

Engineering Materials

Michal Kulka

Current Trends in Boriding

Techniques



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Michał Kulka
Institute of Materials Science
and Engineering
Poznań University of Technology
Poznań, Poland

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*I would like to dedicate this book to
my beloved and understanding wife, Anetta*

Preface

Boriding, as a process of thermochemical treatment, was known for over one hundred years. The intensive development in the techniques of boriding in recent years was the main inspiration to write this book. In the opinion of author, there was a need to exceed the term 'boriding,' taking into account all the available techniques which resulted in the formation of boride layers or boride coatings. The distinction between layers and coatings was also necessary. There was also a need to indicate the materials, subjected to boriding, to classify the boriding techniques, as well as to indicate their effects on the obtained microstructure.

Based on the available literature data, the characterization of all the specified techniques of boriding as well as the analysis of some of their technological aspects was possible. As a consequence, the current trends in thermochemical and physical techniques of boriding could be indicated, taking into account the advantages and disadvantages of each technique.

Of course, it was impossible to analyze all the published works in which the boriding techniques were described. Only the selected literature data could be subjected to analysis. The author hopes that the most important of them were taken into consideration. However, the author would like to apologize to the scientists whose works were omitted in spite of their unquestionable contribution into development of boriding techniques.

The presented monograph will be a first part of the series. The second part, entitled *Current Trends in Boriding: Microstructure*, will describe the microstructure of boride layers and coatings in more detail as well as the growth kinetics of boride layers. The third part, i.e., *Current Trends in Boriding: Properties*, will concern the most important properties of boride layers and coatings as well as the techniques of their investigation. For the cooperation in preparing the two rest parts of series, the author of this monograph is going to invite other scientists who have an essential contribution to the development of boriding.

Poznań, Poland

Michal Kulka

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Contents

1	Introduction	1
	References	3
2	Classification of Boriding Techniques	5
	References	8
3	Borided Materials	9
	References	12
4	Trends in Thermochemical Techniques of Boriding	17
4.1	Boriding in Solid Media	17
4.1.1	Powder-Pack Boriding	17
4.1.2	Paste Boriding	30
4.2	Boriding in Liquid Media	35
4.2.1	Boriding in Chloride, Fluoride or Carbonate Molten Salt Baths Using Reducers with Boron	36
4.2.2	Boriding in Molten Borate Baths Using Reducers with Boron	40
4.2.3	Boriding in Molten Borate Baths Using Reducers Without Boron	44
4.2.4	Electrochemical Boriding in Molten Salt Baths	48
4.2.5	Boriding in Fluidized Bed	58
4.3	Gas Boriding	64
4.3.1	Gas Boriding with the Use of Boron Halides	64
4.3.2	Gas Boriding with the Use of Boranes and Other Boron Sources	78
4.3.3	Thermodynamics of Gas Boriding with the Use of Boron Trichloride as a Boron Source	81
	References	90

5 Trends in Physical Techniques of Boriding	99
5.1 Boriding Under Glow Discharge Conditions	99
5.1.1 Plasma Gas Boriding	100
5.1.2 Plasma Paste Boriding	110
5.1.3 Plasma Electrolytic Boriding	116
5.1.4 Spark Plasma Sintering Boriding	127
5.1.5 Double Glow Plasma Surface Alloying with Boron	131
5.2 Boron Ion Implantation	133
5.2.1 Beam Line Boron Ion Implantation	134
5.2.2 Plasma Immersion Boron Ion Implantation	143
5.3 High-Energy Techniques of Boriding	148
5.3.1 Surface Alloying with Boron	148
5.3.2 Formation of Boride Coatings	193
References	238
6 Developmental Prospects of Boriding	255
6.1 Classification of Surface Layers with Boron in Respect of Microstructure	255
6.2 Indications for the Use of Boriding Techniques	264
References	270
Curriculum Vitae	273
Index	281

About the Author



Michal Kulka was born in 1961 in Poznań, Poland. He studied 'mechanics,' with specialization 'heat treatment and thermochemical treatment' at the Poznań University of Technology. He acquired his M.Sc.Eng. in 'mechanics' in 1985, a Ph.D. in 'construction and operation of machines' in 1993 at the Poznan University of Technology, and D.Sc. in 'materials science and engineering' at the Lodz University of Technology. He works at Poznan University of Technology since 1984. His specialities are as follows: gas boriding, growth kinetics of boride layers, borocarburing, laser surface alloying with boron, plasma paste boriding, gas carburizing, gas nitriding, laser modification of diffusion layers (borided, carburized, and nitrided layers), low-cycle fatigue, wear, mechanical, and nanomechanical properties of the diffusion layers. Since 2012, he works as Associate Professor and Head of Division of Metal Science and Surface Engineering at the Institute of Materials Science and Engineering at the Faculty of Mechanical Engineering and Managements. He has (co-)authored more than 100 scientific papers in international scientific journals, wrote a monograph entitled 'The Gradient Boride Layers Formed by Borocarburing and Laser Surface Modification,' and was a reviewer of over 280 manuscripts, submitted to international scientific journals in his field of science. He often received awards for his scientific work and opinion-forming activity. He can be contacted at: michal.kulka@put.poznan.pl.

Abbreviations

APS	Atmospheric (air) plasma spraying
BFB	Boriding in fluidized bed
BLBII	Beam line boron ion implantation
BLII	Beam line ion implantation
Cp-Ti	Commercially pure titanium
CRTD-Bor	Cathodic reduction and thermal diffusion-based boriding
CVD	Chemical vapor deposition
DAP	Diffusion annealing process
DBI	Dual-beam implantation
DGPB	Double glow plasma boriding
DGPSA	Double glow plasma surface alloying
DGS	Detonation gun spraying
DM	Dynamic mixing
DRM	Dynamic recoil mixing
EB	Electrochemical boriding
EBB	Electron-beam boriding
EBSA	Electron-beam surface alloying
FS	Flame spraying
GB	Gas boriding
HAZ	Heat-affected zone
HVOF	High-velocity oxy-fuel
IAPS	Inert atmosphere plasma spraying
IBD	Ion beam deposition
IBI	Ion beam intermixing
IEPM	Ion enhanced position mixing
LACVD	Laser-assisted chemical vapor deposition
LC	Laser cladding
LEHCII	Low-energy, high-current ion implantation
LSA	Laser surface alloying
MZ	Re-melted zone

PACVD	Plasma-assisted chemical vapor deposition
PB	Paste boriding
PC	Plasma cladding
PEB	Plasma electrolytic boriding (plasma electrolytic saturation with boron)
PEB/C	Plasma electrolytic borocarburing (plasma electrolytic saturation with boron and carbon)
PEB/C/N	Plasma electrolytic borocarbonitriding (plasma electrolytic saturation with boron, carbon, and nitrogen)
PEB/C/N/S	Plasma electrolytic saturation with boron, carbon, nitrogen, and sulfur
PEB/N	Plasma electrolytic boronitriding (plasma electrolytic saturation with boron and nitrogen)
PEBeam	Pulsed electron beam
PEC	Plasma electrolytic carburizing (plasma electrolytic saturation with carbon)
PED	Plasma electrolytic deposition
PEN	Plasma electrolytic nitriding (plasma electrolytic saturation with nitrogen)
PEO	Plasma electrolytic oxidation
PES	Plasma electrolytic saturation
PET	Plasma electrolytic treatment
PGB	Plasma gas boriding
PHEB	Phase homogenization in electrochemical boriding
PIBII	Plasma immersion boron ion implantation
PIII or PI^3	Plasma immersion ion implantation
PIIID	Plasma immersion ion implantation and deposition
PLD	Pulsed laser deposition
PPB	Plasma paste boriding
P-PB	Powder-pack boriding
PS	Plasma spraying
PSA	Plasma surface alloying
PTA	Plasma transferred arc
PVD	Physical vapor deposition
RI	Recoil implantation
SEB	Scanned electron beam
SHS	Self-propagating high-temperature synthesis
SII	Simple ion implantation
SLEB	Swept line electron beam
SPSB	Spark plasma sintering boriding
TEM	Transverse electromagnetic
TWAS	Twin wire arc spraying
VGE	Vapor-gas envelope
VPS	Vacuum plasma spraying
WAS	Wire arc spraying
XRD	X-ray diffraction

Chapter 1

Introduction



Boriding, also called boronizing, is a well-known process of thermochemical treatment, developed and widely applied through the several last decades. Already at the end of the 19th century, Moissan (1895) concluded that it was possible to produce the hard and wear resistant surface layers by diffusion of boron into the steel. Together with carburizing and nitriding, boriding became one of the most intensively studied and implemented processes, in which the diffusion saturation of metallic materials with interstitial elements was used.

Originally, the term “boriding” was defined as an enrichment of the material surface with boron by means of the thermochemical treatment. Using thermal energy and chemical reactions, boron atoms were adsorbed on the surface and introduced into the lattice of base material, and then diffused into the core direction to form borides with the atoms of the substrate (Kunst and Schaaber 1967). However, intensive development in the techniques of boriding caused that this term was extended, including some physical methods in which the diffusion of boron had less importance. The general partition of boriding techniques, including chemical and physical methods, was reported by Przybyłowicz (2000).

Iron alloys, especially steels, were the first materials which were subjected to boronizing. The process was usually carried out in the range of temperature 850–1000 °C (1123–1273 K) for several hours. In general, the process resulted in formation of needle-like microstructure (also called saw-tooth microstructure) consisting of FeB and Fe₂B iron borides of strong zonation. It was possible to produce the single-phase (Fe₂B) or dual-phase (FeB and Fe₂B) microstructure depending on the boriding conditions (temperature, time, boron activity) as well as on the chemical composition of substrate material. The borided steels were characterized by a high hardness (up to 2000 HV) and wear resistance. The unique advantage of borided steels consisted in their high resistance to abrasion which was significantly better than that-obtained after other thermochemical processes, such as carburizing or nitriding (Graf von Matuschka 1977). Additional advantages of the borided layers, produced on steels, were as follows: the advantageous profile of residual stresses, high heat resistance, high corrosion resistance in alkaline and acid

solutions, high resistance to influence of liquid metals and alloys (Graf von Matuschka 1977; Pertek 2001; Przybyłowicz 2000; Sinha 1991; Voroshnin and Lyakhovich 1978; Wierzchoń 1988).

Diffusion boriding was carried out in solid, liquid and gaseous media. Each of them had good and bad features. Powder-pack boriding (Brakman et al. 1989; Campos-Silva et al. 2013), representing the process in solid medium, was most often implemented due to its conducting facility and availability of commercial powders, used as the boron source. However, taking into account the growth kinetics of boride layers, the gas boriding (Pertek 2001; Kulka 2009; Kulka et al. 2013) as well as electrochemical boriding (Kartal et al. 2006) seemed to be more attractive. Additionally, during pack-boriding, the composition of the produced atmosphere couldn't be constant. Therefore, the diffusion flux of boron from the boriding medium was usually changeable for a time of boriding. It was very difficult to assess to what extent it affected the diffusion process, especially, its growth kinetics. In the case of gas boriding, the composition of boriding medium was controlled (Kulka et al. 2012, 2013; Keddām et al. 2014). There was a possibility of keeping this composition at the constant level. It provided the stability of the diffusion flux from the boriding medium.

The typical thermochemical boriding, irrespective of the boron source used, couldn't be carried out for some steels and many other metallic materials. It was the reason for the intensive development in physical methods of boriding, e.g. boriding under glow discharge conditions (Wierzchoń 1988; Makuch et al. 2017; Keddām et al. 2018) or laser surface alloying with boron (Filip et al. 2006; Tian et al. 2008; Kulka et al. 2014, 2016). Laser alloying with boron was developed as an alternative for time- and energy-consuming thermochemical treatment. Thanks to these physical methods, the boride layers could be produced on high-alloy steels or on titanium and its alloys, i.e. on the materials which were easily subjected to passivation.

In recent years, the hybrid layers were also often produced using boronizing. Such layers offered the new advantageous properties which were difficult to attain by the simple method of boriding. First of all, the process of diffusion carburizing was followed by diffusion boriding. Such process was called borocarburizing (Formanek et al. 1994; Pertek and Kulka 2002). The microstructure and properties of borocarburized steels were widely studied. The layers were produced using gas methods of carburizing and boriding (Kulka and Pertek 2008; Kulka et al. 2011, 2012) as well as by plasma electrolytic process (Wang et al. 2013; Kusmanov et al. 2017). Laser surface modification was also used in order to produce hybrid layers with the presence of iron borides. Laser re-melting was carried out after gas boriding (Kulka and Pertek 2003) or borocarburizing (Kulka and Pertek 2004, 2007), and laser alloying with boron after carburizing (Kulka et al. 2015). The more complex hybrid layers were also proposed.

The formation of boride coatings was also taken into account as a special technique of boriding. Coatings were deposited on top of the substrate material using incremental surface treatment. Thermal spraying (Horlock et al. 2002),

detonation gun spraying (Jin et al. 1999) and cladding with boron (Kim et al. 2001) were selected as the most important techniques of coatings' formation.

This work was a first part of the series, devoted to the current trends in boriding. The current trends in the most commonly used techniques of boriding were described and analyzed. The advantages and disadvantages of the presented methods were indicated based on the process conditions. The conclusions were formulated in relation to the developmental prospects of boriding techniques. The preliminary analysis of the obtained microstructure of boride layers and coatings was presented. The microstructure of boride layers and coatings as well as growth kinetics of boride layers will be analyzed in the second part of series, entitled: ***Current Trends in Boriding: Microstructure***. In the future the third part of the series, ***Current Trends in Boriding: Properties***, will be also prepared.

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Chapter 2

Classification of Boriding Techniques



Abstract The simplified classification of the techniques of boriding was presented in this chapter. The two main groups of the methods were indicated: chemical techniques and physical techniques regarding the technological aspects of boriding process. Such a classification was based on how to produce the active atoms or ions of boron, which might be adsorbed on the surface of metal alloys and could diffuse into the substrate. The most intensively developed techniques were put in the boxes drawn in a broken line, indicating the current trends in boriding.

The complete classification of boriding processes was recently proposed by Krukovich et al. (2016). It partially coincided with the classification given by Minkevich (1965). The very complex partition of boriding process took into account the four aspects:

- mechanism of saturating boron atoms generation,
- technological specifics,
- phase composition, structure and properties,
- processing temperature and usage.

The mechanism of saturating boron atoms generation comprised the characteristics of saturating atoms generation process and means for generation of saturating atoms or transportation of subions to a processed surface. Among the processes of generation of saturating boron atoms, the boriding methods were characterized, taking into account: the flow and circulation of gaseous atmosphere, a contact processes in solid and liquid medium, the processes in liquid medium with the use of an electrolysis or not, an electrostatic field (e.g. glow-discharge) or plasma-immersion ion implantation in a plasma medium, laser or electron-beam treatment.

The means for generation of saturating boron or subions transportation were also specified, for example: boron halides—compounds of boron and halogens (BCl_3 , BF_3 , BJ_3 , BBr_3), boranes—compounds of boron and hydrogen (B_2H_2 , B_2H_6), alkyl boron compounds—organic boron compounds ($(\text{CH}_3)_3\text{B}$, $(\text{C}_2\text{H}_5)_3\text{B}$), a powder mixture, a granulated mixture, a compact mixture, water solutions of salts and suspensions, an electromagnetic field. The technological aspect of the classification of

boriding methods included all known techniques and their characteristics. The classification comprised in this regard: the methods and means of boriding and their types as well as the ways of sealing a saturating medium. The aspect, related to phase composition, structure and properties, took into account the morphology (needle-like or smooth) and compactness of boride layers, their phase composition (dual-phase $\text{FeB} + \text{Fe}_2\text{B}$, single-phase Fe_2B , eutectic mixture of borides, α solid solution) as well as the hardness. It was easy to notice that this part of classification corresponded to only boriding of iron alloys.

The last criterion of classification defined also the processes of boriding of iron alloys depending on the temperature at which they were carried out. High-temperature boriding was defined as a process at temperature above 900°C (1173 K). The processes, carried out at the temperatures between A_{c1} (a referential critical point for a particular steel) and 900°C (1173 K), were classified as medium-temperature boriding. Whereas low-temperature boriding was usually carried out at the temperatures in the range of 550°C — A_{c1} .

Przybyłowicz (2000) limited his own classification to the technological aspects, focusing on the most commonly used techniques of boriding. In the present work, the simplified classification, previously formulated by Przybyłowicz (2000), was modified, indicating the main trends in boriding. The boriding processes were divided into the two groups: chemical and physical techniques. The classification based on the mechanism of formation of the free atoms or ions of boron, which could be adsorbed on the surface of metal alloys and could diffuse into the substrate material. Chemical techniques represented the typical thermochemical boriding in solid, liquid and gaseous media. Physical techniques included boronizing under glow-discharge conditions, ion implantation and high energy methods, i.e. surface alloying with boron, typical thermal spraying, detonation spraying and cladding with boron.

The modifications of this classification, proposed in the present work, were shown in Fig. 2.1. They concerned mainly the physical boriding techniques. These methods were divided into the three groups: boriding under glow-discharge conditions, boron ion implantation and high-energy methods. The four methods, carried out under glow-discharge conditions, were distinguished, taking into account the type of boron source (gas, paste, liquid and powder). The ion implantation could be carried out using beam line or plasma immersion process. Instead of laser alloying with boron, the more general term surface alloying with boron was classified as one of the high-energy techniques. In general, the two groups were characteristic of the high-energy techniques: surface alloying with boron and formation of boride coatings. Surface alloying with boron was usually carried out using laser alloying, electron beam alloying and plasma alloying. Boride coatings could be produced using typical thermal spraying, detonation spraying and cladding. Among the methods of powder-pack boriding, the process, carried out using the electrically conductive powder, was also taken into account. Apart from the gas boriding using boron halides, boranes and process under reduced pressure, the additional method was specified, that is the gas boriding using a boron powder under hydrogen atmosphere. Additionally, all the most intensively developed

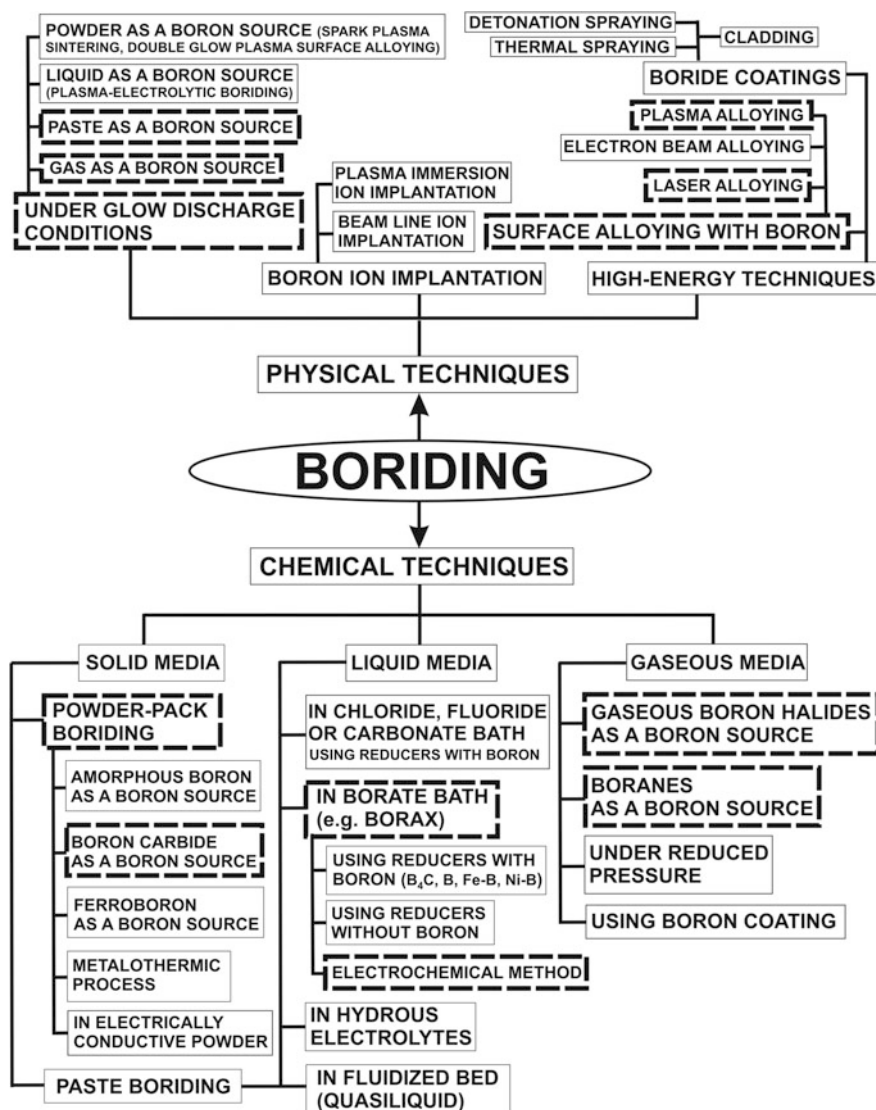


Fig. 2.1 Classification of boriding techniques

methods were put in the boxes drawn in a broken line. In the future part of this work, the most attention was devoted to these methods.

This way, the classification included the two main types of borided surface layers: *technological superficial layers* and *coatings*. Such a distinction was proposed by Burakowski and Wierzchoń (1999) and was consequently used in the present work. The technological superficial boride layers, briefly called *boride layers*, were produced by non-decremental techniques, using all the thermochemical

techniques in solid, liquid or gas media as well as some physical techniques: under glow-discharge conditions and surface alloying with boron. The borides were rarely produced by ion implantation. Therefore, it was difficult to use the term “boride layers” in this case. However, the technological superficial layers with boron were formed by this technique. In general, coatings could be fabricated using different manufacturing techniques, such as: chemical deposition, painting, enameling, electroplating, cladding, thermal spraying, detonation treatment, CVD (chemical vapor deposition) and PVD (physical vapor deposition) techniques, PLD (pulsed laser deposition), hot dip metallization or sol-gel techniques. Among these techniques, the high-energy methods such as thermal spraying, detonation spraying and cladding with boron were selected as the most effective processes in order to produce *boride coatings*.

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Chapter 3

Borided Materials



Abstract All the materials, subjected to boronizing using different techniques, were indicated in this chapter. They were classified into two main groups: iron alloys and non-ferrous materials. The preliminary analysis of the produced microstructure was presented. The most popular materials with boride layers were marked with the boxes drawn in a broken line. Boride coatings could be produced on any metal alloy under certain conditions.

The materials, most often used during producing the boride layers, including iron alloys and non-ferrous alloys, were specified in Fig. 3.1. All the most important materials, taking into account current trends in boriding, were put in the boxes drawn in a broken line. The boriding processes of these materials were described in more detail in the present work.

Iron alloys became the first borided materials because of their most common applying in the mechanical engineering industry. Steels, cast iron as well as cast steels could be successfully subjected to boronizing using all the methods, mentioned above. However, the effects of boriding were evaluated taking into account the quality of the boride layer, its mechanical properties and economical cost-effectiveness as well as the impact of the process on environment. Such an evaluation depended strongly on the boriding method used. In general, all the grades of steels could be borided. The borided layers were produced effectively on the surface of low-carbon (Campos-Silva et al. 2013b; Hernández-Sánchez et al. 2013), medium-carbon (Campos-Silva et al. 2013a; Kusmanov et al. 2017) and high-carbon (Ozbek and Bindal 2002) steels. The low-alloy (Üçisik and Bindal 1997; Campos-Silva et al. 2010) and high-alloy steels (Ozbek and Bindal 2011; Campos-Silva et al. 2011; Rodríguez-Castro et al. 2013) were also subjected to boronizing. Many papers reported boriding of cast iron, including gray cast iron (Campos-Silva et al. 2009; Keddām and Chegroune 2010), ductile (nodular) cast iron (Paczkowska et al. 2010; Mindivan 2016; Azouani et al. 2017), low-alloy ductile cast iron (Mariani et al. 2015a, b) or high-alloy cast iron (Li et al. 2008). Although it was difficult to find the examples of the boriding of cast steels in literature data, these materials were shown in Fig. 3.1 due to the obvious possibility of boride layer formation.

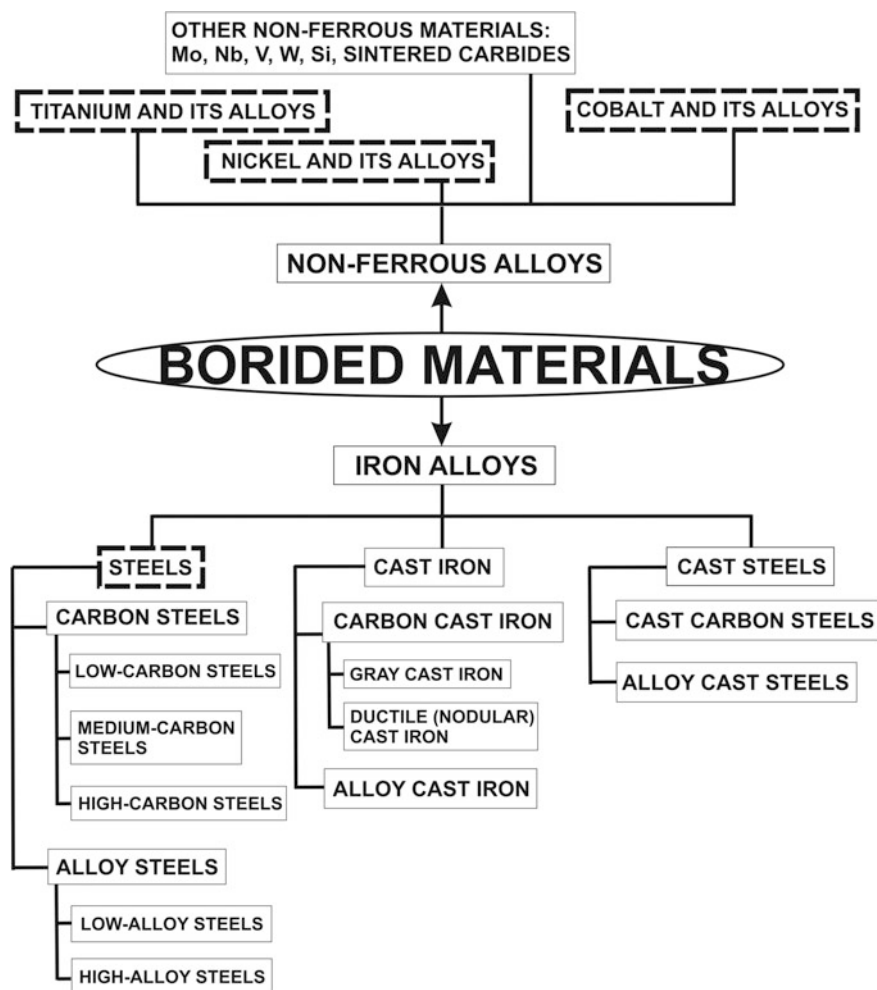


Fig. 3.1 Most commonly used materials during producing the boride layers

According to the Fe–B phase equilibrium diagram (Liao and Spear 1990, 1993), orthorhombic FeB boride and tetragonal Fe₂B boride could appear in the boride layers produced in iron alloys. The majority of the boriding methods resulted in formation of dual-phase (FeB + Fe₂B) or single-phase (Fe₂B) boride layers on the surface of iron alloys. The two-phase layer was usually characterized by strong zonation. The zone with FeB iron borides were formed close to the surface. Fe₂B phase appeared in the second zone, below the first one. Pomel'nikova et al. (2011) reported that rhombic Fe₃B boride and hexagonal FeB₂ boride could also appear during liquid boronizing of steels. Laser alloying with boron (Kulka et al. 2013b) as well as laser re-melting of diffusion borided steel (Kulka and Pertek 2003) resulted

in the formation of eutectic mixture of borides (FeB , Fe_2B and Fe_3B) and martensite. A non-equilibrium iron richer orthorhombic Fe_3B phase was formed during resolidification in some regions of the re-melted zone due to the segregation of boron that took place during re-melting.

The intensive development in mechanical engineering industry was the reason for the more and more great need of applying other materials than iron alloys. Hence, the non-ferrous alloys became very interesting due to their advantageous properties such as high corrosion resistance, high heat resistance or low density compared to iron alloys. However, these alloys also required the high hardness and suitable wear protection under conditions of appreciable mechanical wear. Boriding process became one of the surface treatment processes which could provide them the improved tribological properties without sacrificing the corrosion resistance. The non-ferrous metallic materials, most commonly subjected to boriding, were as follows: titanium and its alloys (Kaestner et al. 2001; Filip et al. 2006; Tikekar et al. 2007; Atar et al. 2008; Kartal et al. 2010; Kulka et al. 2014; Ataibis and Taktak 2015; Makuch et al. 2017), nickel and its alloys (Ueda et al. 2000; Lou et al. 2009; Sista et al. 2013; Kulka et al. 2013a; Makuch and Kulka 2014) as well as cobalt and its alloys (Anthymidis et al. 2002; Campos-Silva et al. 2013c; Çalik et al. 2014; Campos-Silva et al. 2014). Besides, literature data reported the borided layers formed on the pure metals, such as molybdenum (Yu et al. 2006) niobium (Usta 2005; Ribeiro et al. 2006), vanadium (Tarakci et al. 2010) and tungsten (Khor et al. 2005; Usta et al. 2005) as well as on silicon (Milési et al. 2017) or sintered carbides (Johnston et al. 2016).

The diffusion processes of titanium and its alloys usually resulted in the formation of the dual-phase boride layer, containing the compact zone with hexagonal TiB_2 borides close to the surface and orthorhombic TiB whiskers below (Tikekar et al. 2007; Atar et al. 2008; Makuch et al. 2017), according to the Ti-B phase equilibrium diagram (Murray et al. 1986, 1992). Whereas alloying with boron revealed the characteristic composite microstructure with stick-like titanium borides (TiB and TiB_2) among the eutectic mixture, consisting of TiB whiskers and Ti_x , titanium martensite in the re-melted zone (Makuch et al. 2014).

According to the Ni-B phase equilibrium diagram (Liao and Spear 1991), the boriding of nickel and its alloys could result in the formation of a few types nickel borides. The boride layers, produced on pure Ni, were usually composed of only tetragonal Ni_2B phase (Ueda et al. 2000; Lou et al. 2009). After diffusion boriding of Ni-based alloys (Sista et al. 2013; Makuch and Kulka 2014; Makuch et al. 2015a), the more nickel borides have been identified: orthorhombic Ni_3B phase, tetragonal Ni_2B phase, orthorhombic Ni_4B_3 phase and orthorhombic NiB phase. Additionally, the significant concentration of chromium in some Ni-based alloys (e.g. Inconel[®]600, Nimonic[®]90, Nimonic[®]80A) was the reason for the formation of tetragonal Cr_2B and orthorhombic CrB chromium borides. It was characteristic of the diffusion borided nickel alloys that the zonation of the various types of borides did not appear. The borided layer consisted of the mixture of nickel and chromium borides. After laser alloying with boron, the microstructure of re-melted zone usually consisted of the mixture of different borides (nickel and chromium borides

as well as sometimes iron or niobium borides) and Ni–Cr–Fe or Ni–Cr matrix, depending on the chemical composition of Ni-based alloy (Kulka et al. 2013b; Makuch et al. 2015b). However, the suitable selection of laser processing parameters could provide the compact zone with only borides close to the surface.

The diffusion boriding of cobalt and its alloys caused the formation of the boride layer with strong zonation. The orthorhombic CoB phase and tetragonal Co₂B phase were usually identified, according to the Co–B phase equilibrium diagram (Liao and Spear, 1988). The zone with CoB borides appeared close to the surface and was followed by the second zone, containing Co₂B borides (Campos-Silva et al. 2013c, 2014).

As a consequence of boriding process, hard and wear resistant borides were also formed on the surface of other metallic elements and non-ferrous alloys. MoB borides (Yu et al. 2006), NbB₂ and NbB borides (Ribeiro et al. 2006), VB₂ borides (Tarackci et al. 2010) as well as WB borides (Khor et al. 2005; Usta et al. 2005) were identified in the produced boride layers.

In order to produce semiconductors or solar cells, boron ions were often implanted into silicon using the process of beam line ion implantation (Chang et al. 2018) or plasma immersion ion implantation (Milési et al. 2017).

In principle, the boride coatings could be fabricated on all the metal alloys under certain conditions. In the present work, the most attention was devoted to the high-energy techniques of formation of coatings, i.e. typical thermal spraying, detonation spraying and cladding. The iron alloys, most often subjected to thermal spraying with boron, were as follows: low-carbon steels (Horlock et al. 2002; Sakata et al. 2007), medium-carbon steels (Zhao et al. 2018), high-carbon steels (Storozhenko et al. 2017) and high-alloy steels (Huang et al. 2014). Besides, copper (Sharma and Majumdar 2012), Al-based alloys (Dikici and Ozdemir 2012), titanium alloys (Mann et al. 2011) or Ni-based superalloys (Sidhu et al. 2006) were successfully thermally sprayed with boron. Detonation-sprayed coatings were often produced on carbon steels (Jin et al. 1999; Nedaiborshch and Shchepetov 2014), low- and high alloy steels (Kadyrov et al. 1985; Shankar et al. 2010), or on Al-based alloys (Tillmann et al. 2014). Cladding with boron was a popular process which was often carried out on the low-carbon steels (Hemmati et al. 2013), medium-carbon steels (Chen et al. 2008), low-alloy steels (Kim et al. 2001), high-alloy steels (Sudha et al. 2008) as well as on titanium alloys (Majumdar and Li 2010). Plasma cladding and laser cladding were the most commonly techniques of cladding with boron. The composite microstructure of coatings, produced with the use of boron source, usually consisted of the hard phases (including borides) in a soft metallic matrix.

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Chapter 4

Trends in Thermochemical Techniques of Boriding



Abstract All the specified thermochemical techniques of boriding in solid, liquid and gaseous media were characterized and compared in this chapter based on the available literature data. The technological aspects of boriding processes were analyzed, taking into consideration the advantages and disadvantages of each method. The effects of the boriding techniques on the microstructure of borided materials have been indicated. The mechanism of formation of active boron atoms was described. Some issues of the thermodynamics of gas boriding were analyzed. The chemical techniques of boriding were divided into the three groups: boriding in solid media, boriding in liquid media and boriding in gaseous media (see Fig. 2.1). Due to the need of using the elevated temperature during these processes, they were usually recognized as thermochemical techniques. In the present work, the most intensively developed techniques, put in the boxes drawn in a broken line in Fig. 2.1, were described in more detail, taking into account the current trends in boriding. Therefore, the most attention in this chapter was devoted to the powder-pack processes, electrochemical boronizing in borax as well as to the gas boronizing with the use of boron halides or boranes.

4.1 Boriding in Solid Media

4.1.1 Powder-Pack Boriding

The two main techniques of *boriding in solid media* were classified: *powder-pack boriding (P-PB)* and *paste boriding (PB)* (see Fig. 2.1). The first method consisted in the use of a powder mixture, composing of boron source, activator and diluent. Based on the differences in the boron source used, the four techniques of powder-pack boriding were distinguished (Fig. 2.1): with the use of amorphous boron, ferroboration, boron carbide B_4C and boron oxide B_2O_3 (metalothermic method). Sometimes, the mixture of these boriding agents was used. Activator hastened the delivery of boron atoms from the powder mixture to the surface of

borided workpieces. In real conditions, the boron atoms were transported through gas phase. Halides were usually used as the activators (Przybyłowicz 2000), e.g. such compounds as NaF, KF, AlF_3 , NaCl or multicomponent compounds (KBF_4 , KHF, $\text{Na}_2\text{B}_4\text{O}_7$, i.e. borax). The addition of activator usually didn't exceed a few percent by weight. However, this additive was very important due to the reduction in the duration of the boriding process. Diluent, as an inactive substance, was added to the powder mixture in order to prevent its sintering and to diminish the potential of boron. The lower boron potential could eliminate the brittle FeB phase or limit its percentage in borided iron alloys. Aluminum and magnesium oxides, ground chamotte or kaolin as well as silicon carbide SiC were mostly used as diluents.

At first, amorphous boron and ferroboration were used as a boron source (Minkevich 1965). Simultaneously a reducing protective atmosphere was often applied. At elevated temperature, amorphous boron easily formed compounds with oxygen and nitrogen, reducing the effectiveness of the boriding process. Therefore, the use of only boron as boriding powder required the application of the atmosphere, consisting of hydrogen or argon (Przybyłowicz 2000). Such difficulties were limited by the use of vacuum furnace (Zemskov et al. 1964; Krzyminski et al. 1973). Amorphous boron powder could be applied many times if the special complicated procedure of its degassing by vacuum annealing at 1000 °C (1273 K) and reduced pressure (in the range of 10^{-3} – 10^{-2} Pa) was guaranteed. After annealing, argon was introduced into the vacuum chamber, and boron powder was cooled to room temperature. Adsorbed argon protected the amorphous boron powder against the repeated oxidizing during boriding at reduced pressure (Krzyminski et al. 1973). Additionally, amorphous boron has been always relatively expensive. Hence, the powder, containing amorphous boron only, was not adopted for the common use in boriding. So, the various mixtures of amorphous boron with activators and diluents were applied. Minkevich (1965) used the mixture of amorphous boron and 3% of ammonium chloride (NH_4Cl) as an activator, obtaining the relative thick boride layers on Armco iron and low-carbon steel. The boriding agents also consisted of the mixture of amorphous boron, potassium tetrafluoroborate (KBF_4) as an activator and carbon black as a diluent (Bartkowska and Pertek 2014). The thick boride layers of high quality were produced on medium-carbon steel (Bartkowska and Pertek 2014; Bartkowska et al. 2015a) or low-alloy steel (Bartkowska et al. 2015b) using the powder mixture of composition: 4 wt% B, 8 wt% KBF_4 and 88 wt% carbon black.

The use of ferroboration as a boron source didn't provide such difficulties as amorphous boron (Minkevich 1965). Boriding mixture usually consisted of ferroboration powder and activator (ammonium chloride NH_4Cl or hydrochloric acid HCl). The addition of diluent wasn't necessary because of the relatively low boriding potential and resistance to sintering. However, there were some disadvantages of boriding with the use of ferroboration, such as the relatively long duration of the process and the contaminations of the powder by silicon and aluminum, leading to the worsening of the layer quality (Minkevich 1950).

In recent years, the powder mixtures with boron carbide (B_4C) as a boron source have been intensively developed. Although the boron carbide was expensive, it could be used many times, and the containers with powder mixture didn't require the hermetic seal. Even the use of only B_4C powder was possible. However, the effectiveness of such boriding was too low. Therefore, the addition of activators (e.g. KBF_4 or/and $NaCl$) as well as diluents (e.g. Al_2O_3) was usually advisable (Przybyłowicz 2000). The use of about 43 wt% Al_2O_3 diminished the percentage of boron carbide twice, and the boride layer was only slightly thinner. The commercial powder mixtures, such as EKABOR[®] and DURBORID[®], have been specially prepared based on boron carbide. They have been mainly used in the industrial applications as well as in the study of powder-pack boriding through the last decade. The reasons for the use of commercial boriding agents were as follows: good processability, high quality of the boride layers produced, reproducibility of the powder composition and the effects of boriding and cost effectiveness. EKABOR[®], produced by BorTec GmbH, was available in various compositions for a wide range of materials as powder mixture and paste. The five types of powder mixtures were produced: EKABOR[®]I, EKABOR[®]II, EKABOR[®]III, EKABOR[®]HM and EKABOR[®]Ni. These powders differed in the size of particles as well as density (Flichtl 1981). Çalik (2013) reported that EKABOR[®]I, II and III could be characterized by approximately the same chemical composition, consisting of B_4C as boron source, KBF_4 as activator and SiC as diluent. Whereas EKABOR[®]HM and EKABOR[®]Ni were still proprietary and their chemical composition wasn't provided by the supplier. However, the comparison of particle sizes and density of EKABOR[®]I, II, III and HM powders led to the conclusion that the thesis about the same chemical composition had to raise doubts.

Less data were available in relation to the EKABOR[®]Ni and DURBORID[®]G powder mixtures. EKABOR[®]Ni didn't contain SiC (Ueda et al. 2000) and was intended for boriding of nickel and its alloys. DURBORID[®]G was supplied by Durferit GmbH (previously by Degussa) and was characterized as granules. It was only reported that B_4C boron carbide was one of the components of this powder mixture (Campos-Silva et al. 2009). The available data regarding EKABOR[®] and DURBORID[®] boriding agents were specified in Table 4.1.

Boron oxide B_2O_3 was applied as a boron source during the metalothermic technique of boronizing, proposed by Lyakhovich et al. (1974). The addition of a reducer with greater chemical affinity to oxygen than boron (e.g. Al, Ca, Mg, Si, Ti or Zr) was necessary. Aluminum powder was used most often. So, the process was called *aluminothermic technique of boriding*. Then, as a consequence of exothermic reaction of boron oxide with aluminum, the aluminum oxide Al_2O_3 and free boron atoms were formed. It was accompanied by heat emission, and the amount of heat was the temperature-dependent. The most proper Al: B_2O_3 ratio was reported as 35:65 (Voroshnin and Lyakhovich 1978). Besides, the activators typical of the process with the use of B_4C as boron source (e.g. NaF) as well as diluents (e.g. Al_2O_3) were added to the boriding mixture. The main tasks of the diluent were as follows: the decrease in the potential of boron, the protection against sintering, and the partial absorption of the heat of reaction. The detailed study of boriding by

Table 4.1 Available data regarding the chemical composition, particle sizes and density of the EKABOR[®] and DURBORID[®] powders

Boriding agent	Chemical composition (wt%) (Çalik 2013)			Particle size (μm) (Flichtl 1981)	Density (g/cm ³) (Flichtl 1981)
	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	Powder mixture without SiC, unknown components (Ueda et al. 2000)			Unknown	Unknown
DURBORID [®] G	B ₄ C of unknown quantity and unknown other components (Campos-Silva et al. 2009)			Unknown	Unknown

Source Flichtl (1981), Ueda et al. (2000), Campos-Silva et al. (2009), Çalik (2013)

aluminothermic method was carried out by Chochołowski and Przybyłowicz (1984). They used the powder mixture, consisting of B₂O₃, Al, Al₂O₃ and various activators (NaF, NaCl, NaJ, KCl, KBF₄, NaBF₄, Na₂B₄O₇, FeCl₂, AlF₃ and SrCl₂). The most proper composition of the powder mixture was determined as follows: 20–35 wt% B₂O₃, 15–26.3 wt% Al, 2–5 wt% AlF₃, and Al₂O₃ as balance. However, it would be difficult to include this method as one of the leading powder methods, taking into account only the two papers published in the last fifteen years in available journals (Uzunov and Ivanov 2004; Ivanov and Ignatova-Ivanova 2016).

The cleaned workpieces, subjected to powder-pack boronizing, were usually put into the cylindrical case (also called container, crucible, retort, or box), filled with an adequate powder mixture and made of heat-resisting steel or stainless steel (Atar et al. 2008; Campos-Silva et al. 2011, 2013b; Hernández-Sánchez et al. 2013). Sometimes, a fire-clay crucible was used as a container with powder mixture, e.g. during boriding of titanium (Tikekar et al. 2007). Next, this container was heated to a temperature of boriding process in an electric resistance furnace under atmospheric pressure (Ozbek and Bindal 2011), held at this temperature for an adequate time and cooled to ambient temperature outside the furnace. In general, all the previously mentioned materials (see Fig. 2.2) could be pack-borided. Apart from the powder composition, the usually used other parameters of powder-pack boriding were approximately as follows: the wide temperature range of 850–1100 °C (1123–1373 K), and a duration of 2–24 h. These parameters depended on the borided material to a certain degree. The schematic representations of the most effective powder-pack processes were shown in Fig. 4.1, taking into account the methods that were easy to carry out. The containers with the powder mixture and workpieces were usually heated and held at boriding temperature in air, i.e. in the

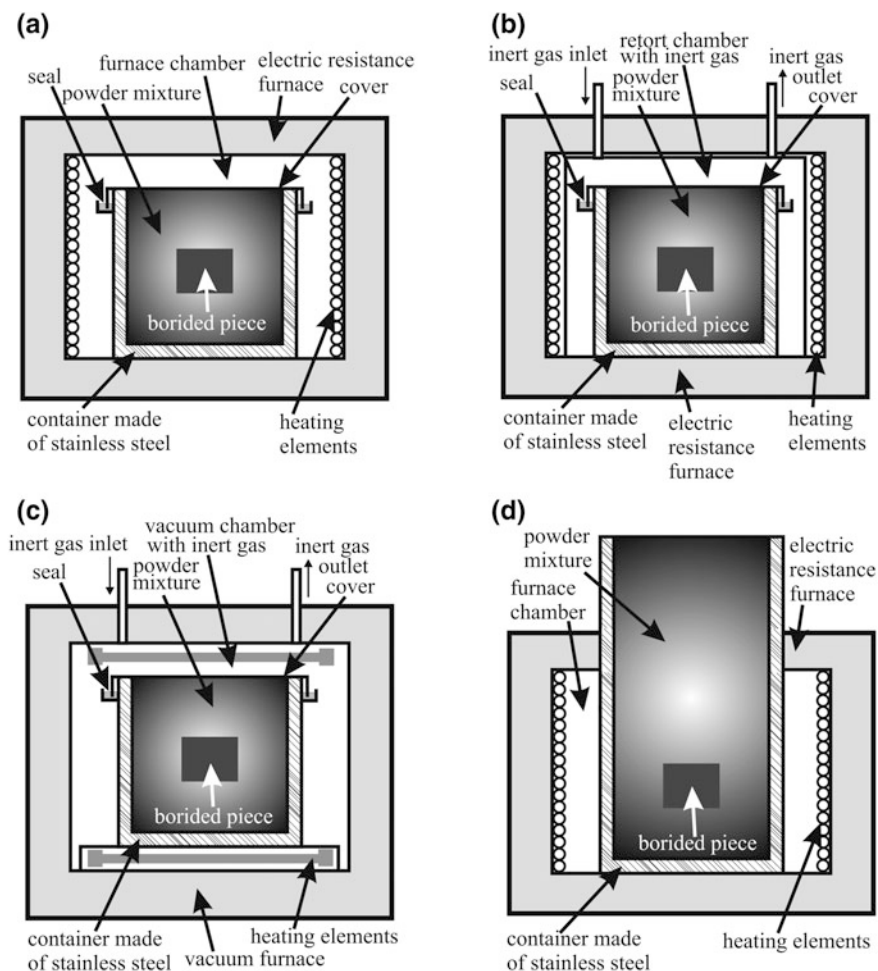


Fig. 4.1 Schematic representations of the most effective and easiest techniques of powder-pack boriding: sealed container in the typical electric resistance furnace using air atmosphere (a), sealed container in the tight retort of electric resistance furnace in the presence of inert gas (e.g. argon) (b), sealed container in the chamber of vacuum furnace in the presence of inert gas (e.g. argon) (c), open retort (container) in the typical electric resistance furnace in air atmosphere (d). *Remark: in the case of methods (a) and (b), the seal of containers was less important if the boron carbide was used as a boron source*

absence of inert gases (Campos-Silva et al. 2009, 2011, 2013a, b; Hernández-Sánchez et al. 2013). Therefore, the seal of containers was often very important due to limit air access to the powder mixture.

The excessive access of air to boriding powder mixture could cause uncontrolled oxidation of borided material what was particularly important during boriding of

such materials as austenitic steels or titanium and its alloys. However, the sealing method of cylindrical cases, crucibles, retorts or other containers, applied during powder-pack process, was usually omitted by authors in experimental procedures, even if the schematic representation of the container with boriding powder mixture was given (Campos-Silva et al. 2013b). Probably, it could result from the common use of the powder mixtures, containing boron carbide (B_4C) as a boron source. In that case, the seal of containers wasn't so important, provided that overpressure appeared in the boriding medium. Therefore, the authors mentioned only about a closed case (Campos-Silva et al. 2009). Przybyłowicz (2000) reported the use of clay with water-glass as well as liquid seals (e.g. enamel, lead glass, lead or labyrinth seal with cast iron turnings) in order to seal the containers. It was assumed that such seal was sometimes necessary, and the effective boriding process in the typical resistance furnace using air atmosphere could proceed as shown in Fig. 4.1a.

Sometimes, the powder-pack boronizing was carried out in the atmosphere of inert gas, e.g. argon (Campos-Silva et al. 2013c). Probably, it required the use of a furnace of special construction with tight retort, as it was characteristic of the thermochemical treatment in gaseous media. However, it was often not reported whether the container with boriding mixture was somehow sealed, probably not because of using B_4C as a boron source. Such boriding process, carried out in the electric resistance furnace with tight retort and using an inert gas was presented in Fig. 4.1b.

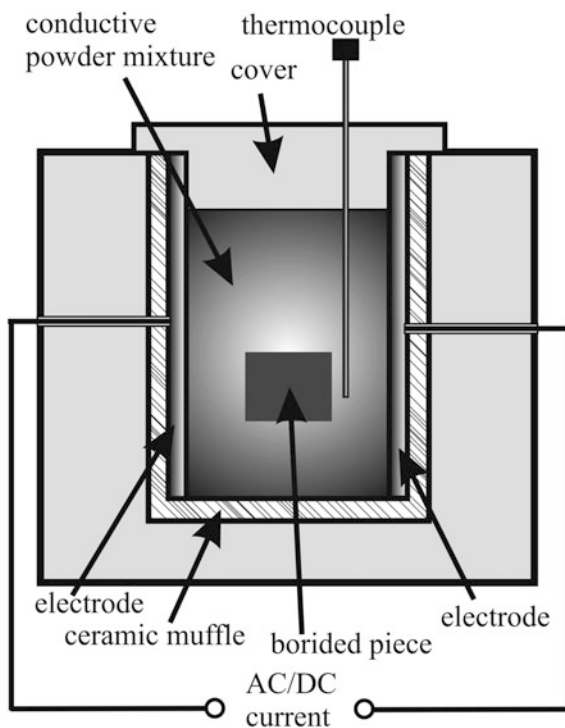
The vacuum furnaces were also applied for a similar purpose by Tarakci et al. (2010). The crucible (container) with powder mixture was tightly sealed to prevent air gas entrance and then loaded into a vacuum furnace. The air was evacuated from the furnace chamber using a mechanical rotary vacuum pump to a pressure of 1×10^{-3} mbar. Subsequently argon gas (99.998%) flowed through the chamber continuously to control the furnace atmosphere. Such method found its schematic representation in Fig. 4.1c. It was also possible to use a vacuum as a protective atmosphere (Torun and Çelikyürek 2009). Usually, the tight retort with inert gas (Fig. 4.1b) as well as the vacuum chamber (Fig. 4.1c) should be equipped with a fan in order to provide the constant flow of inert gas and the constant temperature in the entire chamber volume.

Very interesting method of powder-pack process was described by Młynarczak (2005). It was called the method with open retort and was patented by Jastrzębowski et al. (1988). The process was mainly used for the formation of the diffusion carbide coatings on steels (Młynarczak et al. 2003; Młynarczak 2005) by titanizing, vanadizing and chromizing. However, it was also a very effective method of powder-pack boriding (Nawrocki and Piasecki 2002) or borochromizing (Piasecki and Młynarczak 2003). In this method, the tube-shaped retort with a closed bottom, made of heat-resisting or stainless steel, was filled with borided pieces and powder mixture without an additional seal. Then, it was put into the furnace chamber in such a way that the upper part of the retort extended outside the furnace (Fig. 4.1d). The powder mixture in the upper part of the retort (outside the furnace) became its natural seal. The temperature of the surface of boriding mixture was so low that this mixture

didn't oxidize. The gases, created in the bottom part of the retort, re-sublimated in its cold upper part and, therefore, they didn't get out outside the retort (Młynarczak 2005). The powder mixture usually based on boron carbide as a boron source, containing e.g. 60 wt% B_4C , 0.5 wt% AlF_3 as an activator and 39.5 wt% Al_2O_3 as diluent (Nawrocki and Piasecki 2002). Several times lesser amount of activator was needed during boriding with open retort compared to the other methods of powder-pack boriding.

Powder-pack boriding was also carried out *in electrically conductive boriding agents*. In this case, the powder mixture was heated and activated by the passage of direct or alternating current. The heating was an effect of this current passage through the powder mixture, consisting of B_4C , amorphous boron, diluent (e.g. CaO , Al_2O_3 , MgO or SiO_2) as well as the substance that was electrically conducting, e.g. coke, charcoal, copper or the most preferred—graphite. The method was used in order to form boride layers on steels (Gerasimov and Prosvirin 1972; Voroshnin and Lyakhovich 1978). The device for such a treatment was shown in Fig. 4.2. Borided workpieces were put into ceramic muffle filled with boriding mixture. The muffle was closed by a cover. The electrodes, made of low-carbon steel, were mounted on opposite walls of the muffle. The power source of direct or alternating current with a voltage of 10–50 V was being connected to electrodes. Such powder-pack boriding didn't become the commonly used method, probably

Fig. 4.2 Schematic representation of the powder-pack boriding in electrically conductive boriding agent with the heating by the use of current passage



because of the difficulties regarding the control of temperature. Too high temperature caused local partial melting and the formation of the eutectic mixture of borides.

Increasingly, the nanoboron powder was applied as a boriding agent without activators and diluent (Günen et al. 2014, 2017). Such a powder-pack boriding required the use of the inert gas (argon) in order to protect the nanoboron powder against the oxidation as it was mentioned previously. The process resulted in the formation of the layer of good quality on low-alloy (Günen et al. 2017) and high-alloy steels (Günen et al. 2014), causing shortening of treatment time.

The general characterization of the selected processes of powder-pack boriding of iron alloys was presented in Table 4.2, taking into account the used powder mixture, protective atmosphere, schematic representation of the method in Fig. 4.1, temperature and time of the treatment.

This characterization was based on the available literature data, indicated by the cited References. Current trends in the powder-pack boriding of iron alloys pointed at applying the least complicated method, schematically represented by the Fig. 4.1a and consisting in the use of commercial powder mixtures (EKABOR[®] and DURBORID[®]). The sealed containers (tightly packed) were usually applied, although the use of boron carbide as a boron source didn't require a special seal. The protective atmosphere was only applied if the boriding agent consisted of the nanoboron powder, susceptible to oxidation.

The tendency of the use of commercial powder mixtures was even more visible in powder-pack boriding of non-ferrous alloys (Table 4.3). Cobalt and its alloys as well as pure niobium, vanadium, molybdenum, tungsten or tantalum were efficiently borided using, in principle, only the commercial boriding agents such as EKABOR[®]II, EKABOR[®]III or DURBORID[®]. In the case of nickel and its alloys, the use of typical commercial powder mixture, containing SiC as diluent, were inadvisable because of the formation of nickel silicides of high porosity (Hunger and Trute 1994; Ozbek et al. 2000). Therefore, the special commercial boriding agent EKABOR[®]Ni without SiC was usually applied in order to carry out the successful boronizing of these materials (Ueda et al. 2000; Torun and Çelikyürek 2009). Sometimes, other powder mixtures, not containing silicon carbide, were used (Hunger and Trute 1994; Petrova et al. 2008). Ti-based alloys were subjected to powder-pack boriding process using both commercial boriding agents with SiC (Atar et al. 2008) and the unique powder mixtures, composed of B, Na₂CO₃ as an activator and C as a diluent (Aich and Ravi Chandran 2002; Tikekar et al. 2007) or consisting amorphous boron, borax (Na₂B₄O₇) and C (Sarma et al. 2012).

It was characteristic of non-ferrous alloys, subjected to the powder-pack boriding, that the borided pieces were usually tightly packed into the crucibles, containers, boxes or cases, and the protective atmosphere (argon or vacuum) was used more often than for iron alloys.

The powder-pack boriding of iron alloys usually resulted in the formation of iron boride layers with a strong zonation. In the case of carbon steels, both two-phase (FeB + Fe₂B) and single-phase Fe₂B layers could be produced. The boron richer FeB phase occurred close to the surface, and Fe₂B iron borides were observed in the

Table 4.2 General characterization of powder-pack boriding of iron alloys

Type of material	Powder mixture/Protective atmosphere/Scheme of the method	Temperature (°C)/ Time (h)	References
Low-carbon steels	EKABOR [®] II/absence/ Fig. 4.1a, closed container	1000/4–8	Campos-Silva et al. (2013b)
	DURBORID [®] /absence/ Fig. 4.1a, closed case	1000/6	Hernández-Sánchez et al. (2013)
Medium-carbon steels	4% B, 8% KBF ₄ , 88% carbon black/absence/ Fig. 4.1a	950/4	Bartkowska and Pertek (2014)
	20% B ₄ C, 10% KBF ₄ , 70% SiC/absence/ Fig. 4.1a, closed case	950/8–12	Campos-Silva et al. (2013a)
High-carbon steels	EKABOR [®] I/absence/ Fig. 4.1a	850–1050/1–8	Ozbek and Bindal (2002), Genel et al. (2003)
Low-alloy steels	EKABOR [®] II/absence/ Fig. 4.1a	850–950/2–8	Efe et al. (2008)
	60% B ₄ C, 0.5% AlF ₃ , 39.5% Al ₂ O ₃ /absence/ Fig. 4.1d	950/3	Nawrocki and Piasecki (2002)
	Nanoboron/argon/ Fig. 4.1b	1000/0.5–1.75	Günen et al. (2017)
High-alloy steels	DURBORID [®] /absence/ Fig. 4.1a, closed case	850–1000/2–10	Campos-Silva et al. (2011)
	EKABOR [®] I/absence/ Fig. 4.1a, sealed container	850–1050/2–8	Ozbek and Bindal (2011)
	DURBORID [®] /absence/ Fig. 4.1a, closed case	900–1050/4–8	Campos-Silva et al. (2012)
	DURBORID [®] /absence/ Fig. 4.1a, closed case	950–1050/3–7	Rodríguez-Castro et al. (2013)
	DURBORID [®] /absence/ Fig. 4.1a, sealed container	1000/8	Hudáková et al. (2007)
	EKABOR [®] II/absence/ Fig. 4.1a	850–1050/2–8	Gunes and Kanat (2015)
	Nanoboron/argon/ Fig. 4.1b	950–1000/2–4	Günen et al. (2014)
	95% B, 5% KBF ₄ /argon/ Fig. 4.1c	850–950/1–12	Dybkov (2017)
Gray cast iron	DURBORID [®] /absence/ Fig. 4.1a, closed case	900–1000/2–8	Campos-Silva et al. (2009)
Ductile cast iron	EKABOR [®] II/absence/ Fig. 4.1a, sealed container	900/3	Mindivan (2016)
Alloy cast iron	B ₄ C, KBF ₄ , SiC/absence/ Fig. 4.1a, sealed container	900–950/2–8	Li et al. (2008)

Table 4.3 General characterization of powder-pack boriding of non-ferrous alloys

Type of material	Powder mixture/Protective atmosphere/ Scheme of the method	Temperature (°C)/Time (h)	References
Titanium and its alloys	EKABOR [®] II/absence/Fig. 4.1a, sealed container	1100/2.5	Atar et al. (2008)
	B, Na ₂ CO ₃ , C in different ratios/absence/Fig. 4.1a, sealed crucible	800–1100/1–24	Aich and Ravi Chandran (2002)
	B, Na ₂ CO ₃ , C/absence/Fig. 4.1a, sealed crucible	850–1050/3–24	Tikekar et al. (2007)
	B, C, Na ₂ B ₄ O ₇ /absence/Fig. 4.1a, sealed crucible	850–1050/3–24	Sarma et al. (2012)
Nickel and its alloys	EKABOR [®] Ni/argon/Fig. 4.1b	800–900/2	Ueda et al. (2000)
	EKABOR [®] Ni/vacuum/Fig. 4.1c	900/1–8	Torun and Çelikyürek (2009)
	B ₄ C and KBF ₄ /argon/Fig. 4.1b	950/4	Petrova et al. (2008)
Cobalt and its alloys	EKABOR [®] III/absence/Fig. 4.1a	900–1000/1–6	Çalik et al. (2014)
	DURBORID [®] /argon/Fig. 4.1b, closed case	950–1000/6–10	Campos-Silva et al. (2013c, 2014)
	EKABOR [®] II/absence/Fig. 4.1a, closed case		Rodríguez-Castro et al. (2015)
Niobium	EKABOR [®] /absence/Fig. 4.1a	940/2–8	Ribeiro et al. (2006)
	EKABOR [®] II/absence/Fig. 4.1a	940/2–8	Usta (2005)
Vanadium	5% B ₄ C, 5% KBF ₄ , 90% SiC/argon/ Fig. 4.1c, sealed crucible	1100/4–16	Tarakci et al. (2010)
Molybdenum	EKABOR [®] II/Ar/Fig. 4.1b, sealed box	1000–1100/2–8	Akca and Çalik (2017)
Tungsten	EKABOR [®] II/absence/Fig. 4.1a	940/2–8	Usta et al. (2005)
Tantalum	EKABOR [®] II/absence/Fig. 4.1a	940/4	Ribeiro et al. (2007)

zone below the first one. The formation of Fe₂B monolayer required the use of the boriding agent of special composition, the adequate selection of parameters of boriding or an additional heat treatment after boriding, e.g. diffusion annealing process (DAP). The needle-like (also called saw-tooth) microstructure was characteristic of iron boride layers. It provided the good cohesion of the boride layers. Below the boride layer, the boron concentration was only slightly increased due to the very low solubility of boron (about 0.005 wt%) in Fe_γ austenite (McBride et al. 1954). However, it could have a positive effect on the hardenability of the borided steel.

Hernández-Sanchez et al. (2013) obtained the FeB + Fe₂B layer on the surface of low-carbon steel. Whereas the single-phase layer, composed of only Fe₂B

borides, was formed by Campos-Silva et al. (2013b) on the same steel. The dual-phase composition ($\text{FeB} + \text{Fe}_2\text{B}$) was characteristic of the layers which were fabricated on the surface of a medium-carbon steel (Campos-Silva et al. 2013a; Bartkowska and Pertek 2014). However, the diffusion annealing process (DAP), carried out after powder-pack boriding, could provide the Fe_2B monolayer (Campos-Silva et al. 2013a). During such a process, the samples were inserted into the sealed container with SiC powder which acted as a diluent. The powder-pack boriding of high-carbon steels provided the two-phase or single-phase iron boride layer, depending on the boronizing time. The long duration of the process (above 4 h) resulted usually in the formation of $\text{FeB} + \text{Fe}_2\text{B}$ layer (Ozbek and Bindal 2002; Genel et al. 2003). Whereas the monolayer (Fe_2B) was produced by boriding for shorter time (Ozbek and Bindal 2002). The carbon content in the borided substrate influenced the morphology of borides. Carbon didn't dissolve in FeB borides, and its solubility in Fe_2B boride was very low (Voroshnin and Lyakhovich 1978). Therefore, during boriding of carbon steels, carbon was being moved in a core direction by following the boron diffusion front. Carbon was ejected from interstitial positions by boron. As a consequence, iron borides were formed close to the surface. This phenomenon was accompanied by an increase in carbon concentration beneath iron borides. Hence, sometimes the borocementite $\text{Fe}_3(\text{C},\text{B})$ was observed at the end of boride layer (Brakman et al. 1989). In general, the boron diffusion was hindered by carbon. Hence, the high carbon content in the borided steel resulted in the formation of more smooth interface between the boride layer and the substrate material. Iron borides showed a tendency towards loss of the needle-like nature. Simultaneously, the thickness of boride layer diminished.

Like the increased carbon concentration, high content of alloying elements, especially chromium and nickel, also caused the formation of the relatively flat (smooth) boride layers at their boride/substrate interface (Goeuriot et al. 1982). The thickness of boride layers, produced on high-alloy steels, was decreased in comparison with carbon steels. Although the FeB and Fe_2B iron borides were still predominant phases in borided alloy steels, the borides of other metallic elements often appeared after powder-pack boriding. Efe et al. (2008) produced the layer with FeB , Fe_2B , CrB and Cr_2B borides on the low-alloy steels. The boride layers also contained some amount of chromium carbides of various types. The similar phase composition of boride layer was obtained by Nawrocki and Piasecki (2002). The boride layer, produced by Günen et al. (2017) on the low-alloy steel using nanoboron powder, was composed of FeB and Fe_2B zones in which CrB , Mo_2B and Ni_2B borides were also identified. Campos-Silva et al. (2011) reported the formation of two-phase ($\text{FeB} + \text{Fe}_2\text{B}$) boride layers on a high-alloy austenitic steel, indicating the diminished thickness of the layers as well as their modified morphology and possible formation of other borides. The boride layer, fabricated on AISI M2 high speed steel by Ozbek and Bindal (2011), consisted mainly of FeB , Fe_2B , CrB phases as well as an amount of MoB borides and carbides. Campos-Silva et al. (2012) identified the FeB , Fe_2B , CrB , Cr_2B and V_3B_4 phases in the boride layer with strong zonation after powder-pack boriding of AISI M2 steel. Together with the predominant iron borides (FeB and Fe_2B), the boride layer was

composed of CrB, Cr₂B, MoB, Mo₂B₄ and VB₂ borides as a consequence of boriding of AISI D2 steel (Rodríguez-Castro et al. 2013). The boronized high-alloy tool steel was characterized by the dominant FeB borides (or MeB, where Me was a metallic element) as well as by the minor Fe₂B (Me₂B) and CrB phases (Hudáková et al. 2007). Gunes and Kanat (2015) fabricated on AISI D6 steel the boride layer which contained FeB, Fe₂B, CrB, and Cr₂B phases. Whereas Günen et al. (2014) confirmed the presence of FeB, Fe₂B, CrB as well as Ni₂B borides after powder-pack boriding of AISI 304 austenitic steel. Dybkov (2017) indicated the possibility of formation of complex (Fe,Cr)B and (Fe,Cr)₂B borides with strong zonation in case of boronizing of high-chromium steels. In recent years, powder-pack borided steels were usually not subjected to the further heat treatment. The current trends in powder-pack boriding didn't indicate the need of the use of additional heat treatment. Only sometimes, the borided objects were quenched from an austenitizing temperature and then low-temperature or high-temperature tempered (Bartkowska and Pertek 2014). However, an important advantage of such a treatment was that the diminished hardness gradient between the boride layer and the substrate material could be obtained.

The similar phase composition was obtained after powder-pack boriding of cast irons. Borided gray cast iron was characterized by single-phase Fe₂B boride layer with flake graphite (Campos-Silva et al. 2009). The nodular graphite among the two-phase boride layer (FeB + Fe₂B) was observed in the powder-pack borided ductile cast iron (Mindivan 2016). Iron borides (FeB + Fe₂B) and chromium borides were revealed in borided alloy cast iron (Li et al. 2008).

The powder-pack boronizing of titanium and its alloys usually resulted in the formation of the typical dual-phase boride layer, composed of the compact TiB₂ zone close to the surface and the zone with TiB whiskers below the first one (Tikekar et al. 2007; Atar et al. 2008; Sarma et al. 2012). However, it was also possible to produce the single-phase layer with only TiB whiskers (Aich and Ravi Chandran 2002) by properly selected boriding agent and parameters of the diffusion process. TiB whiskers occurred among the substrate material. Hence, the interface between this zone and substrate material was determined by the sharp tips of TiB whiskers. Only Atar et al. (2008) reported the smooth interface between the two-phase layer (TiB₂ + TiB) and Ti6Al4V alloy substrate.

The boride layer, produced by powder-pack boriding of Ni-based alloys using a proper boriding agent (without SiC), didn't reveal the zonation. The nickel borides usually occurred in the layer as a mixture. The formation of borides of other metallic elements (e.g. chromium borides) was also possible. The borides/substrate interface was smooth. Petrova et al. (2008) identified the mixture of Ni₄B₃, Ni₃B and Ni₂B nickel borides in the layers, produced on Inconel®625 and Inconel®718 alloys. Ueda et al. (2000) reported the presence of only Ni₂B phase after powder-pack boronizing of pure Ni. Whereas the mixture of Ni₂B and Ni₃B borides was obtained on the surface of the same material by Torun and Çelikyürek (2009).

The powder-pack boriding of cobalt and its alloys caused the formation of the boride layer with strong zonation. The CoB and Co₂B phases were usually identified. The zone with CoB borides appeared close to the surface and was followed by

the second zone, containing Co_2B borides (Campos-Silva et al. 2013c, 2014; Çalik et al. 2014; Rodríguez-Castro et al. 2013). If the pure Co was subjected to boronizing (Çalik et al. 2014), the boride layer was characterized by needle-like (saw-tooth) nature like it was observed for borided iron alloys. The more smooth interface between the successive boride zones and between the whole boride layer and the substrate was obtained in case of powder-pack boriding of Co–Cr–Mo–C alloy.

In case of powder-pack borided pure niobium, the boride layer contained only NbB_2 phase of smooth interface with the substrate (Usta 2005; Ribeiro et al. 2006). The single-phase boride layer was also produced by powder-pack boriding of pure vanadium (Tarakci et al. 2010) or pure tungsten (Usta et al. 2005). The layer was composed of VB_2 and WB borides, respectively. The borides/substrate interface was relatively smooth. The two-phase boride layers were usually revealed in borided pure molybdenum (Akca and Çalik 2017) and pure tantalum (Ribeiro et al. 2007). The $\text{Mo} + \text{Mo}_2\text{B}$ boride layer was obtained on pure Mo only at high temperature of boriding (1100 °C, i.e. 1373 K). It was difficult to distinguish these phases in the samples which were borided for shorter times. The reduced boriding temperature could provide MoB monolayer (Akca and Çalik 2017). The borided pure tantalum contained the relatively thin layer with TaB and Ta_2B borides which were also hard to distinguish.

The mechanism of formation of active boron atoms during powder-pack boriding with the use of boron carbide was analyzed by Przybyłowicz (2000). It was assumed that the commercial B_4C powder contained an amount of boron trioxide B_2O_3 (up to 3%). Boriding in the pure boron carbide didn't result in the formation of the appropriately thick boride layer. Simultaneously, the boriding process didn't proceed with the use of the pure B_2O_3 powder. Hence, it was concluded that boron trioxide played a role of an activator during powder-pack boriding using B_4C as a boron source. Analysis with the use of a mass spectrometer indicated that the B_2O_3 and B_2O_2 oxides occurred during powder-pack boriding using the commercial B_4C powder. Hence, the possible reaction was as follows:



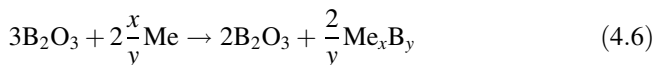
Taking into account the evaporation of boron oxides at high temperature, they were condensed on the surface in the form of vitreous film, containing B^{+2} and B^{+3} ions:



Boriding process could proceed as a consequence of the formation of solid solution Me(B) or metal borides Me_xB_y :

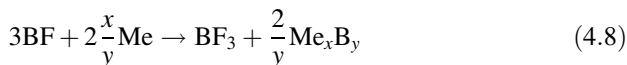
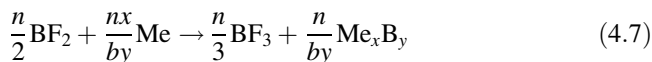


The summary reaction could be as follows (Przybyłowicz 2000):



It was assumed that the similar reactions could also proceed in the case of the use of other boron sources. Even if the boron trioxide didn't occur in the initial stage of boriding, it could be formed as a consequence of boron oxidation because of the presence of air in powder mixture.

In the case of use of halides (e.g. NaF, KF, AlF₃, NaCl, KBF₄, KHF) as activators, the mechanism of formation of active boron atoms was quite different (Voroshnin and Lyakhovich 1978). The volatile boron halides (BF₂, BF) were formed at higher temperature. They were responsible for the transport of boron to the surface of saturated workpieces. Hence, during powder-pack boriding the saturation with boron really occurred through gas phase. The active boron atoms were formed according to the reactions:



The similar reactions could proceed if the chlorides were applied as activators, instead of fluorides.

4.1.2 Paste Boriding

Paste boriding (PB) was usually classified as a process in solid media. However, if the paste contained cryolite (Na₃AlF₆), it could obtain a liquid state (Przybyłowicz 2000), especially at the temperature above 1000 °C (1273 K). Hence, this possibility has been taken into account by the proposed classification of the boronizing methods (Fig. 2.1). The main advantages of paste boronizing were as follows: the possibility of the boride layer formation only on the selected surface, the use of any furnace with the control of temperature, the possibility of the direct quenching of steels after boriding, as well as boron source and energy saving.

Paste boronizing was developed since 1959 to produce the boride layers mainly on steels. At first, the method consisted in coating the material surface with an active paste, containing boron source and cryolite or activator, and next, after

drying the first one, with the second paste, protecting against oxidation. Water glass or hydrolyzed ethyl silicate was usually used as a binder. The protective paste often based on aluminum oxide (Bayazitov et al. 1976). Then, the coated and dried pieces were heated up to temperature of boriding. The paste usually dropped off during the quenching, carried out directly after thermochemical treatment.

Minkevich and Ulybin (1959) used the paste, containing 50 wt% B_4C and 50 wt% of cryolite with hydrolyzed ethyl silicate as a binder. They applied induction heating up to 1200 °C (1473 K) for 2–3 min, obtaining the eutectic boride layer of the thickness of 100 μm and hardness 1000 HV on low-alloy steel. Many different pastes were applied through the several last decades. Their detailed description was reported by Przybyłowicz (2000). It should be mentioned that the boriding paste could be composed of various boron sources, such as amorphous boron, ferroboration or boron carbide, as well as of activators and fillers (diluent).

The use of amorphous boron required to apply the protective atmosphere (e.g. $H_2 + Ar$) like during the powder-pack boriding due to the susceptibility of boron to oxidation. The heating process was often carried out in vacuum (Minkevich 1965). Sometimes, the borided pieces with paste coating were put into the sealed containers, filled with Al_2O_3 or powdered chamotte, to avoid the oxidation. In general, over time, the use of such methods as well as the protective paste was replaced by protective atmospheres. Ferroboration as a boron source was used by Kunst and Schaaber (1967) with the addition of cryolite and water glass. However, the quality of the boride layer was unsatisfactory. Voroshnin and Lyakhovich (1978) have developed a metalothermic paste, containing B_2O_3 . The special heat paste, applied instead of protective paste, was proposed by Prosvirin and Locmanov (1965). It eliminated the need of using the heating unit.

In recent years, the paste, containing the boron carbide (B_4C), was usually used in the practical applications and in the study of the paste boronizing process of steels. The commercial pastes, such as EKABOR[®] and DURBORID[®] (also known as Dur-Ferrit paste), were offered by Bortec GmbH and Durferrit GmbH, respectively, and probably based on boron carbide. However, their chemical composition was not fully known. The available data (Wahl 1975) indicated that DURBORID[®] paste contained boron carbide (B_4C) and cryolite (Na_3AlF_6) with an unknown ratio and a maximum of 10–15% water. Recently, Doñu Ruiz et al. (2015) admitted that this commercial boriding paste was used in their study. Previously, many authors also carried out the boriding process using the paste, consisting of B_4C and Na_3AlF_6 with unknown ratio, mixed with water (Campos et al. 2005, 2006a; Campos-Silva et al. 2008, 2010). However, they didn't provide an information that it could be this commercial DURBORID[®] paste.

The special self-protective boronizing paste was recently developed by Lou et al. (2007) in order to form the boride layers on Ni-based alloys. The boriding of pure nickel and Nimonic[®]90 alloy with the use of such paste resulted in the formation of a boride layer of high quality without porous nickel silicides (Lou et al. 2009). The paste, containing the nanodispersed boron source was also successfully applied (Kostyk 2015).

The schematic representations of the most often used processes of paste boronizing through the last decade were shown in Fig. 4.3, taking into account the methods that were easy to carry out. The workpieces with paste coating were rarely heated and held at boriding temperature in air, i.e. in the absence of inert gases (Doñu Ruiz et al. 2015; Khairulmaini et al. 2015). Such situation required a special procedure during thermochemical treatment. The borided pieces were embedded in a closed cylindrical container made of steel and filled with a Durborid[®] dehydrate

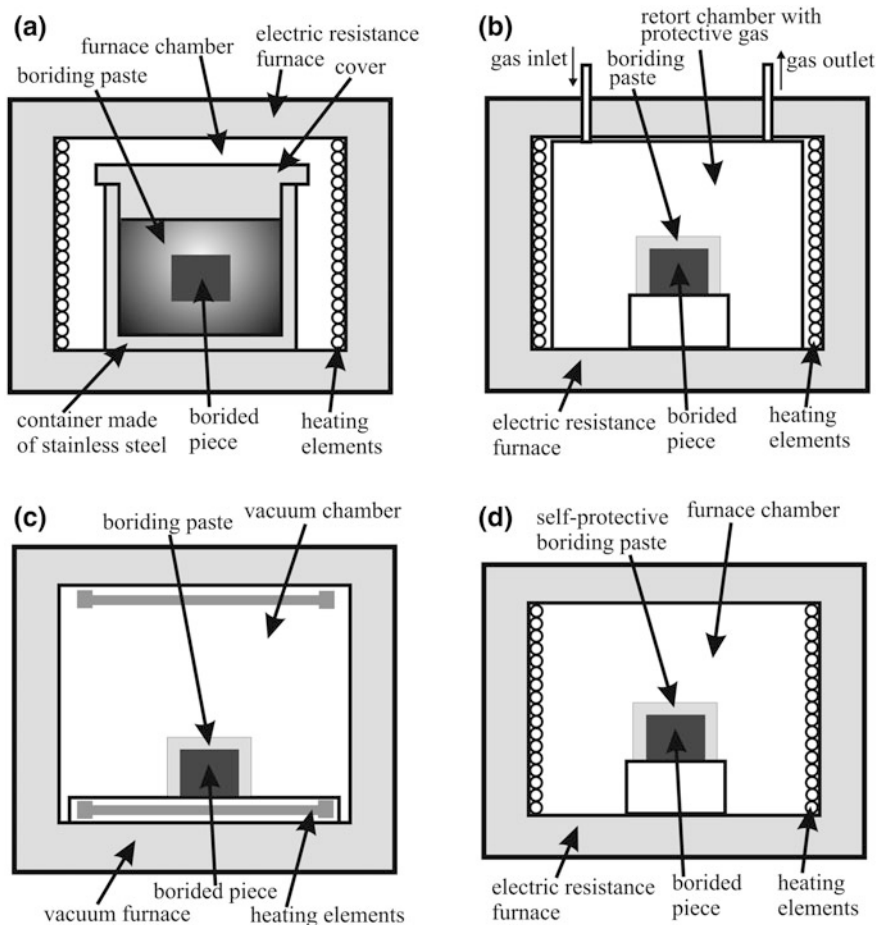


Fig. 4.3 Schematic representations of the most effective and easiest techniques of paste boriding: paste boriding in the typical electric resistance furnace using a closed container under air atmosphere (a), paste boriding in the typical electric resistance furnace in the presence of protective gas (e.g. argon, nitrogen or $N_2 + H_2$ mixture) (b), paste boriding in the chamber of vacuum furnace (c), paste boriding in the typical electric resistance furnace using a self-protective paste under air atmosphere (d). Remark: in the case of methods (b) and (c), the closed containers could also be used

paste, as shown in Fig. 4.3a. The paste boriding was carried out in a conventional electric resistance furnace without inert atmosphere.

However, the most widely used processes of paste boronizing required the use of a protective atmosphere, e.g. argon, nitrogen or $N_2 + H_2$ mixture (Campos et al. 2003, 2005, 2006a; Campos-Silva et al. 2008, 2010; Meneses-Amador et al. 2013). The method of such a boriding treatment was shown in Fig. 4.3b.

Instead of the process, applied in an inert gas, the paste boronizing could be carried out at reduced pressure, i.e. in a vacuum. Hence, such a method of protection against oxidation during paste boriding was also shown in Fig. 4.3c. The use of a special self-protective boriding paste (Lou et al. 2009) enabled to carry out the process in a typical electric resistance furnace without protective atmosphere (Fig. 4.3d).

The general characterization of the selected processes of paste boronizing of various materials was presented in Table 4.4, taking into account the composition of the paste used, its thickness, protective atmosphere, schematic representation of the method in Fig. 4.3, temperature and time of the treatment.

It was easy to notice that in recent years the paste boriding of iron alloys, especially steels, was developed first of all. Nickel and its alloys were the only non-ferrous alloys, which were subjected to this method of boronizing. Apart from the paste composition, the usually used other parameters of paste boriding of steels and Ni-based alloys were approximately as follows: the wide temperature range of 850–1050 °C (1123–1323 K), and a duration of 0.25–8 h. Current trends in paste boriding were represented by the use of the boriding paste, based on the mixture of boron carbide and cryolite ($B_4C + Na_3AlF_6$) with the addition of water. The ratio of B_4C to Na_3AlF_6 was usually not provided. Whereas the ratio of water to the mixture of boron carbide and cryolite was mostly about 1:5.

The most often used paste boriding processes were carried out in the typical electric resistance furnace in the presence of argon as a protective gas and, probably, without the use of container (Fig. 4.3b).

However, the special procedure of covering with a boriding paste was very often applied. The samples were placed in acrylic molds for the impregnation of paste and in order to control the paste thickness (Campos et al. 2005, 2006a, b, 2008a, b). Then, the covered pieces were usually dried at a temperature of 120 °C (393 K) for 20 min, in order to eliminate any water residues in the paste. Such a procedure caused that the paste boriding process became more complicated. After boriding process, the paste borided workpieces were usually directly quenched.

It was characteristic of paste borided Armco iron and carbon steels that the microstructure of boride layer usually consisted of only Fe_2B phase (Meléndez et al. 1997; Campos et al. 2003, 2005, 2008a; Ortiz-Domínguez et al. 2012; Meneses-Amador et al. 2013). Campos et al. (2003) tried to interpret such a situation by relatively low potential of boron. However, it was difficult and even impossible to define the boron potential during boriding in solid media. Probably, the boron supply by the atmosphere was limited compared to the powder-pack boriding. Hence, the single-phase Fe_2B layers were usually produced. The Fe_2B phase had often a needle-like (saw-tooth) nature. Only in case of paste borided

Table 4.4 General characterization of paste boriding

Type of material	Paste and its thickness/Protective atmosphere/Scheme of the method	Temperature (°C)/Time (h)	References
Armco iron	B ₄ C and activator, probably 1.5–3 mm/nitrogen/Fig. 4.3b	950–1050/1–4	Campos et al. (2003)
Low-carbon steels	B ₄ C + Na ₃ AlF ₆ paste, 4 mm/argon/Fig. 4.3b	850–1000/2–8	Ortiz-Domínguez et al. (2012)
	Water and B ₄ C paste with a ratio of 1:5, 4 mm/argon/Fig. 4.3b	850–1000/4–8	Meneses-Amador et al. (2013)
Medium-carbon steels	B ₄ C + Na ₃ AlF ₆ with 10–15% of water, 2–5 mm/N ₂ + H ₂ (90:10 or 95:5)/Fig. 4.3b	920–1000/2–6	Campos et al. (2005)
	Water and B ₄ C + Na ₃ AlF ₆ with a ratio of 1:5, 4 mm/argon/Fig. 4.3b	850–1000/8	Campos et al. (2008a)
High-carbon steels	DURBORID [®] (B ₄ C + Na ₃ AlF ₆) 2 mm/nitrogen/Fig. 4.3b	920/1–5	Meléndez et al. (1997)
Low-alloy steels	Distilled water and B ₄ C + Na ₃ AlF ₆ with a ratio of 1:5, 4 mm/argon/Fig. 4.3b	850–1000/2–8	Campos-Silva et al. (2010)
	80–86% nanodispersed MgB ₂ + 7–10% LiF + 7–10% NaF, 3 mm/unknown/probably Fig. 4.3b	800–900/0.25–2	Kostyk (2015)
High-alloy steels	Water and Dur-Ferrit (B ₄ C + Na ₃ AlF ₆) with a ratio of 1:5, 4–5 mm/argon/Fig. 4.3b	900–1000/4–6	Campos et al. (2006a)
	Water and B ₄ C + Na ₃ AlF ₆ with a ratio of 1:5, 3–4 mm/argon/ Fig. 4.3b	950–1000/2–6	Campos et al. (2006b)
	Water and B ₄ C + Na ₃ AlF ₆ with a ratio of 1:5, 3–4 mm/argon/ Fig. 4.3b	900–1000/4	Campos et al. (2008b)
	Distilled water and B ₄ C + Na ₃ AlF ₆ with a ratio of 1:5, 4–5 mm/argon/Fig. 4.3b	980–1000/2–6	Campos-Silva et al. (2008)
	DURBORID [®] (B ₄ C + Na ₃ AlF ₆) with 10–15% of water, 7 mm/ absence/Fig. 4.3a	900–1000/1–7	Doñu Ruiz et al. (2015)
Nickel and its alloys	Special self-protective paste/ absence/Fig. 4.3d	900–1050/2–5	Lou et al. (2009)

high-carbon steel (Meléndez et al. 1997), the smooth interface between the boride layer and the substrate appeared. The more hindered diffusion of boron in high-carbon substrate could be the reason for such a situation. Both the single-phase (Fe₂B) and the two-phase (FeB + Fe₂B) layers were fabricated on low-alloy steels (Campos-Silva et al. 2010; Kostyk 2015). Whereas the microstructure of paste borided high-alloy steels usually contained FeB and Fe₂B borides (Campos et al. 2006a, b, 2008b; Campos-Silva et al. 2008; Doñu Ruiz et al. 2015).

It was characteristic of the paste boriding process that the treated steels were usually quenched in oil from the boriding temperature. Sometimes, they were also tempered at 200 °C (473 K). The processes, carried out by Campos et al. (2003) and Doñu Ruiz et al. (2015) were the only exceptions. In case of paste borided AISI 304 steel (Campos et al. 2006a) such a treatment was unnecessary because the austenitic structure couldn't be hardened by the conventional heat treatment.

In the boride layer, produced on pure nickel with the use of special self-protective paste (Lou et al. 2009), the Ni_2B nickel borides were identified by XRD. The authors assumed a zonation of this layer and suggested the presence of Ni_3B zone below Ni_2B borides based on the differences in etching of these two zones and WDS analysis of chemical composition. Simultaneously, they confirmed an increased silicon content in the outer layer (Ni_2B) which was characterized by the high porosity. Probably, this porosity could be caused by the presence of nickel silicides (Kulka et al. 2014). It could be the reason for the other effect of etching the outer layer. Maybe, a special paste used for boronizing contained an amount of SiC. However, the authors didn't provide the paste composition. It was possible that the considered layer could consist of the mixture of Ni_3B and Ni_2B borides with some percentage of nickel silicides close to the surface. The XRD analysis of borided Nimonic[®]90-alloy with the use of the same paste confirmed the presence of CrB and Ni_2B borides (Lou et al. 2009). The authors also tried to find the zonation of the produced boride layer, indicating the possible formation of complex $(\text{Cr},\text{Ni},\text{Co})\text{B}$ and $(\text{Ni},\text{Co})_2\text{B}$ borides. However, like in the previous case, the boride layer was probably composed of the CrB + Ni_2B mixture.

Probably, the mechanism of formation of active boron atoms during paste boriding with the use of boron carbide (B_4C) as a boron source was similar to that-described for powder-pack boronizing.

4.2 Boriding in Liquid Media

The four main methods of *boriding in liquid media* were classified (see Fig. 2.1): boriding in chloride, fluoride or carbonate molten salt bath using reducers with boron, in the molten borate bath (e.g. in borax), in hydrous electrolytes and in fluidized bed (as a quasi-liquid method). The main advantages of the use of liquid media were as follows: the possibility of the direct quenching of steels after boriding, as well as energy saving compared to powder-pack boriding because of no need to heat the containers with powder mixture. The adherence of the bath residues to the borided pieces, the need for their removal and the need of continuous adding a fresh mixture to the bath were recognized as the main disadvantages of this boronizing method. Besides, such a process wasn't environmental friendly.

4.2.1 *Boriding in Chloride, Fluoride or Carbonate Molten Salt Baths Using Reducers with Boron*

Voroshnin and Lyakhovich (1978) reported that the *boriding in molten salt baths, not containing boron, with the use of reducers with boron* was proposed in 1949. The base composition of the salt bath could be the same as it was often applied during the typical heat treatment. The bath was composed of chlorides or fluorides (e.g. BaCl_2 , NaCl , KCl , CaCl_2 , NaF , LiF , KF) and could also contain the carbonates of alkaline elements (Li_2CO_3 , K_2CO_3 , Na_2CO_3). Such a method required the additional use of the reducers (reducing agents), containing boron, e.g. boron carbide (B_4C), ferroboration, potassium tetrafluoroborate (KBF_4) or amorphous boron. The increase in the percentage of these reducing agents above 15 wt% wasn't accompanied by the increased thickness of boride layers, produced on steels (Przybyłowicz 2000).

The process of *boriding in chloride, fluoride or carbonate molten salt baths using reducers with boron* was usually carried out at the temperatures in the range of 850–1050 °C (1123–1323 K) for 1–8 h in crucibles made of steels, of graphite or of ceramics (Al_2O_3 , SiO_2). In recent years, the various alloys were borided using this method, and the various molten salt baths were applied, e.g. CaCl_2 with boron to form iron borides on steels (Chernov et al. 1998, 1999), chlorides (KCl , BaCl_2) and sodium fluoride (NaF) with B_2O_3 and ferroboration during boriding of TiAl intermetallic compound (Yokota and Suzuki 2005) or chlorides (NaCl , KCl) and sodium fluoride (NaF) with addition of KBF_4 and boron to produce the boride layers on molybdenum (Kuznetsov et al. 2005) or on MoSi_2 (Kuznetsov et al. 2006). The low-temperature boronizing consisted in the use of the eutectic mixture of chlorides, fluorides or carbonates of alkaline elements with amorphous boron or boron carbide as a boron source. Such a process could be carried out at 550–700 °C (823–973 K) for 6–18 h and was described by Voroshnin and Lyakhovich (1978). They used the salt baths, consisting of fluorides (LiF , NaF , KF) with B_4C or of the same fluorides with B_4C and B_2O_3 . The addition of B_2O_3 caused an increase in the layer thickness. The fluoride and carbonate salt baths, containing tetraborates of alkaline elements (e.g. $\text{Li}_2\text{B}_4\text{O}_7$, $\text{K}_2\text{B}_4\text{O}_7$, $\text{Na}_2\text{B}_4\text{O}_7$) and reducing agents without boron (e.g. Si-Ca , Si-Mn or SiC) were also applied during low-temperature boriding. However, the effectiveness of this process required the significant increase in its duration. Koyama et al. (1983) tried to use the low-temperature process in order to boronize nickel, cobalt, iron, molybdenum, tantalum, titanium, niobium, and Hastelloy[®]B alloy in a salt bath, consisting of KF , KBF_4 and dispersed borides (NiB , FeB , MnB_2 , CrB_2 , ZrB_{12} , and GdB_6). Boronizing of nickel was the most effective, resulting in the formation of a 46 μm thick boride layer at 550 °C (823 K). However, it was related to extending the duration of the process up to 24 h.

In spite of the seeming simplicity, this method often required a special complicated procedure regarding the preparation of salt bath. Kuznetsov et al. (2005) described such a procedure with the use of the molten salts consisting of chlorides (NaCl , KCl), sodium fluoride (NaF) with addition of KBF_4 and B (10 wt%) as

reducing agents. The chemically pure alkali chlorides (NaCl and KCl) were dehydrated by heating (just above the melting point) under gaseous HCl atmosphere in a quartz ampule. Chemically pure NaF was additionally purified by heating in Ar atmosphere to a temperature of 50 °C above the melting point and slow cooling to a temperature of 50 °C below the melting point. At 120 °C (393 K), the re-solidified salt was transferred to a dry glove box, and the impurities were removed mechanically. KBF₄ was re-crystallized from a commercial product in HF, washed in ethyl alcohol and dried in a vacuum. Boron of purity of 99.0 wt% was used without a special treatment. NaCl, KCl, and NaF were blended in the required ratio, placed in a molybdenum crucible and transferred to a hermetically sealed retort made of stainless steel. The pressure in this retort was reduced to 0.67 Pa at room temperature and then the retort was gradually heated to 200, 400, and 600 °C (473, 673 and 873 K). Next, the retort was filled with argon of high purity and the mixture of salts were re-melted, kept at 800 °C (1073 K) for 3 h and cooled down to the room temperature. KBF₄ and boron were added to the crucible with the re-solidified melt.

Only after such a preparation of salt bath, the boronizing process could be carried out. The crucible with salt bath was put into the retort, and the pressure was reduced. Then the flow of argon was activated, and the retort was heated up to the desired temperature. Apart from the complicated procedure of preparation, such salt baths revealed the tendency to separation of the components due to the significant difference in the density of salts and reducing agents. There was also a need to supplement the bath with spent reducing agents. That was why the method of boronizing in chloride, fluoride or carbonate salt baths didn't find the wider application in recent years.

The schematic representations of the most often used processes of boriding in molten chloride, fluoride or carbonate salt baths using reducers with boron were shown in Fig. 4.4, taking into account the methods that were relatively easy to carry out. Due to the lack of accurate literature data, it was assumed that the unsealed crucibles, containing the salt bath and workpieces, were usually heated and held at boriding temperature in a typical electric resistance furnace (Voroshnin and Lyakhovich 1978; Koyama et al. 1983; Yokota and Suzuki 2005) or in an electrode furnace (Chernov et al. 1998, 1999) under air (Fig. 4.4a), i.e. in the absence of protective atmosphere. Protective atmosphere (e.g. argon) during such process, as it was shown in Fig. 4.4b, was applied rarely (Kuznetsov et al. 2005, 2006).

The general characterization of the processes of boronizing in molten salt baths, not containing boron, with the use of reducers with boron was shown in Table 4.5, taking into account the composition of the bath used, protective atmosphere, schematic representation of the method in Fig. 4.4, temperature and time of the treatment. The current trends were difficult to indicate because of the small number of References in relation to the considered boriding method. It could be noticed that there was usually no need to use a protective atmosphere during such a boriding process. Hence, in the majority of the studies, boronizing was carried out according to the scheme in Fig. 4.4a. Iron alloys as well as non-ferrous materials could be

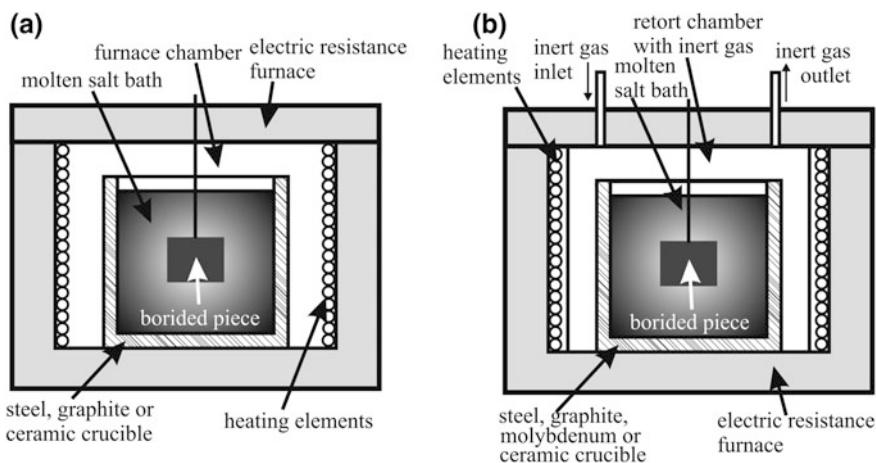


Fig. 4.4 Schematic representations of the most often used and easiest techniques of boriding in molten chloride, fluoride or carbonate salt baths using reducers with boron: boriding in the typical electric resistance furnace under air atmosphere using an unsealed crucible (a), boriding in the typical electric resistance furnace using an unsealed crucible in the presence of protective gas (e.g. argon) (b). *Remark: both the presented methods could be carried out in sealed crucibles or using electrode furnace*

effectively subjected to this method of boronizing. However, the available literature data showed the relatively small popularity of the method, probably, because of the disadvantages, mentioned above.

The low-temperature process of boriding of Armco iron in the fluoride molten salt bath using B_4C as a reducer resulted in the formation of single-phase Fe_2B layer (Voroshnin and Lyakhovich 1978). The addition of B_2O_3 (30 wt%) to such a bath increased the layer thickness and changed the microstructure of boride layer this way that the typical two-phase $FeB + Fe_2B$ layer of strong zonation appeared on the surface of Armco iron. The needle-like boride layers, produced on carbon and low-alloy steels in the chloride molten salt bath using boron as a reducer, were also characterized by the two-phase composition ($FeB + Fe_2B$) and a relatively high thickness (Chernov et al. 1998, 1999). As it was expected, if the high-alloy steel was used as a substrate, the interfaces between the boride zones and between Fe_2B layer and the substrate were smoother. After boronizing, the steels were quenched in aqueous solution of calcium chloride and tempered at a temperature in the range of 200–600 °C (473–873 K) depending on the grade of the steel.

Both the Mo_2B monolayer and the two-phase $MoB + Mo_2B$ boride layer could be produced using boriding of pure molybdenum in molten salt bath of composition: $NaCl + KCl + NaF + KBF_4 + 10 \text{ wt\% B}$ (Kuznetsov et al. 2005). The phase composition strongly depended on the temperature of boriding. The single-phase boride layer (Mo_2B) was produced by boronizing at 850 °C (1123 K). The increase in the boriding temperature up to 950 °C (1223 K) favored the formation of the $MoB + Mo_2B$ layer. Boron richer MoB phase appeared close to the surface.

Table 4.5 General characterization of boriding in chloride, fluoride or carbonate molten salt baths using reducers with boron

Type of material	Composition of the bath/Protective atmosphere/Scheme of the method	Temperature (°C)/Time (h)	References
Armco iron	20.3% LiF + 8.4% NaF + 41.3% KF + 30% B ₄ C/absence/Fig. 4.4a, unsealed crucible	550–700/6–18 Low-temperature process	Voroshnin and Lyakhovich (1978)
	11.6% LiF + 4.8% NaF + 23.6% KF + 30% B ₄ C + 30% B ₂ O ₃ /absence/Fig. 4.4a, unsealed crucible		
Medium-carbon steels	CaCl ₂ + 3% B/absence/Fig. 4.4a, unsealed crucible, electrode furnace	850–1000/1–5	Chernov et al. (1998, 1999)
High-carbon steels			
Low-alloy steels			
High-alloy steels			
Mo	NaCl + KCl + NaF + KBF ₄ + 10% B/argon/Fig. 4.4b, unsealed crucible	850–1050/7	Kuznetsov et al. (2005)
MoSi ₂		800–1000/5–7	Kuznetsov et al. (2006)
TiAl	30% KCl + 30% BaCl ₂ + 15% NaF + 2.3% B ₂ O ₃ + 22.7% ferroboron/absence/Fig. 4.4a, unsealed crucible	950/4–8	Yokota and Suzuki (2005)
Pure Ni, Co, Fe, Mo, Ta, Ti, Nb and Hastelloy®B alloy	KF + KBF ₄ with dispersed borides (NiB, FeB, MnB ₂ , CrB ₂ , ZrB ₁₂ , and GdB ₆)/absence/Fig. 4.4a, unsealed crucible	500–670/up to 24 Low-temperature process	Koyama et al. (1983)

The Mo₂B borides were visible below the MoB zone. The interfaces between these borides as well as between the Mo₂B zone and the substrate material were smooth. The MoSi₂ layer, produced by siliciding of pure Mo, was subjected to boronizing in the same molten salt bath by Kuznetsov et al. (2006). In general, the produced boride layers were composed of the mixture of silicides and borides with smooth interface between the layer and the substrate material (pure Mo). The MoSi₂ phase was partially or completely transformed to the Mo₅Si₃ phase depending on the boriding temperature. At the temperatures equal to or below 950 °C (1223 K), only partial transformation of MoSi₂ phase proceeded. Whereas it was completely transformed to the Mo₅Si₃ and boride phases at 1000 °C (1273 K). Simultaneously, Mo peaks appeared in the XRD pattern. The types of molybdenum borides in the boride layer also depended on the temperature of process. At 750 °C (1023 K) the Mo₂B borides appeared. The increase in the temperature up to 800 °C (1073 K) caused that Mo₂B became the matrix phase, and the increase in duration of boronizing up to 8 h lead to the formation of Mo₂B₅ as the matrix phase. At 900 °C (1173 K) after 5 h, the MoB borides were formed. They transformed into Mo₂B₅ phase after 5 h of the process. At 1000 °C (1273 K) only Mo₂B₅ borides occurred in the boride layer.

The TiAl intermetallic compound was boronized by Yokota and Suzuki (2005) in molten salt bath, containing chlorides, fluorides and reducers with boron. The boride layer contained TiB_2 borides. Below TiB_2 borides, the Al_3Ti phase appeared. The dispersed borides was used by Koyama et al. (1983) as the reducers. Among these borides, NiB seemed to be most effective. A 46 μm thick boride layer was produced on pure nickel at 550 °C (823 K) for less than 24 h.

The mechanism of formation of active boron atoms during boriding in molten salt baths without electrolysis was described in detail by Przybyłowicz (2000). Initially, it was supposed that active boron atoms were formed as a consequence of chemical reaction of the bath with reducer. However, a different mechanism was proposed by Ilyushchenko and Belyaeva (1968) for the formation of active aluminum atoms during aluminizing of steels. It was based on the electrochemical effect and was developed by Lyakhovich et al. (1972) for boronizing in molten salt baths. According to this theory, the formation of boride layers could proceed as a consequence of appearance of boron subions in the salt bath and their diffusion and convection transport to the saturated surface. Simultaneously, in the system: cathode (borided workpiece)—molten and dissociated electrolyte—anode (reducer) the short shorted galvanic cells acted just as corrosive micro-cells. Hence, the active boron atoms could be formed by disproportionation of boron subions on the workpiece surface and by electrochemical reduction (operation of galvanic cells).

In case of the boriding process in molten chloride or fluoride salt baths, not containing boron, with the use of reducers with boron, the first mechanism (i.e. noncurrent transport) predominated (Przybyłowicz 2000). Kuznetsov et al. (2005) described this mechanism for such a boriding process of molybdenum. The formation of lower valence boron at the interface of the boron-containing powder and the ionic melt could proceed as follows:



Boron ions of lower valence reached the metallic substrate by the usual mass-transfer mechanism through the ionic melt and disproportionate at the melt/metal interface giving energetically more favorable borides. Exceeding the formulated reaction (Kuznetsov et al. 2005) to any metal, it would be as follows:



4.2.2 Boriding in Molten Borate Baths Using Reducers with Boron

The more popular boronizing in liquid media was carried out in molten borate baths, especially in borax (sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7$). According to the Fig. 2.1, the three methods of *boriding in molten borate baths* were classified: with the use

of reducing agents containing boron, with the use of reducers without boron and electrochemical process.

As it was reported by Przybyłowicz (2000), *boriding in molten borate baths using reducers with boron* was proposed by Blanter and Besedin (1955). They used borax bath ($\text{Na}_2\text{B}_4\text{O}_7$) with the addition of 40 wt% of boron carbide (B_4C) as a reducer. This method was characterized by a high rate of saturation with boron. Although the addition of 50–55 wt% B_4C seemed to be the most effective (Blanter and Besedin 1955; Voroshnin and Lyakhovich 1978), the too high viscosity of such a bath was observed. Hence, the amount of boron carbide was usually reduced to 30 wt% (Simonenko et al. 1982, 1985; Allaoui et al. 2006; Rayane and Allaoui 2015; Kul et al. 2016). Borax and boron carbide were mixed at ambient temperature. However, boron carbide was very expensive. Therefore, it was often replaced by the even more expensive boron, but added to the borax in smaller quantities (Koyama et al. 2011a, b). Sometimes, the bath consisted of the mixture of $\text{Na}_2\text{B}_4\text{O}_7$ and NaBF_4 (Yokota et al. 2003; Yokota and Suzuki 2005).

Apart from the composition of a bath, the other parameters of boriding in molten borate bath using reducers with boron were similar to those applied during the process in salt baths, not containing boron, with the use of reducing agents with boron. So, the process was usually carried out at the temperatures in the range of 850–1050 °C (1123–1323 K) for 0.5–8 h in steel, graphite or ceramic crucibles. The most often used techniques were schematically represented in Fig. 4.5. Many authors didn't report their methods used in detail. The provided data were usually limited to the main components of a bath (often without their percentage), temperature and duration of the process. Only Yokota and Suzuki (2005) showed the schematic illustration of the proposed boriding, and the construction of crucibles was given by Simonenko et al. (1985).

Hence, it was assumed that some methods were characterized by the use of unsealed crucible under air atmosphere (Fig. 4.5a). The double crucible, composed of graphite crucible inside a protective steel container (Fig. 4.5b), was proposed by Simonenko et al. (1985).

However, recently the sealed ceramic crucible was applied under air atmosphere (Kul et al. 2016). Such a method was shown in Fig. 4.5c, also taking into account the possibility of the use of a protective atmosphere (e.g. an inert gas). The induction heating (Simonenko et al. 1982) could be also used during the considered boriding (Fig. 4.5d).

The general characterization of boronizing in molten borate bath using reducing agents with boron was presented in Table 4.6, revealing the composition of the bath used, protective atmosphere, schematic representation of the method in Fig. 4.5, temperature and time of the treatment. Although the use of other tetraborates was mentioned by Voroshnin and Lyakhovich (1978), the current trends indicated that borax baths were commonly used borate baths, and the boron carbide was still the main reducing agent. No protective atmosphere was usually applied. So, the most often used method has been similar to this presented in Fig. 4.5a. Iron alloys, especially steels and ductile cast iron, could be effectively subjected to this method of boronizing. The non-ferrous materials were also borided with this process, but much more rarely.

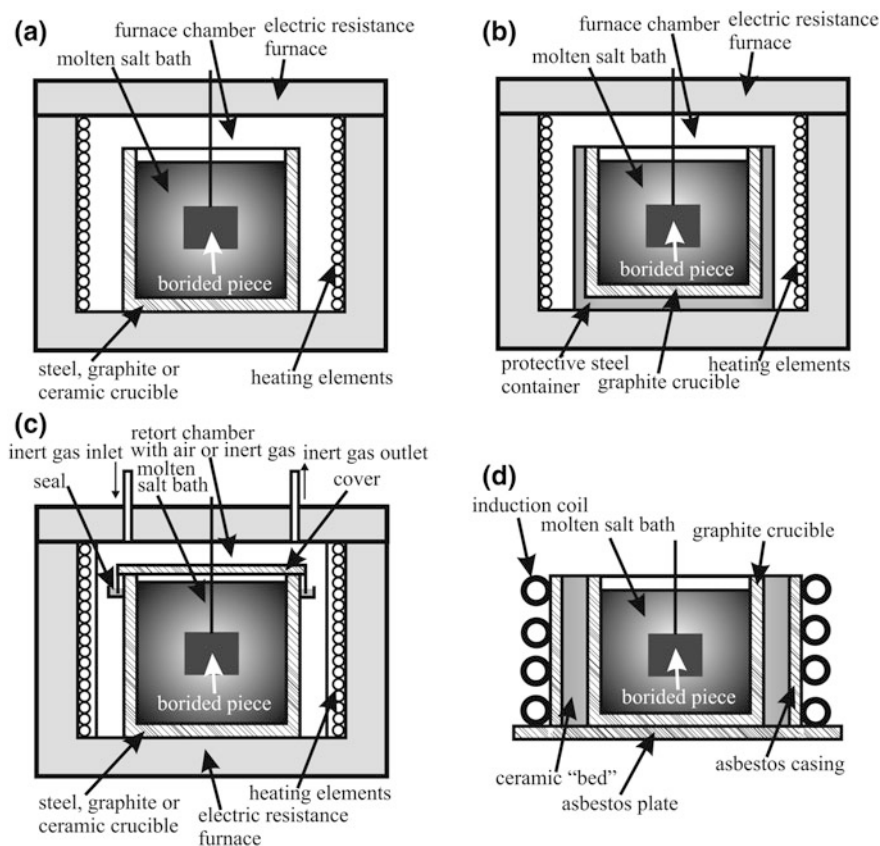


Fig. 4.5 Schematic representations of the most often used and easiest techniques of boriding in molten borate baths using reducers with boron: boriding in the typical electric resistance furnace under air atmosphere using an unsealed crucible **(a)**, boriding in the typical electric resistance furnace under air atmosphere using an unsealed double crucible **(b)**, boriding in the typical electric resistance furnace under air or protective atmosphere using a sealed crucible **(c)**, boriding by the induction heating under air atmosphere using an unsealed crucible **(d)**. *Remark: the presented methods in (a) and (b) could be carried out in sealed crucibles*

Boriding of medium-carbon steel in molten borax bath using B_4C as a reducer resulted in the formation of the typical two-phase $FeB + Fe_2B$ layer with a typical zonation (Allaoui et al. 2006; Rayane and Allaoui 2015). Simonenko et al. (1982, 1985) also obtained the two-phase boride layer ($FeB + Fe_2B$) on the surface of high-carbon steels as well as of low-alloy steels using the same molten borax bath with B_4C . However, the FeB zone was discontinuous. The similar boride layer, with FeB zone close to the surface and Fe_2B zone below the first one, was produced by Kul et al. (2016) on the surface of ductile cast iron with the use of the bath of the same composition. A needle-like (saw-tooth) nature was typical of these iron borides. The authors didn't mention about the heat treatment after boronizing.

Table 4.6 General characterization of boriding in molten borate baths using reducers with boron

Type of material	Composition of the bath/Protective atmosphere/Scheme of the method	Temperature (°C)/Time (h)	References
Medium-carbon steels	70% $\text{Na}_2\text{B}_4\text{O}_7$ + 30% B_4C /absence/Fig. 4.5a, unsealed crucible	950/4	Allaoui et al. (2006)
	70% $\text{Na}_2\text{B}_4\text{O}_7$ + 30% B_4C /absence/Fig. 4.5a, unsealed crucible	850–1050/2–6	Rayane and Allaoui (2015)
High-carbon steels	70% $\text{Na}_2\text{B}_4\text{O}_7$ + 30% B_4C /absence/Fig. 4.5d, unsealed graphite crucible	900/1–3	Simonenko et al. (1982)
	70% $\text{Na}_2\text{B}_4\text{O}_7$ + 30% B_4C /absence/Fig. 4.5a,b, unsealed crucible made of medium-carbon or stainless steel or unsealed graphite crucible in a protective case made of medium-carbon steel	960/1	Simonenko et al. (1985)
Low-alloy steels	70% $\text{Na}_2\text{B}_4\text{O}_7$ + 30% B_4C /absence/Fig. 4.5d, unsealed graphite crucible	900/1–3	Simonenko et al. (1982)
	70% $\text{Na}_2\text{B}_4\text{O}_7$ + 30% B_4C /absence/Fig. 4.5a,b, unsealed crucible made of medium-carbon or stainless steel or unsealed graphite crucible in a protective case made of medium-carbon steel	960/1	Simonenko et al. (1985)
High-alloy steels	$\text{Na}_2\text{B}_4\text{O}_7$ + 1–7% B/absence/Fig. 4.5a, unsealed crucible	927/4	Koyama et al. (2011a)
	$\text{Na}_2\text{B}_4\text{O}_7$ + 4% B/absence/Fig. 4.5a, unsealed crucible	850–950/0.5	Koyama et al. (2011b)
Ductile cast iron	70% $\text{Na}_2\text{B}_4\text{O}_7$ + 30% B_4C /absence/Fig. 4.5c, sealed ceramic crucible	950/4	Kul et al. (2016)
MoSi_2	$\text{Na}_2\text{B}_4\text{O}_7$ + NaBF_4 with ratios 9:1, 4:1, 7:3/absence/Fig. 4.5a, unsealed crucible	1000/3	Yokota et al. (2003)
TiAl	$\text{Na}_2\text{B}_4\text{O}_7$ + NaBF_4 with ratios 1:2, 3:4, 1:1, 3:2, 2:1/absence/Fig. 4.5a, unsealed crucible	950/4–8	Yokota and Suzuki (2005)

The boride layers were also fabricated on the surface of austenitic steel using molten borax bath with boron as a reducer (Koyama et al. 2011a, b). Their phase composition depended on the boron content in the bath as well as on the boriding temperature. The obtained boride zones were smooth because of the high concentration of alloying elements (especially chromium and nickel). The basic phases were FeB and Fe_2B of strong zonation. Besides, chromium borides (CrB , Cr_2B , or even Cr_5B_3) were identified in the boride layer, especially, if the bath contained low boron content (<4%) or if the boriding temperature was relatively low, i.e. up to 900 °C (1173 K). The higher boron content in borate bath as well as the higher temperature of boronizing favored the formation of the thick FeB zone.

The microstructure of the boride layers, produced on the considered non-ferrous materials by boriding in molten borax baths with the use of reducers with boron, was more complex. The MoSi_2 intermetallic compound was fabricated using arc melting by Yokota et al. (2003) and then subjected to boronizing in molten borax bath with addition of NaBF_4 . The starting material also contained Mo_5Si_3 phase. The authors obtained the layer which was composed of Mo_2B_5 borides and Mo_5Si_3 phase. Because of the absence of MoSi_2 in the layer, they concluded that only this phase could be borided.

The TiAl intermetallic compound was borided by Yokota and Suzuki (2005) in molten borax bath with addition of NaBF_4 . The microstructure of the produced layers strongly depended on the boriding time as well as on the $\text{Na}_2\text{B}_4\text{O}_7/\text{NaBF}_4$ ratio. If this ratio was equal to 0.5, the TiB and Ti_3B_4 titanium borides appeared in the layer after boriding for 4 h. The longer duration of the process (8 h) resulted in the formation of TiB_2 borides on the TiAl substrate. The increase in $\text{Na}_2\text{B}_4\text{O}_7/\text{NaBF}_4$ ratio up to 0.75 caused the appearance of Al_3Ti phase below TiB or TiB_2 borides, as a consequence of boriding for 4 or 8 h, respectively. If the ratio of borax to sodium tetrafluoroborate was equal to 1, the titanium borides weren't indicated by XRD. The further increase in this ratio above 1 usually resulted in the formation of TiB_2 titanium borides on the TiAl substrate, irrespective of the applied time of the process. Boriding for 8 h at the $\text{Na}_2\text{B}_4\text{O}_7/\text{NaBF}_4$ ratio equal 2 was an only exception. In this case, the boride layer was composed of TiB borides.

As for the previous method, the active boron atoms also could be formed by disproportionation of boron subions on the workpiece surface and by electrochemical reduction (operation of galvanic cells). Predominance of some of these mechanisms depended on the conditions, determining the possibility of contact of reducer and workpiece as well as on the size of reducer particles (Przybyłowicz 2000).

4.2.3 *Boriding in Molten Borate Baths Using Reducers Without Boron*

In recent years, the very expensive reducers, containing boron (as boron carbide or amorphous boron), were replaced by chemically active metals or their alloys with iron (ferroalloys) as well as by silicon carbide (SiC). Therefore, ***boriding in molten borate baths using reducers without boron*** became the most popular process in liquid media, excluding the ***electrochemical boriding***.

The tetraboranes of alkaline elements (Li , Na , K) could be used to prepare the borate bath (Hill and Stapleton 1965). However, borax ($\text{Na}_2\text{B}_4\text{O}_7$) was most often applied. As it was reported by Przybyłowicz (2000), Ca , Li , Be , Ce , Mg , Al and Ti could become the reducers. However, their chemical affinity to oxygen should be higher than boron. Then, the reduction proceeded and release of boron atoms, required for saturation, occurred. The high chemical affinity of some reducing agents caused that the use of protective atmosphere was required during their

mixing with borax (Przybyłowicz 2000). Voroshnin and Lyakhovich (1978) used the ferroalloys (ferromanganese Fe–Mn or ferrosilicon Fe–Si) as reducers. This prevented the rapid oxidation of a reducer and increased the boriding ability of a bath. The ability to frothing and the ejection of bath during the mixing of the reducing agent with borax was also diminished.

The process of boriding in molten borate baths using the reducing agents without boron was usually carried out at the temperatures in the range of 800–1100 °C (1073–1373 K) for 0.5–8 h in steel, graphite or ceramic crucibles. The most often used techniques were schematically represented in Fig. 4.6. If silicon carbide (SiC) was used as a reducer (Allaoui et al. 2006; Bouaziz et al. 2009) the preparation of a bath could be carried out at ambient temperature without protective gas. Hence, the boriding process also didn't require to use the protective atmosphere (e.g. inert gas) and could be carried in the unsealed crucible under air atmosphere as it was shown in Fig. 4.6a. However, if Al was used as a reducing agent (Allaoui et al. 2006; Koyama et al. 2011c; Mariani et al. 2015a, b; Anzawa et al. 2017), its mixing with borax occurred in the liquid state, and the protective atmosphere seemed to be necessary even though at the stage of mixing. Such a process was also represented by Fig. 4.6a as an optional method. The very popular boriding in $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3 + \text{Fe-Si}$ (ferrosilicon) molten bath was developed by Bindal (1991). However, due to the lack of access to this Reference, it was difficult to classify this method according to the Fig. 4.6. Taking into account that the seal of the crucible was usually indicated by the authors, it was assumed that this process was carried out in the unsealed crucible.

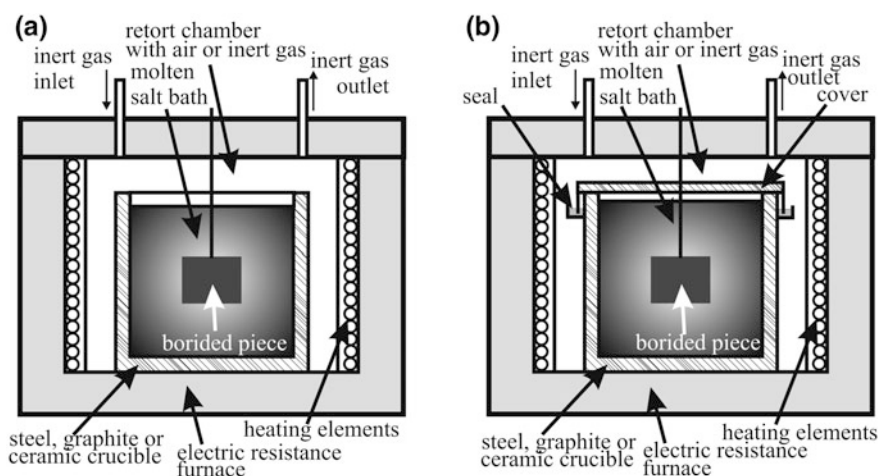


Fig. 4.6 Schematic representations of the most often used and easiest techniques of boriding in molten borate baths using reducers without boron: boriding in the typical electric resistance furnace under air or protective atmosphere using an unsealed crucible (a), boriding in the typical electric resistance furnace under air or protective atmosphere using a sealed crucible (b). *Remark: the protective atmosphere could be used only during the addition of the reducing agent*

However, maybe a protective inert atmosphere was necessary during the mixing of such a borate bath with the reducing agent (Fe–Si). Hence, the methods reported by Üçisik and Bindal (1997), Bindal and Üçisik (1999), Sen et al. (2004), Köksal (2009), Kaouka et al. (2013, 2014) were classified as the boriding under air or argon atmosphere in unsealed crucible (Fig. 4.6a). Although the process with the use of sealed crucible was rarely carried out (Sen 2005; Kul et al. 2016), such a method was shown in Fig. 4.6b with the optional use of protective atmosphere.

The general characterization of boriding in molten borate bath using reducing agents without boron was shown in Table 4.7, taking into account the available literature data regarding the composition of the bath, protective atmosphere, schematic representation of the method in Fig. 4.6, temperature and time of the treatment. The current trends showed that the commonly used borate baths were also composed mainly of borax. The most often used reducers have been as follows: ferrosilicon, silicon carbide and aluminum. The protective atmosphere was usually used only during the mixing of borax with the reducing agent of high chemical affinity (e.g. Al). The predominant method consisted in the use of unsealed crucibles. So, the most often applied methods corresponded to the schematic representation in Fig. 4.6a. Iron alloys, especially steels, ductile cast iron as well as ductile alloy cast iron were effectively borided in molten borax bath using reducing agents without boron. The non-ferrous materials were more rarely subjected to this method. WC–Co sintered carbide represented such a non-ferrous material.

The microstructure of iron alloys after boriding in molten borate baths using reducers without boron was similar to that-obtained by the other thermochemical techniques. The typical two-phase (FeB + Fe₂B) boride layers with strong zonation were produced on the low-carbon steels (Üçisik and Bindal 1997), on medium-carbon steels (Allaoui et al. 2006; Kaouka et al. 2013, 2014) as well as on low-alloy steels (Üçisik and Bindal 1997; Bindal and Üçisik 1999; Anzawa et al. 2017) using ferrosilicon (Fe–Si) or Al as a reducer. Sometimes, the possible formation of borides of alloying elements, such as CrB, Cr₂B, MnB or Mn₂B, was also suggested in case of boriding of low-alloy steels (Üçisik and Bindal 1997; Bindal and Üçisik 1999). After boriding of low-alloy steel, Sen (2005) reported the boride layer which was composed mainly of FeB phase based on the results of XRD. However, the presence of Fe₂B borides at higher depth was also probable. The single-phase Fe₂B layer was usually produced with the use of SiC as a reducer (Allaoui et al. 2006; Bouaziz et al. 2009). The two-phase boride layer, consisting mainly of FeB and Fe₂B phases, was also fabricated on the surface of austenitic steel (Koyama et al. 2011c). However, in this case the significant percentage of CrB and Cr₂B chromium borides was confirmed. The ductile cast iron was borided by Sen et al. (2004) in Na₂B₄O₇ + H₃BO₃ + Fe–Si molten borate bath. The produced two-phase boride layer (FeB + Fe₂B) included the nodular graphite. Kul et al. (2016) used the various molten borate baths and reducers in order to form the boride layer on the same material. The best effect in respect of the hardness and thickness of boride layer was obtained as a consequence of boriding in 65% Na₂B₄O₇ + 10% NaOH + 25% Fe–Si molten borate bath. The boride layer also

Table 4.7 General characterization of boriding in molten borate baths using reducers without boron

Type of material	Composition of the bath/Protective atmosphere/Scheme of the method	Temperature (°C)/Time (h)	References
Low-carbon steels	$\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3 + \text{Fe-Si}$ /absence or argon/Fig. 4.6a, unsealed crucible	940/5–7	Üçisik and Bindal (1997)
Medium-carbon steels	70% $\text{Na}_2\text{B}_4\text{O}_7 + 30\%$ SiC or 70% $\text{Na}_2\text{B}_4\text{O}_7 + 30\%$ Al/absence or argon/ Fig. 4.6a, unsealed crucible	950/4	Allaoui et al. (2006)
	70% $\text{Na}_2\text{B}_4\text{O}_7 + 30\%$ SiC/absence/ Fig. 4.6a, unsealed crucible	850–1000/2–8	Bouaziz et al. (2009)
	60% $\text{Na}_2\text{B}_4\text{O}_7 + 20\%$ $\text{H}_3\text{BO}_3 + 20\%$ Fe–Si/ absence or argon/ Fig. 4.6a, unsealed crucible	800–1000/2–8	Kaouka et al. (2013)
	60% $\text{Na}_2\text{B}_4\text{O}_7 + 20\%$ $\text{H}_3\text{BO}_3 + 20\%$ Fe–Si/ absence or argon/ Fig. 4.6a, unsealed crucible	800–1000/2–8	Kaouka et al. (2014)
Low-alloy steels	$\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3 + \text{Fe-Si}$ /absence or argon/ Fig. 4.6a, unsealed crucible	940/5–7	Üçisik and Bindal (1997)
	$\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3 + \text{Fe-Si}$ /absence or argon/ Fig. 4.6a, unsealed graphite crucible	940/5–7	Bindal and Üçisik (1999)
	$\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3 + \text{Fe-Si}$ /absence or argon/ Fig. 4.6b, sealed crucible	900/4	Sen (2005)
	90% $\text{Na}_2\text{B}_4\text{O}_7 + 10\%$ Al/absence or argon/ Fig. 2.8a, unsealed crucible	1030/0.5–2	Anzawa et al. (2017)
High-alloy steels	90% $\text{Na}_2\text{B}_4\text{O}_7 + 10\%$ Al/absence or argon/ Fig. 4.6a, unsealed crucible	850–950/2	Koyama et al. (2011c)
Ductile cast iron	$\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3 + \text{Fe-Si}$ /absence or argon/ Fig. 4.6a, unsealed graphite crucible	850–950/2–8	Sen et al. (2004)
	65% $\text{Na}_2\text{B}_4\text{O}_7 + 10\%$ Na_2CO_3 (or NaOH or B_2O_3 or CaCl_2) + 25% Fe–Si; 70% $\text{Na}_2\text{B}_4\text{O}_7 + 30\%$ Al or SiC/absence/ Fig. 4.6b, sealed ceramic crucible	950/4	Kul et al. (2016)
Ductile alloy cast iron	90% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + 10\%$ Al/absence or argon/ Fig. 4.6a, unsealed crucible	850–950/2–4	Mariani et al. (2015a, b)
WC–Co	$\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_3\text{BO}_3 + \text{Fe-Si}$ /absence or argon/ Fig. 4.6a, unsealed stainless steel container	900–1100/1–4	Köksal (2009)

consisted of FeB and Fe₂B phases with nodular graphite. The similar microstructure characterized the borided alloy ductile cast iron (Mariani et al. 2015a, b).

The additional heat treatment wasn't usually carried out after boronizing of iron alloys in molten borate baths using reducers without boron. The borided samples were often cooled in air (Bindal and Üçisik 1999; Sen et al. 2004; Sen 2005; Allaoui et al. 2006; Kaouka et al. 2013; Anzawa et al. 2017). Only Mariani et al. (2015a, b) proposed the special heat treatment of boronized ductile alloy cast iron. Boriding process followed by austempering was called boroaustempering. Just after boriding, the samples were transferred to the austempering salt bath. The isothermal austempering was carried out at 240, 300 or 360 °C (513, 573 or 633 K) for 4 h. After this treatment, the samples were removed from the salt bath and cooled in air. Boroaustempering caused the increase in wear resistance of borided ductile alloy cast iron compared to the borided and air cooled material.

WC–Co sintered carbide was the only analyzed non-ferrous material, subjected to boriding in molten borate bath using reducer without boron. The microstructure of borided layer was composed of hard phases, containing boron, such as WCoB, W₂CoB₂, W₂B₅, W₃CoB₃ and CoB. These phases occupied the grain boundary areas in sintered carbide. The presence of WC particles within the diffusion layer indicated that they were more prone to dissolving than the particles of other carbides, such as TiC or Ta(Nb)C.

During boriding in molten borate baths using reducers without boron, the predominant mechanism of active boron formation consisted in electrochemical reduction, i.e. operation of galvanic cells (Przybyłowicz 2000).

4.2.4 *Electrochemical Boriding in Molten Salt Baths*

Electrochemical boriding (EB) in molten salt baths became the most effective and, hence, the most popular method of boriding in liquid media in recent years. The main advantages of such a process concerned the possibility of the use of lower temperature and significantly shorter duration in order to form boride layers on the surface of various materials compared to many other methods.

The process was also called **electrolytic boriding** (Voroshnin and Lyakhovich 1978; Makyta et al. 1984; Fuda et al. 1991; Huang et al. 2013) because of the electrolysis phenomenon used. Electrolysis was well-known as a technique that used a direct electric current (DC) to drive a chemical reaction, being otherwise non-spontaneous. However, during the considered process the electrolytic dissociation was usually accompanied by thermal dissociation, and the adsorption and subsequent diffusion of atomic boron into the interstitial positions of the substrate occurred as a consequence of thermal driving forces and the gradient of boron concentration. Therefore, the term electrochemical boriding seemed to be more

accurate (Bonomi et al. 1973; Matiašovský et al. 1988; Segers et al. 1991; Kartal et al. 2005; Kahvecioglu et al. 2011; Sista et al. 2011).

Yukin (1971) analyzed the first stage of such a process in molten borax, related to the reduction of boron on the cathode, using even the term electroplating with boron. The mechanism of the cathode process was also analyzed by Makyta et al. (1984) in the systems $\text{LiF} + \text{KF} + \text{KBF}_4$ and $\text{LiF} + \text{KF} + \text{B}_2\text{O}_3$. Kartal and Timur (2013) implemented the term CRTD-Bor method (i.e. Cathodic Reduction and Thermal Diffusion based Boriding), including the two main mechanisms of the process. In recent years, the electrochemical boriding was intensively developed. Its modification consisted in applying the two-stage process in which the typical process was followed by phase homogenization (PH) in order to produce the single-phase boride layer (Kartal et al. 2011; Kartal Sireli et al. 2017). Electrochemical boriding was combined with a PH treatment, carried out in the same boriding bath without any extra effort. After a first stage of electrolysis, the source of direct current was turned off and the cathode (borided pieces) was left in the bath without any polarization.

In general, electrochemical boriding could be implemented in molten salt bath, not containing boron, with the use of reducing agents with boron (Bonomi et al. 1973, 1978; Makyta et al. 1984; Matiašovský et al. 1988) as well as in molten borax baths (Segers et al. 1991; Kahvecioglu et al. 2011; Sista et al. 2011), also containing chlorides (Matiašovský et al. 1988; Segers et al. 1991; Kartal et al. 2005, 2006) or carbonates (Kartal et al. 2006, 2010a, b, 2011; Kartal and Timur 2013; Sista et al. 2013; Kilic et al. 2013; Huang et al. 2013; Kartal Sireli et al. 2017). The process was also sporadically carried out in other baths, e.g. the mixture of B_2O_3 and Na_2O (Kartal et al. 2006).

NaCl was added to borax in order to decrease the viscosity of the bath, especially, if the process proceeded at the relative low temperature (Segers et al. 1991). The electrolyte supplementary sodium chloride was stepwise replaced with sodium or potassium carbonate due to the corrosion effect on the electrode connectors (Kartal et al. 2010b; Huang et al. 2013). The carbonates accelerated the boron diffusion into the material and adjusted electrolyte viscosity and conductivity. The electrochemical boriding was usually carried out at the temperatures of 700–1000 °C (973–1273 K) in graphite crucibles, acting as an anode, whereas the borided pieces acted as the cathode. The increased temperature, up to 1200 °C (1473 K), was applied only during boriding of pure titanium (Kartal and Timur 2013; Kilic et al. 2013). However, many authors decided to elevate the process temperature in order to shorten its duration. The time of electrochemical boriding ranged from only 30 s (Segers et al. 1991) to 8 h in case of commercially pure titanium (Huang et al. 2013) or even 10 h for boronized medium-carbon steel (Bonomi et al. 1978). Although the wide range of process duration was studied, the shortest times of treatment (below 10 min) had only a cognitive significance. The cathodic current density was usually given as the next important parameter of electrochemical boronizing. Its values ranged from 5 up to 1120 mA/cm^2 . However, many authors (Kartal et al. 2010a, b, 2011; Kartal and Timur 2013; Sista et al. 2013; Huang et al. 2013; Kartal Sireli et al. 2017) indicated the range of 200–300 mA/cm^2 as the most advisable for practical

applications. The use of the current density above 300 mA/cm^2 usually didn't cause a significant increase in the boride layer thickness. It was observed for both iron alloys (Segers et al. 1991; Kartal et al. 2005) and commercially pure titanium (Kilic et al. 2013). However, the use of the current density up to 500 mA/cm^2 (Kahvecioglu et al. 2011; Kahvecioglu Feridun et al. 2015) still increased the thickness of boride layer produced on nickel aluminide (Ni_3Al) or pure Mo.

The salt bath, used for electrochemical boriding, often required a special preparation. The mixture of fluorides and KBF_4 was dried directly in the cell at a temperature of 400°C (673 K) under argon for 15 h (Bonomi et al. 1973). Next, the temperature was raised to 830°C (1103 K) and then residual water and other impurities of the bath were removed by pre-electrolysis on a copper cathode. The more complicated procedure was applied by Makyta et al. (1984). They used lithium fluoride (LiF), potassium fluoride dihydrate ($\text{KF}\cdot 2\text{H}_2\text{O}$) and potassium tetrafluoroborate (KBF_4) or boron trioxide (B_2O_3) to prepare the salt bath. $\text{KF}\cdot 2\text{H}_2\text{O}$ was preliminary dried over P_2O_5 , at 30°C (303 K) in vacuum for about 150 h, and then at 200°C (473 K) in vacuum for the next 150 h. LiF , KBF_4 and B_2O_3 were dried in vacuum at 200°C (473 K). $\text{Li} + \text{KF}$ mixture was then premelted at 900°C (1173 K) in an inert atmosphere. The final stage in the purification of this basic electrolyte consisted in the pre-electrolysis, which was carried out at 700°C (973 K) for 48 h using graphite anode and cathode. Only then, the adequate amount of the electrochemically active component (KBF_4 or B_2O_3) could be added to the basic electrolyte.

Although the borax bath also required the special procedure of preparation, it was often omitted by many authors. Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) was premelted twice under argon atmosphere (Segers et al. 1991). Huang et al. (2013) mentioned that $\text{Na}_2\text{B}_4\text{O}_7$ and K_2CO_3 were dried at 150°C (423 K) for 24 h before use, and then mixed with an adequate ratio. More details in relation to the preparation of borax baths in industrial steel electrolytic tanks, applied for electrochemical boriding, were provided by Przybyłowicz (2000). At first, the electrolytic tank was usually filled with borax to half its height and heated up to $500\text{--}650^\circ\text{C}$ ($773\text{--}923 \text{ K}$) in order to dry this component of bath. Then, the temperature was increased above the melting point of borax, and the additional portions of sodium tetraborate were evenly scattered on the surface of a bath. Finally, the borax bath was subjected to pre-electrolysis for 10–15 h in order to purify the bath from impurities.

The surface of boronized pieces, acting as a cathode material, were also specially prepared before the process. They could be degreased in ethanol and then etched for two minutes in a 25 vol% hydrochloric acid aqueous solution (Segers et al. 1991). Sometimes, they were only polished in order to degrease the surface and obtain an adequate surface roughness (Kartal et al. 2006; Sista et al. 2011). The most often used preparation of the borided pieces consisted in polishing and ultrasonic degreasing in acetone (Kartal et al. 2010a, b, 2011; Kahvecioglu et al. 2011; Sista et al. 2013; Kartal and Timur 2013; Kartal Sireli et al. 2017).

The main equipment, required to electrochemical boriding, was as follows: direct current source, crucible (usually acting as the anode) filled with salt bath and the borided pieces (acting as the cathode), heating device with temperature control

system and with the optional tight retort, and temperature measurement system. The most often used and most effective techniques of electrochemical boriding in molten salt baths were schematically represented in Fig. 4.7. The simplest method consisted in the use of a typical electric resistance furnace with a single graphite crucible, acting as the anode and with an optional tight retort (Fig. 4.7a). Such a

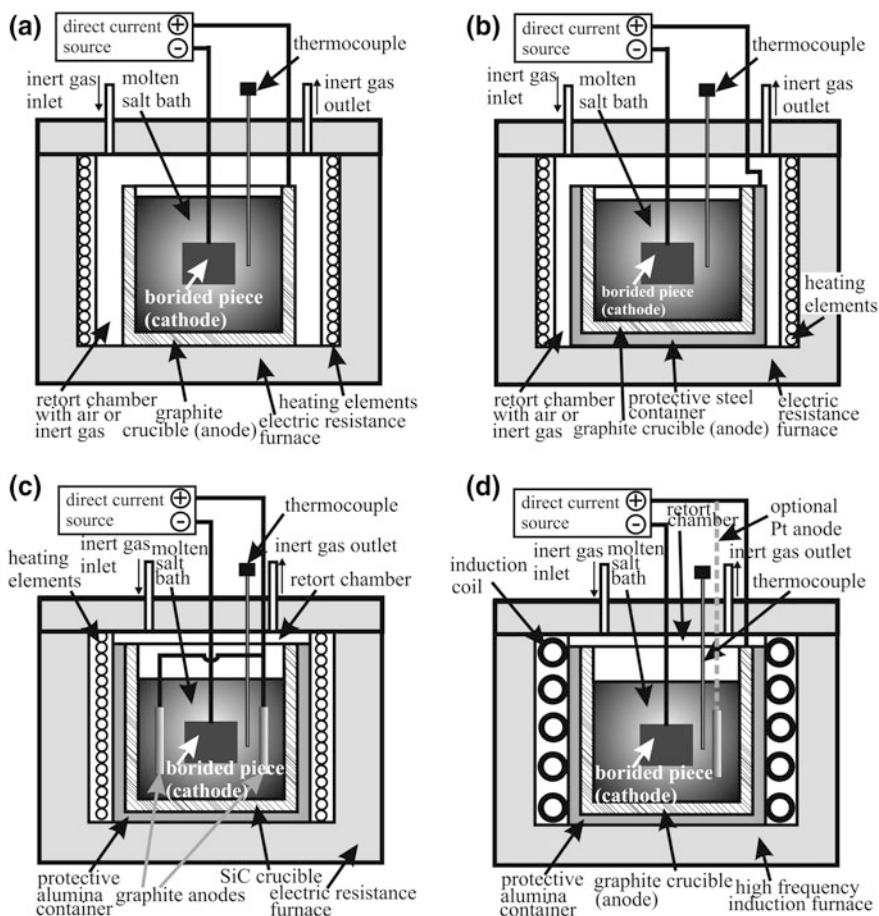


Fig. 4.7 Schematic representations of the most often used and most effective techniques of electrochemical boriding in molten salt baths: boriding in the typical electric resistance furnace under air or protective atmosphere using an unsealed graphite crucible as anode (a), boriding in the typical electric resistance furnace under air or protective atmosphere using an unsealed graphite crucible as anode and a protective steel container (b), boriding in the typical electric resistance furnace under air or protective atmosphere using an unsealed SiC crucible in a protective alumina container and additional graphite anodes (c), boriding by the high frequency induction heating under air or protective atmosphere using an unsealed graphite crucible as anode and a protective alumina container (d). Remark: the method shown in (d) could be carried out using the additional Pt anodes

version of treatment was carried out both in the basic electrolyte, consisting of fluorides (Bonomi et al. 1973, 1978) and in the baths, based on borax (Huang et al. 2013). The protective atmosphere (argon) was used only in case of boriding in fluoride baths. Sometimes, this method was extended this way that a graphite crucible was tightly put into the protective steel container, acting as the anode (Fig. 4.7b). The fluoride salt baths and borax baths (Matiašovský et al. 1988) or salts of alkali metals of unknown composition (Fuda et al. 1991) under protective inert gas (nitrogen) were mainly applied during such a process. The electrochemical boriding could also be carried out in the SiC crucible, not acting as an anode (Fig. 4.7c). SiC crucible was then put into a protective alumina container, and the graphite plates, located in the molten borax bath, acted as anodes. Both steels (Kartal et al. 2011; Sista et al. 2011) and Ni-based materials (Kahvecioglu et al. 2011; Sista et al. 2013) were electrochemically borided this way in molten borax baths. Nitrogen was usually used as a protective atmosphere in order to protect electrodes and crucible from oxidation and corrosive attack of the molten electrolyte (Sista et al. 2011).

In recent years, the high-frequency induction furnace was very often applied to heat the crucibles with electrolyte, based on the molten borax (Fig. 4.7d). The graphite crucible, tightly put into a protective alumina container, usually acted as the anode (Kartal et al. 2010a, b; Kartal and Timur 2013; Kilic et al. 2013; Kartal Sireli et al. 2017). Whereas the other crucibles, e.g. made of Pt-20% Rh alloy (Segers et al. 1991), were implemented sporadically.

Sometimes, the platinum anodes were additionally located in the molten electrolyte (Kartal et al. 2005, 2006). The process didn't require to use a protective atmosphere and was usually carried out under air. Although the use of protective inert gas was rarely reported (Segers et al. 1991), such a variant of treatment was taken into account in Fig. 4.7d. Iron alloys as well as pure titanium were effectively borided using such a method.

The general characterization of electrochemical boriding was shown in Tables 4.8 and 4.9, taking into account the available literature data regarding the composition of the bath, protective atmosphere, schematic representation of the method in Fig. 4.7, temperature and time of the treatment as well as the current density used.

The current trends favored the use of molten borax bath with the addition of carbonates which accelerated the boron diffusion and adjusted electrolyte viscosity and conductivity. The most often applied methods corresponded to the schematic representations in Fig. 4.7c, d. The crucibles with electrolyte could be heated in both the electric resistance furnace and high-frequency induction furnace. The process in the electric furnace (Fig. 4.7c) was characterized by the use of non-conducting crucible (made of SiC). Hence, the graphite plates, put into the molten borax bath, acted as anodes. Crucible and anodes required the adequate protection (inert gas) from oxidation and corrosive attack of the molten electrolyte. If the induction heating was used (Fig. 4.7d), graphite crucible acted as the anode, and usually, the protective atmosphere wasn't required. The electrochemical

Table 4.8 General characterization of selected processes of electrochemical boriding in molten salt baths. Part I

Type of material	Composition of the bath/Protective atmosphere/Scheme of the method	Temperature (°C)/ Time (h)/Current density (mA/cm ²)	References
Armco iron	Na ₂ B ₄ O ₇ or 80% Na ₂ B ₄ O ₇ + 20% NaCl/argon/Fig. 4.7d, Pt-20% Rh crucible as anode in a protective alumina (Al ₂ O ₃) container	900–1000/ 0.0083–3.33/50– 1120	Segers et al. (1991)
Almost pure Fe (0.04% C in low-carbon steel)	80% Na ₂ B ₄ O ₇ + 20% NaCl/absence/ Fig. 4.7d, graphite crucible with Pt anodes	800–1000/1/50– 700	Kartal et al. (2005)
	80–90% Na ₂ B ₄ O ₇ + 10–20% NaCl or B ₂ O ₃ + Na ₂ O with a ratio of 1.25– 2.245 or 90% Na ₂ B ₄ O ₇ + 10% Na ₂ CO ₃ /absence/Fig. 4.7d, graphite crucible with Pt anodes	800–1000/ 0.0167–2/50–700	Kartal et al. (2006)
	90% Na ₂ B ₄ O ₇ + 10% Na ₂ CO ₃ / absence/Fig. 4.7d, graphite crucible as anode	900/0.0167–2/200	Kartal et al. (2010b)
Low-carbon steels	27.3% LiF + 63.6% KF + 9.1% KBF ₄ or 80% Na ₂ B ₄ O ₇ + 20% NaCl/ nitrogen/Fig. 4.7b, graphite crucible in a protective steel container as anode	700–900/1–6/50	Matiašovský et al. (1988)
	90% Na ₂ B ₄ O ₇ + 10% Na ₂ CO ₃ / nitrogen/Fig. 4.7c, SiC crucible in a protective alumina tube, graphite plates as anodes	950/0.25/200	Kartal et al. (2011)
Medium-carbon steels	KF + LiF mixture + 10% KBF ₄ / argon/Fig. 4.7a, graphite crucible as anode	800/0.5–10/5–40	Bonomi et al. (1978)
Low-alloy steels	27.3% Li + 63.6% KF + 9.1% KBF ₄ or 80% Na ₂ B ₄ O ₇ + 20% NaCl/ nitrogen/Fig. 4.7b, graphite crucible in a protective steel container as anode	700–900/1–6/50	Matiašovský et al. (1988)

boriding was commonly used in order to form boride layers on the surface of iron alloys, titanium alloys and nickel alloys.

The boride layers, produced by electrochemical boriding, were usually characterized by typical two-phase or single-phase microstructure with a strong zonation. The relatively short treatment time compared to other boriding techniques was an important advantage of EB processes. Segers et al. (1991) obtained FeB + Fe₂B layer or Fe₂B monolayer on Armco iron depending on the main parameters of the process, i.e. temperature, duration and current density. At the temperature of 1000 °C (1273 K) for 0.5 h using borax bath and current density 50 mA/cm², they

Table 4.9 General characterization of selected processes of electrochemical boriding in molten salt baths. Part II

Type of material	Composition of the bath/Protective atmosphere/Scheme of the method	Temperature (°C)/Time (h)/Current density (mA/cm ²)	References
High-alloy steels	Salts of alkali metals/nitrogen/ Fig. 4.7b, graphite crucible with Pt wire in a protective stainless steel container as anode	850–950/0.5–1.25/400	Fuda et al. (1991)
	27.3% Li + 63.6% KF + 9.1% KBF ₄ or 80%Na ₂ B ₄ O ₇ + 20% NaCl/ nitrogen/ Fig. 4.7b, graphite crucible in a protective steel container as anode	700–900/1–6/50	Matiašovský et al. (1988)
	Na ₂ B ₄ O ₇ /nitrogen/ Fig. 4.7c, SiC crucible in a protective alumina tube, graphite plates as anodes	850–1000/0.25–1/200	Sista et al. (2011)
	90% Na ₂ B ₄ O ₇ + 10% Na ₂ CO ₃ / absence/ Fig. 4.7d, graphite crucible as anode	1000/0.2–0.25/200	Kartal Sireli et al. (2017)
Pure Ti	90% Na ₂ B ₄ O ₇ + 10% Na ₂ CO ₃ / absence/ Fig. 4.7d, graphite crucible as anode	950/0.0833–2/300	Kartal et al. (2010a)
	90% Na ₂ B ₄ O ₇ + 10% Na ₂ CO ₃ / absence/ Fig. 4.7d, graphite crucible as anode	900–1100/0.25–2/200	Kartal and Timur (2013)
	85% Na ₂ B ₄ O ₇ + 15% Na ₂ CO ₃ / absence/ Fig. 4.7d, graphite crucible as anode	900–1200/0.0167–4/50–700	Kilic et al. (2013)
	80% Na ₂ B ₄ O ₇ + 20% K ₂ CO ₃ / absence/ Fig. 4.7a, graphite crucible as anode	950/8/200	Huang et al. (2013)
Nickel-based alloys	90% Na ₂ B ₄ O ₇ + 10% Na ₂ CO ₃ / nitrogen/ Fig. 4.7c, SiC crucible in a protective alumina tube, graphite plates as anodes	950/0.0833–0.25/200	Sista et al. (2013)
Ni ₃ Al	Na ₂ B ₄ O ₇ /nitrogen/ Fig. 4.7c, SiC crucible in a protective alumina tube, graphite plates as anodes	800–950/0.25–1/100–500	Kahvecioglu et al. (2011)
Pure Mo	KF + LiF mixture + 10% KBF ₄ / argon/ Fig. 4.7a, graphite crucible as anode	830/1–5/5.5–30	Bonomi et al. (1973)
	Na ₂ B ₄ O ₇ /nitrogen/ Fig. 4.7c, SiC crucible in a protective alumina tube, graphite plates as anodes	900–1000/0.5–3/500	Kahvecioglu Feridun et al. (2015)

fabricated the single-phase Fe_2B layer. Whereas the increase in the time of boronizing up to 3.33 h resulted in the formation of a two-phase layer.

After electrochemical boriding of almost pure iron (DIN EN 10130-99 DC04 steel), the boride layer was composed of the three successive zones: FeB , Fe_2B and Fe_3B (Kartal et al. 2005, 2006). Kartal et al. (2005) reported the increase in boride layer thickness with increasing current density up to 200 mA/cm^2 . Kartal et al. (2006) determined the most advantageous parameters during electrochemical boriding of almost pure iron as follows: bath composition $90\% \text{ Na}_2\text{B}_4\text{O}_7 + 10\% \text{ Na}_2\text{CO}_3$, temperature 900°C (1173 K), time 1 h and current density 200 mA/cm^2 . Under these conditions, within the first 0.5 h of processing time, more than $90 \mu\text{m}$ thick $\text{FeB} + \text{Fe}_2\text{B}$ boride layer was obtained, and the further increase in process duration favored the formation of thick FeB zone (Kartal et al. 2010b).

Low-carbon steel as well as low- and high-alloy steels were electrochemically borided by Matiašovský et al. (1988). The best effects, providing the two-phase $\text{FeB} + \text{Fe}_2\text{B}$ boride layer, were obtained using $80\% \text{ Na}_2\text{B}_4\text{O}_7 + 20\% \text{ NaCl}$ bath, temperature 900°C (1173 K), time 2 h and current density 50 mA/cm^2 .

Kartal et al. (2011) produced the single-phase Fe_2B layers on low-carbon steel using the two-stage process. The electrochemical boriding (EB) was followed by phase homogenization (PH). Such a process was called phase homogenization in electrochemical boriding (PHEB). After the EB process, the applied current was turned off, and PH was started without any polarization. The samples were left in the same molten bath for 0.25, 0.5 or 0.75 h. After 0.25 h of EB process, carried out in $90\% \text{ Na}_2\text{B}_4\text{O}_7 + 10\% \text{ Na}_2\text{CO}_3$ bath at 950°C (1223 K) and current density 200 mA/cm^2 , the only FeB phase was identified by XRD. The PH for 0.25 h resulted in the formation of a dual phase layer ($\text{FeB} + \text{Fe}_2\text{B}$). The further increase in duration of phase homogenization favored obtaining the Fe_2B monolayer (Kartal et al. 2011).

Both the two-phase and single-phase boride layers were produced on the medium-carbon steel by Bonomi et al. (1978) using electrochemical boriding. The relatively low current density (10 mA/cm^2) and a short treatment time (0.5 h) resulted in formation of only the Fe_2B layer. Whereas with increasing duration of the process (up to 7 h) the FeB and Fe_2B phases were identified in the layer.

The electrochemical boriding of AISI D2 high-alloy steel provided the boride layer of strong zonation, in which the first outer zone consisted of FeB and CrB borides, and the Fe_2B borides occurred in the second zone below the first one (Sista et al. 2011). Kartal Sireli et al. (2017) used the two-stage PHEB process in order to form the boride layer on chromium-silicon martensitic steel. The EB process, carried out in $90\% \text{ Na}_2\text{B}_4\text{O}_7 + 10\% \text{ Na}_2\text{CO}_3$ bath at 1000°C (1273 K) for 0.25 h with current density 200 mA/cm^2 , probably resulted in the formation of two-phase $(\text{Fe,Cr})\text{B} + (\text{Fe,Cr})_2\text{B}$ layer. The complex borides appeared because of the high chromium concentration in the substrate material. However, XRD analysis revealed only FeB , Fe_2B and Cr_2B borides. Additionally, Kartal Sireli et al. (2017) reported the formation of $(\text{Fe,Cr})_2\text{B}$ islands below the continuous $(\text{Fe,Cr})_2\text{B}$ zone. The same phases were observed after PH for 35 min. The increase in duration of PH process up to 40 min caused that only the Fe_2B and Cr_2B phases were identified by phase analysis. Hence, probably the boride layer consisted of only $(\text{Fe,Cr})_2\text{B}$ zone.

However, further increasing the time of the phase homogenization (up to 45 min) influenced the microstructure of the layer this way that only Fe–Cr phase was identified, and the borides weren't observed. The authors suggested probable “deboriding” process as a reason for such a situation.

The special heat treatment wasn't carried out after electrochemical boriding of steels. After the current to electrodes was cut off, the samples, acting as cathode, were usually withdrawn from electrolyte and left in air to cool down (Kartal et al. 2006, 2010b; Sista et al. 2013). The same procedure was used after PHEB processes (Kartal et al. 2011; Kartal Sireli et al. 2017).

The electrochemical boriding of commercially pure titanium provided the two-phase TiB_2 + TiB layer (Kartal et al. 2010a; Kartal and Timur 2013; Kilic et al. 2013). The TiB_2 and TiB titanium borides were visible even after only 5 min of the process which was carried out in 90% $\text{Na}_2\text{B}_4\text{O}_7$ + 10% Na_2CO_3 bath at 950 °C (1223 K) with current density 300 mA/cm² (Kartal et al. 2010a). Like in the case of powder-pack boriding, the TiB_2 zone was compact and continuous. Whereas TiB borides appeared below TiB_2 phase in the form of whiskers and grew toward the substrate. With increasing the time of boronizing, the thickness of TiB_2 layer was higher. The XRD patterns showed that the intensity of peaks, characteristic of this phase, increased, and the intensity of TiB peaks diminished because of the formation of more compact and dense TiB_2 zone. After 2 h of the process, only TiB_2 phase was identified by XRD. The similar effect was caused by the elevated temperature of electrochemical boriding (Kartal and Timur 2013). The increase in the process temperature above 900 °C (1173 K) influenced the phase analysis by XRD this way that the TiB phase wasn't identified. The thicker and more dense TiB_2 zone at elevated temperatures and the lower penetration depth of X-rays with a glancing angle 2° could be the reason for such a situation. The growth of TiB whiskers was also less spectacular when compared to the powder-pack boronizing due to the relatively short duration of the EB processes. Hence, the penetration depth of TiB whiskers was shorter (Kartal et al. 2010a). However, the increase in time of EB process up to 8 h (Huang et al. 2013) could result in a formation of even 230 µm long TiB whiskers at 950 °C (1223 K). Kilic et al. (2013) reported the appreciable influence of boriding temperature on the morphology of TiB whiskers. The relatively thin TiB whiskers were formed at 900 °C (1173 K). At 1100 °C (1373 K) they became thicker and similar to needle-like microstructure. Whereas at 1200 °C (1473 K) they could be converted into an almost continuous layer.

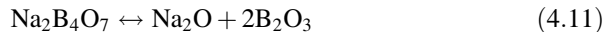
The electrochemical boriding of Ni-based alloy (Inconel®600) in 90% $\text{Na}_2\text{B}_4\text{O}_7$ + 10% Na_2CO_3 bath at 950 °C (1223 K) with current density 200 mA/cm² (Sista et al. 2013) resulted in the formation of the boride layers which were composed of mixture of nickel borides: Ni_3B , Ni_2B , Ni_4B_3 and NiB. The Ni_2B and Ni_3B borides were the predominant phases. The relatively high layer thickness compared to the powder-pack boriding was an important advantage of this boriding technique. After 0.25 h of the EB process, this thickness obtained even 81 µm. After the EB process, the applied current was turned off, and the samples were left in the same molten bath for 1 h without any polarization. It increased the boride layer thickness without essential modification of its phase composition.

The electrochemical boriding as an ultra-fast process was also used in order to produce the boride layers on Ni₃Al nickel aluminide (Kahvecioglu et al. 2011). The EB process of Ni₃Al, carried out in borax bath at 950 °C (1223 K) for 0.25 h with current density 500 mA/cm², resulted in the formation of the boride layer which was composed of nickel borides' mixture (Ni₃B, Ni₂B and Ni₄B₃) and complex Ni₂₀AlB₁₄ phase. The overall thickness of this boride layer was about 260 µm.

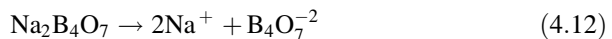
Pure molybdenum was also subjected to electrochemical boriding. The single-phase Mo₂B₅ boride layer was fabricated by Bonomi et al. (1973) and by Kahvecioglu Feridun et al. (2015). The overall thicknesses of boride layers, produced in borax bath for 1 h with current density 500 mA/cm² (Kahvecioglu Feridun et al. 2015), ranged from 34 µm at 900 °C (1173 K) to 47 µm at 1000 °C (1273 K).

The mechanism of formation of active boron atoms during electrochemical boriding was described by Yukin (1971) in detail. Initially, it was generally accepted in the literature on electrolytic boronizing that the following reactions occurred:

- partial thermal dissociation



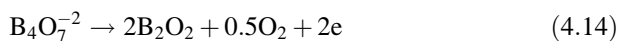
- electrolytic dissociation



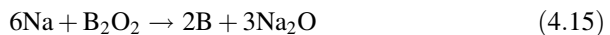
- deposition of sodium on the cathode



- discharge of anions on the anode and evolution of oxygen



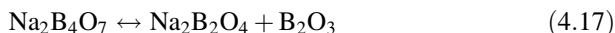
- reduction of boron with sodium on the cathode



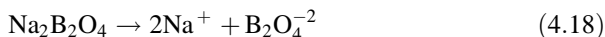
- oxidation of the graphite anode with oxygen



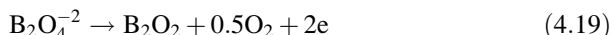
However, Yukin (1971) paid attention that the presence of B₄O₇⁻² ions in molten borates has not been observed and some of these reactions raised doubts. It was confirmed that the monoborate (Na₂B₂O₄) was the most stable compound in molten borates. Hence, the sodium tetraborate partially decomposed at high temperatures with formation of monoborate according to the reaction:



In this case, electrolytic dissociation of monoborate proceeded as follows:



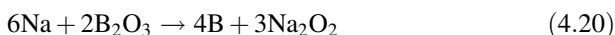
Deposition of sodium on the cathode occurred according to the reaction (4.13), and discharge of boron-containing anions with the formation of boron oxide and evolution of oxygen could be as follows:



Reduction of boron with sodium on the cathode and oxidation of the graphite anode with oxygen proceeded according to the unchanged reactions (4.15) and (4.16), respectively.

Yukin (1971) also formulated six stages of electrochemical boronizing: (1) the diffusion of sodium cations through the layer at the cathode; (2) passage of cations into the double electric layer; (3) loss of electrons to cations and formation of sodium atoms in the double electric layer; (4) adsorption of atoms and migration of atoms on the cathode to places with the lowest energy levels; (5) formation of nuclei of adsorbed atoms- bubbles of sodium vapor and (6) the selective growth of bubbles from the nuclei.

Kartal and Timur (2013) confirmed that the formation of active boron atoms could proceed according to the reactions (4.17), (4.18), (4.13) and (4.19). However, they indicated that the reduction of boron with sodium on the cathode could proceed as follows:



The diffusion of boron into the substrate resulted in the formation of borides:



4.2.5 Boriding in Fluidized Bed

Fluidized bed was admitted as a quasi-liquid state (Przybyłowicz 2000; Winter et al. 2014). Hence, the **boriding in fluidized bed (BFB)** was classified as a process in liquid media with a strong relation to the processes in solid media (see Fig. 2.1). Fluidized bed was usually formed as a consequence of blowing the gas through the retort, containing the fine particles of powder of an adequate composition (Przybyłowicz 2000).

The thermochemical treatment in fluidized bed was most often used to produce the carburized, nitrided, carbonitrided, nitrocarburized, oxynitrided or borided

layers (Jasiński et al. 2007; Babul and Kucharieva 2014; Winter et al. 2014). During these processes, gas was introduced through the special diffuser. As the gas moved up through the fine particles of a fluidized bed, the bed was unlocked and started to behave like a fluid. As the gas velocity increased, the degree of fluidization became smoother (Winter et al. 2014). In order to create the quasi-liquid state, the gas velocity should be higher than the critical velocity of fluidization (Przybyłowicz 2000). This critical velocity of fluidization was approximated by Sagon-King (1991) to a function of the product of square of the particle diameter and particle mass. Past this critical velocity, bubbles started to appear and the surface of the 'bed' became heterogeneous and liquid-like. Such factors as: the uniformity of the gas flow, the constant pressure drop through the retort, and the particle size influenced the fluidization.

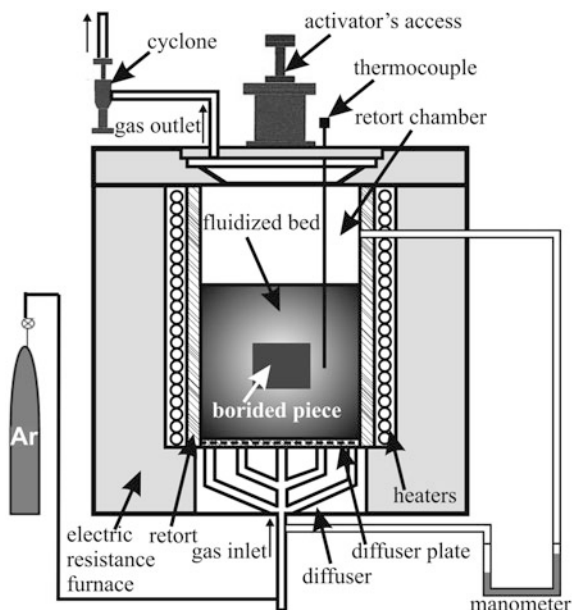
Boronizing in fluidized bed had some advantages, thanks to which it was relatively popular through the two last decades. The bed didn't contaminate the surfaces of borided workpieces. On the contrary, usually hard its particles cleaned the surface from impurities (Przybyłowicz 2000). If the fluidized beds were activated, they behaved very similar to a liquid bath. The quasi-liquid state provided rapid heat and mass transfer to all directions equally (Anthymidis et al. 2001b; Topuz et al. 2016). Fluidized bed furnaces were also easy to maintain, inexpensive to run and relatively safe to operate (Reynoldson 1993).

Boriding in fluidized bed was known since 1968. Gutman et al. (1968) blew argon through the bed, composed of 72–85% ferroboration, 21–23% amorphous boron and 7–12% boron carbide. The process was carried out at the temperature in the range of 950–1100 °C (1223–1373 K) for 5–7 h, and resulted in the formation of iron boride layers of a thickness up to 120 μm. In recent years, the bed was usually composed of B₄C and mixture of solid halogen-containing compounds (Anthymidis et al. 2001a, b; Tsipas et al. 2003), often enriched with Al₂O₃ (Anthymidis et al. 2002a; David et al. 2008).

Among the solid halogen-containing compounds, sodium or ammonium fluorides or chlorides were the most popular (Anthymidis et al. 2002b, c; Balandin 2004, 2005). However, the detailed composition of the bed was often not provided. Topuz et al. (2016) reported the use of the typical EKABOR[®]I powder as the fluidized bed. Argon was commonly applied as a fluidizing gas. Whereas its flow rate, as an important parameter of the process, was rarely given (Anthymidis et al. 2002b, c). Similarly, the size of powder particles (120 μm) was provided only by Balandin (2005). The process of boronizing in fluidized bed was usually carried out in the range of temperatures 800–1050 °C (1073–1323 K) for 0.5–6 h.

The retorts of fluidized bed furnace could be heated in different ways. Those that were externally gas-fired and electrically (by resistance heaters) heated were common. However, for some applications the electrode furnaces were used (Przybyłowicz 2000; Winter et al. 2014). The schematic representation of the most often used processes of boriding in fluidized bed was shown in Fig. 4.8, based on the available literature data (Anthymidis et al. 2001b; Winter et al. 2014). The main components of the fluidized bed reactor system were as follows: fluidized bed reactor unit (retort filled with fluidized bed), electric resistance furnace for heating

Fig. 4.8 Schematic representation of the most often used technique of boriding in fluidized bed



the reactor, the system of gas supply (cylinder, diffuser and diffuser plate) and the unit of providing reactants, the unit of trapping the hazardous substances (cyclone) as well as the control panel and measuring instruments (thermocouple, manometer). Fluidized bed was formed as a consequence of blowing argon through the retort. Balandin (2005) proposed another method of bed fluidization. The retort was mounted in the furnace on a special frame which was rigidly fixed to an electromagnetic vibrator. The bed was fluidized by the vertical vibration of the working retort at a frequency of 15 Hz and amplitude of 3 mm. However, such a method didn't achieve popularity among other researchers.

The general characterization of boriding of iron alloys and non-ferrous alloys in fluidized bed was shown in Tables 4.10 and 4.11, respectively. The available literature data regarding the composition of the bed, fluidizing gas and its flow rate, temperature and time of the treatment were taken into account. The current trends favored the use of B_4C , Al_2O_3 and solid halogen-containing compounds with an unknown ratio as the components of the fluidized bed. The most often applied methods corresponded to the schematic representation in Fig. 4.8. Argon of rarely given flow rate was usually used as a fluidizing gas. The boriding in fluidized bed was commonly applied in order to form boride layers on the surface of iron alloys as well as non-ferrous alloys.

Microstructure of borided alloys in fluidized bed consisted of both two-phase and single-phase boride layers. Balandin (2005) produced the dual phase $FeB + Fe_2B$ boride layer on Armco iron using bed composed of 10% $B_4C + 0.2\% NH_4Cl + Al_2O_3$ and fluidized by the vertical vibration of the working container (retort). The same technique was used in order to fabricate boride layers on

Table 4.10 General characterization of selected processes of boriding of iron alloys in fluidized bed

Type of material	Composition of the bed/Fluidizing gas used/ Flow rate of fluidizing gas (m ³ /h)	Temperature (°C)/Time (h)	References
Pure iron	10% B ₄ C + 0.2% NH ₄ Cl + Al ₂ O ₃ /absence —bed was fluidized by the vertical vibration of the working container (retort) at a frequency of 15 Hz and amplitude of 3 mm	850–1000/ 0.5–2	Balandin (2005)
Medium-carbon steel	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	800–1000/ 1.5	Anthymidis et al. (2001a)
	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	900–1000/1– 6	Tsipas et al. (2003)
	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/1.5	David et al. (2008)
High-carbon steel	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/3	Anthymidis et al. (2002a)
	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/3	David et al. (2008)
Low-alloy steels	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/3	Anthymidis et al. (2002a)
	B ₄ C + 5% NH ₄ Cl + Al ₂ O ₃ /absence—bed was fluidized by the vertical vibration of the working container (retort) at a frequency of 15 Hz and amplitude of 3 mm	800–1000/ 0.5–2	Balandin (2004)
	10% B ₄ C + 0.2% NH ₄ Cl + Al ₂ O ₃ /absence —bed was fluidized by the vertical vibration of the retort	850–1000/ 0.5–2	Balandin (2005)
	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/3	David et al. (2008)
	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/3	Anthymidis et al. (2002a)
High-alloy steels	B ₄ C + 5% NH ₄ Cl + Al ₂ O ₃ /absence—bed was fluidized by the vertical vibration of the working retort	800–1000/ 0.5–2	Balandin (2004)
	10% B ₄ C + 0.2% NH ₄ Cl + Al ₂ O ₃ /absence —bed was fluidized by the vertical vibration of the retort	850–1000/ 0.5–2	Balandin (2005)
	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/3	David et al. (2008)
	EKABOR [®] I powder/argon/unknown	850–1050/1– 4	Topuz et al. (2016)

Table 4.11 General characterization of selected processes of boriding of non-ferrous alloys in fluidized bed

Type of material	Composition of the bed/Fluidizing gas used/Flow rate of fluidizing gas (m ³ /h)	Temperature (°C)/Time (h)	References
Titanium and its alloys	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	1000/6	Anthymidis et al. (2001b)
	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/3–6	Anthymidis et al. (2002a)
	B ₄ C + Al ₂ O ₃ + sodium or ammonium fluoride or chloride/argon/1.4	950/1.5–6	Anthymidis et al. (2002b)
	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	900–1000/1–6	Tsipas et al. (2003)
Nickel and its alloys	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/5	Anthymidis et al. (2002a)
	B ₄ C + Al ₂ O ₃ + sodium or ammonium fluoride or chloride/argon/1.4	950–975/1.5–5	Anthymidis et al. (2002b; 2002c)
Pure Co	B ₄ C + Al ₂ O ₃ + solid halogen-containing compounds/argon/unknown	950/3	Anthymidis et al. (2002a)
	B ₄ C + Al ₂ O ₃ + sodium or ammonium fluoride or chloride/argon/1.4	950/3	Anthymidis et al. (2002b)
Pure Cr	B ₄ C + Al ₂ O ₃ + sodium or ammonium fluoride or chloride/argon/1.4	950/3	Anthymidis et al. (2002b)
Pure Mo	B ₄ C + Al ₂ O ₃ + sodium or ammonium fluoride or chloride/argon/1.4	950/5	Anthymidis et al. (2002b)

low- and high-alloy steels (Balandin 2004, 2005). The diffusion layers were mainly composed of the FeB and Fe₂B borides with strong zonation. Because of the high content of some alloying elements, Cr₂B and Mo₂B phases were also identified in boride layers. There were a few publications which reported the similar results regarding the boriding of medium- and high-carbon steels as well as low- or high-alloy steels in fluidized bed. The medium-carbon steel was subjected to boronizing in fluidized bed which contained B₄C, solid halogen-containing compounds and Al₂O₃ (Anthymidis et al. 2001a; Tsipas et al. 2003; David et al. 2008). The Fe₂B monolayer was produced at 950 °C (1223 K) for 1.5 h on medium-carbon steel. Anthymidis et al. (2002a) and David et al. (2008) reported the very similar effects of the boronizing of a high-carbon steel, two low-alloy steels and high-alloy steel using the same fluidized bed (B₄C + solid halogen-containing compounds + Al₂O₃). The two-phase FeB + Fe₂B boride layer was obtained only in case of high-alloy steel which was treated at 950 °C (1223 K) for 3 h. The other borided materials were characterized by the Fe₂B monolayer which was produced as a consequence of boronizing at the same temperature and duration. The AISI 304 austenitic steel was borided by Topuz et al. (2016) in fluidized bed, containing EKABOR[®]I powder. The boride layer, obtained for 1 h in the temperature range of 850–1050 °C (1123–1323 K), was composed mainly of FeB and Fe₂B iron borides. Besides, the Cr₂Ni₃B₆ and Ni₂B phases were identified by XRD.

The microstructure of borided titanium and its alloys in fluidized bed was reported by Anthymidis et al. (2001b, 2002a, b) as well as by Tspas et al. (2003). In all these cases, the bed was composed of B_4C , solid halogen-containing compounds and Al_2O_3 . The applied solid halogen-containing compounds were identified by Anthymidis et al. (2002b) as sodium fluoride (NaF) or ammonium fluoride (NH_4F) or corresponding chlorides (NaCl, NH_4Cl). The boriding of pure titanium in such a fluidized bed resulted usually in the formation of single-phase TiB layer which was obtained at 950 °C (1223 K) for 3 h (Anthymidis et al. 2002a; Tspas et al. 2003) as well as for 5 h (Anthymidis et al. 2002b). Whereas the boride layer, produced by boriding of titanium alloy (Ti6Al4V), consisted of typical two-phase $TiB_2 + TiB$ boride layer (Anthymidis et al. 2001b, 2002a, b; Tspas et al. 2003). Such a layer was fabricated by boronizing at 950 °C (1223 K) for 6 h (Anthymidis et al. 2002a, b) as well as by the process at 1000 °C (1273 K) for 6 h (Anthymidis et al. 2001b; Tspas et al. 2003). The microstructure of borided nickel and its alloy in fluidized bed was analyzed by Anthymidis et al. (2002a, b, c). The pure nickel, borided in $B_4C + Al_2O_3 +$ solid halogen-containing compounds bed at 950 °C (1223 K) for 5 h, was characterized by the Ni_3B boride layer (Anthymidis et al. 2002a, b, c). Whereas the boronizing of Inconel[®]-alloy of 72% Ni–15% Cr–13% Fe composition in fluidized bed resulted in formation Ni_4B_3 borides according to Anthymidis et al. (2002b). However, the XRD patterns weren't provided.

The pure cobalt, chromium and molybdenum were also borided in fluidized bed (Anthymidis et al. 2002a, b). The boriding process of pure Co in a fluidized bed reactor at 950 °C (1223 K) for 3 h resulted in the formation of Co_3B and Co_4B borides.

Whereas after boriding of pure Cr in a fluidized bed reactor at 950 °C (1223 K) for 3 h, the Cr_5B_3 , Cr_2B and CrB phases occurred in the boride layer. The Mo_2B_5 monolayer was produced as a consequence of boriding in fluidized bed of pure molybdenum (Anthymidis et al. 2002b).

The additional heat treatment which could influence the microstructure of substrate material wasn't carried out after boriding in fluidized bed.

Boriding in hydrous electrolytes was also classified as a method in liquid media (see Fig. 2.1). Such a process based on the known method of surface hardening in hydrous electrolytes (Jasnogorodsky 1949). The modification consisted in the addition of a boron source (in a form of solution or suspension) to the electrolyte (Lyakhovich et al. 1973). In order to boride the iron alloys, the composition of electrolyte contained water and glycerol as well as potassium carbonate. However, the electrolytes, composed of the mixture of boron carbide, water, glycerol and sodium carbonate, were also applied (Voroshnin and Lyakhovich 1978). Because of no representation of this boriding method in recent years, its detailed description will be omitted.

4.3 Gas Boriding

The four main methods of *boriding in gaseous media* were classified (see Fig. 2.1): with the use of gaseous boron halides as a boron source, with the use of boranes as a boron source, with the use of boron coating as a boron source and the process under reduced pressure. Although some technological difficulties were related to gas boronizing, the process was characterized by the advantages that caused its permanent development. The constant chemical composition of the boriding atmosphere, continuously provided to the borided pieces, was recognized as the main reason for these advantages. In case of boriding in solid or liquid media, the boron source became exhausted during the process. In contrast to these processes, gas boriding enabled the permanent supplementing the boron source (boron halides or boranes) due to the continuous flow of the boriding atmosphere through the furnace retort. It provided the constant chemical composition of the atmosphere and the stability of the diffusion flux of boron from the boriding medium to the borided material.

Gas boriding (GB) was initiated by Weintraub (1911) who passed a mixture of BCl_3 and hydrogen over a glowing tungsten wire. Laubengayer et al. (1943) used the reduction of boron tribromide (BBr_3) with hydrogen to produce the crystals of α -tetragonal boron in the form of needles and plates on a hot tantalum filament at temperature of 1300 °C (1573 K) or above. Eipeltauer (1951) studied boronizing in the H_2 - BCl_3 atmosphere as a function of various factors. Martin (1949) tried to use trimethylborane in order to form borides on a heated metal surface, but the layer thus obtained peeled easily from the surface. The thermal decomposition of diborane (B_2H_6) at 500 °C (773 K) resulted in the formation of a thin boride layer of uniform thickness (Moss 1947). The process was accelerated at temperatures of 900–1000 °C (1173–1273 K) by Hurd (1952), though the thickness of boride layer was not so uniform as at 500 °C (773 K).

4.3.1 Gas Boriding with the Use of Boron Halides

Gas boriding (GB) with the use of boron halides as a boron source, especially using boron trichloride (BCl_3), was the most often applied process of gas boronizing through the last two decades. Boron trichloride was well-known as a colorless, toxic gas of sharp odor, fuming in the air. The strong reactivity and high thermal stability were characteristic of this gas. During heating, in the presence of hydrogen, BCl_3 underwent the decomposition to dichloroborane (BHCl_2) and hydrochloric acid (HCl) or, at the temperatures above 1000 °C (1273 K), to boron and HCl (Sezgi et al. 1997; Pertek 2001) according to the reactions:



In a similar way boron trichloride reacted with metals, creating volatile chlorides at elevated temperature.

The cleaned workpieces, subjected to gas boronizing, were usually put into the chamber or into the cylindrical retort of an electric resistance furnace and heated up to the adequate temperature under protective atmosphere (argon or nitrogen) in order to avoid the oxidation. Sometimes before heating, the air was evacuated from the whole system by the vacuum pump. After the workpieces have been heated to the temperature of boriding, the flow of the boriding atmosphere was activated and the gas boriding was started. The composition of the boriding atmosphere could be as follows: hydrogen (H_2) as a carrier gas and boron trichloride (BCl_3) as a boron source (Pchelkina and Lakhtin 1960; Skugorova et al. 1972; Skugorova and Nechaev 1973; Takeuchi et al. 1979; Lyakhovich et al. 1982; Pertek 2001; Kulka et al. 2011), mixture of argon and hydrogen ($\text{Ar} + \text{H}_2$) as a carrier gas and boron trichloride (BCl_3) as a boron source (Pertek 2001) or, finally, mixture of nitrogen and hydrogen ($\text{N}_2 + \text{H}_2$) as a carrier gas and boron trichloride (BCl_3) as a boron source (Hegewaldt et al. 1984; Kulka et al. 2012a, 2014; Makuch and Kulka 2014, 2016; Makuch et al. 2015, 2017a, b). After the workpieces have been held at the process temperature for a desired time, the flow of boriding atmosphere was switched off and the borided parts were cooled under a protective gas (nitrogen or argon) to ambient temperature. In general, almost all the previously indicated materials (see Fig. 2.2) with the exception of austenitic steels and titanium alloys could be gas-borided using boron trichloride as the boron source. The usually used temperatures of gas boriding with the use of BCl_3 ranged from 550 °C (823 K) to 1000 °C (1273 K) for various alloys, and the duration of such a process was in the range of 1–6 h. These parameters depended on the type of borided material or on the type of boriding atmosphere to a certain degree.

The main equipment, required for **gas boriding (GB) using boron trichloride**, was as follows: heating device with temperature control system, i.e. electric resistance tubular furnace or electric resistance chamber furnace (mainly in industrial applications), retort (made of quartz, Ni-based alloy or stainless steel), gas cylinders with boron trichloride, hydrogen, nitrogen or argon, injection nozzle or the system of BCl_3 cooling, off-gas washer (gas scrubber), temperature measurement system and, optionally, a vacuum pump. Sometimes, the furnaces should be equipped with a fan in order to provide the constant flow of boriding atmosphere, its good mixing (the constant chemical composition) as well as the constant temperature in the entire chamber volume. The most often used and most effective techniques of gas boriding with the use of BCl_3 as a boron source were schematically represented in Fig. 4.9.

The process was often carried out according to the scheme shown in Fig. 4.9a (Skugorova et al. 1972; Skugorova and Nechaev 1973; Takeuchi et al. 1979;

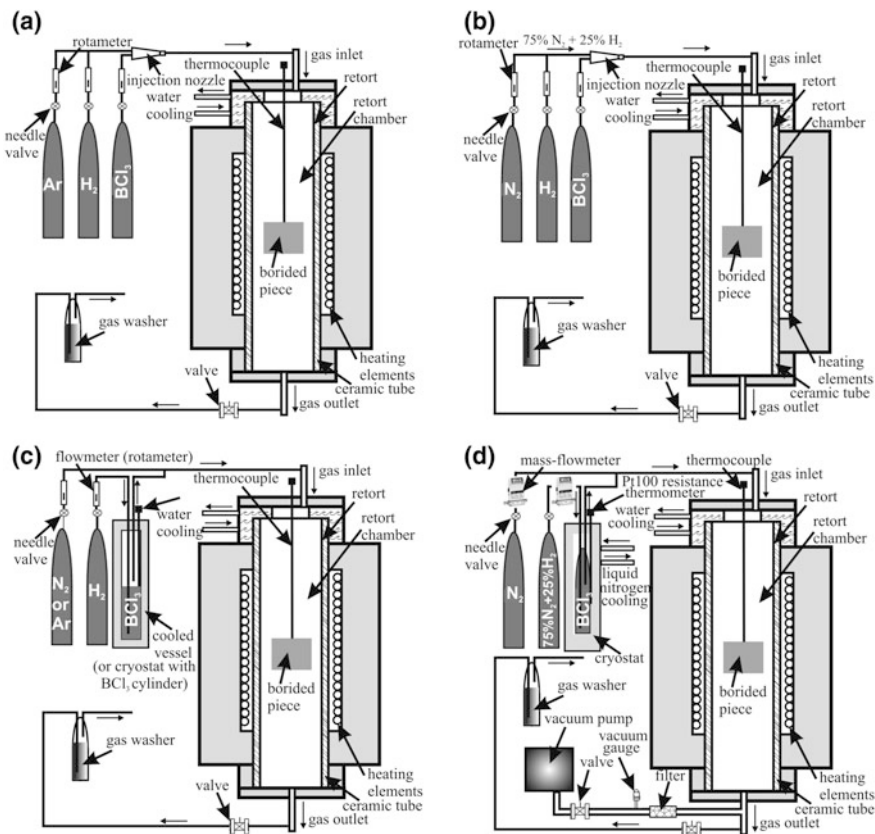


Fig. 4.9 Schematic representations of the most often applied and most effective techniques of gas boriding using boron trichloride (BCl_3): boriding in the typical electric resistance tubular furnace under H_2 – BCl_3 atmosphere (a), boriding in the typical electric resistance tubular furnace under $(75\% \text{ N}_2 + 25\% \text{ H}_2)$ – BCl_3 atmosphere (b), boriding in the typical electric resistance tubular furnace under H_2 – BCl_3 atmosphere using the cooled vessel with boron trichloride or cryostat with BCl_3 cylinder (c), boriding in the typical electric resistance tubular furnace under $(75\% \text{ N}_2 + 25\% \text{ H}_2)$ – BCl_3 atmosphere using the cooled cryostat with BCl_3 cylinder (d). *Remark: all these methods could be carried out in electric resistance chamber furnace, usually equipped with a fan*

Lyakhovich et al. 1982). The boriding atmosphere consisted of hydrogen and boron trichloride which was delivered to the carrier gas directly from the gas cylinder. It was possible because of the lower boiling point of BCl_3 (12.6°C , i.e. 275.6 K) than the temperature of its use (usually ambient temperature). However, BCl_3 was characterized by the relatively high density (1.876 g/cm^3) compared to hydrogen (0.0008988 g/cm^3). Hence, some difficulties usually occurred during the mixing of these gaseous components of boriding atmosphere. The adequate mixing of hydrogen and boron trichloride was necessary in order to form the uniform boride layer on the entire surface of borided workpieces. Therefore, the injection nozzle was usually applied during such a delivery method of BCl_3 to boriding atmosphere.

The second method of gas boriding using the boron trichloride as a boron source consisted in the use of the mixture of nitrogen and hydrogen (75% N_2 + 25% H_2) as a carrier gas (Fig. 4.9b), instead of only hydrogen, previously applied. Such a process for the first time was applied by Hegewaldt et al. (1984) and obviously resulted in improved safety and in diminished addition of BCl_3 to the boriding atmosphere. Taking into account the formation of the borided layer of high quality (i.e. diminished porosity), the ratio of boron trichloride to hydrogen was very important. The most adequate percentage of BCl_3 in relation to H_2 ranged from 1 to 5 vol%, irrespective if 75% N_2 + 25% H_2 mixture (Hegewaldt et al. 1984) or only H_2 (Pertek 2001) was used as a carrier gas. Hence, the use of a mixture of nitrogen and hydrogen enabled to apply the diminished percentage of boron trichloride in relation to the entire boriding atmosphere. Because of the delivery of BCl_3 directly from the gas cylinder, it was advisable to apply the injection nozzle.

Another delivery system of boron trichloride to gas mixture was shown in Fig. 4.9c. Carrier gas (hydrogen) was let in through the special vessel (or cryostat) with liquid BCl_3 , cooled to an adequate temperature. The percentage of boron trichloride in boriding atmosphere (H_2 – BCl_3) depended on its temperature and was diminished with a decrease of BCl_3 temperature. The control of BCl_3 addition to the boriding atmosphere became easier and required to maintain its constant temperature. Simultaneously, it provided the better mixing of hydrogen and boron trichloride. Such a method was proposed by Pchelkina and Lakhtin (1960) and was continued by Pertek (2001). The process was later developed by Pertek and Kulka (2002a, b, 2003a, b), who let the hydrogen in through the gas cylinder with BCl_3 , cooled in the special cryostat using liquid nitrogen as it was shown in Fig. 4.9d. Gas boriding using this method of BCl_3 delivery was still used through the last decade by Kulka and Pertek (2007, 2008) as well as by Kulka et al. (2011, 2012b, 2013).

In recent years, the advantages of the two last processes, i.e. the use of the mixture of nitrogen and hydrogen as a carrier gas as well as the control of BCl_3 addition based on its temperature, have been applied together by Kulka et al. (2012a, 2014). The scheme of such gas boriding process was presented in Fig. 2.11 d. It was the most developed device for gas boriding with the use of boron trichloride. The three basic systems could be specified: heating system with an electric resistance furnace, gas-supply system and systems of regulation and control of temperature. The main device of the heating system was an electric tubular furnace equipped with a quartz retort. The upper part of retort (as the place of loading and unloading of borided workpieces) was cooled by a small coiled tube condenser. The power-supply system with a temperature control consisted of three independent heating zones, which provided a constant temperature along the furnace retort as well as throughout its cross-section. During the boriding process, the temperature was controlled by a personal computer with HTMonit software. Additionally, the separate measuring system with the NiCr–NiAl thermocouple was applied in order to monitor the temperature near the borided workpieces. The control thermocouple was placed in the center of quartz retort. The gas-supply system consisted of the cylinders with gases of a high purity: N_2 and mixture of 75 vol% N_2 and 25 vol% H_2 with a purity of 6.0 as well as boron trichloride BCl_3 with

a purity of 4.0. This system was also equipped with a vacuum pump in order to evacuate air from the gas delivery system before boriding. The pressure was measured by a vacuum gauge. The carrier gas, consisting of 75% N₂ + 25% H₂ mixture, was let in through BCl₃ cylinder, put into cryostat and cooled to the adequate temperature using liquid nitrogen. Liquid nitrogen was delivered from the Dewar flask under overpressure. The percentage of boron trichloride in boriding atmosphere was controlled by its temperature. BCl₃ temperature was measured by Pt100 resistance thermometer and recorded using the DLM Simple software. The appropriately selected flow rate of nitrogen through the Dewar flask enabled to maintain the constant temperature of boron trichloride.

So, the main technological parameters of gas boriding with the use of boron trichloride were as follows: chemical composition of boriding atmosphere (i.e. type of carrier gas and the percentage of BCl₃), temperature and time of boriding. The control of boron trichloride addition was very important, because its too high amount (above 10 vol%) could cause high porosity of the produced layers. Simultaneously, too low percentage of BCl₃ in boriding atmosphere caused slow saturation of the surface with boron and, as a consequence, the thin boride layer was obtained. The percentage of boron trichloride in boriding atmosphere depended on its vapor pressure this way that the increase in vapor pressure caused an increase in BCl₃ percentage. Chemical composition of boriding atmosphere, containing hydrogen and boron trichloride, depended on the vapor pressure of BCl₃, determined by its evaporation pressure, according to the equation (Kubaschewski et al. 1967):

$$\log p_{\text{BCl}_3} = \frac{2115}{T} - 7.04 \log T + 27.56 \quad (4.24)$$

Where: p_{BCl_3} is BCl₃ vapor pressure (mm Hg), T is the absolute temperature (K).

The ratio of mixing (x) BCl₃ to hydrogen resulted from the relation:

$$x = \frac{p_{\text{BCl}_3}}{p_{\text{H}_2}} = \frac{p_{\text{BCl}_3}}{1 - p_{\text{BCl}_3}} \quad (4.25)$$

where: p_{BCl_3} is a vapor pressure of BCl₃ (Pa), p_{H_2} is a vapor pressure of H₂ (Pa).

By analogy, the ratio of mixing BCl₃ to the mixture of nitrogen and hydrogen could be calculated as:

$$x = \frac{p_{\text{BCl}_3}}{p_{\text{N}_2 + \text{H}_2}} = \frac{p_{\text{BCl}_3}}{1 - p_{\text{BCl}_3}} \quad (4.26)$$

The influence of temperature of boron trichloride evaporation on the BCl₃ vapor pressure and its content in boriding atmosphere was shown in Fig. 4.10. The addition of nitrogen to the carrier gas didn't influence the BCl₃ content in relation to the entire atmosphere. However, the content of boron trichloride in relation to hydrogen could be significantly increased in this case, especially if the percentage of nitrogen was appreciable. It was marked in Fig. 4.10 with dashed line. The most

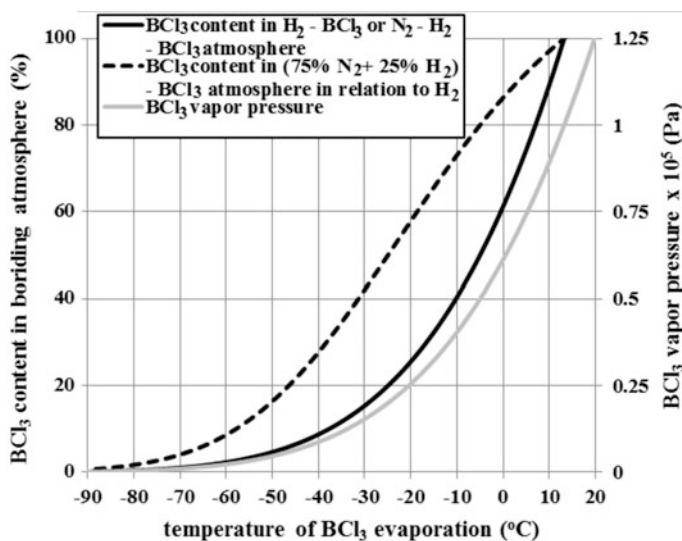


Fig. 4.10 BCl₃ vapor pressure and its content in boriding atmosphere versus the temperature of its evaporation

often used (75% N₂ + 25% H₂)-BCl₃ atmosphere was taken into account during calculations. In order to obtain the commonly used 5 vol% of BCl₃ in relation to H₂, it was sufficient to add only 1.3 vol% of boron trichloride in relation to the entire (75% N₂ + 25% H₂)-BCl₃ atmosphere.

The important problem during gas boriding was the toxicity of boron trichloride and the need to neutralize the off-gas. The use of carrier gas, composed of 75% N₂ + 25% H₂ mixture enabled to diminish the percentage of BCl₃ in relation to the entire boriding atmosphere. As it was reported by Hegewaldt et al. (1984), the off-gas consisted of hydrogen, nitrogen and 2–3% HCl. In order to neutralize HCl by its absorption, the off-gas could be let in through the scrubber (washer), containing water. Pertek (2001) used another substance to neutralize the off-gas. However, its composition was not given.

The general characterization of gas boriding of iron alloys with the use of boron trichloride was shown in Table 4.12, taking into account the available literature data regarding the composition of the carrier gas, percentage of BCl₃ in relation to the entire boriding atmosphere, schematic representation of the method in Fig. 4.9 as well as the temperature and time of the treatment. Although the use of H₂-BCl₃ atmosphere with the control of BCl₃ addition based on its temperature (Fig. 4.9c) predominated through the last two decades, the current trends favored the use of 75% N₂ + 25% H₂ mixture as a carrier gas using the same method of boron trichloride addition, according to the scheme in Fig. 4.9d (Kulka et al. 2017). The similar tendency was observed in case of hybrid layers, produced on steels by carburizing or carbonitriding followed by gas boriding (Table 4.13). The method of gas boriding, represented by Fig. 4.9d, also seemed to be most perspective.

Table 4.12 General characterization of selected processes of gas boriding of iron alloys with the use of boron trichloride

Type of material	Composition of the carrier gas/ BCl_3 percentage/Scheme of the method	Temperature ($^{\circ}\text{C}$)/Time (h)	References
Armco iron	$\text{H}_2/1\text{--}50\% \text{BCl}_3/\text{Fig. 4.9c}$ or $\text{Ar} + \text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	800–1000/1–5	Pertek (2001)
	$\text{H}_2/9\% \text{BCl}_3/\text{Fig. 4.9c}$	950/2	Kulka et al. (2006)
	$\text{H}_2/9.1\% \text{BCl}_3/\text{Fig. 4.9c}$	800–1000/1.33–4	Kulka et al. (2013), Keddarn et al. (2014)
	75% N_2 + 25% $\text{H}_2/1.35\% \text{BCl}_3/\text{Fig. 4.9d}$	920/3	Kulka et al. (2017)
Low-carbon steels	$\text{H}_2/4.76\% \text{BCl}_3/\text{Fig. 4.9c}$	750–950/3–6	Pchelkina and Lakhtin (1960)
	$\text{H}_2/6.25\% \text{BCl}_3/\text{Fig. 4.9a}$	920/2	Skugorova et al. (1972)
	$\text{H}_2/6.25\% \text{BCl}_3/\text{Fig. 4.9a}$	700–1000/0.5–7	Skugorova and Nechaev (1973)
	$\text{H}_2/1\text{--}6\% \text{BCl}_3/\text{Fig. 4.9a}$	850–1050/1–6	Lyakhovich et al. (1982)
Medium-carbon steels	$\text{H}_2/4.76\% \text{BCl}_3/\text{Fig. 4.9c}$	750–950/3–6	Pchelkina and Lakhtin (1960)
	$\text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9a}$	550–800/0.5–1	Takeuchi et al. (1979)
	$\text{H}_2/1\text{--}6\% \text{BCl}_3/\text{Fig. 4.9a}$	750–1050/1–6	Lyakhovich et al. (1982)
	75% N_2 + 25% $\text{H}_2/0.05\text{--}6\% \text{BCl}_3/\text{Fig. 4.9b}$	650–850/0.0833–4.67	Hegewaldt et al. (1984)
	$\text{H}_2/1\text{--}50\% \text{BCl}_3/\text{Fig. 4.9c}$ or $\text{Ar} + \text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	800–1000/1–5	Pertek (2001)
High-carbon steels	$\text{H}_2/4.76\% \text{BCl}_3/\text{Fig. 4.9c}$	750–950/3–6	Pchelkina and Lakhtin (1960)
	$\text{H}_2/1\text{--}6\% \text{BCl}_3/\text{Fig. 4.9a}$	850–1050/1–6	Lyakhovich et al. (1982)
	$\text{H}_2/1\text{--}50\% \text{BCl}_3/\text{Fig. 4.9c}$ or $\text{Ar} + \text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	800–1000/1–5	Pertek (2001)
Low-alloy steels	$\text{H}_2/6.25\% \text{BCl}_3/\text{Fig. 4.9a}$	700–1000/0.5–7	Skugorova and Nechaev (1973)
	$\text{H}_2/1\text{--}50\% \text{BCl}_3/\text{Fig. 4.9c}$ or $\text{Ar} + \text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	800–1000/1–5	Pertek (2001)
	$\text{H}_2/5\text{--}9\% \text{BCl}_3/\text{Fig. 4.9c}$	950/2–3	Kulka and Pertek (2003a, b, c, 2007, 2008), Pertek and Kulka (2002a, b, 2003a, b)

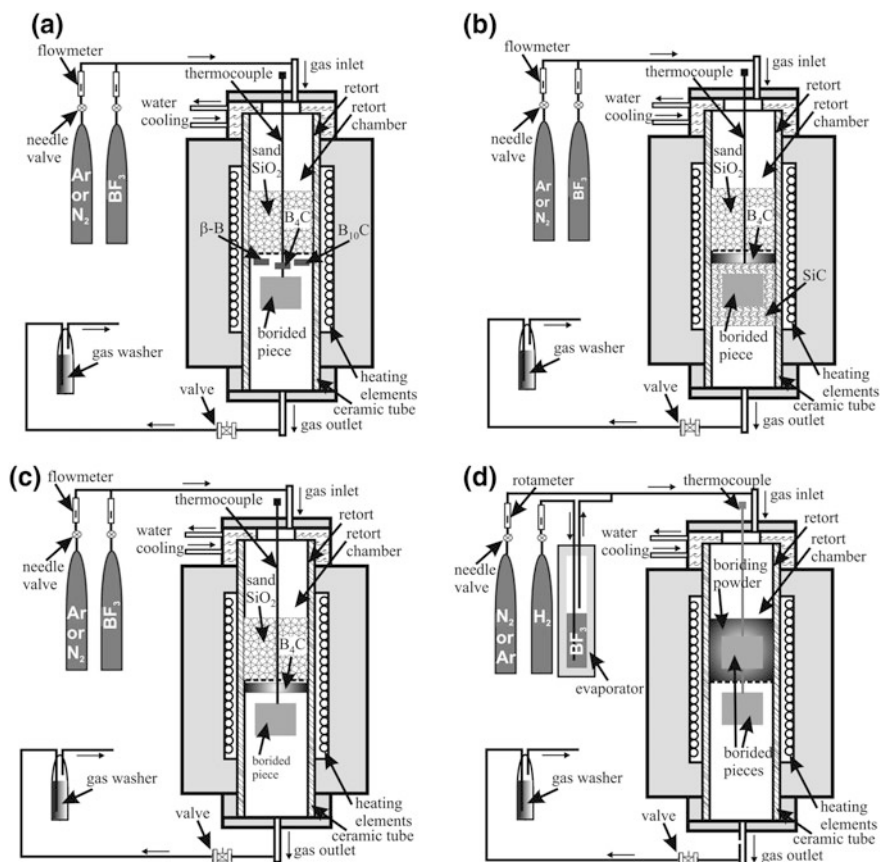


Fig. 4.11 Schematic representations of the most often applied and most effective techniques of gas boriding using boron trifluoride (BF₃): boriding in the typical electric resistance tubular furnace using SiO₂ moderator and β -B, B₄C or B₁₀C obtained by hot pressing under BF₃ atmosphere (a), boriding in the typical electric resistance tubular furnace using SiO₂ moderator, B₄C and SiC under BF₃ atmosphere (b), boriding in the typical electric resistance tubular furnace using SiO₂ moderator and B₄C under BF₃ atmosphere (c), boriding in the typical electric resistance tubular furnace using the boriding powder mixture under H₂-BF₃-O₂ atmosphere (d)

Kulka et al. (2012a) applied this method during the two-stage gas boriding, consisting in saturation with boron and diffusion annealing process (DAP). These stages of the relatively short duration (0.25 h) were alternately repeated. Such a process was used in order to accelerate the boron diffusion and to reduce the thickness of more brittle FeB phase.

The trends in gas boriding with the use of BCl₃ as a boron source, mentioned above, were confirmed in the case of Ni-based alloys, subjected to such a process (Table 4.14). All the available literature data reported the gas boriding of these alloys in N₂-H₂-BCl₃ atmosphere with the carrier gas, consisting of

75% N_2 + 25% H_2 mixture (Fig. 4.9d). At first, gas boriding was applied using the two-stage method, i.e. saturation with boron and diffusion annealing (Kulka et al. 2014). It resulted in the formation of nickel borides only of the relatively low concentration of boron (Ni_3B and Ni_2B). The nickel borides of higher boron concentration (Ni_4B_3 and NiB) occurred after a continuous process of gas boriding without diffusion annealing (Makuch et al. 2015; Makuch and Kulka 2016).

It should be noticed that the percentage of boron trichloride in relation to the entire (75% N_2 + 25% H_2)– BCl_3 boriding atmosphere, usually ranged from 1.34 to 2.3%. However, in relation to hydrogen, the content of BCl_3 was higher, obtaining 5.16–8.6%. It well corresponded to its usually used percentage in the H_2 – BCl_3 atmosphere (5–9%). In general, gas boriding with the use of boron trichloride was commonly used in order to form boride layers on the surface of iron alloys (excluding austenitic steels), carburized or carbonitrided steels and Ni-based alloys. The process was inadvisable for austenitic steels as well as for titanium alloys because of the difficulties in activation of the passivated surface as well as strong corrosive attack of boriding atmosphere, containing HCl and metal chlorides (Hegewaldt et al. 1984; Pertek 2001).

The gas boriding of iron alloys with the use of boron trichloride always resulted in the formation of two-phase FeB + Fe_2B boride layer with strong zonation. The reasons for such a situation will be analyzed and explained in the Sect. 4.3.3. The needle-like FeB and Fe_2B borides appeared in the boride layers produced on technically pure iron (Pchelkina and Lakhtin 1960) as well as on Armco iron (Pertek 1994, 2001; Kulka et al. 2006, 2013; Keddarn et al. 2014). Directly after boriding, the similar microstructure was obtained on the surface of low-carbon steels (Pchelkina and Lakhtin 1960; Skugorova et al. 1972; Skugorova and Nechaev 1973; Lyakhovich et al. 1982), medium-carbon steels (Pchelkina and Lakhtin 1960; Takeuchi et al. 1979; Lyakhovich et al. 1982; Hegewaldt et al. 1984; Pertek 2001) as well as high-carbon steels (Pchelkina and Lakhtin 1960; Lyakhovich et al. 1982; Pertek 2001). The low-alloy steels, subjected to gas boronizing using BCl_3 , were also characterized by typical FeB + Fe_2B layer (Skugorova and Nechaev 1973; Pertek 2001; Kulka and Pertek 2003a, b, c, 2007, 2008; Pertek and Kulka 2002a, b, 2003a, b).

The same phenomena, described for powder-pack borided layers, also proceeded in the steel substrate in the case of gas boriding, that is the increase of carbon concentration below the boride layer as well as the formation of more smooth interface between the layer and the substrate after boriding of high-carbon steels.

The formation of a Fe_2B monolayer on iron alloys required the additional heat treatment, i.e. diffusion annealing process (DAP). The DAP was successfully implemented in order to produce the single-phase boride layer on Armco iron (Pertek 2001; Kulka et al. 2013) or medium-carbon steel (Takeuchi et al. 1979).

Pertek (2001) confirmed an advantageous influence of an additional heat treatment after boriding, such as thermal hardening or toughening, on the profile of stresses in the borided steels or wear resistance of borided layers. Hence, the gas borided pieces made of steels were often reheated, quenched and low-temperature

Table 4.13 General characterization of selected processes of gas boriding of carburized or carbonitrided steels with the use of boron trichloride

Type of material	Composition of the carrier gas/ BCl_3 percentage/ Scheme of the method	Temperature ($^{\circ}\text{C}$)/Time (h)	References
Carburized low-alloy steels	$\text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	950/2	Pertek and Kulka (2002b, 2003b)
	$\text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	950/2.5	Kulka and Pertek (2003b)
	$\text{H}_2/9\% \text{BCl}_3/\text{Fig. 4.9c}$	950/2.5	Kulka and Pertek (2004), Kulka et al. (2006)
	$\text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	950/3	Pertek and Kulka (2002a), Kulka and Pertek (2007), Kulka et al. (2011, 2012b)
	$\text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	950/2–3	Kulka and Pertek (2008)
	75% N_2 + 25% $\text{H}_2/2.3\% \text{BCl}_3/\text{Fig. 4.9d}$	910/2 (including 1 h of diffusion annealing)	Kulka et al. (2012a)
Carbonitrided low-alloy steels	$\text{H}_2/5\% \text{BCl}_3/\text{Fig. 4.9c}$	950/3	Kulka and Pertek (2003c)

(Pertek 2001; Pertek and Kulka 2002a, b; Kulka and Pertek 2003b, c, 2007, 2008) or high-temperature tempered (Pertek 2001; Pertek and Kulka 2003b) after gas boriding.

The typical boride layers, produced on the previously carburized or carbonitrided low-alloy steels by gas boriding using BCl_3 (see Table 4.13), were also composed of the FeB and Fe_2B borides. Only Kulka et al. (2012a) obtained the boride layer with limited thickness of FeB zone as a consequence of two-stage process of gas boriding in which the saturation with boron (i.e. delivery of BCl_3) was temporarily stopped and followed by the diffusion annealing in $\text{N}_2\text{--H}_2$ atmosphere. Each of these two stages lasted 15 min. The stages were alternately repeated for 2 h. At the interface between the boride layer and the carburized surface the borocementite $\text{Fe}_3(\text{C},\text{B})$ often appeared (Kulka et al. 2012a).

The gas borided nickel and its alloys in $\text{N}_2\text{--H}_2\text{--BCl}_3$ atmosphere were usually characterized by the smooth boride layer, containing the mixture of borides. All the phases occurring in Ni--B equilibrium system, i.e. Ni_3B , Ni_2B , Ni_4B_3 and NiB nickel borides, as well as Cr_2B and CrB chromium borides were identified in gas borided layers, produced on both Inconel[®]600 and Nimonic[®]80A-alloy at 920 $^{\circ}\text{C}$ (1193 K) for 2 h (Makuch et al. 2015, 2017a, b; Makuch and Kulka 2016). The precipitates of borides were also visible at the grain boundaries below the compact boride layer. It could indicate the important role of grain-boundary boron diffusion compared to its volume diffusion at the used temperature of the process. This way, the whole diffusion zone was composed of compact boride layer and the zone with nickel and chromium borides at grain boundaries.

Table 4.14 General characterization of selected processes of gas boriding of nickel and its alloys with the use of boron trichloride

Type of material	Composition of the carrier gas/ BCl ₃ percentage/Scheme of the method	Temperature (°C)/Time (h)	References
95.5% pure Ni (Nisil)	75% N ₂ + 25% H ₂ /2.3% BCl ₃ / Fig. 4.9d	910/2 (including 1 h of diffusion annealing)	Kulka et al. (2014)
Inconel [®] 600-alloy	75% N ₂ + 25% H ₂ /1.34% BCl ₃ / Fig. 4.9d	920/2 (including 1 h of diffusion annealing)	Makuch and Kulka (2014)
Nimonic [®] 80A-alloy Inconel [®] 600-alloy	75% N ₂ + 25% H ₂ /1.36% BCl ₃ / Fig. 4.9d	920/2	Makuch et al. (2015)
Nimonic [®] 80A-alloy	75% N ₂ + 25% H ₂ /1.36% BCl ₃ / Fig. 4.9d	920/2	Makuch and Kulka (2016)
Nimonic [®] 80A-alloy	75% N ₂ + 25% H ₂ /1.36% BCl ₃ / Fig. 4.9d	920/2	Makuch et al. (2017a)
Nimonic [®] 80A-alloy	75% N ₂ + 25% H ₂ /1.36% BCl ₃ / Fig. 4.9d	920/2	Makuch et al. (2017b)

It was a typical observation that the chemical composition of Ni-based alloy strongly influenced the thickness of the boride layer, irrespective of the boriding technique used. The increase in chromium content in Ni-based alloy usually resulted in the diminished depth of boride layer because of the higher activation energy which was needed in order to form chromium borides. Therefore, boron diffusion into Ni-based alloys, containing chromium, was hindered. Hence, the highest depth of boride layer was obtained for pure Ni if the same boriding technique at the same parameters was applied. For the same reason, i.e. the higher chromium concentration, the depth of gas borided layer, produced on Nimonic[®]80A-alloy, was diminished compared to the layer obtained on Inconel[®]600-alloy at the same boriding parameters (Makuch et al. 2015).

The microstructure of Inconel[®]600-alloy, subjected to the alternately repeated two-stages of boriding process (saturation with boron and diffusion annealing) by Makuch and Kulka (2014), didn't differ from the microstructure of boride layers mentioned above. The boride layer was composed of the same nickel and chromium borides. Although the homogenization of phase composition wasn't observed, the thickness of the layer was only slightly lower compared to continuous gas boriding (Makuch et al. 2015). The important advantage is the lower consumption of toxic boron trichloride.

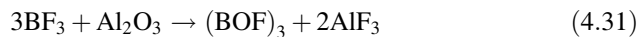
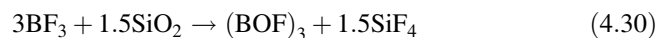
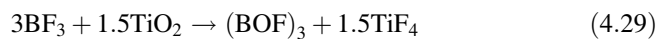
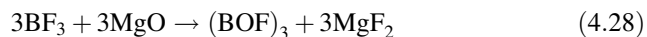
95.5% pure nickel, and more specifically the Ni–4.4Si–0.1 Mg (wt%) alloy called Nisil, was subjected to the same two-stage process of gas boriding (Kulka et al. 2014). The microstructure of boride layer consisted mainly of the mixture of

Ni_2B and Ni_3B nickel borides. In this case, the reduction of boron concentration within the layer during the second stage (diffusion annealing) could affect the phase composition of boride layer. The lack of chromium in the substrate made the diffusion of boron easier. Hence, the Ni_4B_3 or NiB borides (with higher concentration of boron) did not appear within the layer.

In general, the thicknesses of gas borided layers using BCl_3 as a boron source usually exceeded those obtained with the use of other thermochemical techniques at the same temperature and for the same time, excepting the electrochemical boriding.

Gas boriding (GB) using boron trifluoride (BF_3) was less often applied. Like boron trichloride, BF_3 was well-known as a pungent and colorless toxic gas, fuming in the air. Its boiling point was equal to -100.3°C (172.7 K). Hence the control of BF_3 addition based on its temperature was more difficult compared to boron trichloride. Obtaining boron by thermal decomposition of BF_3 or by its reduction with hydrogen was impossible because of the high positive values of the free enthalpy of these reactions (Pertek 2001). Hence, the formation of metal borides in the $\text{H}_2\text{--BF}_3$ atmosphere didn't occur. The presence of oxygen in boriding atmosphere was required in order to produce boride layers.

Oxygen could be delivered to the atmosphere in the different ways. One of them consisted in the passage of BF_3 through the moderator, containing oxygen. BF_3 accepted pairs of electrons. Oxygen could provide these pairs (Goeuriot et al. 1981). Baumgarten and Bruns (1939) reported that different oxides, e.g. B_2O_3 , MgO , TiO_2 , Al_2O_3 , SiO_2 and carbonates, reacted with BF_3 at temperatures above 450°C (723 K), forming boron oxyfluoride $(\text{BOF})_3$. The corresponding reactions could be as follows:



The thermal stability of boron oxyfluoride was not clearly defined. It was assumed that the following reaction could occur:

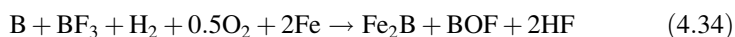


The electron pairs associated with the oxygen of these compounds could also be attached to BF_3 molecules which have not reacted with the oxide. Hence, a set of equilibrium chemical reactions defined a given partial pressure of boron trifluoride. BF_3 quantity, just sufficient for the activation of B_4C , could thus be liberated by

acting on these chemical equilibria. Goeuriot et al. (1981) proposed the boriding process called Borudif in which silica (SiO_2) was selected as the oxide moderator. Boron trifluoride alone was let in through this moderator. However, boron fluoride didn't form the boride layer even if it was passed through heated SiO_2 what resulted in the formation of $(\text{BOF})_3$. As it was reported by Goeuriot et al. (1981), the moderated BF_3 should react with additional activator, i.e. the solid boriding agent or the adequate powder. The three different types of boriding agents were used: solid boriding agents ($\beta\text{-B}$, B_4C and B_{10}C) obtained by hot pressing, $\text{B}_4\text{C} + \text{SiC}$ powder or only B_4C powder. The techniques were schematically represented in Fig. 4.11a–c, respectively.

Another method was proposed by Pertek (2001). Hydrogen was used as a carrier gas, which was let in through the evaporator with liquid boron trifluoride, similarly, as it was applied in the case of boron trichloride. The control of BF_3 addition required the adequate selection of its temperature. However, the temperature of boron trifluoride was unknown. Such $\text{H}_2\text{--BF}_3$ atmosphere was passed through boriding powder, consisting of only amorphous boron or amorphous boron and carbon black (4% B + 96% C or 50% B + 50% C). This powder also contained oxygen, needed for the formation of borides. It could be concluded that the gas boriding was carried out in the $\text{H}_2\text{--BF}_3\text{--O}_2$ atmosphere in the presence of amorphous boron. The technique was shown in Fig. 4.11d.

The main reactions during such a gas boriding of iron alloys were as follows (Pertek 2001):



Such compounds as FeF_3 and H_2O were also present in the gas phase (Pertek 2001).

The general characterization of gas boriding of iron alloys with the use of boron trifluoride was shown in Table 4.15, taking into account the available literature data regarding the composition of the carrier gas, percentage of BF_3 in relation to the entire boriding atmosphere, oxide moderator, activator and powder components, schematic representation of the method in Fig. 4.11 as well as the temperature and time of the treatment. It was difficult to determine the current trends in gas boriding with the use of boron trifluoride based on the two available References. The process wasn't popular in recent years, probably, because of more complicated device in comparison with gas boriding using boron trichloride. The literature data reported only the process, carried out on iron alloys. However, the boriding of some non-ferrous alloys would also be possible.

The microstructure of the gas borided layers, produced on all the analyzed iron alloys with the use of BF_3 , could be both two-phase ($\text{FeB} + \text{Fe}_2\text{B}$) and single phase (Fe_2B). Pertek (2001) suggested that the two-phase boride layer was obtained if the activity of boron in the boriding atmosphere under the powder mixture was relatively high. In this case, the boron atoms, adsorbed by the surface of substrate

Table 4.15 General characterization of selected processes of gas boriding of iron alloys with the use of boron trifluoride

Type of material	Carrier gas/BF ₃ percentage/oxide moderator/activator and powder components/Scheme of the method	Temperature (°C)/Time (h)	References
Armco iron	H ₂ /BF ₃ with unknown percentage/–4% B + 96% C, containing O ₂ /Fig. 4.11d	850–1000/1–6	Pertek (2001)
	H ₂ /BF ₃ with unknown percentage/–50% B + 50% C, containing O ₂ /Fig. 4.11d	850–1000/1–6	Pertek (2001)
	H ₂ /BF ₃ with unknown percentage/–100% B, containing O ₂ /Fig. 4.11d	850–1000/1–6	Pertek (2001)
Low-carbon steels	–/100% BF ₃ /SiO ₂ /B ₄ C/Fig. 4.11c	1000/2	Goeuriot et al. (1981)
Medium-carbon steels	–/100% BF ₃ /SiO ₂ /β-B, B ₄ C, B ₁₀ C/Fig. 4.11a	1000/18	Goeuriot et al. (1981)
	–/100% BF ₃ /SiO ₂ /B ₄ C, borided piece in SiC/Fig. 4.11b	1020/2.5	Goeuriot et al. (1981)
	H ₂ /BF ₃ with unknown percentage/–4% B + 96% C, containing O ₂ /Fig. 4.11d	850–1000/1–6	Pertek (2001)
	H ₂ /BF ₃ with unknown percentage/–50% B + 50% C, containing O ₂ /Fig. 4.11d	850–1000/1–6	Pertek (2001)
	H ₂ /BF ₃ with unknown percentage/–100% B, containing O ₂ /Fig. 4.11d	850–1000/1–6	Pertek (2001)
High-alloy steels	–/100% BF ₃ /SiO ₂ /B ₄ C, borided piece in SiC/Fig. 4.11b	1020/2.5	Goeuriot et al. (1981)

material, caused the quick formation of FeB phase. The Fe₂B phase was formed below FeB because of the further grain-boundary diffusion of boron into the substrate through the FeB layer. During producing the single-phase boride layer (Fe₂B), the activity of boron in the atmosphere was initially also high, resulting in the formation of the very thin FeB layer. Then, the activity of boron was reduced and maintained at a constant level. So, the boron concentration on the surface was relatively low and didn't cause the further growth of FeB phase. However, the growth of Fe₂B phase still occurred because of the grain-boundary diffusion of boron.

Goeuriot et al. (1981) reported the Fe₂B monolayer after boriding of low-carbon and medium-carbon steels with the use of boron trifluoride. They indicated the accepted effect of the boriding technique with the use of solid boriding agent, containing B₄C + SiC powder (see Fig. 4.11b). Such a boriding resulted in the formation of thick needle-like Fe₂B layer (up to 130 μm for low-carbon steel, and up to 90 μm for medium-carbon steel). The two-phase FeB + Fe₂B boride layer, also including CrB phase, was produced on the high-alloy steel. However, the effect

of boriding of austenitic steel was unsatisfactory because of producing the non-adherent multiphase layer.

The control of the chemical composition of boriding atmosphere, i.e. the activity of boron, was very difficult in such complex system of boriding. Hence the gas boriding with the use of BF_3 was less popular than the process which used BCl_3 as a boron source.

4.3.2 Gas Boriding with the Use of Boranes and Other Boron Sources

Gas boriding (GB) with the use of boranes was also much less popular compared to the process in atmospheres, containing the boron trichloride. The main gaseous boron sources, classified as boranes and used for boronizing, were as follows: diborane B_2H_6 , trimethyl borane $(\text{CH}_3)_3\text{B}$ or triethyl borane $(\text{C}_2\text{H}_5)_3\text{B}$. Sometimes trimethyl borate $(\text{OCH}_3)_3\text{B}$ could be also applied.

B_2H_6 was known as a colorless, highly chemically unstable and pyrophoric gas at room temperature with a repulsively sweet odor and boiling point $-92.5\text{ }^\circ\text{C}$ (180.7 K). Diborane could be well mixed with air, easily forming explosive mixtures. In moist air at ambient temperature B_2H_6 would ignite spontaneously. This gas could slowly decompose even at room temperature, and above $500\text{ }^\circ\text{C}$ (773 K) its full thermal dissociation into boron and hydrogen occurred (Zhigach et al. 1959; Casadesus et al. 1979) according to the reaction:



Trimethyl borane was a toxic, pyrophoric gas at room temperature. Its boiling point was equal to $-20.2\text{ }^\circ\text{C}$ (253 K). Triethyl borane was an organoborane (i.e. a compound with a B–C bond). At ambient temperature, it was usually a colorless pyrophoric liquid because of the relatively high boiling point, obtaining $95\text{ }^\circ\text{C}$ (368 K), and melting point of $-93\text{ }^\circ\text{C}$ (180 K). Trimethyl borate was known as the compound with the formula $\text{B}(\text{OCH}_3)_3$, being a colorless liquid of the boiling point in the range of $68\text{--}69\text{ }^\circ\text{C}$ (341–342 K) that burned with a green flame. However, trimethyl borane, triethyl borane or trimethyl borate were applied more often during plasma boriding (Küper et al. 2000) than in the case of typical gas boriding.

The main equipment, applied during **gas boriding (GB) using diborane**, consisted of: heating device with temperature control system, i.e. electric resistance furnace (tubular or chamber furnace) or high frequency induction furnace, retort (made of quartz, Ni-based alloy or stainless steel), gas cylinders with diborane, hydrogen and argon, off-gas washer (gas scrubber) and temperature measurement system. Sometimes, the fan was applied in order to provide the constant flow of boriding atmosphere, its good mixing and the constant temperature in the entire chamber volume.

The available in literature data methods of gas boriding with the use of B_2H_6 as a boron source were schematically represented in Fig. 4.12a, b. These schemes differed only in the heating device. Electric resistance furnace (Fig. 4.12a) was applied by Lakhtin and Pchelkina (1961). Whereas Zhigach et al. (1959) used the high frequency induction furnace (Fig. 4.12b). The boriding atmosphere consisted of hydrogen as a carrier gas and diborane which was delivered directly from the gas cylinder. It was possible because of the lower boiling point of B_2H_6 than the ambient temperature. The difference in the density of diborane (0.001216 g/cm^3) and hydrogen (0.0008988 g/cm^3) wasn't so great. Hence, the use of injection nozzle wasn't necessary. The relation of B_2H_6 to H_2 was usually 1:25, i.e. the percentage of diborane was equal to 3.85%.

Borane triethyl amine complex $BH_3-N(C_2H_5)_3$ was used as a boron source during the *gas boriding (GB) under reduced pressure* (Küper et al. 2000), also called low-pressure gas boriding. In this case, the boron source was delivered to the carrier gas (Ar or Ar + H_2) using an evaporator, and the equipment contained the vacuum pump (Fig. 4.12c). The high frequency induction furnace was applied as a heating device. The last gas boriding method, reported by literature data, consisted in the use of the boron-containing coating as a boron source. Lyakhovich et al. (1982) carried out such a process in a hydrogen atmosphere, and the coating contained amorphous boron (Fig. 4.12d).

The general characterization of the mentioned above processes of gas boriding was presented in Table 4.16, taking into account the available literature data regarding the composition of the carrier gas, percentage of B_2H_6 in relation to the entire boriding atmosphere or other boron source, schematic representation of the method in Fig. 4.12 as well as the temperature and time of the treatment. It was difficult to formulate the conclusion regarding the current trends in these methods of gas boriding because of the small number of References available in literature data. The process with the use of diborane (Zhigach et al. 1959; Lakhtin and Pchelkina 1961) wasn't popular in recent years, probably, due to the possibility of the self-ignition at ambient temperature in the presence of moist air. The low-pressure gas boriding with the use of borane triethyl amine complex resulted in the formation of the relatively thin boride layers (Küper et al. 2000). Although the annealing of the pieces, coated with amorphous boron, in H_2 atmosphere provided the thick boride layers (Lyakhovich et al. 1982), such process wasn't developed in recent years. The difficulties in the control of the growth kinetics of boride layers, depending on the thickness of boron coating, was probably the reason for such situation.

The gas boriding of medium-carbon steel with the use of diborane resulted in the formation of the boride layer of good quality if the temperature of the process was at least 650°C (923 K) or higher (Zhigach et al. 1959). The thicknesses of the boride layers increased with increasing the temperature of boriding. The phase composition of the produced layers wasn't provided. Based on the hardness measurements, probably the two-phase $FeB + Fe_2B$ layers were fabricated. Some high-alloy steels were subjected to gas boronizing using B_2H_6 by Lakhtin and Pchelkina (1961). They suggested the mechanism of boronizing of complex

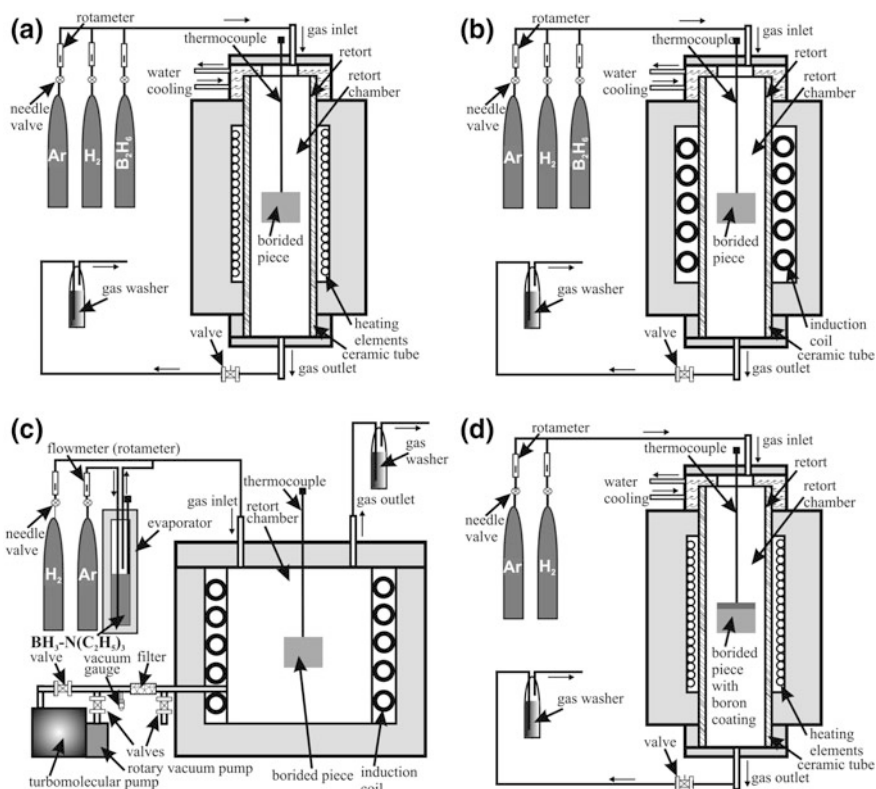


Fig. 4.12 Schematic representations of the other techniques of gas boriding: boriding in the typical electric resistance tubular furnace under H_2 - B_2H_6 atmosphere (a), boriding in the high frequency induction tubular furnace under H_2 - B_2H_6 atmosphere (b), boriding under reduced pressure in the high frequency induction chamber furnace using borane triethyl amine complex $BH_3-N(C_2H_5)_3$ (c), boriding in the typical electric resistance tubular furnace under H_2 atmosphere using the amorphous boron coating (d). *Remark: gas boriding under reduced pressure (c) could be also carried out with the use of trimethyl borane, triethyl borane or trimethyl borate*

austenitic steels with high concentration of Ni, Cr and other elements. If the saturation limit for boron in the alloyed solid solution was reached, borides appeared at the surface alongside the saturated α -solution. The formation of borides was usually accompanied by a depletion of the solid solution in boride-forming elements. The borides located within the solid solution, and grew within the layer because of the boron diffusion into the substrate. As a consequence, the continuous boride layer was formed close to the surface and an austenite with boron appeared below. The authors also indicated the phase composition of the produced boride layers. The proposed boronizing provided the two-phase microstructure of the boride layer with a formation of complex borides. So, the borides of the types $(Fe, Cr)B$ and $(Fe, Cr)_2B$ were formed on the high-chromium steel. Whereas boronizing of high-nickel steel was accompanied by the formation of $(Fe, Ni)B$ and $(Fe, Ni)_2B$.

Table 4.16 General characterization of selected processes of gas boriding of iron alloys with the use of diborane or other boron sources

Type of material	Composition of the carrier gas/B ₂ H ₆ percentage or other boron source/ Scheme of the method	Temperature (°C)/Time (h)	References
Medium-carbon steels	H ₂ /3.85% B ₂ H ₆ /Fig. 4.12b	550–1050/2–10	Zhigach et al. (1959)
	H ₂ /boron coating/Fig. 4.12d	600–1050/1–4	Lyakhovich et al. (1982)
	Ar or Ar + H ₂ /BH ₃ –N(C ₂ H ₅) ₃ borane triethyl amine complex/Fig. 4.12c, under reduced pressure	800–1000/1–10	Küper et al. (2000)
High-carbon steels	H ₂ /boron coating/Fig. 4.12d	600–1050/1–4	Lyakhovich et al. (1982)
High-alloy steels	H ₂ /3.85% B ₂ H ₆ /Fig. 4.12a	950/6	Lakhtin and Pchelkina (1961)

borides. Consequently, the (Fe,Ni,Cr)B and (Fe,Ni,Cr)₂B phases occurred in boride layer if the steel was characterized by high chromium and high nickel concentration. The possibility of producing the boride layers on the austenitic steels was the important advantage of gas boriding with the use of diborane compared to the processes of boriding which used boron halides as a boron source.

The *gas boriding using boron coating* as a contact method of boriding, consisting in the use of boron-containing coating as a boron source, was an intermediate technique between the gas and pack-powder boriding (Lyakhovich et al. 1982). The saturation with boron from a coating (amorphous boron) in hydrogen atmosphere resulted in the formation of single-phase Fe₂B layer on the medium- or high-carbon steel.

The quality of the boride layers, produced by gas boriding under reduced pressure using borane triethyl amine complex as a boron source (Küper et al. 2000), was unsatisfactory. The relatively thin Fe₂B monolayer was formed.

4.3.3 Thermodynamics of Gas Boriding with the Use of Boron Trichloride as a Boron Source

Gas boriding was the only method which enabled the permanent delivery of the boron source to the atmosphere, providing its constant chemical composition and the stability of the diffusion flux of boron from the boriding medium to the borided material. The analysis of the current trends in gas boronizing indicated the process with the use of boron trichloride as the most popular and developed method through the last two decades. Therefore, the thermodynamics of such a process should be presented in more detail.

Thorough thermodynamic analysis of the gas boriding process of pure iron under H_2 - BCl_3 atmosphere was carried out by Pertek (2001). The four systems: BCl_3 - H_2 , BCl_3 - H_2 -B, BCl_3 - H_2 -Fe and BCl_3 - H_2 - $FeCl_2$ were taken into account. The free enthalpy (Gibbs free energy) of possible reactions, proceeding in these systems, were calculated and the most probable reactions were indicated. The influence of temperature, pressure and chemical composition of the reactants on the equilibrium conditions between solid and gas phase was analyzed.

The possible reactions in the BCl_3 - H_2 system were provided by Pertek (2001), based on the calculations of their free enthalpy ΔG_T^0 . Many reactions, relating to the formation of such compounds as: $BHCl_2$, HCl , B_2Cl_4 , BCl_2 , BCl of B_2H_6 , could proceed in the BCl_3 - H_2 gaseous mixture. However, according to the data, reported by Pertek (2001), the main components of gas phase under equilibrium conditions were as follows: H_2 , $BHCl_2$, HCl and BCl_3 . The other components occurred in trace amounts. It well corresponded to the results, presented by Katagiri (1969) or Bartsch and Wolf (1979) regarding the infrared spectra of gaseous reaction products. The thermodynamic analysis enabled to formulate the conclusion that only one reaction proceeded in BCl_3 - H_2 system (Pertek 2001), according to the Eq. (4.22). This reaction was characterized by the smallest positive values of free enthalpy ΔG_T^0 in the wide range of temperatures, according to the equation:

$$\Delta G_T^0 = -0.0232 \cdot T + 37.643 \quad (4.36)$$

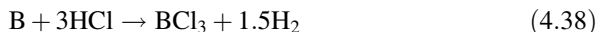
where: ΔG_T^0 is the free enthalpy (Gibbs free energy) in (kJ/mol), T is an absolute temperature (K).

The Gibbs free energy of reaction (4.23) was higher in the whole temperature range, and its dependence on the temperature was as follows:

$$\Delta G_T^0 = -0.0514 \cdot T + 82.083 \quad (4.37)$$

The influence of temperature on the values of Gibbs free energies, calculated by Pertek (2001) for these reactions was shown in Fig. 4.13. Pertek (2001) also determined the chemical composition of reaction products at 900 °C (1173 K). The increase in BCl_3 percentage in reactants (in relation to H_2), i.e. its evaporation temperature, resulted in reduced content of hydrogen and increased contents of $BHCl_2$, HCl and BCl_3 in reaction products.

The equilibrium conditions of boriding mixture with boron were also analyzed by Pertek (2001) in detail. The possible reactions in the BCl_3 - H_2 -B system were as follows:



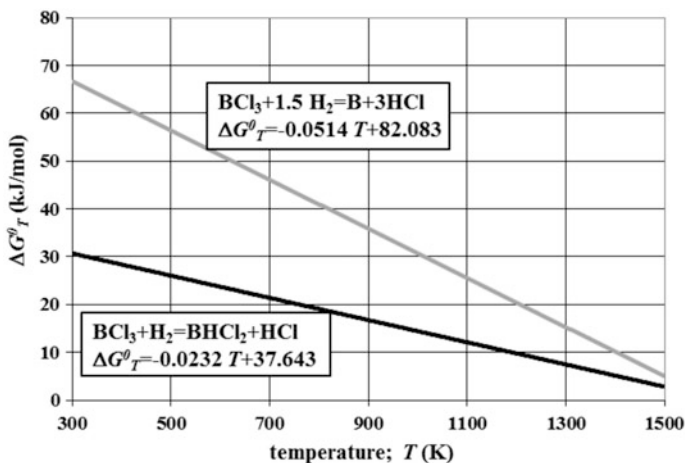
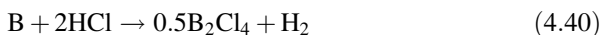


Fig. 4.13 Free enthalpy of reactions (4.22) and (4.23) versus temperature (Pertek 2001)



As for the $\text{BCl}_3\text{--H}_2$ system, Pertek (2001) calculated the chemical composition of reactants, defining the equilibrium of reaction products with boron. The increase in BCl_3 content in reactants was accompanied by the higher temperature, at which the equilibrium of gas phase with boron was obtained. It enabled to show the influence of temperature and BCl_3 percentage in reactants on the chemical composition of the gas phase under equilibrium conditions with boron. The increase in temperature, corresponding to the higher content of BCl_3 in the reactants, caused the diminished percentage of hydrogen and the higher contents of BCl_3 , BHCl_2 , HCl and B_2Cl_4 . The amount of diborane (B_2H_6) was unchanged. However, the main components of the atmosphere were: H_2 , BCl_3 , BHCl_2 and HCl , as it was also observed in the $\text{BCl}_3\text{--H}_2$ system. B_2Cl_4 and B_2H_6 occurred in trace amounts.

The conditions for the equilibrium of the $\text{BCl}_3\text{--H}_2$ atmosphere with boron could be determined based on the results of calculation of chemical composition of gas phase under thermodynamic equilibrium conditions (Pertek 2001). If the reaction (4.38) with boron was considered, the equilibrium constant K of this reaction could be written as:

$$K = \frac{p_{\text{BCl}_3} \cdot p_{\text{H}_2}^{1.5}}{p_{\text{HCl}}^3 \cdot a_{\text{B}}} \quad (4.42)$$

where: p_{BCl_3} , p_{H_2} , p_{HCl} are the partial pressures of gaseous components, a_{B} is the activity of boron.

Assuming that:

$$r = \frac{p_{\text{BCl}_3} \cdot p_{\text{H}_2}^{1.5}}{p_{\text{HCl}}^3} \quad (4.43)$$

the equilibrium constant K could be expressed as:

$$K = \frac{r}{a_{\text{B}}} \quad (4.44)$$

where: r is the quotient of the partial pressures of gaseous components.

Hence, the activity of boron, related to the pure boron, could be defined as follows:

$$a_{\text{B}} = \frac{r}{K} = \frac{p_{\text{BCl}_3} \cdot p_{\text{H}_2}^{1.5}}{p_{\text{HCl}}^3 \cdot K} \quad (4.45)$$

Pertek (2001) calculated the equilibrium constant (K) at various temperatures based on the free enthalpy of reaction (2.38):

$$\Delta G_T^0 = -119,214 \cdot T + 74.79 \quad (4.46)$$

where: ΔG_T^0 is the free enthalpy (Gibbs free energy) in (J/mol), T is an absolute temperature (K).

Simultaneously, the free enthalpy could be expressed as:

$$\Delta G_T^0 = -R \cdot T \cdot \ln K \quad (4.47)$$

where: R is the gas constant equal to $8.314462 \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$, T is an absolute temperature (K), and K is the equilibrium constant.

Taking into account Eqs. (4.46) and (4.47), the equilibrium constant of the reaction (4.38) was calculated according to:

$$K = \exp\left(\frac{119,214 \cdot T - 74.79}{R \cdot T}\right) \quad (4.48)$$

The quotient of the partial pressures (r) was calculated by Pertek (2001) at various temperatures for the selected chemical compositions of gas mixtures in the $\text{BCl}_3\text{--H}_2$ system under equilibrium conditions. These results were generalized in this work in order to enable the calculations of the r values for any chemical composition of the $\text{BCl}_3\text{--H}_2$ gas mixture. It was assumed that the quotient of the partial pressures (r) could be expressed versus the absolute temperature (T) as:

$$r = a \cdot T^b \quad (4.49)$$

where: a and b are the corresponding coefficients.

The coefficients in Eq. (2.49) depended on the chemical composition of H_2 – BCl_3 atmosphere, i.e. on the percentage of boron trichloride in the reactants:

$$a = (0.00312715 \cdot \%BCl_3^2 - 0.003595971 \cdot \%BCl_3 + 0.60724844) \times 10^{15} \quad (4.50)$$

$$b = 0.00016364 \cdot \%BCl_3^2 - 0.02409091 \cdot \%BCl_3 - 4.07363636 \quad (4.51)$$

where: $\%BCl_3$ is the content of boron trichloride in H_2 – BCl_3 atmosphere (vol%).

The results of calculations of equilibrium constant K , according to Eq. (4.48), and the quotient of the partial pressures r at the various percentages of BCl_3 in H_2 – BCl_3 atmosphere, according to Eqs. (4.49), (4.50) and (4.51), were shown in Fig. 4.14a versus the boriding temperature. The calculated values of r , provided by Pertek (2001), were marked with black squares, triangles, circles or rhombi, depending on the analyzed BCl_3 content. These values well corresponded to the results, marked with the gray lines and obtained with the use of Eqs. (4.49), (4.50) and (4.51), representing the generalized model. According to Hegewaldt et al. (1984), it was assumed that nitrogen didn't participate in the reactions of gas boriding. Therefore, the content of boron trichloride in relation to hydrogen was also most important. In such a case, the mentioned above Eqs. (4.42), (4.43), (4.44), (4.45), (4.46), (4.47), (4.48), (4.49), (4.50) and (4.51) could be also accepted for $(75\% N_2 + 25\% H_2)$ – BCl_3 atmosphere. The only difference consisted in a diminished percentage of BCl_3 in this atmosphere compared to H_2 – BCl_3 mixture. However, the contents of boron trichloride in relation to hydrogen were the same in the both cases. The results of calculations of equilibrium constant (K) and the quotient of the partial pressures (r) were shown in Fig. 4.14b versus the boriding temperature at the various percentages of BCl_3 in $(75\% N_2 + 25\% H_2)$ – BCl_3 atmosphere. The intersections of the K curve with individual curves of the r quotient for the given contents of the boron trichloride appointed the equilibrium conditions of the considered gaseous atmosphere with boron.

The generalization of the relationship between r values and the temperature as well as BCl_3 percentage enabled to predict the boron activity for any temperature and any BCl_3 content in the boriding atmosphere, irrespective if the H_2 – BCl_3 or $(75\% N_2 + 25\% H_2)$ – BCl_3 gas mixture was applied. Activity of boron versus the temperature of boriding was shown in Fig. 4.15 at various percentages of boron trichloride in relation to H_2 (Fig. 4.15a) as well as in relation to $75\% N_2 + 25\% H_2$ mixture (Fig. 4.15b). It should be noticed that the BCl_3 contents in relation to hydrogen in the case of $(75\% N_2 + 25\% H_2)$ – BCl_3 gas mixture corresponded to the boron trichloride contents in the H_2 – BCl_3 atmosphere. The influence of BCl_3 percentage in relation to the whole boriding atmosphere on the boron activity at

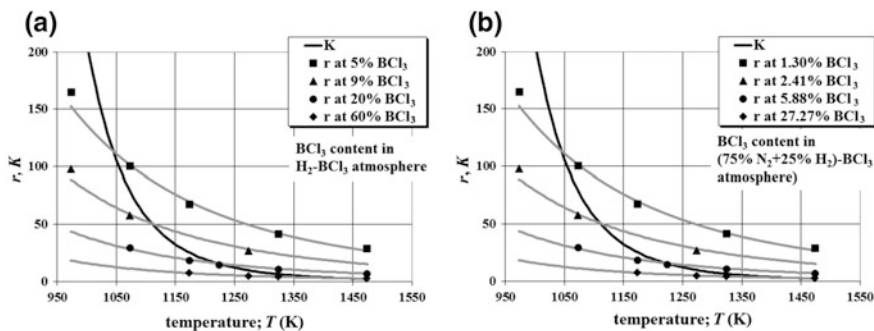


Fig. 4.14 Equilibrium constant K and the quotient of the partial pressures r versus temperature at various BCl_3 percentages in H_2 - BCl_3 atmosphere (a) and in $(75\% N_2 + 25\% H_2)$ - BCl_3 atmosphere (b). The values of quotient r , calculated by Pertek (2001), are marked with black squares, triangles, circles and rhombi

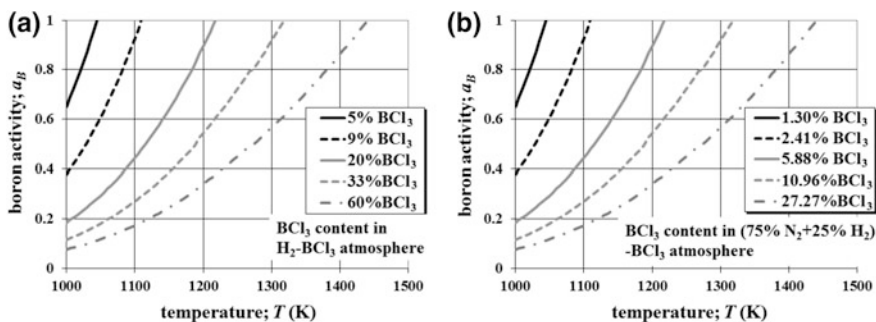


Fig. 4.15 Activity of boron versus temperature at various BCl_3 percentages in H_2 - BCl_3 atmosphere (a) and in $(75\% N_2 + 25\% H_2)$ - BCl_3 atmosphere (b)

different temperatures was shown in Fig. 4.16a, b for H_2 - BCl_3 and $(75\% N_2 + 25\% H_2)$ - BCl_3 gas mixtures, respectively. If the boron trichloride content in relation to hydrogen would be taken into consideration for $(75\% N_2 + 25\% H_2)$ - BCl_3 atmosphere, the diagram in Fig. 4.16b wouldn't differ from it shown in Fig. 4.16a.

The influence of boriding temperature on the boron trichloride percentage in the considered H_2 - BCl_3 and $(75\% N_2 + 25\% H_2)$ - BCl_3 atmospheres at equilibrium conditions with boron ($r = K$) was presented in Fig. 4.17. The determined relationships were very important, taking into account the possibilities of the control of boron activity during the process in the used atmosphere. Based on Figs. 4.15, 4.16 and 4.17, it could be concluded that the most often used temperature of gas boriding, i.e. 800–1000 °C (1073–1273 K), as well as the most commonly applied BCl_3 contents in the H_2 - BCl_3 atmosphere (5–9%) or in $(75\% N_2 + 25\% H_2)$ - BCl_3 gas mixture (1.34–2.3%) corresponded to the activity of boron equal to 1 or to the values slightly smaller than 1. Under such conditions, the ability to

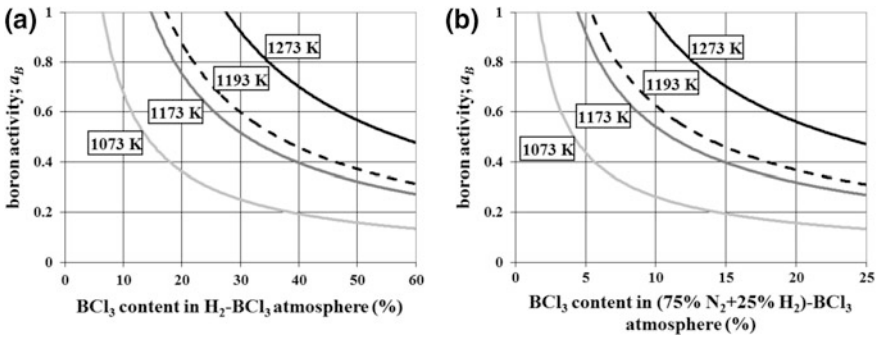


Fig. 4.16 Activity of boron versus BCl_3 percentage in H_2 - BCl_3 atmosphere (a) and in $(75\% \text{N}_2 + 25\% \text{H}_2)$ - BCl_3 atmosphere (b) at various temperatures

regulate activity of boron was limited. Boron activity influenced the microstructure of the boride layer this way that the higher its value favored the formation of borides of high boron concentration, e.g. FeB iron borides were produced close to the surface in the case of boriding of iron alloys. The reduced activity of boron could result in formation of only less brittle Fe_2B phase. The decrease of boron activity required to increase the BCl_3 content in the atmosphere or to diminish the boriding temperature (look at the arrows in Fig. 4.17). However, the increased percentage of boron trichloride (above 10 vol%) in relation to hydrogen provided the boride layers of high porosity (Hegewaldt et al. 1984; Pertek 2001). Whereas the boriding temperature below 800 °C (1073 K) influenced the growth kinetics of boride layers, reducing their thickness.

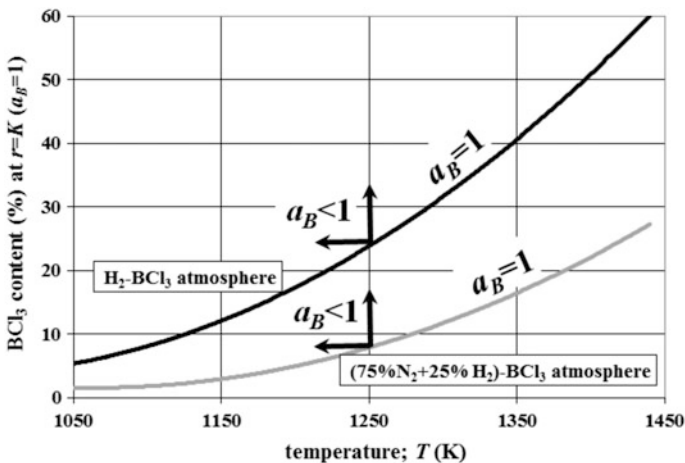


Fig. 4.17 Influence of the boriding temperature on the BCl_3 percentage in H_2 - BCl_3 atmosphere and in $(75\% \text{N}_2 + 25\% \text{H}_2)$ - BCl_3 atmosphere at boron activity equal to 1, i.e. at $r = K$

Pertek (2001) also analyzed the $\text{BCl}_3\text{--H}_2\text{--Fe}$ system in order to determine the equilibrium conditions of $\text{H}_2\text{--BCl}_3$ atmosphere with iron borides (FeB and Fe_2B). The formation of iron borides could proceed according to the reactions:



The corresponding Gibbs free energy ΔG_T^0 versus absolute temperature T was described by the equations (Pertek 2001):

– for reaction (4.52)

$$\Delta G_T^0 = -79.61 + 0.0105 \cdot T \quad (4.55)$$

– for reaction (4.53)

$$\Delta G_T^0 = -87.99 + 0.0184 \cdot T \quad (4.56)$$

– for reaction (4.54)

$$\Delta G_T^0 = -8.38 + 0.0079 \cdot T \quad (4.57)$$

where: ΔG_T^0 is the free enthalpy (Gibbs free energy) in (kJ/mol), T is an absolute temperature (K).

The influence of the temperature on the Gibbs free energy was presented in Fig. 4.18 for the two most probable reactions of iron borides' formation (4.52) and (4.53). The values of Gibbs free energy of reaction (4.54) were significantly higher, ranging from -0.48 to 3.47 kJ/mol. Therefore, the formation of Fe_2B phase directly from FeB was excluded. The free enthalpy of reaction (4.52), responsible for FeB phase formation, was lower than that of reaction (4.53) in the range of the most commonly used temperatures of gas boriding, i.e. $800\text{--}1000$ °C ($1073\text{--}1273$ K). It led to the conclusion that boriding atmosphere could be in thermodynamic equilibrium only with the FeB iron boride. Hence, this phase was formed firstly in iron alloys during gas boriding. Such thesis was confirmed by XRD patterns, obtained after a short duration of gas boriding in $\text{H}_2\text{--BCl}_3$ atmosphere (Pertek 1994). The nucleation of FeB boride occurred promptly on the surface of the Armco iron after about 4 s. After 8 s of boriding, FeB and Fe_2B phases coexisted, and the entire surface of the sample was full of the crystal nuclei of borides.

The main components of the gas atmosphere in the $\text{BCl}_3\text{--H}_2\text{--Fe}$ system under equilibrium with FeB phase were as follows: H_2 , BCl_3 , BHCl_2 , HCl and FeCl_2 . The other components (B_2Cl_4 , BCl_2 , Cl , Cl_2 and BCl) occurred in traces. The reactions,

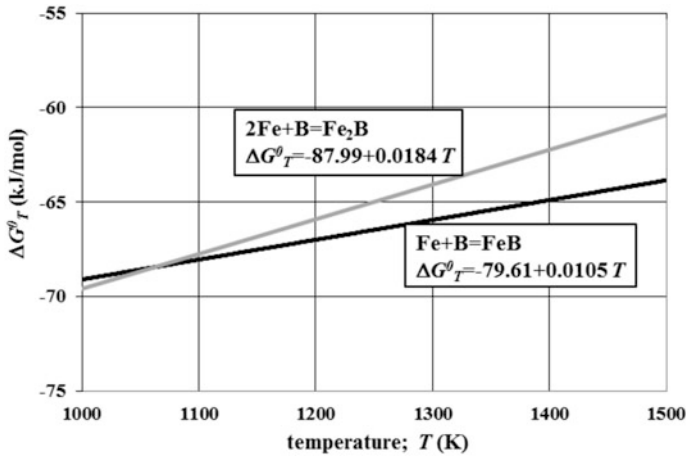
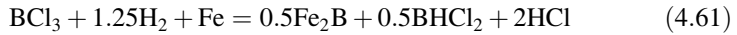
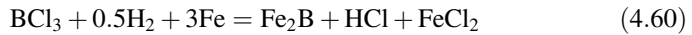
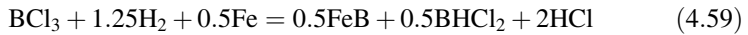


Fig. 4.18 Free enthalpy of reactions (4.52) and (4.53) versus temperature (Pertek 2001)

proceeding in this system and responsible for the formation of FeB + Fe₂B layer, were defined by Pertek (2001):



Therefore, producing the single-phase Fe₂B layer in H₂–BCl₃ atmosphere usually required to apply the two-stage process (Pertek 2001), consisting of the saturation with boron (i.e. typical gas boriding with the high boron activity) and diffusion annealing (i.e. the process under atmosphere without boron trichloride). The first stage resulted in the formation of the two-phase layer (FeB + Fe₂B), and the second stage reduced or completely eliminated the more brittle FeB phase. The two-stage gas boriding with the use of boron trichloride was developed by Kulka et al. (2012a) this way that the (75% N₂ + 25% H₂)–BCl₃ atmosphere was used during the first stage of process, and the saturation with boron and diffusion annealing were alternately repeated.

The BCl₃–H₂–FeCl₂ system was also analyzed by Pertek (2001) because of the formation of ferrous chloride (FeCl₂) as a consequence of reactions (4.58) and (4.60). It was assumed that the main components of the gas atmosphere were the same, as it was observed for BCl₃–H₂–Fe system (i.e. H₂, BCl₃, BHCl₂, HCl, FeCl₂) and, additionally, ferric chloride (FeCl₃). The higher BCl₃ percentage in reactants caused the increase in the content of BCl₃, BHCl₂ and HCl in the reactions' products. Simultaneously, the decrease in H₂ content occurred. The FeCl₂

percentage was only slightly lower in the products than that in the reactants, and the content of FeCl_3 was very low (below 0.01 vol%). The increased percentage of HCl and FeCl_2 was inadvisable because of the possible corrosion attack (Hegewaldt et al. 1984; Pertek 2001). That was why the use of the BCl_3 percentage above 10 vol% in relation to H_2 favored the formation of more porous iron boride layers.

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Chapter 5

Trends in Physical Techniques of Boriding



Abstract All the specified physical techniques of boriding, i.e. carried out under glow discharge conditions, boron ion implantation and high-energy techniques were characterized and compared in this chapter based on the available literature data. The technological aspects of boriding processes were analyzed, taking into consideration the advantages and disadvantages of each method. The effects of the boriding methods on the microstructure of borided materials were shown. The mechanism of formation of active boron atoms or ions and the phenomena during re-melting of alloying material together with the substrate were described. The three main groups of physical techniques of boriding were specified: boriding under glow discharge conditions, boriding by ion implantation and the high-energy methods of boriding. The most intensively developed physical techniques were put in the boxes drawn in a broken line in Fig. 2.1. They were described in more detail, taking into account the current trends in boronizing. Hence, the most attention was devoted to the boriding under glow discharge conditions, especially plasma gas (or paste) boriding, and surface alloying with boron, especially, laser (or plasma) surface alloying.

5.1 Boriding Under Glow Discharge Conditions

The process of *boriding under glow discharge conditions* could be classified, taking into account the various boron sources. The four techniques of such boriding were developed: with the use of gas, powder, paste and liquid as a boron source (see Fig. 2.1). These techniques were often called also plasma boriding or ion boriding. The main advantages of the use of boronizing under glow-discharge were as follows: the reduction of the process temperature and the decreased percentage of toxic gases in the atmosphere compared to the typical gas boriding.

5.1.1 Plasma Gas Boriding

The first technique, called *plasma gas boriding (PGB)* in the present work, consisted in the use of gaseous boron sources. As the gaseous boron sources, used for boronizing under glow-discharge conditions, both boron halides, e.g. boron trichloride BCl_3 or boron trifluoride BF_3 , and boranes, e.g. diborane B_2H_6 , trimethyl borane $(\text{CH}_3)_3\text{B}$ or triethyl borane $(\text{C}_2\text{H}_5)_3\text{B}$, were applied. Sometimes trimethyl borate $(\text{OCH}_3)_3\text{B}$ could be also used. Electrically ionized gases have been studied for a number of years (Engel 1965; Brown 1994). In recent years, they played a significant role in the thermochemical treatment of metals and its alloys. So-called plasma-assisted processes used electrically ionized or excited reactive gases such as nitrogen, hydrocarbons, or chlorides for various surface chemical modifications, including the formation of diffusion nitrided (Roliński 2014), carburized (Winter 2014) or borided layers (Wierchoń 1988).

The cleaned workpieces, subjected to plasma gas boronizing, were usually put into the tubular reactor, which was then evacuated from the air by the vacuum pumping system. This system enabled to carry out the plasma boriding process under reduced pressure. At first, pure hydrogen, pure argon or the $\text{H}_2 + \text{Ar}$ mixture was introduced into the reactor, and DC power supply was switched on with the use of an adequate voltage. The borided workpiece was connected to the plasma power supply as the cathode. Whereas the reactor wall acted as the anode. In such an atmosphere, the sputter cleaning of the surface could occur during simultaneous heating. After the workpiece was heated up, the flow of gaseous boron source was activated. BCl_3 was the most popular boron source (Wierchoń et al. 1980, 1995; Dearnley et al. 1986; Wierchoń 1988; Fillit et al. 1995; Miyashita and Yokota 1996; Sikorski et al. 1998; Nam et al. 1998; Bartsch and Leonhardt 1999; Cabeo et al. 1999; Kaestner et al. 2001; Filep and Farkas 2005, Yang et al. 2013). BF_3 (Hunger and Löbig 1997; Basturk et al. 2010), B_2H_6 (Casadesus et al. 1979; Ballinger and Catledge 2015; Johnston et al. 2015, 2016; Johnston and Catledge 2016) or other evaporated compounds (Küper et al. 2000; Qiao et al. 2000) were also often applied. When the DC voltage operated, the reactor was lighted up and a glow discharge (cold plasma), containing the active species (ions, atoms, radicals and other excited species), appeared close to the surface of the borided parts (Lebrun 2014). As a consequence of impingement of ions or neutrals at the surface, their kinetic energy was converted into heat. This caused an increase in the temperature of the borided pieces. The kinetic energy of the ions and the other rapid particles was sufficient in order to clean the surface of borided piece, i.e. to remove the atoms of impurities from the treated surface (sputtering) during the first stage of the process (without the use of boron source). It was important, especially in the case of metal alloys which easily was subjected to passivation (e.g. stainless steels or titanium alloys). Sputter cleaning caused depassivation of their surface. Thanks to such a clean surface and such active species, boron atoms could be adsorbed at the surface of borided material. In general, plasma gas boriding was carried out at lower temperatures compared to the typical gas boriding. Whereas the duration of

these processes was comparable. The wide ranges of the pressure (133–10,000 Pa) and voltage (400–1400 V) were used. These parameters depended on the type of borided material or on the type of boriding atmosphere to a certain degree.

The main equipment, required for plasma gas boriding, was as follows: tubular reactor, plasma generator, gas cylinders with hydrogen and argon, a gaseous boron source in gas cylinder or in evaporator, gas mixing chamber (sometimes with injection nozzle) or the system of cooling of boron source, off-gas washer (gas scrubber), vacuum pump, temperature control and measurement system. At first, a DC power supply has been commonly used for the generation of a glow discharge during plasma boriding. The glow discharge was in the region of the anomalous glow discharge which could be very unstable and could change to an arc discharge (Rie 1999).

During the 1980s, the very important improvement was introduced, consisting in the use of the pulsed current generators (Burakowski and Wierzchoń 1998; Rie 1999; Lebrun 2014). The advantages of pulsed DC over unpulsed DC were specified by Rie (1999). If the pulsed DC was used, the treatment temperature could be varied by changing the pulse duration and repetition time without altering plasma parameters such as the voltage across the electrodes. However, the additional heating of the reactor was then advised. The transfer of an anomalous glow discharge into an arc discharge was also less probable. The proper selection of the ratio of pulse duration to pulse repetition could influence the phase composition of the layer and enabled to use even a hollow-cathode discharge for a workpiece of cylindrical shape without its damage as a consequence of overheating. This ratio also influenced the amount of ionized species, excited atoms, molecules and neutrals. If the correct pressure was used, the “glow seam” followed the contours of the borided workpiece, even in deep slots and narrow holes (Rie 1999).

Burakowski and Wierzchoń (1998) distinguished the two types of reactors: with cold wall (i.e. with additional cooling or without additional heating only) and with hot wall (i.e. with additional heating). In the present work, another classification of reactors was accepted. The types of reactors, specified by Lebrun (2014), were shown in Fig. 5.1. **Cold wall** (Fig. 5.1a) and **hot wall** (Fig. 5.1b) **reactors** belonged to the first generation of reactors. In case of cold wall reactor the additional cooling was applied, and the hot wall reactor was used without water jackets as well as without an additional heating system. The second generation were the **reactors with an additional heating by convection** (Fig. 5.1c). Whereas the **reactors with an additional heating by radiation** (Fig. 5.1d) belonged to the third generation of the reactors. With the use of additional heating systems, the risks of electrical arcs, hollow cathode or overheating were strongly reduced, but still existed (Lebrun 2014). The various devices, applied for the treatment under glow discharge conditions, were described in detail by Burakowski and Wierzchoń (1998). In the present work, the methods of boriding under glow discharge conditions with the use of gaseous boron sources were generalized, taking into account recent trends.

The most often used and most effective techniques of plasma gas boriding with the use of various boron sources were schematically represented in Fig. 5.2. Although only the methods with hot wall reactor (without additional heating or

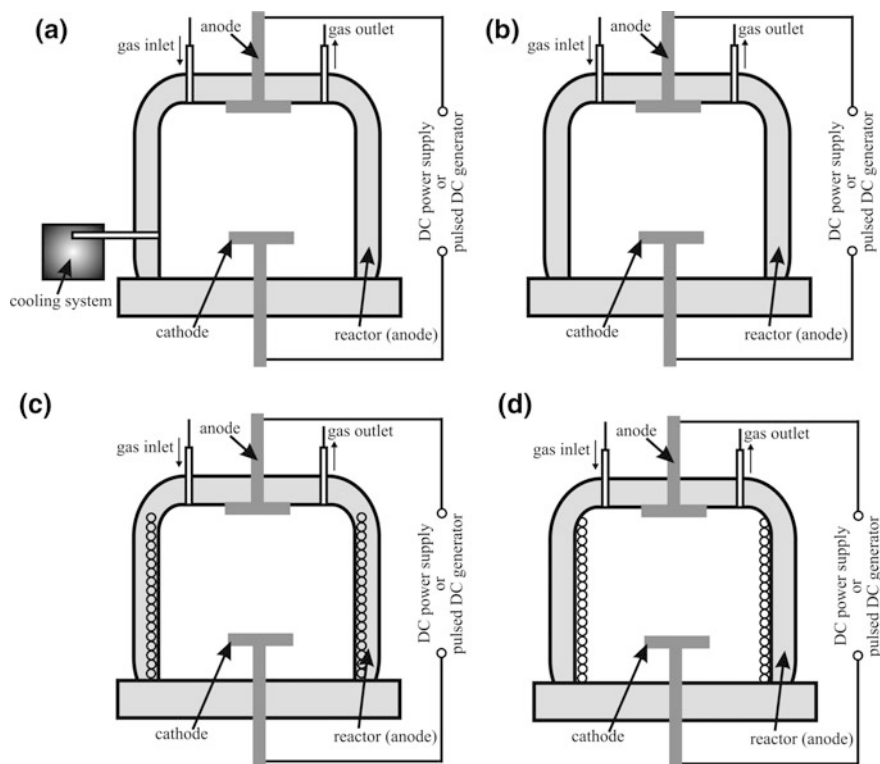


Fig. 5.1 Types of plasma reactors: cold wall reactor (a), hot wall reactor (b), reactor with additional heating by convection (c), reactor with additional heating by radiation (d)

cooling) were shown, the cold wall reactors as well as the reactors with additional heating were commonly applied. Sometimes, the microwave-plasma CVD (chemical vapor deposition) reactors were used for plasma gas boronizing. The process was often carried out according to the scheme shown in Fig. 5.2a (Casadesus et al. 1979; Dearnley et al. 1986; Miyashita and Yokota 1996; Hunger and Löbig 1997; Nam et al. 1998; Bartsch and Leonhardt 1999; Cabeo et al. 1999; Kaestner et al. 2001; Filep and Farkas 2005; Basturk et al. 2010; Yang et al. 2013; Ballinger and Catledge 2015; Johnston et al. 2015, 2016; Johnston and Catledge 2016).

The gaseous boron sources (BCl_3 , BF_3 , or B_2H_6) were delivered to the atmosphere directly from the gas cylinder. The gas mixing chamber was usually used in order to ensure the adequate mixing of carrier gas and gaseous boron source. Sometimes, the injection nozzle could be applied, if boron trichloride was delivered to the boriding atmosphere, as it was applied in the case of common gas boriding. DC power supply or pulsed DC generator with the ability to choose a frequency between 50 and 50,000 Hz usually acted as plasma generator. Other plasma generators, such as a pulsed microwave generator (Ballinger and Catledge 2015;

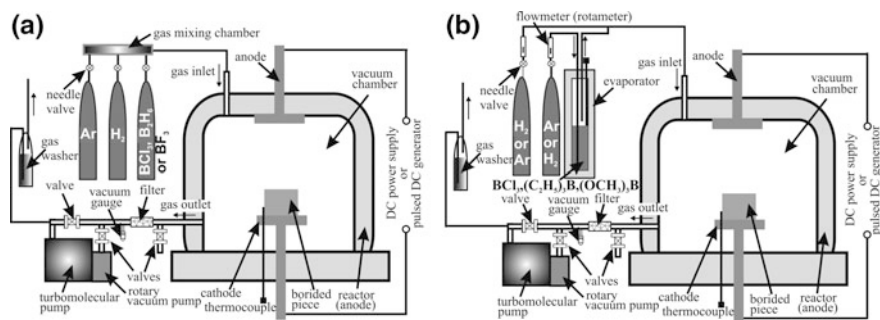


Fig. 5.2 Schematic representations of the most often applied and most effective techniques of plasma gas boriding (PGB): boriding in the vacuum chamber using BCl_3 , BF_3 or B_2H_6 (a), boriding in the vacuum chamber using evaporated boron trichloride BCl_3 , triethyl borane $(\text{C}_2\text{H}_5)_3\text{B}$ or trimethyl borate $(\text{OCH}_3)_3\text{B}$ (b). *Remark: Apart from the presented methods with hot wall reactor, the methods with cold wall and with additional heating by convection or radiation were also applied*

Johnston et al. 2015, 2016; Johnston and Catledge 2016) or pulsed r.f. generator (Miyashita and Yokota 1996), were applied sporadically.

The second method of plasma gas boriding differed from the first one taking into account the delivery of boron source to boriding atmosphere (Fig. 5.2b). Carrier gas (hydrogen or argon) was passed through the evaporator, containing the liquid boron trichloride BCl_3 (Wierzchoń et al. 1980, 1995; Fillit et al. 1995; Sikorski et al. 1998), triethyl borane $(\text{C}_2\text{H}_5)_3\text{B}$ (Küper et al. 2000) or trimethyl borate $(\text{OCH}_3)_3\text{B}$ (Küper et al. 2000; Qiao et al. 2000). The amount of boron source in boriding atmosphere was controlled by its evaporation temperature, as it was described for typical gas boriding.

The general characterization of plasma gas boriding of iron alloys was shown in Tables 5.1 and 5.2, taking into account the available literature data regarding the composition of the carrier gas, the type and percentage of gaseous boron source in relation to the entire boriding atmosphere, schematic representation of the method in Fig. 5.2, type of reactor, temperature and time of the treatment as well as pressure, voltage and type of plasma generator. Because of a number of important parameters and a number of variants of treatment as well as an incidental use of plasma gas boriding by some authors, it was difficult to indicate the current trends in plasma gas boronizing of iron alloys definitely.

However, taking into consideration the development in the technical possibilities of the devices, without a doubt it could be concluded that the use of reactor with additional heating as well as the pulsed DC generator was most advisable and perspective. The carrier gas usually included hydrogen or the mixture of argon and hydrogen.

Boron trichloride was most often used as a source of boron, and its delivery using an evaporator (Fig. 5.2b) still seemed to be most perspective because of the most effective control of its percentage in boriding atmosphere.

Table 5.1 General characterization of selected processes of plasma gas boriding of iron alloys. Part I

Type of material	Composition of carrier gas/ gaseous boron source/scheme of the method/type of reactor	Temperature (°C)/time (h)/pressure (Pa)/voltage (V)/plasma generator	References
Armco iron	H ₂ /BCl ₃ of unknown percentage/ Fig. 5.2b/hot wall reactor	900/0.83/9000/400–750/ DC power supply	Wierchoń et al. (1980)
	50% Ar + 50% H ₂ /0.1–0.3% BCl ₃ /Fig. 5.2a/heated reactor	700–800/1.75–2.5/500/ 550/DC power supply	Dearnley et al. (1986)
	Ar/∼40% BCl ₃ /Fig. 5.2a/heated reactor	500–700/0.5–2/133/ unknown voltage/pulsed r.f. generator	Miyashita and Yokota (1996)
	Ar + H ₂ /BCl ₃ of unknown percentage/Fig. 5.2a/cold wall reactor	520–560/1.5–3/170/ unknown voltage/pulsed DC generator	Bartsch and Leonhardt (1999)
Low-carbon steels	H ₂ /0.05–2% B ₂ H ₆ /Fig. 5.2a/ cold wall reactor	600–950/0.5–10/140– 1400/400–1000/pulsed DC generator	Casadesus et al. (1979)
	H ₂ /BCl ₃ of unknown percentage/ Fig. 5.2b/hot wall reactor	900/0.83/9000/400–750/ DC power supply	Wierchoń et al. (1980)
	0–98% Ar + 0–85% H ₂ /0.5– 20% BF ₃ /Fig. 5.2a/heated reactor	750–800/3.5/800–1200/ 400–600/pulsed DC generator	Hunger and Löbige (1997)
	Ar + H ₂ /1–5% BCl ₃ /Fig. 5.2a/ heated reactor	800/1–4/400–1000/600– 950/pulsed DC generator	Nam et al. (1998)
	Ar + H ₂ /2.5–15% BCl ₃ / Fig. 5.2a/heated reactor	700–850/2.5/300–1500/ 500–850/pulsed DC generator	Cabeo et al. (1999)
	H ₂ /0.5–2.5% BCl ₃ /Fig. 5.2a/hot wall reactor	750–800/2/520–550/900– 1400/pulsed DC generator	Filep and Farkas (2005)
Medium-carbon steels	Ar + H ₂ /1–5% BCl ₃ /Fig. 5.2a/ heated reactor	800/1–4/400–1000/600– 950/pulsed DC generator	Nam et al. (1998)
	Ar + H ₂ /BCl ₃ of unknown percentage/Fig. 5.2a/cold wall reactor	520–560/1.5–2/170/ unknown voltage/pulsed DC generator	Bartsch and Leonhardt (1999)

For the same reason, the use of triethyl borane or trimethyl borate gained in importance. Diborane, delivered to the boriding atmosphere directly from the gas cylinder, still seemed to be attractive as a boron source. Whereas boron trifluoride has been applied incidentally.

Table 5.2 General characterization of selected processes of plasma gas boriding of iron alloys. Part II

Type of material	Composition of carrier gas/gaseous boron source/scheme of the method/type of reactor	Temperature (°C)/time (h)/pressure (Pa)/voltage (V)/plasma generator	References
Low-alloy steels	0–98% Ar + 0–85% H ₂ /0.5–20% BF ₃ /Fig. 5.2a/heated reactor	750–800/3.5/800–1200/400–600/pulsed DC generator	Hunger and Löbig (1997)
	Ar + H ₂ /BCl ₃ of unknown percentage/Fig. 5.2a/cold wall reactor	520–560/1.5–3.67/170/unknown voltage/pulsed DC generator	Bartsch and Leonhardt (1999)
	Ar + H ₂ /2.5–15% BCl ₃ /Fig. 5.2a/heated reactor	700–850/2.5/300–1500/500–850/pulsed DC generator	Cabeo et al. (1999)
	Ar + H ₂ /(C ₂ H ₅) ₃ B or (OCH ₃) ₃ B/Fig. 5.2b/unknown reactor	800–1050/1–10/200–800/~ 550/pulsed DC generator	Küper et al. (2000)
	83.3%Ar + 16.7% H ₂ /(OCH ₃) ₃ B/Fig. 5.2b/heated reactor	830/1/800/unknown voltage/pulsed DC generator	Qiao et al. (2000)
High-alloy steels	Ar/~ 40% BCl ₃ /Fig. 5.2a/heated reactor	500–700/0.5–2/133/unknown voltage/pulsed r. f. generator	Miyashita and Yokota (1996)
	38.1% Ar + 61.9% H ₂ /3% BF ₃ /Fig. 5.2a/heated reactor	580/4/650–750/550/DC power supply	Yang et al. (2013)
	H ₂ /0.04% B ₂ H ₆ /Fig. 5.2a/microwave-plasma CVD reactor	550–825/0.1667–1/5300–10,000/unknown voltage/pulsed microwave generator	Ballinger and Catledge (2015)

PGB process has been applied more rarely in regard to non-ferrous materials. The general characterization of the treatment of such materials was shown in Table 5.3. Only isolated cases, concerning plasma gas boriding of titanium and its alloy, nickel-based alloy, Ni and Ni–P coatings on steel substrate (i.e. formation of hybrid boride layers), CoCrMo alloy and WC–Co sintered carbide, were reported. The conclusion in relation to the current trends had to be the same as for iron alloys.

The microstructure of plasma gas borided iron alloys was mostly two-phase, containing FeB and Fe₂B iron borides with characteristic zonation. The PGB process of Armco iron usually resulted in the formation of such a boride layer using both the technique presented in Fig. 5.2a (Dearnley et al. 1986; Miyashita and Yokota 1996; Bartsch and Leonhardt 1999) and the method from Fig. 5.2b (Wierzchoń et al. 1980).

The same FeB + Fe₂B boride layer was characteristic of plasma gas borided low-carbon steels (Casadesus et al. 1979; Wierzchoń et al. 1980; Hunger and Löbig 1997; Nam et al. 1998; Cabeo et al. 1999; Filep and Farkas 2005) and medium-carbon steels (Nam et al. 1998; Bartsch and Leonhardt 1999). The

Table 5.3 General characterization of selected processes of plasma gas boriding of non-ferrous materials

Type of material	Composition of carrier gas/gaseous boron source/scheme of the method/type of reactor	Temperature (°C)/time (h)/pressure (Pa)/voltage (V)/plasma generator	References
Titanium and its alloy	Ar + H ₂ /BCl ₃ of unknown percentage/Fig. 5.2a/heated reactor	700–900/4–8/300–1500/500–750/pulsed DC generator	Kaestner et al. (2001)
Nickel alloy	0–98% Ar + 0–85% H ₂ /0.5–20% BF ₃ /Fig. 5.2a/heated reactor	750–800/3.5/800–1200/400–600/pulsed DC generator	Hunger and Löbig (1997)
Ni or Ni–P coating on steel substrate	H ₂ /up to 5% BCl ₃ /Fig. 5.2b/hot wall reactor	650–850/2/500/unknown voltage/DC power supply	Wierzchoń et al. (1995) and Fillit et al. (1995)
	H ₂ /up to 5% BCl ₃ /Fig. 5.2b/hot wall reactor	650–850/4/500/unknown voltage/DC power supply	Sikorski et al. (1998)
CoCrMo alloy	H ₂ /0.06% B ₂ H ₆ /Fig. 5.2a/microwave-plasma CVD reactor	500–800/0.0028–2/unknown pressure/unknown voltage/pulsed microwave generator	Johnston et al. (2015)
WC–Co sintered carbide	55.6% H ₂ + 44.4% Ar/10% BF ₃ /Fig. 5.2a/heated reactor	600–850/1–6/unknown pressure/unknown voltage/DC power supply	Basturk et al. (2010)
	H ₂ /0.06% B ₂ H ₆ /Fig. 5.2a/microwave-plasma CVD reactor	700–1100/1/4000–8000/unknown voltage/pulsed microwave generator	Johnston and Catledge (2016)
	H ₂ /0.06% B ₂ H ₆ /Fig. 5.2a/microwave-plasma CVD reactor	700–1100/1/4000–8000/unknown voltage/pulsed microwave generator	Johnston et al. (2016)

single-phase Fe₂B layer was produced only by Nam et al. (1998) on the surface of low-carbon steel using the relatively low content of boron trichloride in the Ar–H₂–BCl₃ atmosphere (about 1%).

Although the boride layers, formed on low-alloy steels, were mainly composed of FeB and Fe₂B iron borides (Hunger and Löbig 1997; Bartsch and Leonhardt 1999; Cabeo et al. 1999), the Fe₂B monolayer was obtained with the use of trimethyl borate (Küper et al. 2000; Qiao et al. 2000) or triethyl borane (Küper et al. 2000) as a boron source.

In spite of the unquestionable advantages of plasma gas boriding, i.e. the diminished process temperature and decreased percentage of the used toxic gases, the microstructure of borided Armco iron as well as borided low-carbon and low-alloy steels seemed to be characterized by the worse quality (e.g. larger porosity) than the microstructure of the same materials after typical gas boriding. The additional heat treatment was usually not applied after PGB of low-carbon as well as low-alloy steels.

The high-alloy steels were characterized by more complex microstructure after plasma gas boriding. The basic composition of the boride layers, fabricated on high-speed steels as well as austenitic stainless steel (Miyashita and Yokota 1996), consisted of FeB and Fe₂B phases. However, the Cr₂B and MoB borides were identified in plasma gas borided high-speed steel. Whereas the presence of CrB and Cr₂B chromium borides as well as Ni₄B₃ nickel borides was confirmed in plasma gas borided austenitic steel.

Ballinger and Catledge (2015) used plasma gas boriding in order to form the boride interlayer between the substrate, made of austenitic or martensitic stainless steel, and the nanostructured diamond thin film. PBG of austenitic steel at 550 °C (823 K) resulted in formation of only CrB borides. The boride layer, produced at 750 °C (1023 K), was composed of Fe₂B phase. The further increase in boriding temperature up to 825 °C (1098 K) caused that the CrB borides also appeared in boride layer. The phase composition of borided martensitic stainless steel wasn't provided in detail. However, the FeB and Fe₂B borides were identified after deposition of thin film with nanostructured diamond.

Plasma gas boriding at 580 °C (853 K) was also carried out on the AISI H13 steel with a nanostructured surface layer produced by air blast shot peening (Yang et al. 2013). The continuous, smooth and thin boride layer was composed of FeB and Fe₂B phases.

Plasma gas boriding of pure titanium and the TiAl6V4 titanium alloy usually provided the typical two-phase microstructure of boride layer, consisting of TiB₂ and TiB phases (Kaestner et al. 2001). After boriding at the relatively low temperature, i.e. 800 °C (1073 K), only TiB₂ borides were identified by XRD. Whereas the use of diminished voltage (500 V) resulted in the formation of only TiB borides because of the reduced boron concentration at the surface.

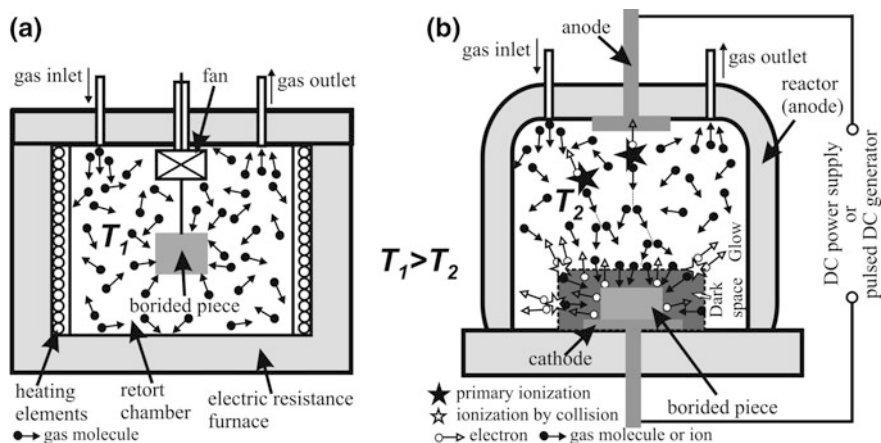
The phase composition of boride layer, produced on Ni-based alloy (Hastelloy C4) by Hunger and Löbig (1997), wasn't studied in detail. Based on the image of microstructure and hardness measurements, it could be concluded that the smooth boride layer consisted of the mixture of nickel and chromium borides. The plasma gas borided layers were fabricated on the Ni or Ni-P coatings deposited on the steel substrate (Wierzchoń et al. 1995; Fillit et al. 1995; Sikorski et al. 1998). On the surface of nickel-coated steel, borided at 650 °C (923 K), a thin zone of Ni₄B₃ nickel boride appeared. This zone was followed by the complex (Fe,Ni)B and (Fe,Ni)₂B phases. The increase in the boriding temperature to 850 °C (1123 K) enhanced the diffusion of the iron atoms through the nickel coating. So, only (Fe, Ni)B and (Fe,Ni)₂B borides constituted the fabricated layers. Johnston et al. (2015) used plasma gas boriding in order to form the boride interlayer between the CoCrMo alloy and the nanostructured diamond thin film. The produced microstructure was composed mainly of two-phase CoB + Co₂B layer with a characteristic zonation. Additionally, the CrB and MoB borides appeared in the boride layer.

WC-Co sintered carbide has been often borided using the plasma gas technique. Basturk et al. (2010) didn't studied the phase composition of the boride layers, fabricated on the surface of cutting tools. Johnston and Catledge (2016) analyzed

the microstructure evolution at various temperatures of boriding. As a consequence of PGB at 700 °C (973 K), the surface layer was composed of CoB borides with the phases typical of WC–Co material, i.e. WC tungsten carbide and Co. The increase in the process temperature up to 800 °C (1073 K) resulted in the formation of the layer which consisted of CoB and WCoB borides as well as WC. After PGB at 900 °C (1173 K), the main identified phases were as follows: WCoB, W_2CoB_2 , WB_2 and WC. The surface layer, fabricated at 1000 °C (1273 K), was composed of WCoB and W_2CoB_2 borides and WC tungsten carbide. Finally, the use of the temperature of 1100 °C (1373 K) resulted in the formation of WCoB and Co_3B borides among WC phase. Johnston et al. (2016) improved nanostructured diamond adhesion on the cemented tungsten carbide with boride interlayers.

The advantage of the use of plasma gas boriding was reported by Dearnley et al. (1986) in comparison to the typical gaseous process. The basic differences between gas and plasma treatments were described for plasma gas carburizing by Booth et al. (1983), and adopted for the PGB process by Dearnley et al. (1986). In opinion of Dearnley et al. (1986), during the simple gas boronizing, the interaction between the molecules and the surface of borided workpiece was random. Whereas during plasma boriding, the partial dissociation and ionization of the gas ensured the forced attraction toward the workpiece surface. Even if only a small percentage of molecules was dissociated and ionized, their collisions with neutral molecules caused that the majority of gas molecules drifted toward the workpiece. It caused that the use of diminished temperature was possible. Dearnley et al. (1986) concluded that, for a given pressure, the higher net flux of ions or molecules interacted with the surface than for typical gas boriding. However, it should be noticed that the flow of gas molecules had a directional character at gas inlet or outlet, irrespective of the technique used. Besides, during a simple gas boriding the flow of the atmosphere was often forced by a fan. It caused the good mixing of the components, temperature stabilization, acceleration of gas molecules and more frequent interaction between the molecules and the surface. Therefore, the growth kinetics of boride layer also seemed to be satisfactory. Some differences between GB and PGB processes were illustrated in Fig. 5.3 in real conditions. The arrow indicated the direction of molecule, ion or electron motion. The primary ionizations and ionizations by collision were marked according to Dearnley et al. (1986).

During PGB process in the H_2 – BCl_3 atmosphere, the reduction of the boron trichloride by hydrogen played the decisive role with regard to the formation of the boride layer (Wierzchoń et al. 1983). Under glow-discharge conditions at reduced pressure, the dynamic equilibrium was obtained between the amount of boron, delivered to the workpiece surface, and its chemisorption and diffusion into the borided material. The considerable excess of hydrogen percentage in an atmosphere caused that the reduction of BCl_3 was more probable (Wierzchoń et al. 1982), and the presence of atomic hydrogen intensified proceeding this reduction (Wierzchoń et al. 1983). The first stage of the reduction reaction could proceed in two ways (Wierzchoń et al. 1982):



The Gibbs free energy $\Delta G_{T_s}^0$, calculated by Wierzczoń et al. (1982) at 727 °C (1000 K), was equal to 126.60 and 39.01 kJ/mol for reactions (5.1) and (5.2), respectively. Hence, it could be concluded that the reduction of BCl_3 was initiated by reaction (5.2). The next reduction reactions proceeded as follows (Wierzczoń et al. 1982):



The calculations of the temperature dependence of free enthalpy (ΔG_T^0) for the reactions (5.2), (5.3), (5.4), (5.5) and (5.6) indicated just such a course of reduction of boron trichloride (Wierzchoń et al. 1982). Simultaneously, under conditions of the possible deficiency of hydrogen in the atmosphere, the produced layers on iron alloys contained a brittle FeB phase. Wierzchoń et al. (1982) suggested that in this case the following reaction could predominate at the first stage of reduction:



Summarizing, the course of the PGB process in $\text{H}_2\text{--BCl}_3$ atmosphere was determined by the reduction of boron chlorides (BCl_3 , BCl_2 and BCl). The presence of atomic hydrogen accelerated the reduction reactions. As a consequence, the fast chemisorption of boron proceeded on the surface of a borided workpiece as this surface was activated by sputtering, and the formation of borides was accelerated (Wierzchoń et al. 1982).

During plasma gas boriding the molecules and atoms of the treatment gas were excited, dissociated and ionized, producing the typical luminous phenomenon known as glow discharge. Cabeo et al. (1999) analyzed the cathodic boundary of the discharge with the use of the emission spectroscopy method. They examined optical emission from a $\text{BCl}_3\text{--H}_2\text{--Ar}$ glow discharge. The results showed emission lines from argon in an excited state (Ar^*) and in an ionized excited state (Ar^{+*}). Simultaneously, the presence of the Balmer lines (H_α , H_β , H_γ) indicated the presence of atomic hydrogen. It confirmed the possible important role of atomic hydrogen, evaluated thermodynamically by Wierzchoń et al. (1983) with respect to BCl_3 reduction and borides' formation. Boron-containing species were identified as atomic boron in an excited state (B^*) and excited boron monochloride (BCl^*). Additionally, the presence of ionized atomic chlorine in an excited state (Cl^{+*}) was reported. Cabeo et al. (1999) analyzed the influence of voltage on the ratios $\text{B}^*/\text{Cl}^{+*}$ and BCl^*/B^* . They reported that the microstructure of best quality, i.e. a non-porous boride layer, was obtained under glow discharge with a high ratio of $\text{B}^*/\text{Cl}^{+*}$. The discharge potential should be selected this way that it should result in a maximum of B^* intensity and a relatively low Cl^{+*} intensity.

5.1.2 Plasma Paste Boriding

The plasma boriding was also carried out with the use of paste containing boron. The mixture of hydrogen and argon was usually applied as an ionized gas during such a process, called *plasma paste boriding (PPB)*.

The cleaned workpieces, subjected to PPB process, were specially prepared. They were usually ground using 800 mesh SiC abrasive paper in order to obtain a suitable adhesive joint of the paste with a base material. Then, the specimens were coated with a paste (containing boron) of an adequate thickness and dried for a long time (up to 24 h) at room temperature. The composition of the paste could be as follows: borax (Gunes et al. 2011, 2013b; Gunes 2014; Ataibis and Taktak 2015; Keddām et al. 2016, 2017; Keddām and Taktak 2017; Makuch et al. 2017), mixtures of borax and SiC or B_4C (Gunes et al. 2013b), mixture of borax and amorphous boron (Yoon et al. 1999), B_2O_3 (Gunes et al. 2013a; Keddām et al. 2018), and, finally, mixtures of B_2O_3 and SiC or B_4C (Gunes et al. 2013a). The prepared samples were placed in the reactor this way that they had a contact with the cathode.

Prior to gas input, the reactor chamber was evacuated of air with a vacuum pumping system obtaining a reduced pressure. The special valve was used in order to control the pressure in the range of 100–10,000 Pa during the process. The temperature was measured using a thermocouple that was placed at the bottom of the treated samples. Before the PPB process, a cleaning process was applied to minimize contamination and remove the dense oxide layer formed naturally on the surface of some materials by exposure to the air. The cleaning consisted in the bombardment of Ar^+ ions with the use of a high voltage (over 900 V) for 10 min at low gas pressure. Then, the mixture of argon and hydrogen with various ratios was introduced into the reactor and the plasma paste boriding started with an adequate voltage (potential difference) at reduced pressure. Plasma paste boriding was usually carried out at the temperature of 700–850 °C (973–1123 K) for 2–7 h. After the PPB process, the samples were cooled in the reactor chamber in the Ar or N_2 atmosphere.

The main equipment, used during plasma paste boriding, consisted of: tubular reactor, plasma generator, gas cylinders with hydrogen, argon and nitrogen, gas mixing chamber, vacuum pumping system as well as temperature control and measurement system. The typical technique of plasma paste boriding was schematically represented in Fig. 5.4. Although only the method with hot wall reactor (without additional heating or cooling) was shown, the cold wall reactors as well as the reactors with additional heating could be also applied. Plasma paste boriding was carried out with the use of the mixture of argon and hydrogen. Whereas nitrogen was sporadically applied as a cooling gas.

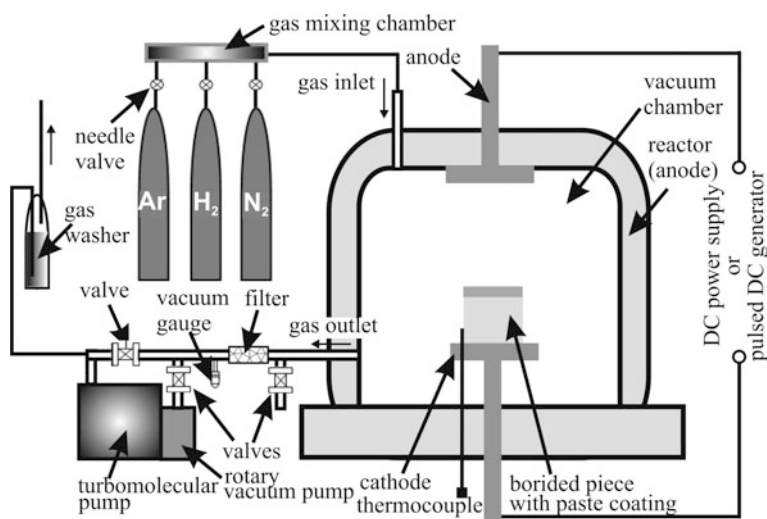


Fig. 5.4 Schematic representation of the most often applied and most effective technique of plasma paste boriding (PPB) in the vacuum chamber using paste as a boron source. *Remark: Apart from the plasma paste boriding with hot wall reactor, the methods with cold wall and with additional heating by convection or radiation could be also applied*

The general characterization of selected processes of plasma paste boriding of iron alloys and of titanium and its alloys was shown in Tables 5.4 and 5.5, respectively, taking into account the available literature data regarding the composition of the ionized gas, the paste composition and its thickness, schematic representation of the method, type of reactor, temperature and time of the treatment as well as pressure, voltage and type of plasma generator. The most often used ionized gas consisted of 70% H_2 + 30% Ar, and borax paste was a predominant boron source.

Despite all the references, indicating the use of quite simple method of PPB process with DC power supply and hot wall reactor without additional heating, it

Table 5.4 General characterization of selected processes of plasma paste boriding of iron alloys

Type of material	Composition of ionized gas/paste composition/paste thickness (μm)/ scheme of the method/type of reactor	Temperature ($^{\circ}C$)/time (h)/ pressure (Pa)/voltage (V)/ plasma generator	References
Low-carbon steels	70% H_2 + 30% Ar/ $Na_2B_4O_7$ of unknown thickness/Fig. 5.4/hot wall reactor	700–800/3–5/400/unknown voltage/DC power supply	Gunes et al. (2011)
	70% H_2 + 30% Ar/ B_2O_3 or 30–70% B_2O_3 + 30–70% SiC or 30–70% B_2O_3 + 30–70% B_4C /150/ Fig. 5.4/hot wall reactor	700–800/2–7/1000/unknown voltage/DC power supply	Gunes et al. (2013a)
	70% H_2 + 30% Ar/ $Na_2B_4O_7$ or 30–70% $Na_2B_4O_7$ + 30–70% SiC or 30–70% $Na_2B_4O_7$ + 30–70% B_4C /150/ Fig. 5.4/hot wall reactor	700–800/2–7/1000/unknown voltage/DC power supply	Gunes et al. (2013b)
Low-alloy steels	70% H_2 + 30% Ar/ $Na_2B_4O_7$ of unknown thickness/ Fig. 5.4/hot wall reactor	700–800/3–5/400/unknown voltage/DC power supply	Gunes et al. (2011)
	70% H_2 + 30% Ar, 50% H_2 + 50% Ar, 30% H_2 + 70% Ar/ $Na_2B_4O_7$ /150/ Fig. 5.4/hot wall reactor	800/5/500/unknown voltage/ DC power supply	Gunes (2014)
High-alloy steels	66.7% Ar + 33.3% H_2 / $Na_2B_4O_7$ + amorphous B of various ratios and of unknown thickness/ Fig. 5.4/unknown reactor	750–950/up to 7/unknown pressure/unknown voltage/ unknown plasma generator	Yoon et al. (1999)
	70% H_2 + 30% Ar/ $Na_2B_4O_7$ of unknown thickness/ Fig. 5.4/hot wall reactor	800/3–5/400/unknown voltage/DC power supply	Gunes et al. (2011)
	70% H_2 + 30% Ar/ $Na_2B_4O_7$ / 1000/ Fig. 5.4/hot wall reactor	700–800/3–7/1000/400–800/ DC power supply	Keddham et al. (2017)
	70% H_2 + 30% Ar/ B_2O_3 /1000/ Fig. 5.4/hot wall reactor	700–800/3–7/1000/400–800/ DC power supply	Keddham et al. (2018)

Table 5.5 General characterization of selected processes of plasma paste boriding of titanium and its alloys

Type of material	Composition of ionized gas/paste composition/paste thickness (μm)/scheme of the method/type of reactor	Temperature ($^{\circ}\text{C}$)/time (h)/pressure (Pa)/voltage (V)/plasma generator	References
Titanium and its alloys	70% H_2 + 30% Ar/ $\text{Na}_2\text{B}_4\text{O}_7$ /1000/ Fig. 5.4/hot wall reactor	700–800/3–7/500/400–800/ DC power supply	Ataibis and Taktak (2015)
	70% H_2 + 30% Ar/ $\text{Na}_2\text{B}_4\text{O}_7$ /1000/ Fig. 5.4/hot wall reactor	700–800/3–7/500/400–800/ DC power supply	Keddad et al. (2016)
	70% H_2 + 30% Ar/ $\text{Na}_2\text{B}_4\text{O}_7$ /1000/ Fig. 5.4/hot wall reactor	700–800/3–7/500/400–800/ DC power supply	Keddad and Taktak (2017)
	50% H_2 + 50% Ar/ $\text{Na}_2\text{B}_4\text{O}_7$ /1000/ Fig. 5.4/hot wall reactor	750–850/3–6/500/300–550/ DC power supply	Makuch et al. (2017)

would be better to apply the pulsed DC generator and a reactor with additional heating because of the advantages, mentioned previously. In the future, such modified equipment should be taken into consideration.

In general, the microstructure of plasma paste borided iron alloys didn't differ from their microstructure obtained with the use of other previously described boriding techniques. However, the formation of a single-phase Fe_2B layer wasn't reported.

Plasma paste boriding of low-carbon steels resulted in producing the two-phase FeB + Fe_2B layer in case of the use of both paste based on borax $\text{Na}_2\text{B}_4\text{O}_7$ (Gunes et al. 2011, 2013b) and paste based on boron trioxide B_2O_3 (Gunes et al. 2013a) even if such a paste also contained a significant percentage of SiC and B_4C .

The boride layers, produced on the low-alloy steels, were also composed of the FeB + Fe_2B iron borides (Gunes et al. 2011; Gunes 2014). Gunes (2014) fabricated these two-phase layers using various compositions of ionized gases.

The additional heat treatment of low-carbon or low-alloy steels wasn't applied after plasma paste boriding.

The more complex microstructure characterized plasma paste borided high-alloy steels. The boride layer, produced by Gunes et al. (2011) and Keddad et al. (2017) on AISI 440C steel, contained mainly FeB and Fe_2B iron borides. However, the CrB and Cr_2B chromium borides were also identified, and the strong zonation of boride layers was confirmed by Keddad et al. (2017). Hence, the formation of complex $(\text{Fe,Cr})\text{B}$ and $(\text{Fe,Cr})_2\text{B}$ phases in the separate zones was also possible.

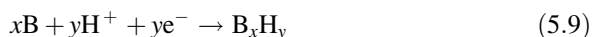
The two boride zones were also observed after plasma paste boriding of austenitic steels (Yoon et al. 1999; Keddad et al. 2018). However, the obtained phase composition differed. Yoon et al. (1999) reported that the first zone contained FeB borides, and the zone with Ni_3B and CrB borides appeared below the first one. The

Fe₂B phase wasn't identified. Whereas Keddarn et al. (2018) indicated the presence of both FeB and Fe₂B borides with strong zonation as well as other metal borides (CrB, Cr₂B and Ni₃B) which appeared in these zones as precipitates. Also in this case, the formation of complex borides was very probable.

The microstructure of plasma paste borided both commercially pure titanium (Ataibis and Taktak 2015; Keddarn et al. 2016; Makuch et al. 2017) and Ti6Al4V titanium alloy (Ataibis and Taktak 2015; Keddarn and Taktak 2017) consisted of a typical two-phase TiB₂ + TiB layer. The TiB₂ titanium borides were observed close to the surface as a compact zone. Whereas the TiB phase appeared below TiB₂ zone in the form of characteristic whiskers.

As it was reported for typical paste boriding, the possibility of the boride layer formation only on the selected surface was an important advantage of PPB process. This boriding technique was also simpler and environmentally friendlier than plasma gas boriding. Besides, the microstructure of the better quality, i.e. without cracks and pores, was usually produced.

Gunes (2014) reported that during plasma paste boriding of iron alloys borax reacted with active hydrogen (H⁺) in glow discharge, forming boron hydride, and the reactions occurred as follows:



Under glow discharge conditions, atomic boron was also produced through the decomposition of the boron hydride (B_xH_y) from the paste:



This atomic boron became the active boron (B⁺) within the glow discharge. Finally, this active boron, B⁺, diffused and reacted with Fe to form the boride layer on iron alloy (Gunes 2014):



In case of plasma paste boriding of titanium or its alloys, the reactions (5.8), (5.9) and (5.10) also proceeded (Ataibis and Taktak 2015). Aich and Ravi Chandran (2002) reported that the titanium borides could be formed according to the reactions:



They calculated the Gibbs free energy (ΔG_T^0) of the reactions (5.13), (5.14) and (5.15) at various temperatures. Their results were approximated in the present work by linear dependence of ΔG_T^0 versus absolute temperature in the range of 300–1600 K. The obtained equations were as follows:

- for reaction (5.13)

$$\Delta G_T^0 = -285.04 + 0.0199 \cdot T \quad (5.16)$$

- for reaction (5.14)

$$\Delta G_T^0 = -22.826 - 0.0024 \cdot T \quad (5.17)$$

- for reaction (5.15)

$$\Delta G_T^0 = -162.74 + 0.0054 \cdot T \quad (5.18)$$

where: ΔG_T^0 is the free enthalpy (Gibbs free energy) in (kJ/mol), T is an absolute temperature (K).

The results of calculations were shown in Fig. 5.5. The reaction (5.13) was characterized by the lowest values of Gibbs free energy (ΔG_T^0). It could indicate that boron richer TiB_2 boride was the first phase, formed on the surface (Ataibis and Taktak 2015) as it was observed earlier in case of boron richer FeB phase during gas boriding of Armco iron (Pertek 1994; Kulka et al. 2013a; Keddami et al. 2014). Under glow discharge conditions, the reaction (5.13) could proceed as follows:



Next, the TiB phase could be formed according to the reaction (5.14). The formation of TiB phase, according to the reaction (5.15) was less probable but still possible. In glow discharge, it could be written as:

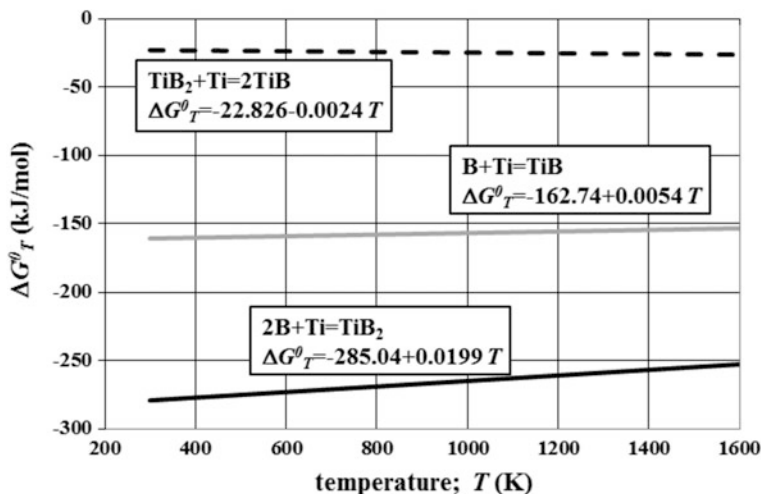


Fig. 5.5 Free enthalpy of reactions (5.13), (5.14) and (5.15) versus temperature, based on calculations of Aich and Ravi Chandran (2002)



5.1.3 Plasma Electrolytic Boriding

Plasma electrolytic treatment (PET) was classified by Yerokhin et al. (1999). Among the PET processes, they specified plasma-enhanced heat treatment and melting, welding, cleaning, etching and polishing, diffusion depletion and **plasma electrolytic deposition (PED)**. The PED group comprised **plasma electrolytic oxidation (PEO)** and **plasma electrolytic saturation (PES)**. The PES methods included such processes as **plasma electrolytic carburizing (PEC)**, **plasma electrolytic nitriding (PEN)** and **plasma electrolytic boriding (PEB)**. Boriding under glow discharge conditions with the use of liquid electrolytes, called plasma electrolytic boriding (PEB), was still developing in recent years, representing an important technique of plasma electrolytic saturation.

The two variants of such a treatment could be distinguished. If the borided workpieces acted as an anode, i.e. were connected at the positive output (Béjar and Henríquez 2009; Kusmanov et al. 2016, 2017b), the process was commonly called **anode plasma electrolytic boriding (anode PEB)**. Hence, the term **cathode plasma electrolytic boriding (cathode PEB)** was accepted in the present work for the processes, in which the borided workpieces were connected at the negative output, acting as the cathode (Aliev and Sabour 2007; Béjar and Henríquez 2009; Taheri et al. 2007a, b; Tavakoli et al. 2015). The typical microstructure, characteristic of the diffusion borided layers and comparable to that produced with the use of the

previously described methods of boriding, was obtained after cathode PEB processes. The anode PEB usually resulted in the formation of gradient surface layers, composed of the oxides close to the surface and borides below the oxidized zone.

The cleaned workpieces, subjected to PEB processes, were connected at negative (cathode PEB) or positive (anode PEB) output of DC power supply. They were inserted into the stainless steel container or Pyrex container, filled with an electrolyte. The stainless steel container acted as anode (during cathode PEB) or as cathode (during anode PEB). The bath, made of Pyrex, was applied for cathode PEB (Taheri et al. 2007a, b). In this case, the additional stainless steel plate played the role of anode. The electrolyte consisted of aqueous solutions of: borax $\text{Na}_2\text{B}_4\text{O}_7$ (Aliev and Sabour 2007; Béjar and Henríquez 2009; Taheri et al. 2007b; Tavakoli et al. 2015), borax and sodium hydroxide NaOH (Béjar and Henríquez 2009; Taheri et al. 2007a) or boric acid H_3BO_3 and ammonium chloride NH_4Cl (Kusmanov et al. 2016, 2017b) with various concentrations of components. Borax and boric acid were used as boron sources, and sodium hydroxide was added in order to provide the desirable conductivity. The addition of ammonium chloride intensified anodic dissolution. This way, it reduced the thickness of an oxide layer, which hindered diffusion of boron during anode PEB. Hence, the growth of a boride layer was promoted (Kusmanov et al. 2017a). Plasma electrolytic boriding was usually carried out at the temperature in the range of 800–950 °C (1073–1223 K) for 5–15 min using an adequate voltage (potential difference). After PEB the borided workpieces were usually quenched in the electrolyte. In case of iron alloys, it resulted in hardening.

The main equipment, applied for plasma electrolytic boriding, was as follows: container (bath) with electrolyte, plasma generator, cooling system of the electrolyte with the use of water jacket or heat exchanger as well as temperature control and measurement system. The typical techniques of plasma electrolytic boriding were schematically represented in Fig. 5.6a, b regarding the cathode and anode PEB process, respectively. In case of cathode PEB, shown in Fig. 5.6a, the stainless steel container was equipped with a water jacket in order to cool the electrolyte. Whereas a heat exchanger provided the adequate cooling of electrolyte during anode PEB (Fig. 5.6b) as it was reported for anode PET (Shadrin and Belkin 2012) or anode PEC (Kusmanov et al. 2014). However, both cooling systems could be used interchangeably in the two presented methods of plasma electrolytic boriding.

The general characterization of selected processes of plasma electrolytic boriding was presented in Table 5.6, taking into account the available literature data regarding the composition of electrolyte, schematic representation of the method in Fig. 5.6, type of the process (cathode or anode PEB), temperature and time of the treatment as well as voltage and type of plasma generator. The current trends indicated the common use of electrolytes which consisted of aqueous solutions of borax $\text{Na}_2\text{B}_4\text{O}_7$ (as a boron source) with an optional addition of sodium hydroxide NaOH (to improve the conductivity) during cathode PEB processes. Such a composition of the electrolyte was sporadically applied during anode PEB. For this method of plasma electrolytic boriding, the aqueous solutions of boric acid H_3BO_3 (as a boron source) and ammonium chloride NH_4Cl (to intensify the anodic

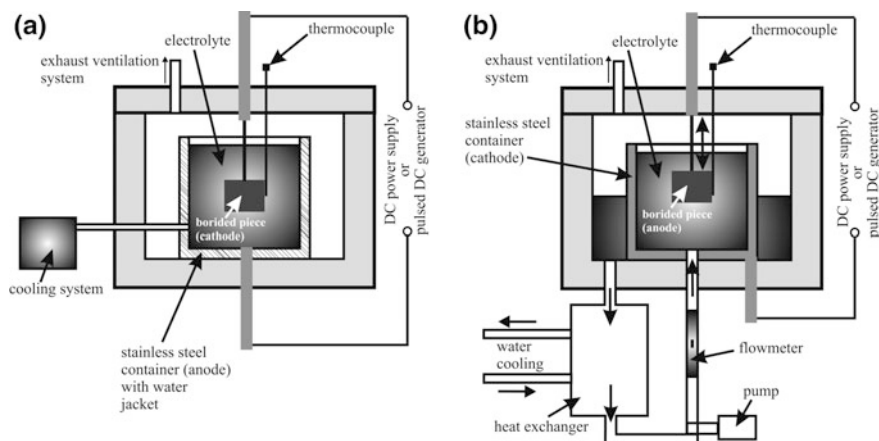


Fig. 5.6 Schematic representations of the most often applied and most effective techniques of plasma electrolytic boriding: cathode plasma electrolytic boriding (cathode PEB) in the stainless steel container using aqueous electrolyte as a boron source (a), anode plasma electrolytic boriding (anode PEB) in the stainless steel container using aqueous electrolyte as a boron source (b). *Remark: If the container was made of Pyrex, the additional stainless steel plate was used as anode during cathode PEB. The two cooling systems (with water jacket or heat exchanger) could be used interchangeably in the cathode or anode PEB process*

Table 5.6 General characterization of selected processes of plasma electrolytic boriding

Type of material	Composition of electrolyte/ scheme of the method and type of process	Temperature (°C)/ time (min)/voltage (V)/plasma generator	References
Low-carbon steels	5–10% $\text{Na}_2\text{B}_4\text{O}_7$ + 0.5% NaOH or 15% $\text{Na}_2\text{B}_4\text{O}_7$ aqueous electrolytes/Fig. 5.6a—cathode PEB, Fig. 5.6b—anode PEB	Unknown temperature/7–15/ max 600/DC power supply	Béjar and Henríquez (2009)
	10–25% $\text{Na}_2\text{B}_4\text{O}_7$ aqueous electrolyte/Fig. 5.6a—cathode PEB	900/10/185–230/DC power supply	Tavakoli et al. (2015)
Medium-carbon steels	5–10% $\text{Na}_2\text{B}_4\text{O}_7$ + 0.5% NaOH or 15% $\text{Na}_2\text{B}_4\text{O}_7$ aqueous electrolytes/Fig. 5.6a—cathode PEB, Fig. 5.6b—anode PEB	Unknown temperature/7–15/ max 600/DC power supply	Béjar and Henríquez (2009)
	5% H_3BO_3 + 10% NH_4Cl aqueous electrolyte/Fig. 5.6b— anode PEB	800–950/5/140–220/ DC power supply	Kusmanov et al. (2016)
	3% H_3BO_3 + 10% NH_4Cl aqueous electrolyte/Fig. 5.6b— anode PEB	850–950/5/~200/ DC power supply	Kusmanov et al. (2017b)

(continued)

Table 5.6 (continued)

Type of material	Composition of electrolyte/ scheme of the method and type of process	Temperature (°C)/ time (min)/voltage (V)/plasma generator	References
Low-alloy steels	5–10% $\text{Na}_2\text{B}_4\text{O}_7$ + 0.5% NaOH or 15% $\text{Na}_2\text{B}_4\text{O}_7$ aqueous electrolytes/Fig. 5.6a—cathode PEB, Fig. 5.6b—anode PEB	Unknown temperature/7–15/ max 600/DC power supply	Béjar and Henríquez (2009)
High-alloy steels	$\text{Na}_2\text{B}_4\text{O}_7$ + NaOH aqueous electrolyte (with unknown concentrations of components)/ Fig. 5.6a—cathode PEB, Pyrex bath, stainless steel plate as anode	900–960/10–15/ 204–233/DC power supply	Taheri et al. (2007a)
	$\text{Na}_2\text{B}_4\text{O}_7$ (with unknown concentration) aqueous electrolyte/Fig. 5.6a—cathode PEB, Pyrex bath, stainless steel plate as anode	900–950/3–6/150– 170/DC power supply	Taheri et al. (2007b)
Titanium	$\text{Na}_2\text{B}_4\text{O}_7$ (with unknown concentration) aqueous electrolyte/Fig. 5.6a—cathode PEB	Unknown temperature/ unknown time/600/ pulsed DC generator	Aliev and Sabour (2007)

dissolution) were more popular as electrolytes. The different kinds of steels as well as commercially pure titanium were subjected to PEB processes.

Among the PES processes, the combined treatment was also intensively developed for steels and titanium alloys. The process of simultaneous saturation with boron and carbon was called *plasma electrolytic borocarbonizing (PEB/C)*. In order to saturate the workpieces with boron and nitrogen or with boron, carbon and nitrogen, the *plasma electrolytic boronitriding (PEB/N)* or *borocarbonitriding (PEB/C/N)* was carried out, respectively. The saturated workpieces usually acted as cathode. However, they were also connected at the positive output during *anode PEB/C* as well as *anode PEB/C/N/S* (simultaneous saturation with carbon, nitrogen, boron and sulfur). In general, such processes differed in the electrolyte composition from the typical PEB. The general characterization of selected processes of plasma electrolytic saturation with different non-metallic elements was shown in Table 5.7, taking into account the available literature data regarding the same parameters as for PEB processes.

For cathode PEB/C process, the aqueous solutions of borax $\text{Na}_2\text{B}_4\text{O}_7$ (as a boron source) and glycerin $\text{C}_3\text{H}_8\text{O}_3$ (as a carbon source) were usually applied (Wang et al. 2013a, b, 2015a; Liu et al. 2014). Sometimes, calcium carbonate CaCO_3 was used as a carbon source instead of glycerin (Taheri et al. 2007c). Anode PEB/C (Kusmanov et al. 2017a) was carried out in the aqueous electrolyte, containing boric acid H_3BO_3 (as a boron source), glycerin $\text{C}_3\text{H}_8\text{O}_3$ (as a carbon source) and ammonium chloride NH_4Cl (added in order to intensify the anodic dissolution).

Table 5.7 General characterization of selected processes of plasma electrolytic saturation with boron and other elements (C, N, S)

Type of material	Composition of electrolyte/ scheme of the method and type of process	Temperature (°C)/time (min)/voltage (V)/plasma generator	References
Low-carbon steels	15% $\text{Na}_2\text{B}_4\text{O}_7$ + $\text{C}_3\text{H}_8\text{O}_3$ (unknown concentration) aqueous electrolyte/Fig. 5.6a— cathode PEB/C	Unknown temperature/5– 30/290/DC power supply	Wang et al. (2013a)
	30% $\text{Na}_2\text{B}_4\text{O}_7$ + carbon containing organic compound aqueous electrolyte/Fig. 5.6a— cathode PEB/C	Unknown temperature (over 950)/30/330/DC power supply	Wang et al. (2013b)
	30% $\text{Na}_2\text{B}_4\text{O}_7$ + 15% $\text{C}_3\text{H}_8\text{O}_3$ aqueous electrolyte/Fig. 5.6a— cathode PEB/C, stainless steel plate as anode	Unknown temperature/15/ 330/pulsed DC generator	Liu et al. (2014)
	30% $\text{Na}_2\text{B}_4\text{O}_7$ + $\text{C}_3\text{H}_8\text{O}_3$ (unknown concentration) aqueous electrolyte/Fig. 5.6a— cathode PEB/C	Unknown temperature/5– 30/330/DC power supply	Wang et al. (2015a)
	15% $\text{CO}(\text{NH}_2)_2$ + 15% NH_4Cl + 10% H_3BO_3 + 10% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous electrolyte/ Fig. 5.6b—anode PEB/C/N/S	650–800/5/170–230/DC power supply	Kusmanov et al. (2015a)
	5% H_3BO_3 + 4–12% $\text{C}_3\text{H}_8\text{O}_3$ + 7.5–17.5% NH_4Cl aqueous electrolyte/Fig. 5.6b— anode PEB/C	800–920/5/170–250/DC power supply	Kusmanov et al. (2017a)
High-alloy steels	$\text{Na}_2\text{B}_4\text{O}_7$ + Na_3N (unknown concentrations) aqueous electrolyte/Fig. 5.6a—cathode PEB/N, Pyrex bath, stainless steel plate as anode	900/15/unknown voltage (over 150)/DC power supply	Taheri et al. (2007c)
	$\text{Na}_2\text{B}_4\text{O}_7$ + CaCO_3 (unknown concentrations) aqueous electrolyte/Fig. 5.6a—cathode PEB/C, bath and anode as before	900/15/unknown voltage (over 150)/DC power supply	Taheri et al. (2007c)
	$\text{Na}_2\text{B}_4\text{O}_7$ + $\text{CO}(\text{NH}_2)_2$ (unknown concentrations) aqueous electrolyte/Fig. 5.6a— cathode PEB/C/N, bath and anode a.b.	900/15/unknown voltage (over 150)/DC power supply	Taheri et al. (2007c)
γ -TiAl alloy (Ti48Al 2Cr2Nb)	Solution of $\text{Na}_2\text{B}_4\text{O}_7$ and H_3BO_3 in $\text{C}_3\text{H}_8\text{O}_3$ /Fig. 5.6a, b—pulsed bipolar nanocrystalline PEB/C	Unknown temperature/10– 30/voltage of bipolar pulses/pulsed current generator	Aliofkhazraei et al. (2009)

Solution of $\text{Na}_2\text{B}_4\text{O}_7$ and H_3BO_3 in glycerin $\text{C}_3\text{H}_8\text{O}_3$ was used during pulsed bipolar nanocrystalline PEB/C process (Aliofkhazraei et al. 2009) in which duty cycles of cathodic direction and anodic direction were alternately repeated with an adequate frequency.

The electrolyte, used for cathode PEB/N process, contained borax as a boron source and sodium nitride Na_3N as a nitrogen source (Taheri et al. 2007c). Whereas the aqueous solution of borax (boron source) and carbamide $\text{CO}(\text{NH}_2)_2$ as carbon and nitrogen source became the electrolyte used for plasma electrolytic borocarbonitriding (PEB/C/N) process (Taheri et al. 2007c).

Anode plasma electrolytic saturation with boron, carbon, nitrogen and sulfur (anode PEB/C/N/S) was reported by Kusmanov et al. (2015a). They used an electrolyte, composed of an aqueous solution of boric acid (boron source), carbamide (carbon and nitrogen source) and sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$ (sulfur source).

The microstructure of the layers, produced by plasma electrolytic boriding, strongly depended on the polarity of the treated pieces. Bejar and Henriquez (2009) reported the cathodic polarity as more effective than the anodic one, taking into account only the obtained hardness profiles. They didn't provide either the phase compositions and micrographs of the borided low-carbon, medium-carbon or low-alloy steels. However, based on the hardness profiles the significant percentage of iron borides could be produced with the use of 15 wt% borax aqueous electrolyte. The lower content of borax in electrolyte resulted probably in the formation of limited percentage of borides, and the measured hardness was characteristic of the mixture of borides and martensite.

The low-carbon steel was borided using cathode PEB by Tavakoli et al. (2015). They reported that the turbulence, existing in electrolyte, could impede the boron diffusion into the steel surface. The intensification of turbulence in electrolyte could lead to the direct contact of the electrolyte with the electrode surface because of the possible disappearance of vapor envelope around the electrode. As a consequence, the electrode surface could be cooled. Hence, the formation of the boride layer in the plasma electrolytic process differed essentially from the other techniques of boriding. The influence of a borax percentage in an aqueous electrolyte on the phase composition of boride layer was analyzed (Tavakoli et al. 2015). The satisfied effect, i.e. the formation of two-phase $\text{FeB} + \text{Fe}_2\text{B}$ layer, was obtained after boriding at the high borax percentage in electrolyte (25 wt%). However, the needle-like nature of the boride layer (similar to the conventional methods) was not observed. The interface between the boride layer and the substrate was smooth.

The high-alloy AISI H13 steel was borided by Taheri et al. (2007a, b) using cathode plasma electrolytic process. The boride layer was composed mainly of nanocrystalline FeB and Fe_2B borides with characteristic zonation. The presence of CrB and Cr_2B chromium borides as well as Fe_3B phase was also confirmed. The nanocrystalline titanium borides were observed after cathode PEB of commercially pure titanium (Aliev and Sabour 2007). However, the phase composition of boride layer wasn't studied.

The microstructure of the layers, fabricated by anode PEB process, differed significantly from the mentioned above. Kusmanov et al. (2016, 2017b) reported that such a layer on medium-carbon steel consisted of the two characteristic zones: top oxide layer and so-called boride-martensite layer below the first one. This way the gradient surface layer was produced. The oxide layer was composed of FeO and Fe₃O₄ oxides. Whereas boride-martensite layer contained FeB and Fe₂B iron borides as well as martensite with retained austenite.

The more complex microstructure of the boride layers was produced using plasma electrolytic saturation with boron and other elements, such as C, N and S. As in the previous case, the microstructure strongly depended on whether the treated sample worked as a cathode or anode. The cathode PEB/C process of low-carbon steel in aqueous electrolyte containing 15 wt% of borax and unknown percentage of C₃H₈O₃ (Wang et al. 2013a) provided the microstructure which consisted of the three characteristic zones: loose top layer, boride layer and the transition layer. The loose top layer contained FeB and Fe₃C phases as well as Fe₂O₃ oxides and was easy to remove by polishing. After polishing, the boride layer containing Fe₂B borides remained close to the surface. The transition layer was composed of Fe₃C and Fe_α phases and appeared below the boride layer. The similar boride layer was produced by Wang et al. (2013b) with the use of electrolyte of higher borax content (30 wt%). Only the Fe₃O₄ oxide appeared additionally in the loose top layer. Liu et al. (2014) didn't report the phase composition of borocarbureted low-carbon steel by cathode PEB/C process using the similar electrolyte. They only confirmed the presence of the loose top layer, boride layer and transition layer. Wang et al. (2015a) identified additionally Fe₂B phase in the loose top layer after PEB/C of low-carbon steel. Whereas the composition of the boride layer was still the same (Fe₂B).

The cathode plasma electrolytic borocarbureting (PEB/C) of high-alloy AISI H13 steel in Na₂B₄O₇ + CaCO₃ aqueous electrolyte resulted in the formation of boride zone close to the surface and carburized zone below (Taheri et al. 2007c). The boride layer was composed of nanocrystalline FeB and Fe₂B borides which showed their less needle-like nature. Whereas the phase composition of carburized zone wasn't investigated. After cathode plasma electrolytic boronitriding (PEB/N) of the same steel using Na₂B₄O₇ + Na₃N aqueous electrolyte, the only difference consisted in the formation of nitrided layer of unknown composition (Taheri et al. 2007c) below the similar top boride layer (FeB + Fe₂B). The phase composition of the layers, produced by cathode plasma electrolytic borocarbonitriding (PEB/C/N) using Na₂B₄O₇ + Co(NH₂)₂ aqueous electrolyte, wasn't studied in detail. It was reported that the FeB and Fe₂B phases occurred in the boride layer, and the borocarbonitrided layer was observed below (Taheri et al. 2007c).

The anode plasma electrolytic borocarbureting (PEB/C) provided the gradient surface layer in which the zones were revealed as follows: top oxide layer, boride layer and diffusion layer (Kusmanov et al. 2017a). The Fe₃O₄ oxide, which was formed as a result of high-temperature oxidation, appeared in the oxide layer. The boride layer consisted of FeB iron borides. Whereas the diffusion layer contained martensite with retained austenite.

In the case of anodic plasma electrolytic saturation with boron, carbon, nitrogen and sulfur (PEB/C/N/S), the phase composition wasn't studied in detail (Kusmanov et al. 2015a). Only the presence of gradient surface layer was indicated. The top oxide layer, probably composed of FeO and Fe₂O₃ oxides, was followed by the diffusion layer in which the borides coexisted with martensite and retained austenite.

Yerokhin et al. (1999) reported that the electrolysis of aqueous solutions was accompanied by a number of electrode processes. These processes were often considered using a simplified model, in which the electrode-electrolyte interface was represented by a two-phase system (i.e. metal-electrolyte or oxide-electrolyte couple) with a single phase boundary consisting of a double-charged layer. The liberation of gaseous oxygen as well as metal oxidation could occur on the anodic surface. The electrolyte chemical activity in respect to the metal determined, whether the surface dissolution or oxide film formation was a predominant process. Simultaneously, the liberation of gaseous hydrogen and reduction of cations could be observed on the cathodic surface. The processes, occurring in the gaseous environment near the electrode or in its surface layers, influenced the effects of the electrolytic treatment. Hence, the simplified model, mentioned above, was not always justifiable (Yerokhin et al. 1999).

The two types of current-voltage characteristic during the processes of plasma electrolytic treatment were reported by Yerokhin et al. (1999) and Nie et al. (2001). They were shown in Fig. 5.7. The first current-voltage diagram was marked as (a) in Fig. 5.7 and represented the metal-electrolyte system with initial gas liberation on the cathode or anode surface (Yerokhin et al. 1999). The second diagram (b) was characteristic of a system in which oxide film formation appeared

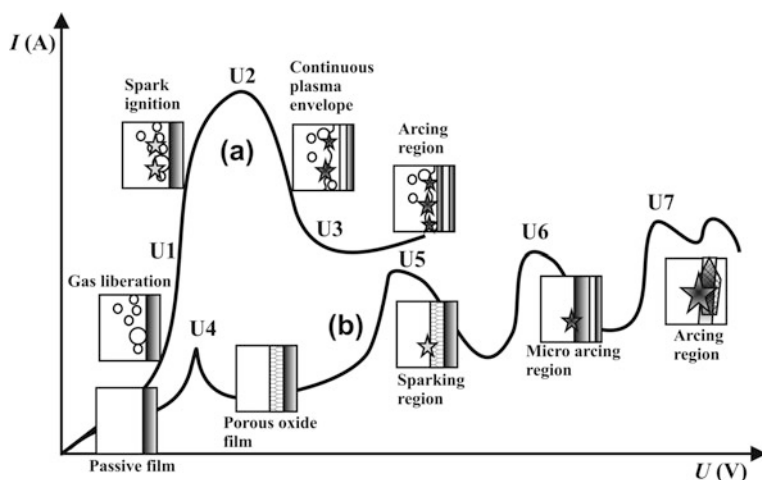


Fig. 5.7 Current-voltage characteristic curves of the plasma electrolytic process (Yerokhin et al. 1999 with permission) in the near-electrode area (a) and in the dielectric film on the electrode surface (b); I —electrode current; U —inter-electrode voltage

(Yerokhin et al. 1999). At relatively low voltages (in the range of 0–U₁), the kinetics of the electrode processes for both systems obeyed Faraday's laws. The current–voltage characteristics varied according to Ohm's law, i.e. an increase in voltage was accompanied by a proportional increase in the current. The further course of the curves differed much.

In the case of (a) system, an increase in voltage from U₁ to U₂ led to current oscillation accompanied by luminescence. The shielding action of gaseous reaction products (H₂ or O₂) partially limited the increase in current intensity. However, the current intensity still increased in areas where the electrode surface was still in contact with electrolyte. It caused local boiling of the electrolyte adjacent to the electrode. With the increase in potential up to U₂, the electrode was surrounded by a continuous plasma vapor-gas envelope of low electrical conductivity. In order to initiate the ionization processes in vapor-gas envelope (VGE), the electric field strength E within this region should reach a sufficient value (between 10⁶ and 10⁸ V/m). At first, the ionization appeared as a rapid sparking in scattered gaseous bubbles. Next, the ionization was transformed into a uniform glow through the continuous plasma envelope. After exceeding the potential U₂ (in the U₂–U₃ region), the drop in current intensity was observed because of the hydrodynamic stabilization of the VGE. If the voltage was increased above U₃, the glow discharge transformed into the intensive arc discharge accompanied by a characteristic low-frequency acoustic emission.

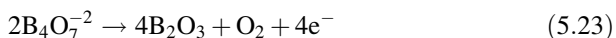
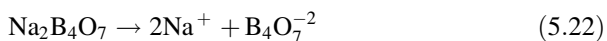
The current-voltage characteristic curve of the electrolyte-oxide film system (b) was more complicated (Fig. 5.7). Its probable interpretation was also provided by Yerokhin et al. (1999). At potential U₄, corresponding to the corrosion potential of the material, the passive film started to dissolve. The range of potentials U₄–U₅ corresponded to the region of repassivation. The growth of a porous oxide film was observed. The voltage drop occurred across this film. At potential U₅, the electric field strength obtained an adequate value to break the oxide film through because of the impact or tunneling ionization. Simultaneously, small luminescent sparks, moving quickly on the film surface, were observed. If the potential obtained U₆ value, the mechanism of impact ionization was supported by thermal ionization processes and by larger arc discharges. In the region U₆–U₇, thermal ionization was partially blocked by the buildup of negative charge in the more and more thick oxide film. It resulted in discharge decay and shorting of the substrate. Such effect caused the relatively low power and duration of the resultant arc discharges, i.e. micro-discharges. Because of this “micro-arcing” the film was gradually fused and alloyed with elements contained in the electrolyte. Above the potential U₇, negative charge blocking effects no longer occurred, and the arc micro-discharges could penetrate to the substrate and transform into powerful arc discharges. It might cause the destruction of the film, e.g. as a consequence of thermal cracking.

During plasma electrolytic saturation (PES), gaseous hydrogen was liberated on the cathode according to the reaction (Li and Han 2006; Liu et al. 2014):

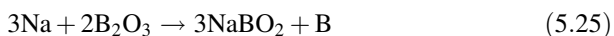


Simultaneously, a large amount of vapor appeared due to the generation of Joule heat. The electrolyte was locally boiled around the electrodes with a smaller surface area, which was surrounded by a vapor-gas envelope (VGE). It enabled the generation of electrolytic plasma (Belkin et al. 2016). So, the vapor mixed with hydrogen gradually formed the VGE around the borided sample during cathode PEB. As the applied voltage increased, the vapor-gas envelope was broken down to generate plasma discharge with high temperature and electron concentration as described above (Liu et al. 2014).

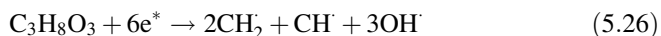
The formation of active boron atoms during plasma electrolytic boriding (PEB) in aqueous solution of borax could be analyzed based on the reactions, which were reported for PEB/C process by Liu et al. (2014). The boiling borax adjacent to the borided workpiece (cathode) quickly decomposed according to the following reactions:



Then sodium metaborate NaBO_2 and active boron atoms were formed on the surface of a borided workpiece as a consequence of reactions (Liu et al. 2014):



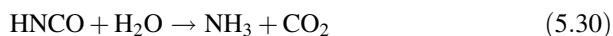
Cathode PEB/C process was often carried out in the aqueous solution of borax and glycerin. In this case, the active boron atoms were provided according to the reactions mentioned above. Whereas the boiling glycerin decomposed as follows (Liu et al. 2014):



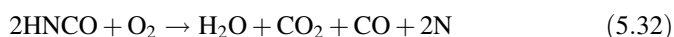
The asterisk in Eq. (5.26) represented the excited state of electrons in the plasma discharge zone, and the breaking positions of covalent bonds were marked with the small dots. Liu et al. (2014) reported that the active radicals CH_2 and OH were unstable. Hence, they were hard to detect by an optical emission spectrometer (OES). The CH_2 and CH radicals were further thermally decomposed into active carbon and hydrogen atoms at the cathode due to the frequent collision reactions in plasma discharge envelope:



Carbamide (urea) $\text{CO}(\text{NH}_2)_2$ was the widespread compound used as carbon and nitrogen source during PEB/C/N process. In an aqueous solution at temperatures of higher than 50 °C (323 K), carbamide could dissociate to produce ammonia NH_3 and isocyanic acid HCNO (Kusmanov et al. 2015b; Belkin et al. 2016):



Such reactions were quite probable because of the detection of isocyanate ions in the electrolyte (Kusmanov et al. 2015b). Active nitrogen atoms were formed as a consequence of the decomposition of the adsorbed ammonia and oxidation of isocyanic acid (Kusmanov et al. 2015b; Belkin et al. 2016):



The adsorbed carbon monoxide could be a carbon source after its decomposition (Kusmanov et al. 2015b):



The possible reactions in electrolyte and in discharge VGE around the saturated surface during cathode PEB, PEB/C and PEB/C/N processes were shown in Fig. 5.8 according to the electrolytes mentioned above. The plasma discharges provided a high-temperature and high-pressure environment combined with a strong electric field in envelope around the saturated surface of treated material, which resulted in the active species such as boron, carbon and nitrogen atoms. Then these active atoms quickly diffused into the surface to form the hardened surface layer, saturated with boron (Fig. 5.8a), with boron and carbon (Fig. 5.8b) or with boron, carbon and nitrogen (Fig. 5.8c) by the interstitial and grain-boundary diffusion mechanisms.

The cathodic polarization techniques were used in order to avoid surface oxidation. However, the electrolytes applied during the cathodic formation of boride layers were generally more complex and also required the use of toxic or combustible organic substances to be effective (Yerokhin et al. 1999). Therefore, the anode PEB (Kusmanov et al. 2016, 2017b), PEB/C (Kusmanov et al. 2017a) and PEB/C/N/S (Kusmanov et al. 2015a) processes were also often used. The plasma electrolytic saturation of anodic surfaces with nonmetallic elements was usually carried out using aqueous solutions of inorganic acids, suitable salts containing the desired elements (B, C, N, S) and certain organic compounds. The diffusing species were chosen this way that they became negatively ionized in the electrolyte. Thus, they were drawn into the vapor-gas envelope under the influence of the applied

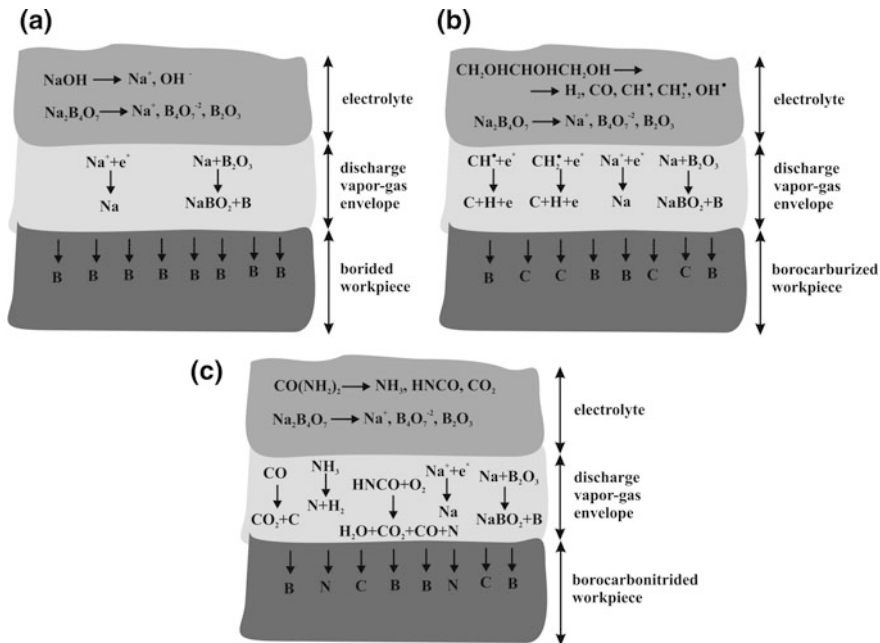


Fig. 5.8 Schematic diagram of possible reactions in electrolyte and in discharge envelope resulting in diffusion processes during the cathode plasma electrolytic saturation: PEB (a), PEB/C (b) reported by Liu et al. (2014) for Q235 steel (with permission) and PEB/C/N (c)

electric field and were accelerated across the voltage drop in order to bombard the electrode surface. Interstitial and grain-boundary diffusion mechanisms also occurred during the growth of the boride layer on the anode surface.

The limited content of diffusing active species into the anode surface resulted from their concentration in the adjacent VGE. Furthermore, boride layer formation on the anode was often also accompanied by an oxidation process. Hence, an oxide layer was often produced on top of the borided, borocarbured or borocarbonitrided layer. It disadvantageously influenced the hardness of the diffusion layer. Therefore, the use of cathode PES with boron as well with carbon or nitrogen seemed to be more advisable. Both cathode and anode plasma electrolytic saturation with boron and other nonmetallic elements was very attractive because of the relatively short duration of the processes, which was comparable to the duration of the electrochemical boriding.

5.1.4 Spark Plasma Sintering Boriding

Plasma boriding could be also carried out using the powders as a boron source. One of such methods was called *spark plasma sintering boriding (SPSB)*.

Spark plasma sintering (SPS) was well-known as a sintering technology in powder metallurgy which was capable to sinter metal and ceramic powders quickly to a high density at a fairly low temperature due to its unique features (Johnson 1991; Risbud and Shan 1995; Gao et al. 1999; Hebda 2012). During SPS, the graphite sintering die was filled with the raw material powder, and was placed between the two electrodes. The lower and upper electrodes acted as loaded punches. A pulsed plasma was provided using an external DC pulse generator in order to activate the surface of the sintering particles. Alternate charging and discharging the spaces between powder particles with electrical energy effectively generated a high temperature spark discharge or plasma. Because of the direct heating of the sintering graphite die and powder materials by the large spark pulse current, the SPS was characterized by a very high thermal efficiency and resulted in the consolidation of a homogeneous and high-quality compacts (Yu et al. 2002; Hebda 2012). The uniform heating, surface purification and activation made by dispersing the spark points also advantageously influenced the quality of compacts. The SPS was usually carried out at the relatively low voltage (about a few volts) and high current intensity (up to 60,000 A) with pressing force up to 3000 kN.

Spark plasma sintering boriding (SPSB) consisting in the use of powders characteristic of the powder-pack methods, i.e. powders containing a boron source, during typical spark plasma sintering (Yu et al. 2002; Khor et al. 2005). The typical powder-pack boriding resulted in the activation of boron atoms from the powder media and in diffusion into the workpiece. The additional use of plasma could certainly enhance the process.

The advantages of SPSB process were as follows (Yu et al. 2002): the generation of spark plasma highly activated the boron atoms; the presence of the electrical field and a high level of electric current accelerated boron diffusion into the workpieces due to the high-speed migration of ions; rapid Joule heating provided and maintained a homogeneous temperature during boriding. The principle of plasma generation in SPSB process was shown in Fig. 5.9 according to Yu et al. (2002). Pulsed current flowed through the particles of boriding powder, resulting in generation of Joule heat and micro-plasma discharges.

The cleaned workpieces, subjected to SPSB processes, were inserted into the sintering graphite die, filled with the boriding powder. This powder was pressed by the lower and upper punches (electrodes) with an adequate load. The electrodes were connected to the pulsed DC generator, one of them at negative output, and the second at positive output. The boriding media usually consisted of the mixture of B_4C and SiC powders (Yu et al. 2002, 2006; Khor et al. 2005; Chen et al. 2008b) in which boron carbide was a boron source and silicon carbide was a diluent. According to the previous consideration (Sect. 4.1.1), B_4C powder had to contain an amount of boron trioxide B_2O_3 (up to 3%), acting as an activator. However, sometimes an unknown additional activator was used (Yu et al. 2005). Spark plasma sintering boriding was carried out at the temperatures in a wide range of 700–1400 °C (973–1673 K) for 5–240 min using an adequate voltage, current intensity and load. The temperature of SPSB process strongly depended on the borided material.

Fig. 5.9 Principle of plasma generation during SPSB process (Yu et al. 2002 with permission)

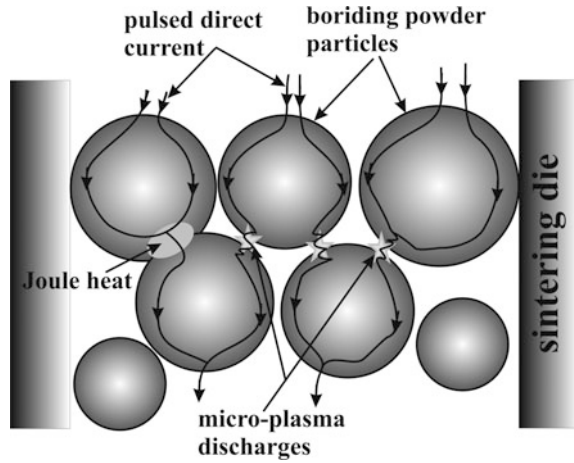
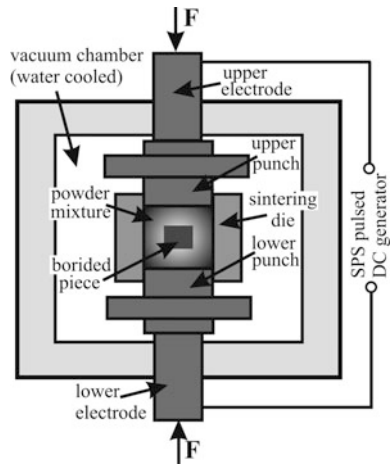


Fig. 5.10 Schematic representation of the spark plasma sintering boriding (SPSB) using the powder mixture as a boron source (Yu et al. 2002 with permission)



The main equipment, used for spark plasma sintering boriding, consisted of: water cooled vacuum chamber, sintering graphite die filled with boriding powder mixture, lower and upper punches (acting as electrodes), pressing system with an adequate load F as well as temperature control and measurement system. The typical technique of SPSB process was schematically represented in Fig. 5.10 (Yu et al. 2002).

The general characterization of selected processes of spark plasma sintering boriding was shown in Table 5.8, taking into account the available literature data regarding the composition of powder mixture (boriding agent), schematic representation of the method, temperature and time of the treatment, voltage, current intensity as well as the type of plasma generator. The current trends indicated the common use of powder mixtures which were composed of boron carbide B_4C

Table 5.8 General characterization of selected processes of spark plasma sintering boriding

Type of material	Powder mixture/scheme of the method	Temperature (°C)/time (h)/voltage (V)/current (A)/plasma generator	References
Low-carbon steels	B ₄ C + SiC with unknown ratio/Fig. 5.10	700–1000/0.5/unknown voltage and current/DC pulsed generator	Yu et al. (2002)
	B ₄ C + SiC + unknown activator with unknown ratio/Fig. 5.10	850/0.0833–4/unknown voltage and current/DC pulsed generator	Yu et al. (2005)
	B ₄ C + SiC with unknown ratio/Fig. 5.10	850/0.5–4 without refreshment of powder mixture or 1–3 with refreshment of powder mixture every 0.5 h or 4.5–5 with refreshment of powder mixture after 4 h/unknown voltage and current/DC pulsed generator	Chen et al. (2008b)
Tungsten	B ₄ C + SiC with unknown ratio/Fig. 5.10	1000–1400/0.5/unknown voltage and current/DC pulsed generator	Khor et al. (2005)
Molybdenum	B ₄ C + SiC with unknown ratio/Fig. 5.10	1000–1400/0.5/unknown voltage and current/DC pulsed generator	Yu et al. (2006)

(as a boron source) and silicon carbide SiC (as diluent). The temperature of SPSB process strongly depended on the borided material. In case of low-carbon steels, the temperature ranged from 700 to 1000 °C (973–1273 K). However, usually the temperature has been equal to 850 °C (1123 K). Whereas commercially pure tungsten or molybdenum were borided using the high temperature of 1000–1400 °C (1273–1673 K). The voltage and current intensity were usually not provided. It could only assume that the voltage didn't exceed a few volts, and a high current intensity was applied (about tens of thousands of amperes). Sometimes, the refreshment in a powder mixture (boriding agent) was applied during SPSB. It resulted in thicker boride layers produced on low-carbon steel (Chen et al. 2008b).

The microstructure of low-carbon steels, subjected to SPSB process, consisted of the typical two-phase FeB + Fe₂B boride layers with strong zonation and a needle-like nature (Yu et al. 2002, 2005; Chen et al. 2008b). The influence of boriding temperature on the thickness of the boride layer was analyzed by Yu et al. (2002). They used a process duration of only 0.5 h. As a consequence of boriding at 700 °C (973 K), the very thin boride layer was produced (about 2 μm). The increase in process temperature up to 1000 °C (1273 K) resulted in the formation of a 59 μm thick boride layer. The influence of boriding time on the phase composition of the boride layers was investigated by Yu et al. (2005). The two-phase composition (FeB + Fe₂B) of boride layer appeared even if the duration of SPSB process was equal to only 5 min. The boron diffusion into the low-carbon steel substrate could be accelerated by the use of refreshment of the powder mixture (Chen et al. 2008b). The various variants of such a treatment consisted in the refreshment of powder every 0.5 h or at the end of SPSB process not before after 4 h. Finally, the thickness of boride layer reached even 130 μm. However, the time

of boriding was significantly longer (4 or 5 h). Although there was no doubt that the refreshment of powder increased the thickness of the boride layer, it was difficult to evaluate the effectiveness of the SPSB in comparison with the typical powder-pack boriding.

The SPSB of pure tungsten at the temperature range from 1000 °C (1273 K) to 1400 °C (1673 K) resulted in the formation of a single-phase WB boride layer (Khor et al. 2005). The thickness of the layer increased with increasing the process temperature. The boride layer obtained a needle-like nature after SPSB at the temperatures in the range of 1000–1200 °C (1273–1473 K). Simultaneously, the cracks occurred in the boride layer parallel to the surface. The elevated temperature up to 1300 °C (1573 K) or 1400 °C (1673 K) caused changes in the morphology of tungsten borides. The interface between WB layer and the substrate became smoother, and the boride layer was free from cracks. Additionally, the WC carbides appeared in the produced layer due to the diffusion of carbon which was adsorbed on the surface from the boriding powder. The process of annealing of boride layers at 1000 °C (1273 K) for 0.5 h in vacuum furnace didn't influence the phase composition.

The similar effects were obtained after SPSB of pure molybdenum (Yu et al. 2006). The process resulted in the formation of a single-phase MoB boride layer. The increase in the temperature of the process from 1000 °C (1273 K) to 1400 °C (1673 K) caused the increase in layer thickness up to 150 µm. Like in the case of borided pure tungsten, the boride layer, produced on pure molybdenum at the temperatures in the range of 1000–1200 °C (1273–1473 K), was characterized by a needle-like morphology as well as the cracks parallel to the surface. The SPSB at elevated temperature, i.e. at 1300 °C (1573 K) or 1400 °C (1673 K), resulted in the formation of a relatively smooth MoB layer.

5.1.5 Double Glow Plasma Surface Alloying with Boron

In recent years, the *double glow plasma surface alloying process (DGPSA)* has been intensively developed (Xu et al. 2002; Qin et al. 2007). In general, DGPSA was a process in which alloying element particles were sputtered from a source cathode, then they were transported through plasma space and diffused into the workpiece, also acting as cathode. So, the three electrodes were inserted into the vacuum chamber: the anode and two negatively charged cathodes, namely the workpiece cathode and the source cathode. Hence, the two power supplies were necessary. If they were switched on, both workpiece cathode and source cathode were surrounded by glow discharge. Such phenomenon was called the “double glow discharge”. One glow discharge caused the sputtering of the desired alloying elements from the source cathode by bombardment of the ions. Whereas the second glow discharge heated the workpiece (substrate) in order to enable the process of alloying. The sputtered alloying elements (by the first glow discharge) travelled to

the workpiece cathode and diffused into its surface. This way, the formation of the alloyed layer occurred (Xu et al. 2007).

The source cathode could be made both of one metallic element, e.g. niobium (Wang et al. 2014) or chromium (Wei et al. 2015), and of the two or more metallic elements, e.g. nickel and molybdenum (Lin et al. 2017) by powder metallurgy. The temperature of the heated workpiece cathode (alloyed substrate) ranged from 800 to 1100 °C (1073–1373 K), depending of the alloying elements used.

DGPSA with nonmetallic elements, such as carbon and nitrogen, was also possible (Zhang et al. 2005). If the source cathode was made of a compound, containing boron, the *double glow plasma surface alloying with boron* could be carried out, resulting in the formation of a diffusion borided layer (Qin et al. 2006, 2012, 2013). During the process, called *double glow plasma boriding* (DGPB), FeB compound in the shape of blocks was used as a sputtering target (Qin et al. 2006, 2013). The enhanced process was carried out with the use of an additional metal (Mo) as alloying element (Qin et al. 2012). So, the main equipment, applied for DGPSA with boron, was as follows: tubular reactor with anode and two cathodes (source cathode and workpiece cathode), two DC power supplies, gas cylinder with argon, vacuum pumping system as well as temperature control and measurement system. The schematic representation of such a method of boriding was shown in Fig. 5.11.

The two steps of cleaning the workpiece were usually applied before such boriding process (Qin et al. 2013). During the first step, the workpieces were supersonically cleaned in acetone and ethanol solution. The second step consisted in sputtering them by Ar^+ ion bombardment under high voltage over 900 V for 10 min at low gas pressure in order to minimize contamination and remove the oxide layer, especially in case of the use of titanium alloy as substrate material

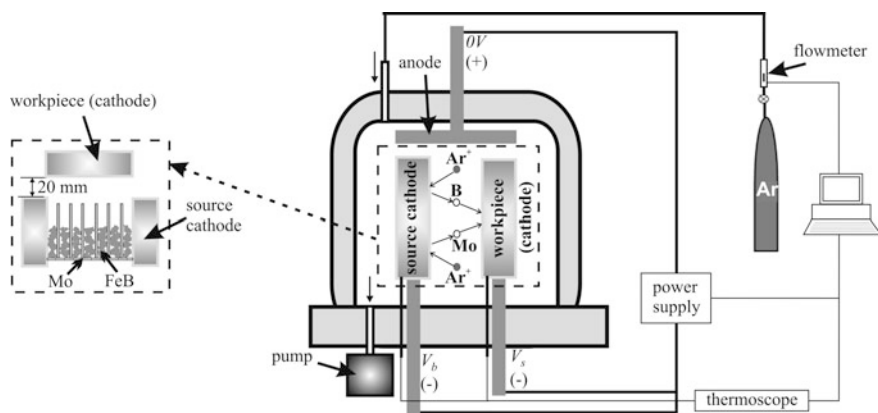


Fig. 5.11 Schematic representation of the double glow plasma surface alloying (DGPSA) with boron and molybdenum using solid FeB blocks as a boron source and Mo rods (Qin et al. 2012 with permission). Remark: The use of only FeB blocks as precursor resulted in double glow plasma surface alloying with boron, also called double glow plasma boriding (Qin et al. 2013)

(workpiece cathode). The DGPB process of Ti6Al4V alloy was carried out at 870 °C (1143 K) for 3 h using Ar gas pressure of 48 Pa, work-piece cathode bias voltage of −600 V, and source cathode bias voltage of −900 V. After the double glow plasma boriding, the samples were naturally cooled in the furnace. The process resulted in the formation of typical diffusion layer, containing mainly titanium borides TiB₂ and TiB close to the workpiece surface (Qin et al. 2013) as a consequence of boron diffusion into the substrate material. The small quantities of Ti₃B₄, Fe₃B and FeB phases were also detected. Iron borides were observed because of the simultaneous sputtering of Fe and B atoms from the source cathode and their deposition on the workpiece cathode.

The modification of this process was proposed by Qin et al. (2012) in order to form the diffusion layer on AISI 5140 low-alloy steel. Molybdenum was applied as the additional alloying element. In this case, the parameters of the treatment were as follows: source cathode voltage in the range of −800 to −700 V, workpiece cathode voltage in the range of −400 to −300 V, substrate (workpiece) temperature 950 °C (1223 K), treatment time 3 h, working pressure 45 Pa, and the distance between the two cathodes equal to 20 mm. Qin et al. (2012) reported that the process resulted in the formation of an inner Mo–B diffusion layer and an outer Fe–Mo–B deposition coating. FeMo₂B₂ and Fe₂B borides were detected by XRD. The simultaneous sputtering of Mo, Fe and B atoms from the source cathode and their deposition on the workpiece cathode as well as the high iron content in the substrate material (5140 low-alloy steel) was responsible for such a phase composition of the diffusion layer.

Although the DGPSA with boron has been rarely applied up to now, this process had an important advantage. The compounds used for boriding were only argon gas, FeB blocks and Mo rods (optionally). So, the undesirable gases and other waste weren't produced. This way, such boriding process was environmentally friendly (Qin et al. 2012).

5.2 Boron Ion Implantation

Ion implantation was well-known low-temperature process by which ions of one element were accelerated into a solid target (workpiece). As a consequence, the physical, chemical, or electrical properties of the target were modified. If the ions differed in composition from the target, they could stop and remain in it, changing its chemical composition. Ion implantation could cause also chemical and physical changes when the ions affected the workpiece at high energy. The crystal structure of the target (workpiece) could be damaged or even destroyed by the energetic collision cascades, and ions of sufficiently high energy (tens of MeV) could cause a nuclear transmutation. The most common applications of ion implantation were as follows: semiconductor device fabrication (Brahma et al. 2016; Chang et al. 2018), solar cells' fabrication (Milési et al. 2017), metal finishing (Dearnaley 1982; Tarasenko et al. 1998), as well as the formation of surface layers (Kluge et al. 1989;

Kern et al. 1997). The ion implantation was carried out with the use of two main methods: *beam line ion implantation (BLII)* and *plasma immersion ion implantation (PIII or PI^3)*, also called (Ensinger 1996) plasma source ion implantation (PSII), plasma ion implantation (PII), plasma immersion implantation (PII), plasma based ion implantation (PBII) or plasma doping (PD).

5.2.1 Beam Line Boron Ion Implantation

The typical equipment for beam line ion implantation (BLII), usually called *ion beam implanter*, consisted of: an ion source (with discharge chamber, ion extractor and DC power supply), ion mass separator, focusing and accelerating system, system of ion deflection, vacuum target chamber (working chamber), vacuum pumping system and a control system. The various types of the implanters were described in detail by Burakowski and Wierchoń (1998). They classified the two main types of implanters: *continuous ion beam implanters* and *pulsed ion beam implanters*, depending on the nature of ion beam. During pulsed ion implantation, the unstable nature of ion beam impact on the solid, resulting from the very short pulse of ions of very high energy, caused re-melting of a thin surface layer. The ions were implanted into the melted surface (Burakowski and Wierchoń 1998).

An example of a continuous implanter was shown in Fig. 5.12 (Burakowski 1988, 1989; Burakowski and Wierchoń 1998). The ions of the desired element were produced by an ion source in the discharge chamber. The three main groups of

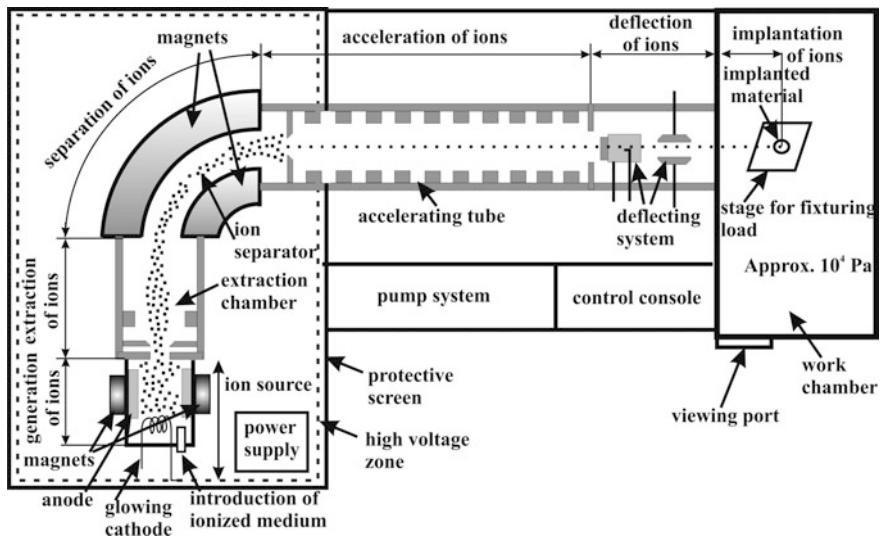


Fig. 5.12 Schematic representation of the ion beam implanter with electric deflection of ion beam (Burakowski and Wierchoń 1998 with permission)

ion sources were indicated by Burakowski and Wierzchoń (1998): with discharge in the gas phase (called plasma ion sources), with thermal emission of ions from the solid surfaces (called ion sources with thermionic emission) and with the surface ionization (called field ion sources). The ion source produced the vapor of the element, which was intended for implantation. This vapor was ionized by the electrons, emitted by the incandescent cathode (Przybyłowicz 2000). The extractor was used for extracting the ions from the ionization zone, their initial formation into a beam and directing the beam towards the separator and accelerator. The mass separator was used for precise selection of ions in the beam, based on the analysis of their mass. Only ions with an adequate ratio of charge to mass were passed through the separator using the influence of magnetic field, limited by two plains (so-called magnetic lens). The ions were accelerated to a high energy and formed into the circle-shaped beam in an electric field, produced by focusing and accelerating system, consisting of high-voltage power supply and ionic-optical system. The deflection system was used in order to direct the ion beam to the desired position of the workpiece (target). The ions impinged on the workpiece (the implanted material) in target chamber.

Ion implantation could be considered a special case of particle radiation. Each ion was typically a single atom or molecule. Thus the actual amount of ions, implanted in the workpiece, was the integral over time of the ion current. This amount was usually called the dose and given as ions/cm² (Madakson 1985; Reuther et al. 1988; Kluge et al. 1989; Ballhause and Wolf 1989; Wang et al. 1991; Lee et al. 1992; Shulov 1994; Jain and Shrivastava 1995; Dimitrova 1995; Davis et al. 1998; Uglov et al. 1998; Zhu et al. 2002; Kholmetskii et al. 2003; Werner et al. 2003; Milési et al. 2017; Piñero et al. 2017; Stepanov et al. 2017; Trzciński et al. 2017). Sometimes, the term ion fluence was also applied (Iwaki 1987; Kern et al. 1997; Rao et al. 1994; Soltani-Farshi et al. 1998; Ynsa et al. 2017; Jang et al. 2017). The currents supplied by implanters were small. They were given as beam current density (Lee et al. 1992; Shulov 1994; Davis et al. 1998; Uglov et al. 1998; Kholmetskii et al. 2003; Stepanov et al. 2017; Trzciński et al. 2017), dose rate (Jain and Shrivastava 1995; Shrivastava 1996) or ion flux (Rao et al. 1994; Soltani-Farshi et al. 1998) and expressed in $\mu\text{A}/\text{cm}^2$. Hence, the dose which could be implanted in a reasonable process duration was relatively small. Therefore, ion implantation was applied in cases where the required chemical change was small.

The penetration of implanted ions depended on their energy, the type of ion species as well as the composition of the target. The usually used ion energies ranged from 20 to 500 keV, i.e. 3200–80,000 aJ (Marest 1998). The values in the range of 1–20 keV (160–3200 aJ) were also acceptable. However the low ion energies resulted in the penetration depth of only a few nanometers. Higher energies could also be applied. Accelerators capable of 5 MeV (800,000 aJ) were commonly used. However, the great structural damage to the target often occurred, and the change in the composition was small at any point in the target (workpiece) because of the broad depth distribution (Bragg peak). In general, the monoenergetic ion beam had a broad depth distribution. The average penetration depth was usually called the range of the ions. Under typical conditions ion ranges were between

10 nm and 1 μm . So, ion implantation was especially useful in such cases where the chemical or structural change was desired to be near the surface of the target (workpiece). During the travel through the workpiece, ions gradually lost their energy. The occasional collisions with target atoms (which caused abrupt energy transfers) and a mild drag from the overlap of electron orbitals (which was a continuous process) were a reason for the degradation of ions' energy. This loss of ion energy in the target (workpiece) was called stopping and could be simulated with the binary collision approximation method.

Burakowski and Wierzchoń (1998) specified the four main techniques of beam line ion implantation: *simple ion implantation (SII)*, *recoil implantation (RI)*, *ion beam intermixing (IBI)* and *dynamic mixing (DM)*, known also as *dynamic recoil mixing (DRM)* or *ion enhanced position mixing (IEPM)*. The selected variants of these methods were schematically represented in Fig. 5.13.

Simple ion implantation (SII), i.e. implantation of primary ions (Fig. 5.13a), as the oldest and best known technique of implantation was used for alloying of metallic materials with no prior coating. It was possible to implant between 10 and 20% of primary ions of alloying element, depending on the type of ions and the type of implanted workpiece. This method of ion implantation wasn't accompanied by measurable dimensional and roughness changes of the surface of implanted workpiece.

Recoil implantation (RI), i.e. implantation of secondary ions, meant recoil by a previously deposited coating. The process consisted in bombarding a thin coating, produced by electrolysis, CVD (chemical vapor deposition) or PVD (physical vapor deposition) techniques on the surface of implanted material, by ions of noble gases. The atoms of the deposited coating could attain high energy due to the collisions with ions. As a consequence, they penetrated into the substrate, i.e. implanted material. After implantation the preplaced coating disappeared (see Fig. 5.13b). The suitable selection of the process parameters could result in *ion mixing (IM)*, also called an *ion beam mixing (IBM)*. During such a process, recoil implantation was accompanied by a simultaneous simple ion implantation (Fig. 5.13c). Both RI and IM processes didn't cause the changes in the geometry of implanted material.

Ion beam intermixing (IBI) was carried out for the previously deposited coatings of greater thickness in order to obtain a gentle transition between this coating and the substrate (the implanted material). As a consequence, the previously produced coating partially remained close to the surface, and the implanted ions improved its adhesion to the substrate due to the presence of a transition zone (see Fig. 5.13d).

Dynamic Mixing (DM) was a version of ion mixing, in which the ions were mixed during the simultaneous implantation using two or more ion beams (Fig. 5.13e) or during deposition of coating on the surface (Fig. 5.13f) by evaporation or sputtering (Burakowski and Wierzchoń 1998). If the two ion beams were applied, the process was called *dual beam implantation (DBI)*. The second variant of DM was often a combination of ion implantation and a PVD method of deposition, i.e. the PVD process was ion beam-aided. Hence, such a treatment was known as *ion beam deposition (IBD)*.

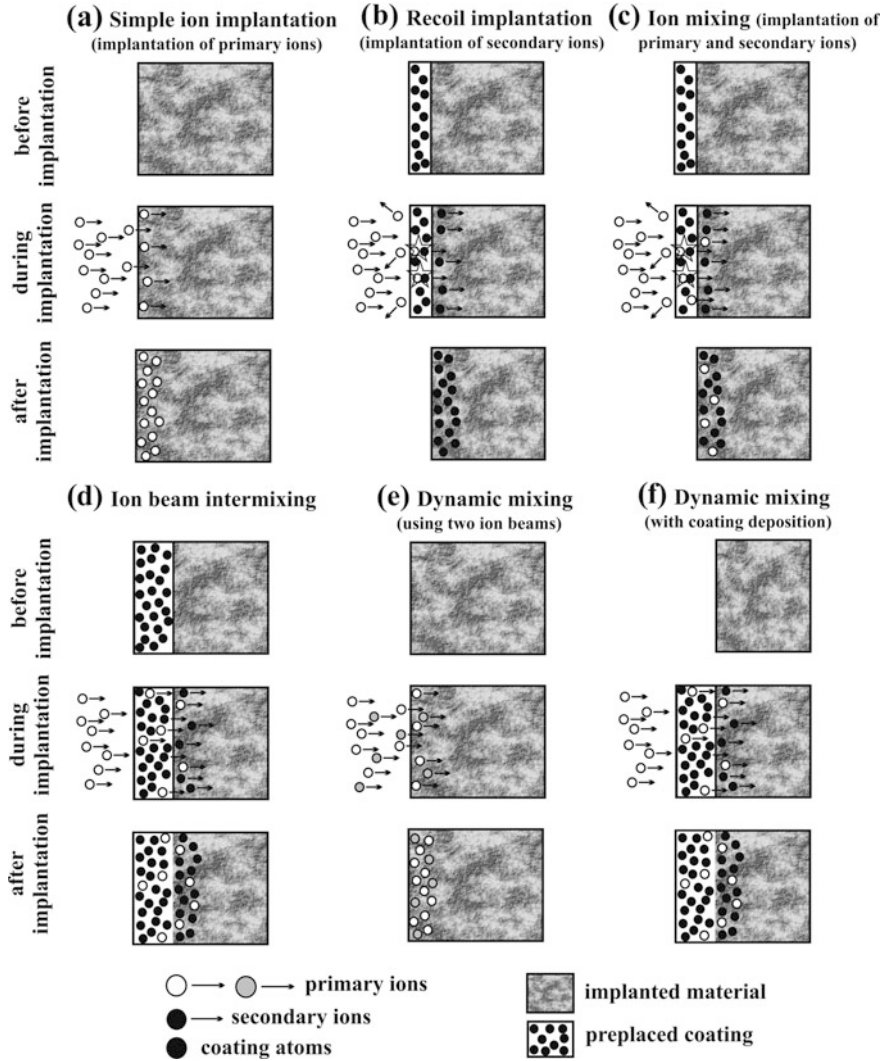


Fig. 5.13 Schematic representation of the selected techniques of beam line ion implantation, (b) and (d) based on Burakowski and Wierchoń (1998)

The beam line ion implantation was characterized by many advantages (Marest 1998; Burakowski and Wierchoń 1998). The main of them were as follows: a possibility of implantation of any atomic species into almost any material in a short duration at any temperature, a possibility of the use of low temperatures of implanted material below 200 °C (473 K), a possibility of obtaining the high concentrations of alloying elements (exceeding their solubility in implanted material), a possibility of precise control of these concentrations by programming the

dose and ion energy, a control and reproducibility of the penetration depth (range of ions), a possibility of creation the new crystalline phases or amorphous structure, a formation of high compressive stresses due to the creation of numerous defects, the unchanged dimensions and surface finish of the treated material, no adhesion problems due to the gradual changes of concentration of implanted species throughout the implanted layer, non-pollution of the environment and low electrical energy consumption.

Simultaneously, the main limitations of the BLII process (Marest 1998; Burakowski and Wierzchoń 1998) were as follows: a relatively low range of ions (penetration depth), a line-of-sight nature of the process which caused the impossibility of easy implantation of materials with complex geometrical shapes (target manipulation arrangements were necessary to obtain the uniform implantation of the entire surface), very high cost of ion implanters and high operating cost of implantation as well as a necessity to use radiological shields, protecting the operator from X-ray radiation.

The ions of non-metallic elements, such as carbon, nitrogen and boron, could be implanted into interstitial positions of the crystal lattice. Therefore, they were very often used for ion implantation of metals (Reuther et al. 1988; Dearnaley 1990) because of the relatively high penetration depth (range of ions) in comparison with substitutional atoms of metallic elements of higher atomic diameter.

Beam line boron ion implantation (BLBII) has been intensively developed through the last three decades. Such a process was commonly applied in order to form the surface layers on iron alloys (Madakson 1985; Iwaki 1987; Kluge et al. 1989; Ballhause and Wolf 1989; Wang et al. 1991; Ohtani et al. 1993; Shulov 1994; Rao et al. 1994; Dimitrova 1995; Jain and Shrivastava 1995; Shrivastava et al. 1995, 1996; Kern et al. 1997; Davis et al. 1998; Uglov et al. 1998, 2002; Kholmetskii et al. 2003; Fedorishcheva et al. 2007). Whereas the other metal alloys were rather sporadically implanted with boron ions (Soltani-Farshi et al. 1998). Boron ion implantation had also a special importance during fabrication of Si-based semiconductor devices (Chang et al. 2018), Si(n) based solar cells fabrication (Milési et al. 2017) as well as in order to obtain p-type doping of diamond (Piñero et al. 2017) and graphene (Jang et al. 2017), to obtain diamond optical elements (DOEs) on a polished surface of synthetic diamond (Stepanov et al. 2017) or to generate superconductivity on diamond (Ynsa et al. 2017). Polymers were also implanted with boron ions, e.g. in order to improve the wear resistance of poly (ether-ether-ketone)—PEEK and poly-ether-imide—Ultem (Lee et al. 1992) or to change the optical characteristics of PMMA (polymethylmethacrylate) nanocomposite (Trzciński et al. 2017).

The general characterization of selected processes of beam line boron ion implantation (BLBII) was shown in Tables 5.9, 5.10 and 5.11, taking into account the available literature data regarding the method of implantation, ion source, implanted ions, type of implanter, ion energy, ion dose, beam current density and temperature of implanted substrate material. However, many authors didn't report the full data regarding the used methods and parameters of beam line ion implantation.

Table 5.9 General characterization of selected processes of beam line boron ion implantation of iron alloys. Part I

Type of material	Method of implantation/ion source/implanted ions/type of implanter	Ion energy (keV)/Dose (ions/cm ²)/current density (μA/cm ²)/temperature (°C)	References
Pure α-iron (99.9%)	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	50/10 ¹⁶ –10 ¹⁸ /unknown current density/room temperature	Reuther et al. (1988)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /T51-200/ZK	150/10 ¹⁷ –4 × 10 ¹⁷ /unknown current density and temperature	Wang et al. (1991)
	DM (3 ion beams) — Fig. 5.13e/unknown ion source/B ⁺ , Ni ⁺ and Mo ⁺ /T51-200/ZK	150/10 ¹⁷ –4 × 10 ¹⁷ (B ⁺), 10 ¹⁷ –3 × 10 ¹⁷ (Ni ⁺), 10 ¹⁷ (Mo ⁺)/unknown current density and temperature	Wang et al. (1991)
Pure α-iron (99.5%)	SII—Fig. 5.13a (LEHCII)/boron pellets/B ⁺ /unknown implanter	20/unknown dose/500/600–950	Davis et al. (1998)
Low-carbon steels	SII—Fig. 5.13a/HCl (or CCl ₄) + B powder, HCl (or CCl ₄) + B ₂ O ₃ /B ⁺ /unknown implanter	75/2.2 × 10 ¹⁷ –7.9 × 10 ¹⁷ /1–3/below 30 or 600–700	Kern et al. (1997)
Low-alloy steels	SII—Fig. 5.13a/unknown ion source/B ⁺ /Varian/Extrion 350 DF	100/1 × 10 ¹⁷ –4 × 10 ¹⁷ /unknown current density/below 150	Kluge et al. (1989)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	60/1 × 10 ¹⁷ –6 × 10 ¹⁷ /unknown current density/50–100	Ballhause and Wolf (1989)
	DM (2 ion beams)—Fig. 5.13e (DBI)/unknown ion source/B ⁺ and Cr ⁺ /unknown implanter	80/unknown dose, current density and temperature	Fedorishcheva et al. (2007)
White cast iron	SII—Fig. 5.13a/HCl (or CCl ₄) + B powder, HCl (or CCl ₄) + B ₂ O ₃ /B ⁺ /unknown implanter	75/2 × 10 ¹⁷ –7.9 × 10 ¹⁷ /1–3/below 30 or 600–700	Kern et al. (1997)

In case of iron alloys, implanted with boron ions (Tables 5.9 and 5.10), simple ion implantation (SII) was a predominant method applied. Moreover, dynamic mixing (DM) using the two or three ion beams (Wang et al. 1991; Rao et al. 1994; Fedorishcheva et al. 2007) was sporadically carried out. Much attention has been devoted to the beam line boron ion implantation of high-alloy steels (Table 5.10) due to the difficulties during the typical diffusion boriding of such materials. So, the high-chromium steels (Iwaki 1987; Ballhause and Wolf 1989; Ohtani et al. 1993; Rao et al. 1994), high-speed steels (Madakson 1985; Ballhause and Wolf 1989; Dimitrova 1995) or austenitic steels (Jain and Shrivastava 1995; Shrivastava 1995; Davis et al. 1998) were commonly subjected to BLBII processes. The ion energy

Table 5.10 General characterization of selected processes of beam line boron ion implantation of iron alloys. Part II

Type of material	Method of implantation/ion source/implanted ions/type of implanter	Ion energy (keV)/dose (ions/cm ²)/current density (μA/cm ²)/temperature (°C)	References
High-alloy steels	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	200/10 ¹³ –10 ¹⁸ /unknown current density and temperature	Madakson (1985)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	75/1 × 10 ¹⁷ –5 × 10 ¹⁷ /unknown current density and temperature	Iwaki (1987)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /Varian/Extrion350 DF	100/1 × 10 ¹⁷ –4 × 10 ¹⁷ /unknown current density/below 150	Kluge et al. (1989)
	SII—Fig. 5.13a/unknown ion source/B/unknown implanter	60/1 × 10 ¹⁷ –6 × 10 ¹⁷ /unknown current density/50–100	Ballhause and Wolf (1989)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	30–180/4.4 × 10 ²⁰ –6 × 10 ²¹ /unknown current density and temperature	Ohtani et al. (1993)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	40/10 ¹⁸ /10–40/650	Shulov (1994)
	DM (2 ion beams)—Fig. 5.13e (DBI)/unknown ion source/B ⁺ and N ⁺ /unknown implanter	400 (B ⁺), 550 (N ⁺)/2.3 × 10 ²⁰ /below 0.2/below 100	Rao et al. (1994)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /Vezuvium or ILU-4	50/1 × 10 ¹⁶ –1 × 10 ¹⁷ /unknown current density/50–100	Dimitrova (1995)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /Varian DF 3000	100/2 × 10 ¹⁷ /3.3/unknown temperature	Jain and Shrivastava (1995), Shrivastava et al. (1995, 1996)
	SII—Fig. 5.13a/HCl (or CCl ₄) + B powder, HCl (or CCl ₄) + B ₂ O ₃ /B ⁺ /unknown implanter	75/2 × 10 ¹⁷ –7.8 × 10 ¹⁷ /1–3/below 30 or 600–700	Kern et al. (1997)
	SII—Fig. 5.13a (LEHCII)/boron pellets/B ⁺ /unknown implanter	20/unknown dose/500/600–950	Davis et al. (1998)
	SII—Fig. 5.13a (LEHCII)/unknown ion source/B ⁺ /unknown implanter	20/2 × 10 ¹⁸ /530/500	Uglov et al. (1998, 2002) Kholmetskii et al. (2003)

Table 5.11 General characterization of selected processes of beam line boron ion implantation of non-ferrous materials

Type of material	Method of implantation/ion source/implanted ions/type of implanter	Ion energy (keV)/dose (ions/cm ²)/current density (μA/cm ²)/temperature (°C)	References
Titanium and its alloys	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	100–185/10 ¹⁶ –10 ¹⁸ /20/unknown temperature	Soltani-Farshi et al. (1998)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	40/2 × 10 ¹⁷ /10–40/450	Shulov (1994)
Nickel alloys	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	40/3.7 × 10 ¹⁶ /10–40/600	Shulov (1994)
TiAlN	IBI—Fig. 5.13d/unknown ion source/B ⁺ /unknown implanter	75/10 ¹⁷ –10 ¹⁸ /unknown current density and temperature	Zhu et al. (2002)
TiN	IBI—Fig. 5.13d/unknown ion source/B and Si/unknown implanter	80 (B ⁺), 200 (Si ⁺)/5 × 10 ¹⁶ –2 × 10 ¹⁷ /unknown current density and temperature	Werner et al. (2003)
Si wafers	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	3–5/2.07 × 10 ¹⁵ –4.2 × 10 ¹⁵ /unknown current density and temperature	Chang et al. (2018)
Si(n) based solar cells	SII—Fig. 5.13a/unknown ion source/B ⁺ /VIISTA HCP	10/10 ¹⁴ –10 ¹⁵ /unknown current density and temperature	Milési et al. (2017)
Synthetic diamond	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	20–150/8.5 × 10 ¹⁴ –1 × 10 ¹⁶ /unknown current density/300	Piñero et al. (2017)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /ILU-3	40/1.43 × 10 ¹⁸ /15/unknown temperature	Stepanov et al. (2017)
	SII—Fig. 5.13a (HEII)/unknown ion source/B ⁺ /unknown implanter	8000/1 × 10 ¹⁵ –57 × 10 ¹⁵ /unknown current density and temperature	Ynsa et al. (2017)
PMMA/ Graphene/ Cu stack	SII—Fig. 5.13a/unknown ion source/B ⁺ /unknown implanter	35/0.5 × 10 ¹⁰ –5 × 10 ¹¹ /unknown current density/room temperature	Jang et al. (2017)
Polymers	SII—Fig. 5.13a/unknown ion source/B ⁺ /Van de Graaff	200/2.3 × 10 ¹⁴ –2.2 × 10 ¹⁵ /less than 0.1/room temperature	Lee et al. (1992)
	SII—Fig. 5.13a/unknown ion source/B ⁺ /ILU-3	40/6.25 × 10 ¹⁴ –2.5 × 10 ¹⁶ /less than 2/room temperature	Trzciński et al. (2017)

ranged from 40 to 200 keV during the typical SII process. Whereas the DM process was characterized by the ion energy even up to 400 keV (Rao et al. 1994). The beam current density usually didn't exceed 3.3 μA/cm² if it was reported by authors of published papers. The temperature of boron ion implanted iron alloys was

usually below 150 °C (423 K). The ion dose ranged from 10^{13} to 6×10^{21} ions/cm². However, such a boron ion implantation resulted in a relatively low range of ions (80–450 nm). It usually excluded the formation of hard metal borides in the implanted iron alloy. The implanted region was characterized by amorphous state. As it was reported by Ballhause and Wolf (1989), the transformation of the amorphous state into a crystalline one was possible as a consequence of annealing of implanted alloy at the temperature above 280–300 °C (553–573 K). Reuther et al. (1988) suggested that depending on the temperature there was a critical dose above which the amorphous iron borides could be transformed into metastable or stable crystalline iron borides. Hence, only the use of the relative high dose (Ohtani et al. 1993) or high beam current density (10–40 $\mu\text{A}/\text{cm}^2$) with the increased temperature of the substrate (Shulov 1994) favored the appearance of metal borides (Fe_2B or CrB , respectively) in boron ion implanted steels by the typical SII process. Dynamic mixing (DM) with simultaneous implantation of B and Cr ions also provided a little amount of borides (CrB , Cr_2B , Cr_3B_3).

Therefore, the modified BLBII processes were proposed (Davis et al. 1998; Uglov et al. 1998, 2002; Kholmetskii et al. 2003) with the use of the low ion energy (20 keV) and high current density (500–530 $\mu\text{A}/\text{cm}^2$) at elevated temperature of implanted material up to 500–950 °C (773–1223 K). Such a process was called (Uglov et al. 1998) the *low energy high current ion implantation (LEHCII)* and enabled to increase the range of ions (penetration depth of ions) up to 0.8–40 μm . LEHCII process usually provided an amount of iron borides in implanted material. