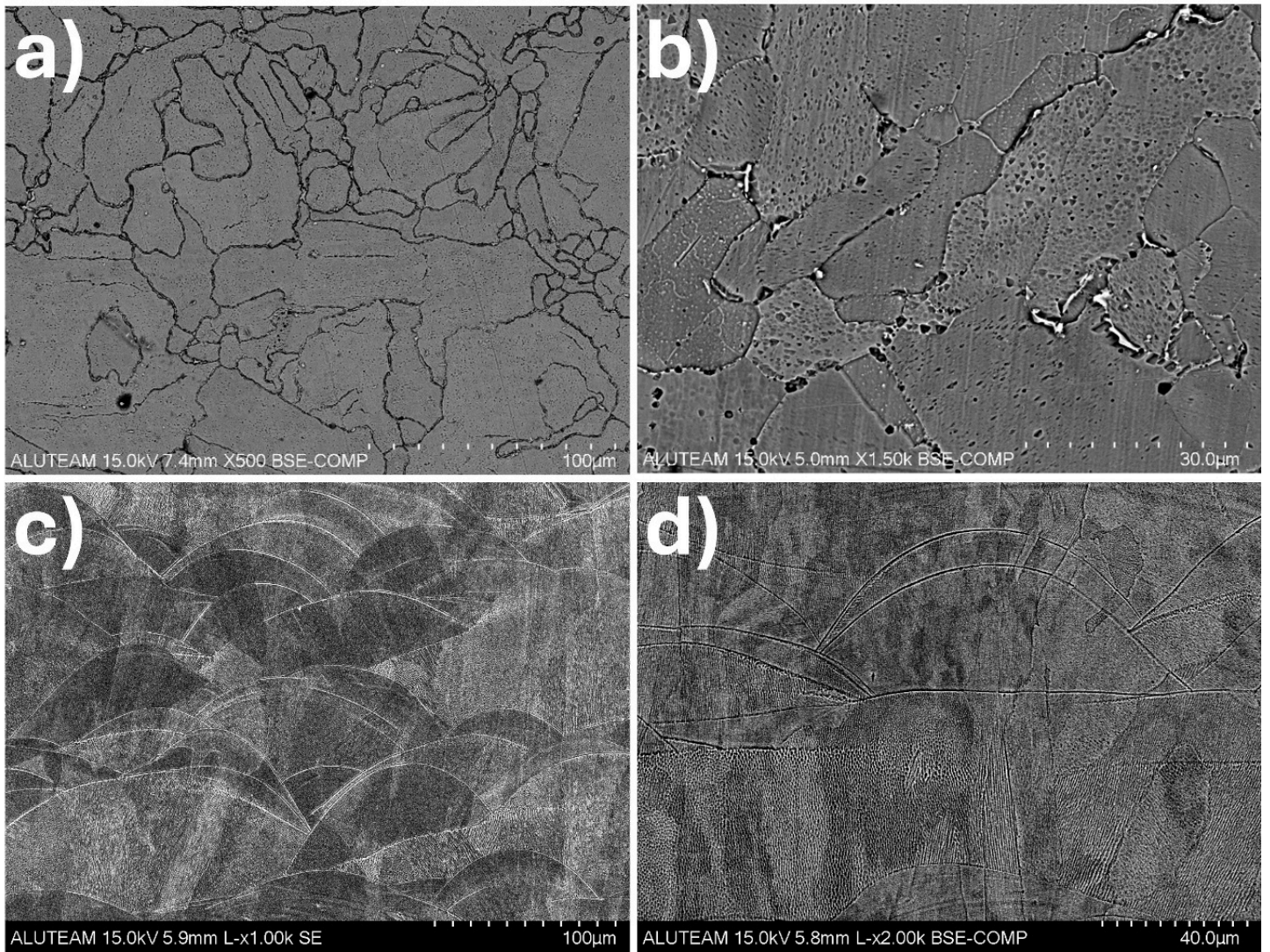


Figure 2

Comparative SEM images at different magnifications of the initial matrix microstructures of AISI 316L austenitic stainless steel samples in the as-built/unborided state: (a, b) sample produced by conventional method (CM) and (c, d) sample produced by selective laser melting (LPBF-AM) method

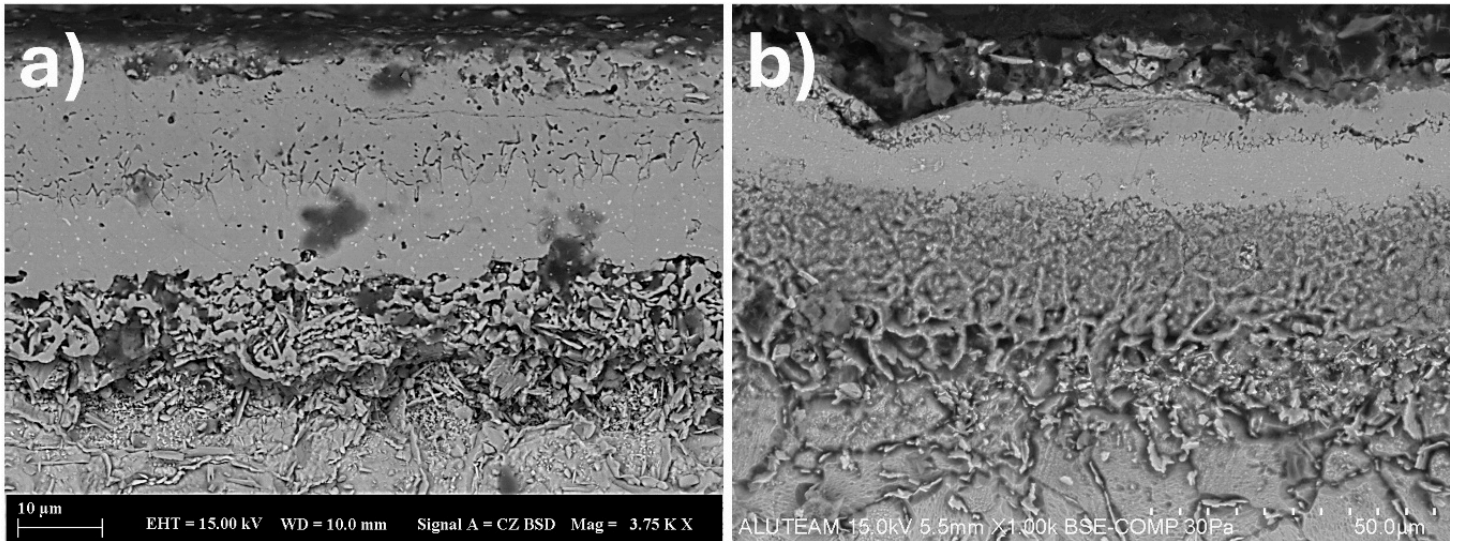


Figure 3

Cross-sectional microstructural SEM (BSE) images of AISI 316L stainless steels borided at 900 °C for 2 hours: (a) Sample produced by conventional method (CM) and (b) sample produced by additive manufacturing (AM)

