

Review Article

Advances in Solid-State Boriding of AISI 304, 316, and 316L Stainless Steels: Progress and Challenges

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Abstract

Boriding, or boronizing, is a thermochemical surface treatment that enhances the hardness, wear resistance, and corrosion properties of austenitic stainless steels such as AISI 304, 316, and 316L, which are widely used in biomedical, nuclear, and chemical applications despite their inherent limitations in tribological performance. This review synthesizes over 60 peer-reviewed articles to examine recent advances in solid-state boriding technologies, specifically powder-pack and paste boriding methods, highlighting their mechanisms, process parameters, and impacts on tribological integrity, mechanical properties, and corrosion mitigation. Key classifications of boriding operations are discussed, including physical and chemical processes, with emphasis on overcoming diffusion barriers posed by high Cr and Ni content in these steels. The review details the compositions of boriding agents, schematic configurations for practical implementation, and comparative advantages of paste boriding over powder-pack methods, such as selective application and energy efficiency. Challenges, including oxidation risks, inconsistent layer formation, and process optimization, are critically analyzed alongside progress in achieving boride layers (FeB and Fe₂B) with superior hardness exceeding 2000 HV. The findings underscore boriding's potential to extend component service life in demanding environments, while identifying gaps for future research to enhance industrial scalability and environmental sustainability.

Keywords

Powder-pack Boriding, Paste Boriding, Mechanical Properties, Tribological Properties, Corrosion Properties, Boride Layer

1. Introduction

Boriding (also called boronizing) is a high-temperature surface modification in which boron atoms diffuse into a metal, forming a hard iron-boride layer [1, 2]. By forming FeB and Fe₂B phases on the surface, boriding can multiply a steel's surface hardness by an order of magnitude [3, 4]. For austenitic stainless steels (AISI 304 and AISI 316), which are valued

for corrosion resistance but have relatively low hardness and are unsuitable for friction-based applications with other materials, boriding offers a route to produce hard, wear-resistant skins. However, their high Cr and Ni content tends to form passive oxides and secondary borides (Cr₂B, Ni₂B), which act as diffusion barriers [5] by increasing their activation energies,

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and consequently causing lower boride layer thickness compared to carbon steel materials [6-8]. Recent years have seen a renewed interest in advanced boriding of 304/316/316L stainless steel materials, driven by the needs of biomedical implants, the nuclear and chemical industries, and wear-critical components.

Additionally, various boriding technologies have been developed and employed in diverse studies to improve the surface properties of samples, including plasma paste, salt bath, laser alloying, box or pack, microwave-assisted methods, etc., to overcome diffusion limits [9-16]. Figure 1 presents the physical and chemical process-based classifications of boriding operation. This review deliberately restricts its scope to

solid-state boriding (powder-pack and paste methods) due to their greater industrial relevance for austenitic stainless steels compared to plasma, gas, or molten-salt techniques. Solid-state methods require only conventional furnaces, avoid toxic gases (e.g., diborane in gas boriding) or hazardous molten salts, offer lower capital and operational costs, and enable easier implementation in small-to-medium enterprises without specialized containment or exhaust systems [17, 18]. These attributes make powder-pack and paste boriding particularly suitable for cost-sensitive applications and selective treatment of complex geometries, despite requiring longer processing times than plasma or gas methods [18, 19].

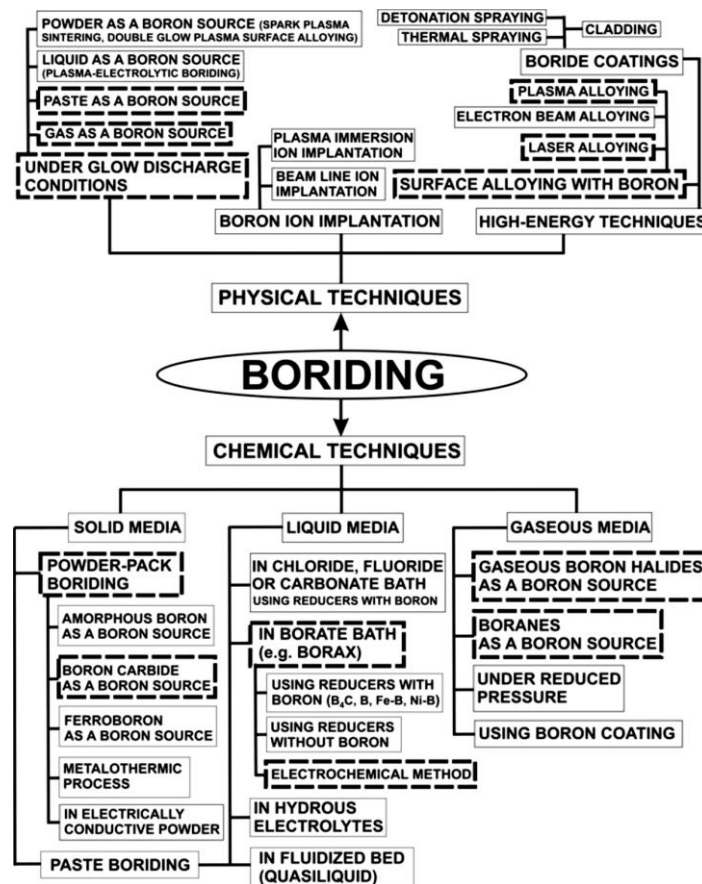


Figure 1. The various classifications of boriding operation [18].

The boriding operation is usually performed within the temperature range of 850-1000°C for a holding time of 1-10 hrs. [20]. The box-boriding method has been reported to be cost-effective and efficient [21, 22]. The boride layer produced on the material's surface consists of an outer and inner phase, which are respectively FeB (with an orthorhombic crystal structure) and Fe₂B (with a tetragonal crystalline structure) [23-25].

The microstructural characteristics of stainless steel materials are known to be of three basic types: ferritic, austenitic, and martensitic [20]. These patterns form the bedrock of the

material's behaviours when deployed to service applications, as they inherently inform about the mechanical and tribological properties of the material. For example, a stainless steel material with a microstructural architecture that reveals poor homogeneity of the constituent mix indicates a negative effect on its properties. Among all the stainless steel family, the AISI 304 austenitic stainless steel (which is non-magnetic) is the most widely applied steel type, considering its diverse areas of deployment, such as nuclear reactors, the food industry, medical applications, etc., and it is very sensitive to a chloride environment [20, 26-28]. AISI 316L steel is used as an implant

material due to its biocompatibility and corrosion resistance [5]. However, its low wear resistance limits its application.

Therefore, this review synthesizes over 60 peer-reviewed articles on solid-state boriding technologies, extracting information on various advances in such boriding operations on AISI 304, 316, and 316L steels, the progress in terms of structural integrity improvement (mechanical and tribological properties), and corrosion rate mitigation. The review also covered the challenges of these technologies. Additionally, while comprehensive works on boriding techniques exist, no prior review has systematically focused on solid-state (powder-pack and paste) boriding applied specifically to AISI 304, 316, and 316L austenitic stainless steels, synthesizing recent progress (2000–2025) across mechanical, tribological, and corrosion performance from over 60 peer-reviewed studies. This review addresses this gap by critically evaluating diffusion barriers unique to high Cr/Ni alloys, comparing powder-pack and paste methods for industrial viability, and identifying specific challenges in layer uniformity, brittleness, and scalability that limit broader adoption in biomedical, nuclear, and chemical sectors.

2. Materials and Methods

The literature considered in this review comprised peer-reviewed journal articles addressing solid-state boriding technologies applied to AISI 304, 316, and 316L stainless steels. Relevant studies were retrieved from the Scopus and Crossref databases, which were selected for their comprehensive coverage of high-quality, high-impact publications relevant to surface engineering and materials science. These databases provide reliable access to studies that clearly define research challenges and propose systematic approaches for addressing them. The review methodology followed the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) framework to ensure transparency and reproducibility in literature selection (see Figure 3). An initial total of 688 articles was identified through a structured search strategy covering publications from 2000 to 2025. This time frame was selected to capture both foundational and recent advances in solid-state boriding technologies. The search strategy employed Boolean operators combining the following keywords: “solid-state boriding” OR “powder-pack boriding” OR “paste boriding” AND “AISI 304” AND “AISI 316” AND “AISI 316L” AND “mechanical properties” AND “tribological properties” AND “corrosion resistance.” The retrieved records were systematically screened to exclude articles lacking clearly defined methodologies, insufficient experimental data on mechanical, tribological, or corrosion performance, or studies not based on solid-state boriding techniques (powder-pack or paste boriding). After the screening and eligibility assessment, 624 articles were excluded, resulting in 64 studies that met the inclusion criteria. These 64 peer-reviewed articles formed the final dataset for the present review on solid-state

boriding technology. Figure 2 presents an outline for the review methodology.

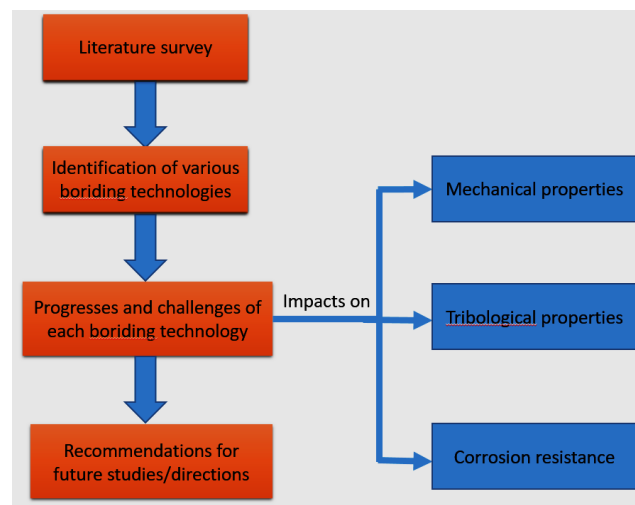


Figure 2. The methodology of the review.

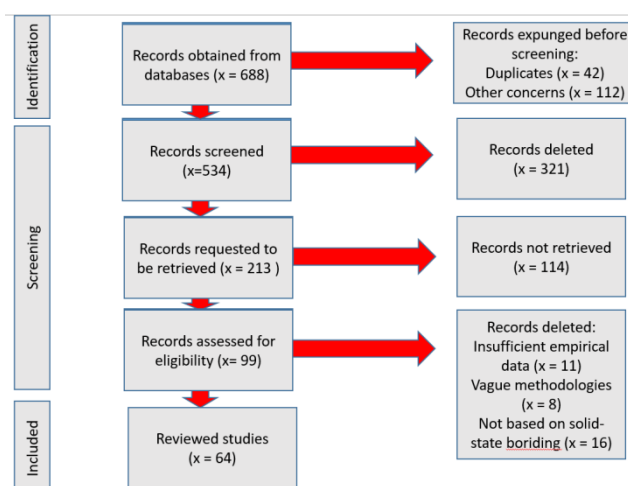


Figure 3. PRISMA FLOW diagram used in selecting suitable literatures for the study.

3. An Overview of Various Boriding Technologies: Impact Extent and Limitations

This section of the study presents a detailed review of the two types of solid-state boriding methods used to improve the mechanical, tribological, and corrosion properties of stainless steel materials. For each method, the successes and challenges were discussed and supported with relevant literature.

3.1. Powder-Pack Boriding Technology

This is one of the main types of boriding in solid media/sys-

tems. The boriding source, comprising a boron source, activator, and diluent, is used in the powdered state and is kept inside a box containing the specimen, which is heated to a temperature range of 850-1100°C for a holding time of 2-24hrs. In some studies (see Table 2), a combination of these components was employed, while some did not. There are basically four (4) primary techniques of powder-pack boriding, and the difference in the methods is based on the source of the boron: the use of amorphous boron, ferroboration, boron carbide (B_4C), and boron oxide (B_2O_3) as presented in Figure 1. The activator component facilitates the movement of boron atoms (which in real situations exists in gaseous phase) from the powder mixture to the surface of the workpieces, thereby reducing the reaction time, and the activators are usually Halides such as NaF, KF, AlF_3 , NaCl or multi-constituent compounds (KBF_4 , KHF, $Na_2B_4O_7$ -borax) [18]. The application of the activator into the boriding mixture is mainly in a few weight percentages as indicated in Table 1. Additionally, the diluent component helps to prevent sintering of the boriding mixture and reduces the potential of boron atoms by eliminating the brittle FeB phase

or decreasing its percentage in the borided material [29, 30]. The most commonly used diluents are Al_2O_3 , MgO, Kaolin, and SiC. However, the commonly applied boriding agents include the EKABOR® I, II, III, EKABOR® Ni, and DURBORID® G. Table 1 clearly displayed the compositions, particle sizes, and densities of these agents.

From Table 1, it is evident that the core difference between the boriding agents lies in the compositional build, particle size, and density. The EKABOR® Ni is essentially used for boriding Ni and Ni alloys. The powder-pack boriding parameters, such as the boriding temperature, holding time, and the weight percentages of the components of the boriding agent, are very critical in achieving optimal boriding. Sequel to, the process also depends on the material type (to be borided) and the type of containment used for the boriding agent. Some materials negatively influence the process through their reaction with the boriding agents. Figure 4 presents the schematic diagram of the most effective powder-pack boriding processes as reported by Kulka et al. [18].

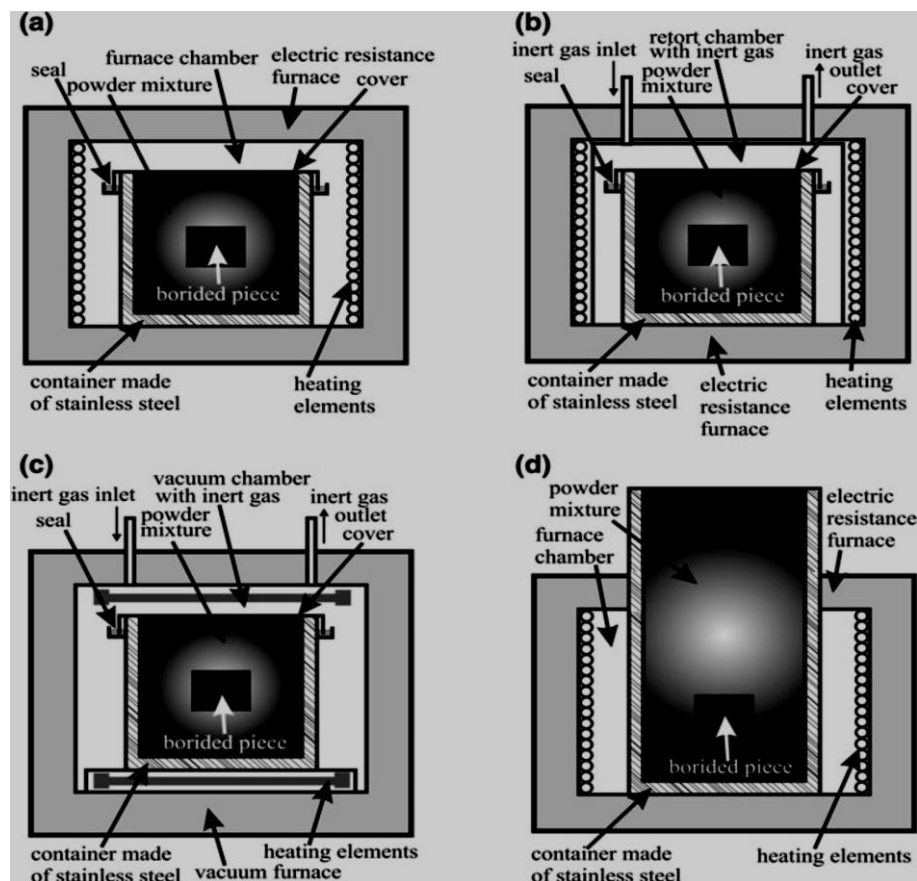


Figure 4. Schematic illustrations of the most practical and widely adopted powder-pack boriding techniques include the following configurations: (a) a sealed container placed in a conventional electric resistance furnace operating in an air atmosphere; (b) a sealed container housed within a tightly closed retort in an electric resistance furnace under an inert gas environment, such as argon; (c) a sealed container located inside the chamber of a vacuum furnace with an inert gas atmosphere, typically argon; and (d) an open retort or container positioned in a conventional electric resistance furnace under air atmosphere. It should be noted that for configurations (a) and (b), strict container sealing becomes less critical when boron carbide is employed as the boron source.

Table 1. Information on the boriding agents [18, 31-34].

Boriding agent	Chemical compositions (wt. %)			Particle size (μm)	Density (g/cm^3)
	B ₄ C	KBF ₄	SiC		
EKABOR®I	5	5	90	≤ 150	1.9
EKABOR®II	5	5	90	≤ 850	1.7
EKABOR®III	5	5	90	≤ 1400	0.95
EKABOR®HM	Unknown			≤ 150	0.95
EKABOR®Ni	The powder mixture had no SiC, and other constituents are unknown			Unknown	Unknown
DURBORID®G	Unknown quantity of B ₄ C and other components are unknown			Unknown	Unknown

In the first case (Figure 4a), the containment was completely sealed, devoid of air or inert gas entrance point(s). Excessive air access to the boriding mixture could result in uncontrolled oxidation of the borided material. Powder-pack boronizing has, in some cases, been conducted under an inert gas atmosphere, such as argon, as reported by Campos-Silva et al. [35]. This approach likely necessitates the use of a specially designed furnace equipped with a tightly sealed retort, similar to those employed in gaseous thermochemical treatment processes. Nevertheless, many studies do not explicitly indicate whether the container holding the boriding mixture was sealed, which is possibly attributed to the use of boron carbide (B₄C) as the boron source, given its relative stability under atmospheric conditions. A representative configuration of this boriding method, involving an electric resistance furnace with a tight retort operating under an inert gas environment, is illustrated in Figure 4b. Additionally, Vacuum furnaces have also been utilized for powder-pack boronizing applications, as demonstrated by Tarakci et al. [36]. In this method, the crucible containing the boriding powder mixture is hermetically sealed to prevent air ingress before being placed inside the vacuum furnace. The furnace chamber is evacuated using a mechanical rotary vacuum pump to a pressure of approximately 1×10^{-3} mbar. Subsequently, high-purity argon gas (99.998%) is continuously introduced into the chamber to regulate and maintain a controlled processing atmosphere. This boronizing configuration is schematically illustrated in Figure 3c. Alternatively, a vacuum environment alone can serve as a protective atmosphere during boriding, as reported by Torun and Çelikyürek [37]. In both the inert gas-assisted tight retort system (Figure 4b) and the vacuum chamber configuration (Figure 4c), the inclusion of a circulation fan is recommended to ensure uniform temperature distribution and consistent gas

flow throughout the furnace chamber [18]. Furthermore, a novel powder-pack technique was reported by Młynarczak [38], originally developed for producing diffusion carbide coatings on steels through titanizing, vanadizing, and chromizing processes [38, 39]. This approach was later demonstrated to be highly effective for powder-pack boriding [40]. In this method, a tubular retort with a sealed bottom, fabricated from heat-resistant or stainless steel, was loaded with the components to be borided along with the powder mixture, without the use of any additional sealing mechanism. The retort was positioned in the furnace such that its upper section protruded outside the heated zone (Figure 4d). The powder mixture located in the exposed upper section functioned as a self-forming seal. Owing to the relatively low temperature at the surface of the powder in this region, oxidation was avoided. Gaseous species generated in the heated lower section of the retort re-sublimated upon reaching the cooler upper region, thereby preventing their escape from the retort [38]. The boriding mixture was typically formulated using boron carbide as the boron source, for example, 60 wt.% B₄C, 0.5 wt.% AlF₃ as an activator, and 39.5 wt.% Al₂O₃ as a diluent [40]. Compared with conventional powder-pack boriding techniques, this open-retort method required a substantially lower quantity of activator. Furthermore, a critical comparison of the configurations (Figure 4) reveals that inert gas (Figure 4b) and vacuum (Figure 4c) atmospheres provide superior oxidation control and layer uniformity by minimizing O₂ ingress, yielding dense, reproducible layers with <5% porosity. Air-atmosphere sealed containers (Figure 4a) risk oxide scale formation and inhomogeneous diffusion, while the open-retort method (Figure 4d) offers excellent reproducibility with reduced activator consumption but requires precise temperature zoning to prevent gaseous species escape [18, 41].

Table 2. An extensive review of the progress and challenges of the powder-pack boriding method.

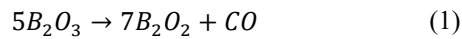
Authors/references	Study topic	Progress/achievements	Challenges/limitations
Hernandez-Sanchez et al [42]	Effect of the boriding surface-hardening process of AISI 304L on the viability of HFoB cells	Wear rate and corrosion reduction even in Cl-rich environments, hardness improved from 1992.4-2397.54HV, and better cellular proliferation was observed in borided samples compared to the unborided.	The interplay between the boride phases (FeB, Fe ₂ B, CrB, Cr ₂ B, NiB, and Ni ₃ B) was provided through the XRD analysis, but an in-depth knowledge of their impacts on surface property improvements and their individual thicknesses was not presented.
Gunen et al [4]	The investigation of corrosion behavior of borided AISI 304 austenitic stainless steel with nanoboron powder	The study formed smooth, homogeneous boride layers on AISI 304 steel via nanoboron powder. Layers achieved thicknesses of 49.29–67.29 µm and hardness of 1880–2200 HV. XRD identified main phases as FeB and Fe ₂ B with traces of CrB and Ni ₂ B. Acid corrosion resistance improved up to 4.3 times over untreated steel. Salt spray tests showed up to 100% reduced weight loss compared to untreated samples.	Cracks and porosity in boride layers sped up acid corrosion at higher temperatures. Borided samples oxidized 40% faster in salt spray due to Cr and Ni depletion, impairing Cr ₂ O ₃ regeneration. Acid resistance declined with rising boriding temperature. The 1273 K, 4-h sample suffered flaking and stress cracking in acid. Prior literature on boriding's anti-corrosion effects was absent.
Gunen et al [43]	Friction and wear behaviour of borided AISI 304 stainless steel with nano particle and micro particle size of boriding agents.	The study formed smooth, homogeneous boride layers on AISI 304 steel using nano and micro boriding agents. Layers reached thicknesses of 23–67 µm and hardness of 1020–2200 HV. XRD confirmed phases like FeB and Fe ₂ B with traces of CrB and Ni ₂ B. Friction coefficients dropped for borided samples. Wear resistance rose 5 times with EKabor and 8 times with Nanoboron over untreated steel.	FeB phase brittleness caused cracks and spalling under load. Longer process times boosted FeB formation, reducing wear resistance. EKabor samples showed complete layer spillage in wear tests. Nanoboron caused local pitting and scars. Lack of prior research on particle size effects on friction and wear.
Gunen et al [44]	Corrosion behavior of borided AISI 304 austenitic stainless steel.	The study formed flat boride layers on AISI 304 steel with thicknesses of 23-33 µm and hardness of 1020-1264 HV. XRD confirmed phases like FeB and Fe ₂ B with traces of CrB. Acid corrosion resistance improved up to seven times over untreated steel. Observed carbide precipitation in the transition zone.	Boride layers spalled in salt spray tests due to poor adhesion and Cr depletion. Early oxide formation in salt spray led to similar or worse performance. Porosity and cracking sped up corrosion in salt environments. Future work is needed to enhance coating adhesion.
Resendiz-Calderon et al [45]	Micro-Abrasion wear resistance of borided 316L stainless steel and AISI 1018 Steel.	The study formed biphasic FeB/Fe ₂ B layers on 316L stainless steel and mono-phase Fe ₂ B on AISI 1018 steel. Boriding enhanced the micro-abrasion wear resistance of 316L stainless steel. Wear rates were determined for FeB and Fe ₂ B phases using SiC slurry tests. Wear mechanisms like rolling and grooving abrasion were identified. Transient conditions between wear modes were outlined in wear mode maps.	Limited prior research on the wear resistance of borided 316L stainless steel. FeB influence on Fe ₂ B not directly evaluated on 316L, requiring AISI 1018 proxy. Focused only on micro-abrasion, ignoring other wear types. Transient conditions for rolling and grooving abrasion vary with load and concentration.
Arteaga-Hernandez et al [46]	Study of boriding surface treatment in the tribological behavior of an AISI 316L stainless steel.	The study synthesized boride layers on AISI 316L steel at 850-1050°C for 2-6 hours. It characterized surfaces with SEM, XRD, micro/nano-hardness, and roughness measurements. Tribological tests showed all borided samples had lower wear rates than untreated ones. Differences in wear	Wear debris and oxides cause performance issues in medical uses like prostheses. Metallic ion release leads to implant loosening and bone damage. Focused on tribology but noted the need for better corrosion resistance via boriding. Potential microcracks in layers

Authors/references	Study topic	Progress/achievements	Challenges/limitations
Zouzou and Keddou [47]	Application of integral method for investigating the boriding kinetics of AISI 316 steel.	performance among borided conditions were discussed. Boriding improved tribological behavior for biomedical applications.	from prior studies. Future work on optimizing parameters for specific applications.
		The study modeled boriding kinetics of AISI 316 steel using the integral method over 1123–1273 K. It estimated boron diffusion coefficients in FeB, Fe ₂ B, and the diffusion zone. Activation energies were calculated as 210.26, 193.80, and 140.55 kJ/mol, aligning with literature values. The model was validated experimentally for two additional conditions at 1243 K for 3 and 5 hours, showing good agreement in layer thicknesses.	The model does not account for carbon's effect on boron diffusion in the diffusion zone. It ignores the precipitation of chromium and nickel borides within the boride layer. Assumes planar interfaces, potentially simplifying actual morphologies. Observed slight discrepancies in simulated diffusion zone thicknesses. Suggests extension to other ferrous and non-ferrous alloys for future work.
Simooglu et al [48]	The effect of different powder mixtures used in the boriding process on the surface properties of AISI 304 stainless steel material.	The study created boriding layers on AISI 304 steel using mixtures of B ₄ C, KBF ₄ , SiC, and graphite in six ratios. It achieved smooth, compact morphology with dominant FeB/Fe ₂ B phases plus CrB and Ni ₃ B confirmed by EDX and XRD. Best mixture F (20% B ₄ C, 50% KBF ₄ , 10% SiC, 20% graphite) gave highest thickness of 70.13 µm and hardness of 1994 HV. Layer thickness increased by 63% and hardness by 11% compared to other mixtures. Lowest wear rate of 0.77 mm ³ /m in F, over three times better than the highest rate.	B ₄ C below 20% prevents boriding layer and double phase formation. FeB phase brittleness reduces wear resistance compared to Fe ₂ B. Some mixtures showed higher wear rates up to 3.38 mm ³ /m and increasing friction coefficients. Wear residues and marks were observed on certain samples. Requires optimal ratios like minimum 20% B ₄ C and 10% SiC for best performance.
Kayali et al [49]	Investigation of corrosion behaviors at different solutions of boronized AISI 316L stainless steel.	The study boronized AISI 316L SS at 800°C and 900°C for 2 and 6 hours using Ekabor powder. It formed smooth, flat boride layers with thicknesses of 2.3–25 µm containing FeB, Fe ₂ B, CrB, Cr ₂ B, NiB, and Ni ₂ B phases via SEM-EDS and XRD. Corrosion resistance significantly increased in 1 mol dm ⁻³ HCl solution via Tafel and linear polarization. Corrosion resistance of borided samples improved with longer immersion times in all solutions including NaOH and NaCl.	No initial positive effect on corrosion resistance in 0.9% NaCl and 1 mol dm ⁻³ NaOH solutions. Porosities and microcracks in boride layers negatively affected performance. Thicker boride layers from higher temperatures and times led to easier separation and cracking. Corrosion rates increased with boronizing temperature and time in NaOH.
Turkoglu and Ay [20]	Investigation of mechanical, kinetic and corrosion properties of borided AISI 304, AISI 420 and AISI 430.	The study pack borided AISI 304, 420, and 430 steels at 850–1000°C for 2–6 hours. It achieved maximum hardness of 1736 HV for AISI 304, 1659 HV for 420, and 1572 HV for 430. XRD confirmed phases like FeB, Fe ₂ B, CrB, and MnB. Boride layers showed planar, compact morphology. Activation energies were calculated for the coatings. Corrosion resistance remarkably increased in 10% HCl compared to untreated samples.	Pitting corrosion mechanism initiated rapid penetration in untreated materials. Intergranular corrosion limited untreated stainless steel applications. Oxide formations like chromium and iron oxides observed post-corrosion.

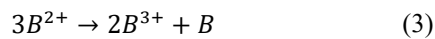
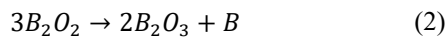
Based on the study of Kulka et al [18], the mechanism responsible for the generation of active boron species during

powder-pack boriding when boron carbide was employed as

the boron source was investigated. It was proposed that commercially available B_4C powder contains a measurable fraction of boron trioxide (B_2O_3), typically up to about 3 wt.%. Experimental observations revealed that boriding conducted using pure boron carbide alone did not produce a sufficiently thick boride layer. Likewise, no effective boride layer formation was observed when boriding was performed using only B_2O_3 powder. Based on these findings, it was inferred that boron trioxide functions as an activator in powder-pack boriding processes involving B_4C . Mass spectrometric analysis further confirmed the presence of B_2O_3 and suboxide B_2O species during boriding with commercial B_4C powder, indicating their participation in the generation of active boron atoms. Consequently, the boriding reaction mechanism was attributed to the formation and transport of these boron oxide species as presented in equation (1).



A further breakdown of the B_2O_2 at higher temperatures could result in equations (2) and (3).



3.2. Paste Boriding

The paste boriding operation was often classified as a solid media process, but transitions to liquid media when the paste contains cryolite (Na_3AlF_6) [50], and the temperature exceeds its melting point ($\sim 1012^\circ C$), enabling molten-phase boron transport and altered kinetics (see classification in Figure 1). Paste boriding operation has the following main characteristics: only the selected surface can be borided, the choice to use any furnace type with temperature control feature, direct quenching of the substrate after boriding is possible, and energy saving potentials [18].

In addition, paste boriding, also known as paste boronizing, is a thermochemical surface hardening process that involves the application of a boron-containing paste to the substrate material, followed by high-temperature diffusion to form iron boride layers, primarily Fe_2B and occasionally FeB , on ferrous alloys such as steels and irons. The process begins with the preparation of a paste typically composed of boron carbide (B_4C) as the boron source, mixed with activators like cryolite or other fluxes to enhance boron release, and binders to achieve a suitable consistency for application; this paste is then brushed, sprayed, or dipped onto cleaned and degreased workpiece surfaces to a thickness of approximately 1.5–4 mm [51], enabling selective treatment of specific areas without the need for full immersion or enclosure. Unlike gaseous or liquid boriding methods that require specialized equipment to handle toxic gases or molten salts, paste boriding is conducted in a conventional furnace under a protective atmosphere such as

argon, hydrogen, nitrogen, or their mixtures to prevent oxidation, with typical processing temperatures ranging from 1123 K to 1323 K (850 – $1050^\circ C$) and treatment durations of 1–10 hours [18, 52], depending on the desired layer thickness, substrate composition, and boron potential in the paste. During heating, boron atoms are liberated from the paste through thermal decomposition and reduction reactions, diffusing into the substrate where they react with iron to form boride phases. The importance of paste boriding lies in its ability to significantly enhance the tribological and corrosion properties of engineering components, imparting surface hardness exceeding 2000 HV (Vickers) [53], low friction coefficients (0.1–0.3 against steel) [18], and superior resistance to abrasive, adhesive, and erosive wear, often extending service life by 3–10 times [35, 54] in harsh environments such as those encountered in extrusion dies, forging tools, gears, and agricultural machinery; this is particularly critical in industries like automotive, aerospace, and mining, where component failure due to surface degradation leads to substantial economic losses, and borided surfaces maintain integrity at elevated temperatures ($>1000^\circ C$), allowing for subsequent heat treatments like quenching without delamination. Furthermore, borided layers exhibit excellent corrosion resistance in acidic and alkaline media, attributed to the chemical stability of iron borides and minimal porosity when properly formed, making the process indispensable for applications involving molten metals or aggressive chemicals.

Furthermore, compared to the traditional powder pack boriding method, which involves embedding the workpiece in a sealed container filled with a powder mixture of boron sources (e.g., B_4C or amorphous boron), activators (e.g., KBF_4), and diluents (e.g., SiC or Al_2O_3) before heating, paste boriding offers several distinct advantages, including greater flexibility for selective boriding of complex geometries or specific regions without the need for masking or full packing, reduced material consumption since only the treated area requires paste application, simplified handling and cleanup as there is no loose powder residue or need for specialized retorts, and lower manual labor requirements for high-volume production, potentially halving processing times under equivalent conditions due to more efficient boron delivery and atmospheric control [18]. Additionally, paste boriding minimizes environmental impact by avoiding the generation of hazardous powder wastes and enables easier automation through precise paste deposition techniques, while maintaining comparable layer quality and uniformity; however, it requires careful control of paste composition and thickness to prevent inconsistencies, and its diffusion-limited nature still demands high temperatures, though advancements in paste formulations continue to optimize energy efficiency and layer properties for broader industrial adoption [52, 54, 55]. Additionally, paste boriding exhibits high sensitivity to applied thickness (optimal 1.5–4 mm) and composition variability; thicknesses less than 1.5 mm yield insufficient boron potential and thin/irregular layers, while thicknesses greater than 4 mm cause cracking, uneven decomposition, and reduced diffusion efficiency [56],

and the corrosion resistance is maximized at a paste thickness of 4mm for a treatment time of 4h [57]. Variability in binder or cryolite content alters boron release rates, leading to reproducibility issues and porosity up to 10–15% in non-optimized formulations. Figure 5 delineates the schematic representations of the various effective and easy-to-implement paste boriding methods. The schematic representation in Figure 5a illustrates paste boriding conducted in a standard electric resistance furnace without an inert atmosphere, typically employing a sealed container under ambient air conditions to provide partial isolation from oxygen; this approach implies a cost-effective and straightforward setup accessible with conventional equipment, minimizing the need for specialized gas handling or vacuum systems, which can reduce operational expenses compared to more advanced methods, and facilitates scalability for small-scale or prototype applications in industries like tool manufacturing where rapid implementation is

prioritized. However, the implications include heightened susceptibility to substrate oxidation due to residual oxygen within the container, leading to the formation of oxide scales (e.g., Fe_2O_3) that act as diffusion barriers, thereby retarding boron atom penetration and resulting in inhomogeneous boride layers with increased porosity, reduced hardness, and compromised adhesion at the interface, which can exacerbate crack propagation under cyclic loading and diminish overall wear resistance in abrasive environments, as quantified in tribological tests [58]; furthermore, this method may necessitate post-treatment cleaning to remove oxide residues, increasing environmental impact through waste generation, and is less suitable for high-performance components in aerospace or automotive sectors where microstructural integrity is paramount, potentially limiting service life.

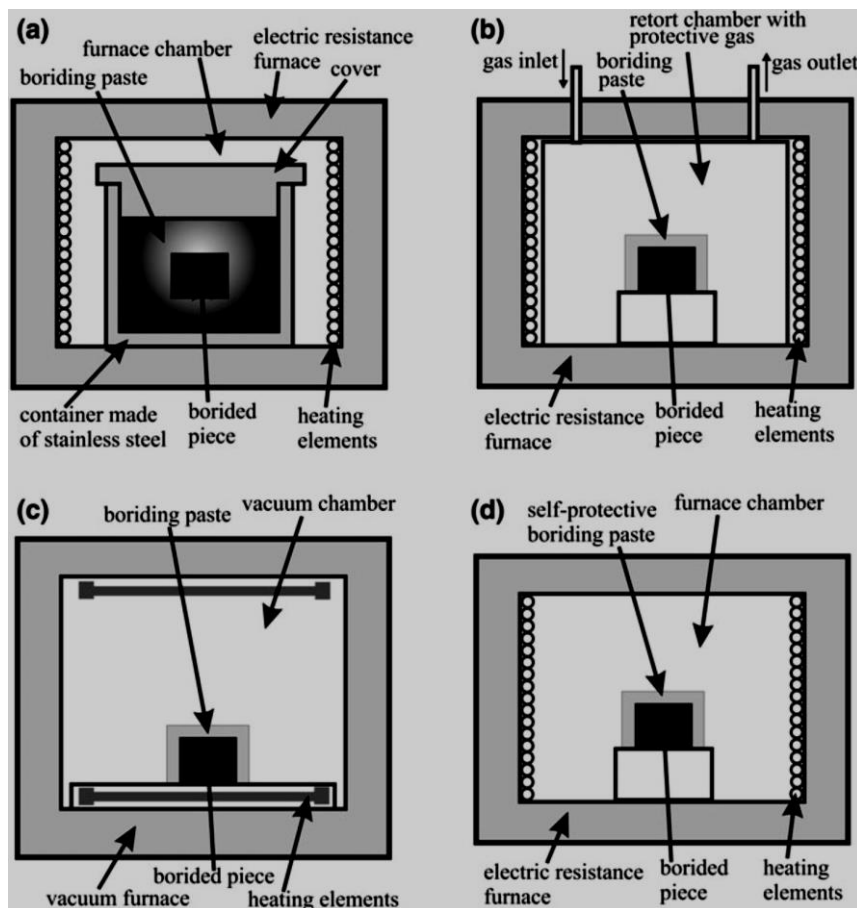


Figure 5. Diagrams illustrating the most efficient and straightforward methods for paste boriding include: paste boriding performed in a standard electric resistance furnace within a sealed container in an air environment (a) paste boriding in a standard electric resistance furnace with a shielding gas (such as argon, nitrogen, or a blend of N_2 and H_2) (b) paste boriding inside a vacuum furnace chamber (c) and paste boriding in a standard electric resistance furnace employing a self-shielding paste in an air environment (d). Note: for techniques (b) and (c), sealed containers may optionally be employed as well [18].

In contrast, Figure 5b depicts the predominant paste boriding process utilizing a shielding atmosphere such as argon, ni-

trogen, or $\text{N}_2 + \text{H}_2$ mixtures [52, 59-63] in a conventional electric resistance furnace, often with or without a closed container,

to create an oxygen-free or reducing environment. This technology encompasses enhanced process reliability and superior boride layer quality, as the inert gas prevents oxidation kinetics by maintaining a low O_2 partial pressure, enabling unhindered solid-state diffusion of boron with parabolic growth rates, yielding dense, uniform Fe_2B -dominated layers with minimal defects, improved hardness, and tribological performance. Additionally, Figure 5c represents an alternative configuration for paste boriding under reduced pressure in a vacuum furnace chamber, which evacuates atmospheric contaminants to safeguard against oxidation. This technique yields exceptional control over the diffusion environment, as low pressure minimizes oxygen availability, suppressing oxide nucleation and allowing for lower processing temperatures or shorter durations [18, 64], which preserves substrate microstructure, reduces thermal distortion in heat-sensitive alloys, and lowers energy consumption by 15–25% through efficient heat transfer in vacuum, while facilitating the formation of compact, low-porosity boride phases (e.g., single-phase Fe_2B with <5% voids) exhibiting superior mechanical properties [18, 65]. Furthermore, Figure 5d delineates paste boriding utilizing a dedicated self-shielding boriding paste in a conventional electric resistance furnace without any protective atmosphere, where the paste incorporates additives that form an in-situ barrier upon heating [66]. The implications underscore operational simplicity and versatility, as the self-protective formulation (e.g., with SiC or carbonaceous fluxes) generates a vitreous slag layer at 600–800°C that seals the surface against oxygen diffusion, eliminating the need for gases or

vacuum and enabling treatment in open-air furnaces, accelerates setup times, and enhances applicability for selective boriding of large or irregular components like agricultural tools or armor plates, while maintaining good layer thicknesses and mechanical properties. Figure 6 shows the relationship between time and boride layer thickness for Fe and steel materials borided with $B_4C - Na_2B_4O_7 - Na_3AlF_6$ using paste boriding method at 1000°C, and the graph depicts a linear relationship between time and boride layer thickness. Table 3 presents a comprehensive review of the progress and challenges of paste boriding technology reported in several studies.

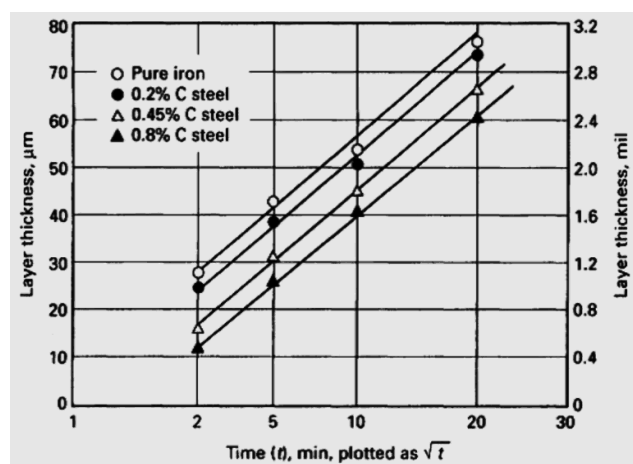


Figure 6. Relationship between boride thickness and time for paste borided samples [67].

Table 3. Progresses and challenges of paste boriding technology.

Authors/references	Study topic	Progress/achievements	Challenges/limitations
Mohammad et al [68]	Wear properties of paste boronized 316 stainless steel before and after shot blasting process	The study applied paste boronizing to 316 SS, forming protective FeB and Fe_2B layers that increased wear resistance compared to unboronized steel. Shot blasting enhanced boron dispersion through surface deformation, resulting in thicker boride layers and further improved wear properties. Higher boronizing temperature (950°C) led to greater boride thickness and reduced weight loss/friction coefficient in pin-on-disc tests. XRD confirmed boride phases with higher intensity at elevated temperatures. Overall, combined treatments maximized component usability in industries by reducing repair needs.	Initial poor wear resistance of 316 SS requires surface treatments to prevent thinning, cracks, and malfunctions under load. Density slightly decreased due to atom dislocation and high-temperature heating, though changes were minor. Process demands long durations (8 hours) and high temperatures, potentially limiting scalability. Single boronizing without shot blasting was less effective in boron dispersion and wear improvement.
Alias et al [69]	Effect of surface attrition on hardness and wear properties of 304 stainless steels	The study applied surface attrition via shot blasting before paste boronizing 304 stainless steel. It formed thicker boride layers with FeB and Fe_2B phases compared to non-attrited samples. Microhardness reached 1815 HV at FeB, a 600% increase over the substrate. Denser borides restricted wear during pin-on-disc tests. Surface deformation enhanced boron diffusion through grain refinement and defects. Paste	COF values increased inversely with boride layer thickness. Some boronizing methods have high toxicity and complex setups. Brittle Fe_3B phase nature noted despite hardness gains. No direct mention of future work or additional explicit limitations.

Authors/references	Study topic	Progress/achievements	Challenges/limitations
Martinez-Baltodano et al [70]	Study of surface treatment by ionic plasma and self-protective pastes of AISI 304 and 316L stainless steels: chemical, microstructural and nanohardness evaluation	boronizing proved cost-effective with denser layers.	
		The study successfully demonstrated that both self-protective paste nitriding (SPN) and ion plasma nitriding (IPN) significantly altered the surface chemistry and microstructure of AISI 304 and 316L stainless steels, leading to improved surface properties. SPN, in particular, produced a complex oxynitrided surface layer containing iron oxides, carbides, and nitrides, which resulted in the highest enhancement in nanohardness. The improvement was especially remarkable for AISI 316L, where SPN increased nanohardness by more than 360%, clearly outperforming IPN. By applying both treatments under identical conditions, the study provided a robust and systematic comparison, highlighting SPN as an effective, economically attractive, and scalable surface treatment for enhancing wear resistance, especially in large stainless steel components.	Despite these achievements, the study primarily emphasized nanohardness as the key performance metric, with limited direct evaluation of actual wear behavior and long-term corrosion resistance. The investigation was restricted to a single processing temperature and duration, which limits understanding of optimal treatment windows and process flexibility. The observed reduction in nanohardness for IPN-treated AISI 304 stainless steel was not thoroughly explained, leaving mechanistic questions unresolved. Additionally, important aspects such as residual stresses, fatigue performance, and long-term stability of the modified layers were not examined. Finally, the absence of validation under real service or industrial operating conditions represents a gap in assessing practical applicability.
Campos et al [60]	Evaluation of the corrosion resistance of iron boride coatings obtained by paste boriding process.	The study successfully formed iron boride layers (FeB and Fe ₂ B) on AISI 304 steel using the paste boriding process. It systematically evaluated the effects of boron paste thickness, treatment temperature, and exposure time on corrosion resistance. Electrochemical tests confirmed a clear dependence of polarization resistance on processing parameters. The results identified optimal conditions, showing that a 4 h treatment time with a 4 mm boron paste thickness maximized corrosion resistance in a chloride environment.	The investigation was limited to corrosion behavior in a single NaCl concentration, restricting environmental relevance. Mechanical properties such as hardness, wear, or coating adhesion were not assessed alongside corrosion resistance. Long-term corrosion performance and coating stability were not examined. The influence of boride layer thickness and phase distribution on corrosion mechanisms was not explicitly analyzed.
Mohammad et al [71]	Effect of shot blasting on paste boronizing of 316L stainless steel.	The study showed that paste boronizing produces boride layers (FeB and Fe ₂ B) on 316L stainless steel that significantly increase surface microhardness, improving mechanical performance. Shot blasting prior to boronizing was found to enhance boron diffusion into the surface, leading to increased boride layer depth and higher microhardness with increasing blasting pressure. Microstructural analysis confirmed that shot blasting altered the steel surface favorably, supporting stronger boride formation and improved case development.	The study focused mainly on microstructure and microhardness, without reporting other performance metrics such as wear, corrosion, or fatigue behavior after treatment. The investigation was limited to a single boronizing temperature and soaking time, so optimization of process parameters across broader conditions was not addressed. Long-term stability and real-world performance of shot-blasted and boronized layers were not evaluated.

Additionally, the boriding operation offers superior surface mechanical properties than the carburization technique, which is a carbon diffusion technology into the surface of the substrate [72], hence the need to advance studies on boriding technology to improve further the applicability of not just the stainless steel materials, but other engineering materials covering a wide range of uses.

4. Conclusions

This review has comprehensively evaluated the advancements in solid-state boriding technologies for AISI 304, 316, and 316L stainless steels, demonstrating significant progress in enhancing surface properties through powder-pack and

paste methods. By addressing diffusion limitations and optimizing process parameters, these techniques have proven effective in forming robust FeB and Fe₂B layers, thereby improving hardness, wear resistance, and corrosion performance for applications in biomedical implants, nuclear reactors, and chemical processing. The following key conclusions are drawn:

- 1) Powder-pack boriding remains a cost-effective and widely adopted method, with configurations under inert gas or vacuum atmospheres yielding uniform boride layers up to 200 μm thick, though challenges such as oxidation and activator dependency necessitate careful control of boron sources like B₄C and activators (e.g., KBF₄) to minimize brittle FeB phases and ensure structural integrity.
- 2) Paste boriding offers superior flexibility for selective surface treatment and energy savings, achieving comparable hardness values (>2000 HV) with reduced material consumption and simplified handling compared to powder-pack approaches, particularly when self-shielding pastes or protective atmospheres are employed to prevent oxidation and promote consistent diffusion.
- 3) Both methods significantly mitigate corrosion rates in aggressive environments by forming dense, low-porosity boride layers that outperform untreated stainless steels, with paste boriding showing potential for direct quenching post-treatment, enhancing applicability in high-volume production sectors like automotive and mining.
- 4) Contradictory corrosion behavior in chloride environments arises mechanistically from chromium depletion in the substrate beneath the boride layer (Cr content dropping to <12 wt.% in the transition zone) and residual porosity/micro-cracks that enable Cl⁻ penetration and localized attack. Dense, Fe₂B-dominated layers with minimal porosity provide cathodic protection and superior resistance, whereas FeB-rich or porous layers exacerbate pitting via galvanic coupling and Cr-depleted zones.
- 5) Halide-based activators (e.g., KBF₄, NaF) pose environmental and safety risks through potential HF evolution during processing and fluoride-containing waste. These concerns necessitate the development of low-halide or halide-free formulations to reduce ecological impact and comply with increasingly stringent regulations on fluoride emissions and disposal.
- 6) Despite advancements, limitations such as high processing temperatures (850–1100°C) and extended holding times (1–24 hours) highlight the need for mechanistic insights into boron oxide species (e.g., B₂O₃ and B₂O₂) to refine reaction kinetics and reduce environmental impacts from waste generation.
- 7) Overall, solid-state boriding surpasses carburizing (typical hardness 600–900 HV, poorer abrasive wear resistance) and nitriding (1000–1200 HV, better fatigue but inferior high-temperature stability) in delivering extreme

surface hardness (>2000 HV) and 3–10× service life extension in abrasive/tribological applications. However, higher processing temperatures and brittleness limit direct competition in fatigue-critical components, positioning boriding as the preferred choice for severe wear environments in biomedical, nuclear, and chemical industries.

5. Recommendations/Directions for Future Studies

This study recommends the following extensions for further examination of solid-state boriding technology to achieve enhanced mechanical, tribological, and corrosion performance of stainless steel materials, as well as improved applicability.

Investigate hybrid boriding techniques, such as combining powder-pack or paste methods with emerging technologies like microwave-assisted or laser alloying, to reduce processing times and temperatures while maintaining or enhancing boride layer uniformity and adhesion on AISI 304, 316, and 316L steels.

Explore the development of eco-friendly boriding agents and activators with lower halide content to minimize environmental hazards and waste, including the use of biodegradable binders in paste formulations for sustainable industrial applications.

Conduct long-term in-situ performance evaluations of borided stainless steels under simulated service conditions, such as cyclic loading in biomedical implants or corrosive environments in nuclear settings, to quantify durability improvements and failure mechanisms.

Utilize advanced characterization tools, including synchrotron X-ray diffraction and atom probe tomography, to elucidate the role of secondary borides (e.g., Cr₂B, Ni₂B) in diffusion barriers and optimize alloy compositions for tailored boride phase distributions.

Assess the scalability of paste boriding for large-scale manufacturing through automation and process modeling, focusing on cost-benefit analyses and integration with additive manufacturing for complex geometries in aerospace and automotive industries.

Examine the biocompatibility and toxicity profiles of borided surfaces for medical applications, incorporating cellular and animal studies to ensure compliance with regulatory standards and expand usage in orthopedic and dental implants.

Abbreviations

HV	Vickers Hardness
Mm	Micro Meter
SPN	Self-Protective Paste Nitriding
IPN	Ion Plasma Nitriding
AISI	American Iron and Steel Institute
SS	Stainless Steel

XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
EDS	Energy-Dispersive X-ray Spectroscopy
SEM-EDS	Scanning Electron Microscopy Coupled with Energy-Dispersive X-ray Spectroscopy

Conflicts of Interest

The authors declare no conflicts of interest.

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