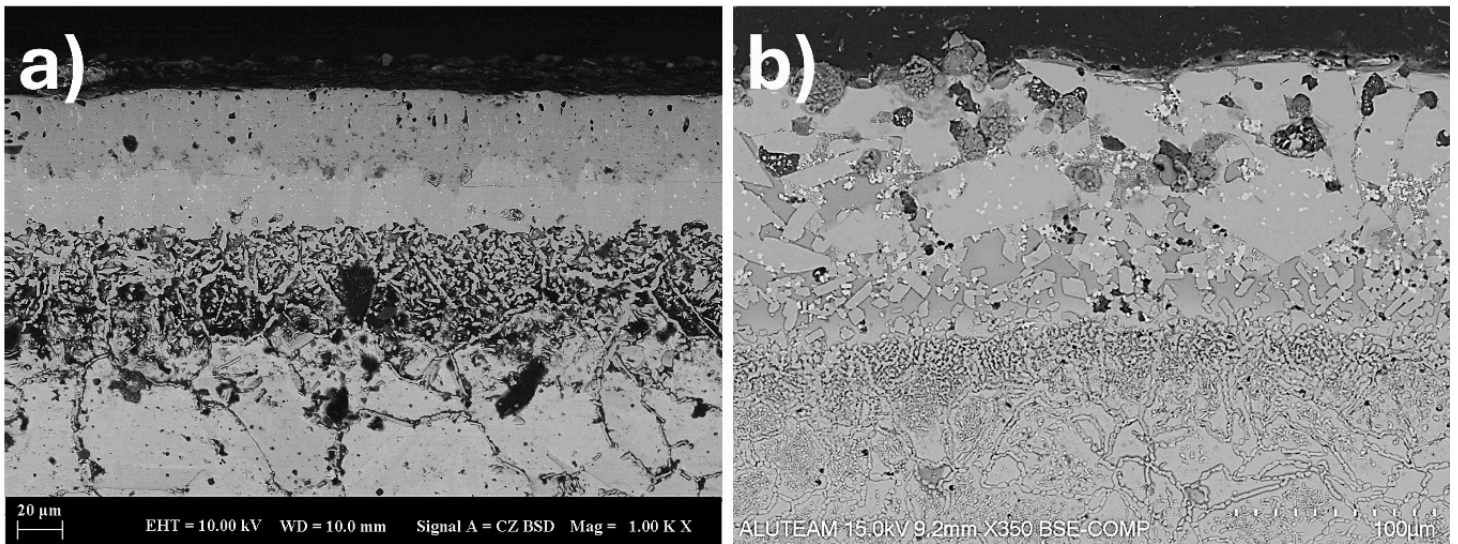


Figure 4

Cross-sectional microstructural SEM (BSE) images of AISI 316L stainless steels borided at 1100 °C for 2 hours: (a) Sample produced by conventional method (CM) and (b) Sample produced by additive manufacturing (AM)

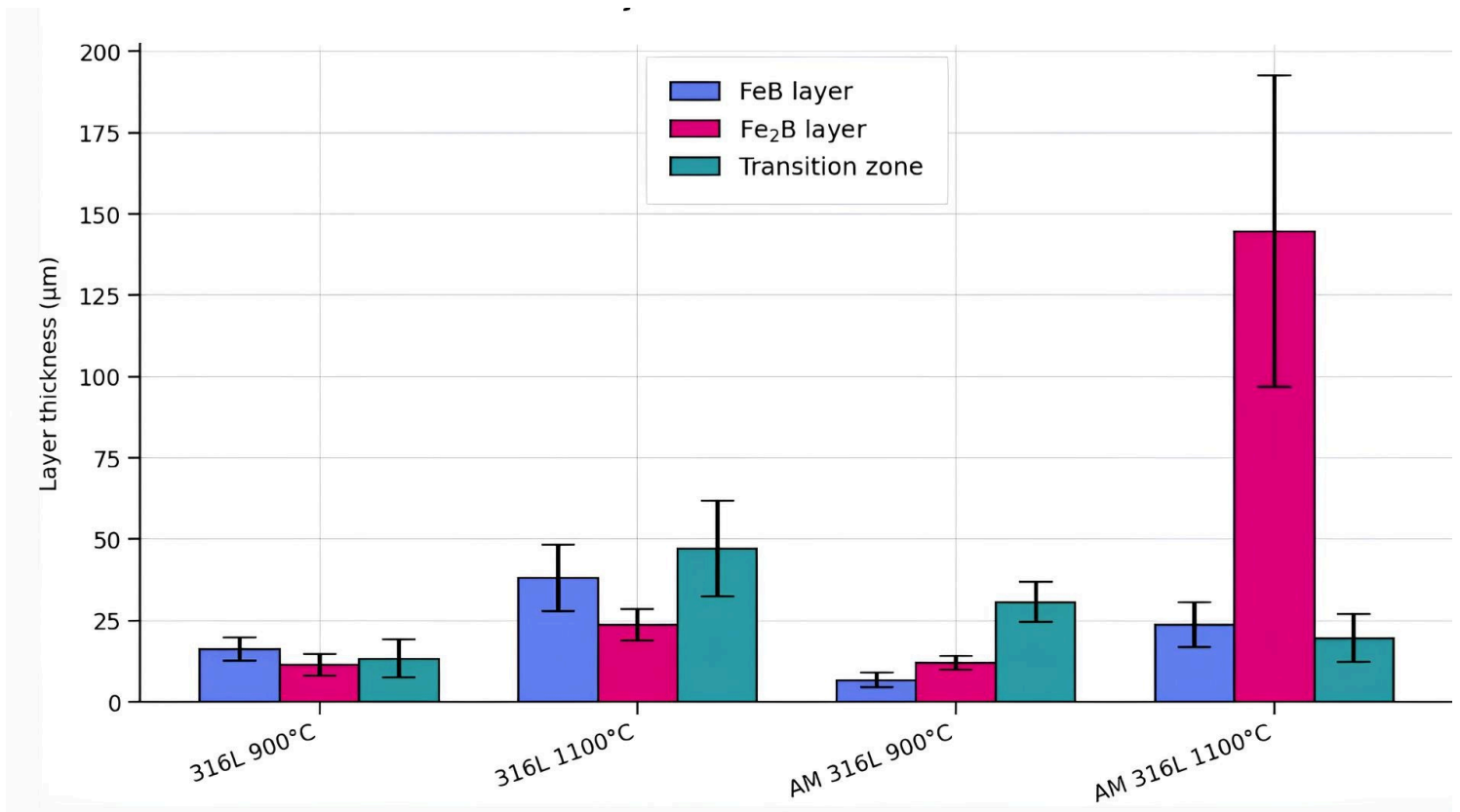


Figure 5

Graph of average FeB, Fe₂B, and transition zone thicknesses measured from cross-sections after boriding conventional CM and layered fabrication AM AISI 316L steels at 900 °C and 1100 °C for 2 hours

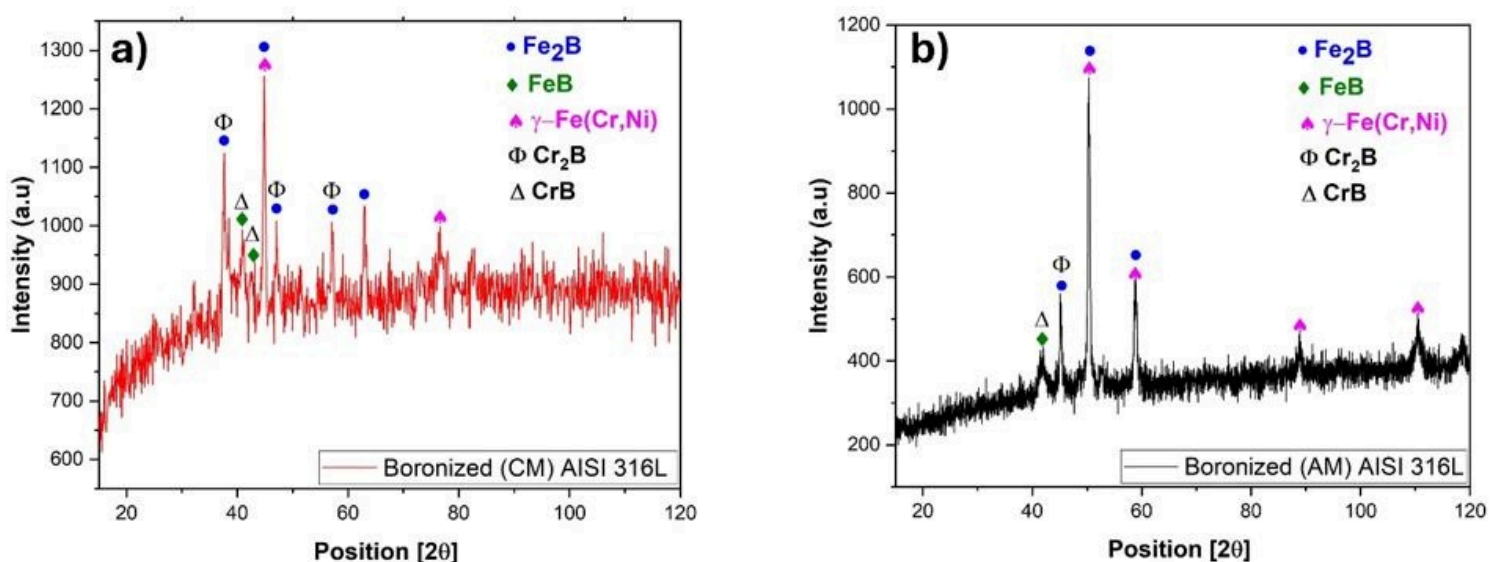


Figure 6

XRD diffraction patterns taken from the surface of AISI 316L steels borided at 1100 °C for 2 hours: (a) Sample (CM) produced by the conventional method and (b) Sample (AM) produced by layered manufacturing

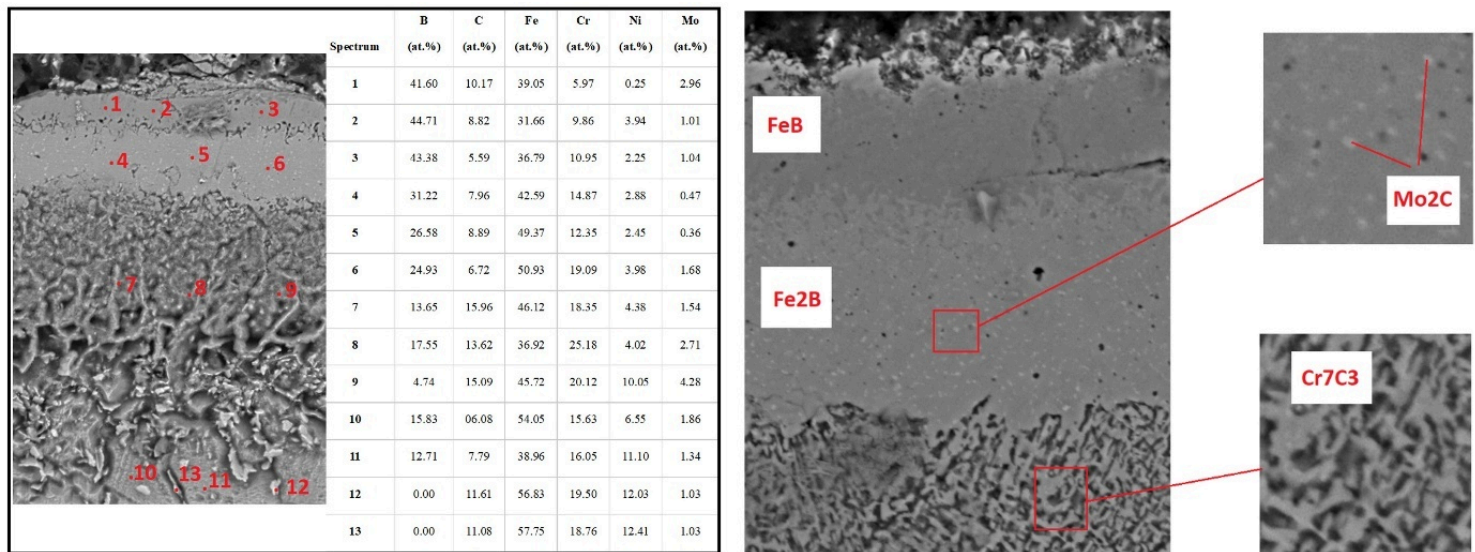


Figure 7

Point EDX measurement locations subjected to stoichiometric analysis as shown in Table 3 on the cross-sectional SEM (BEI) image of the AM AISI 316L stainless steel sample borided at 900 °C for 2 hours

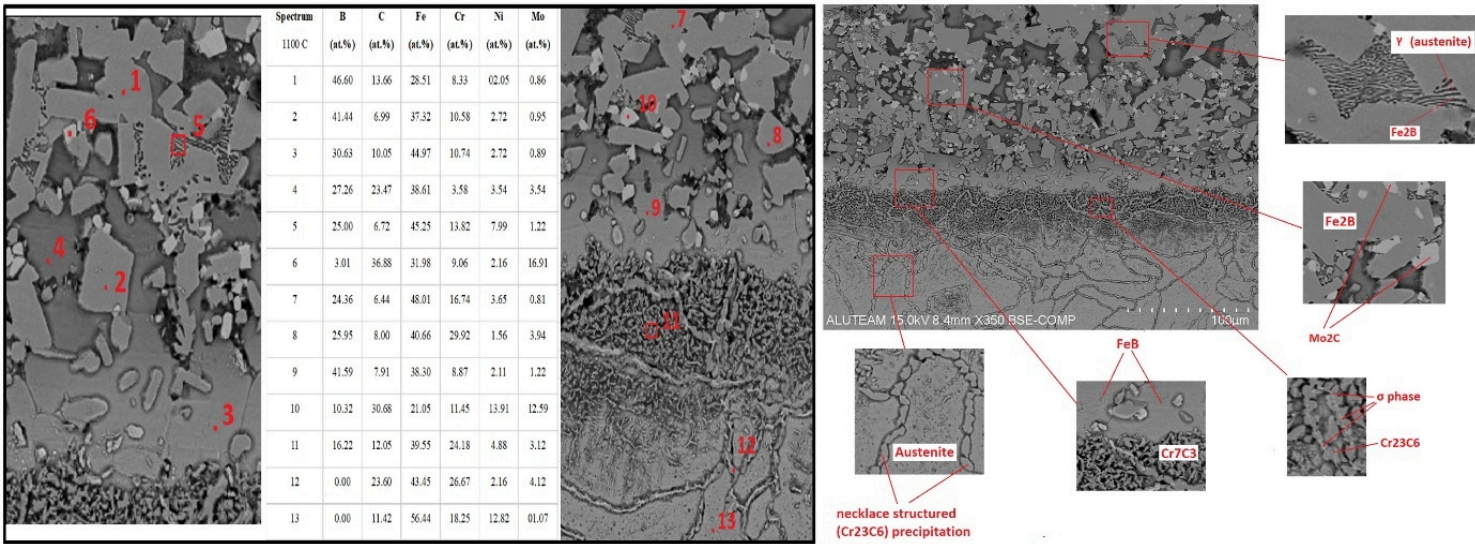


Figure 8

Point EDX measurement locations subjected to stoichiometric analysis as shown in Table 3, on a cross-sectional SEM (BSE) image of an AM AISI 316L stainless steel sample borided at 1100 °C for 2 hours

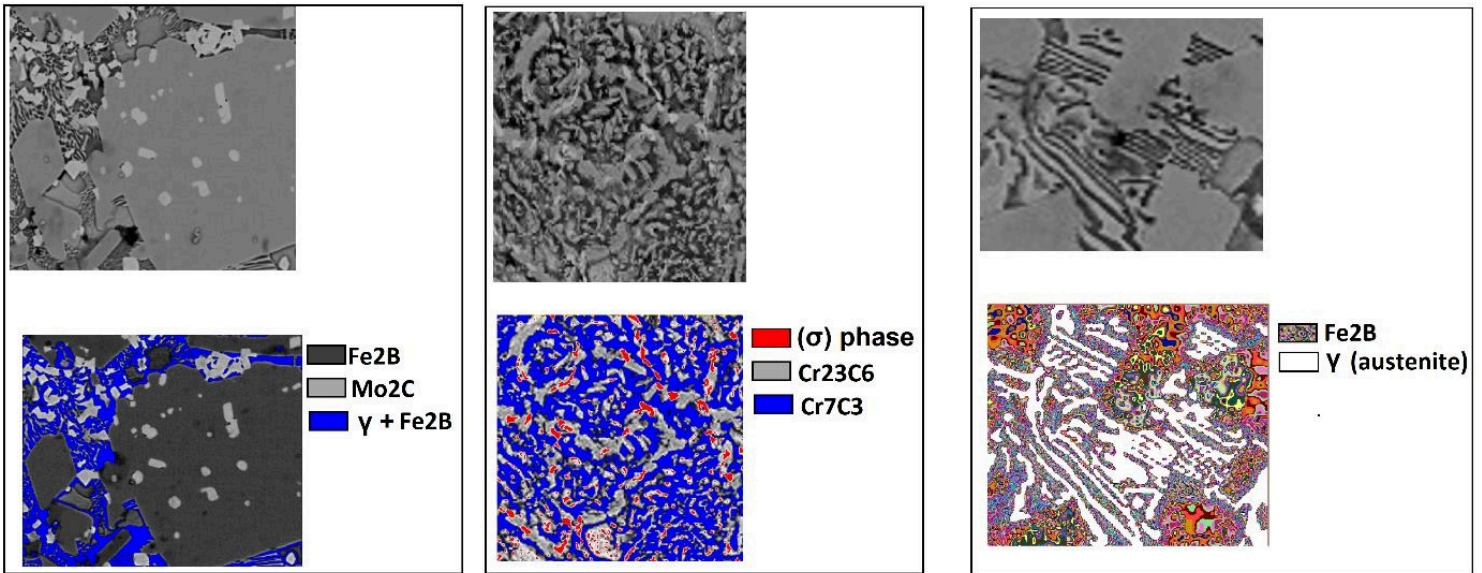


Figure 9

High-resolution detailed SEM (BSE) images showing the complex and multilayered boride-carbide surface architecture, microsegregation mechanisms, eutectic lamellae, and grain boundary carbide precipitations formed in the cross-section of an AM AISI 316L stainless steel sample borided at 1100 °C for 2 hours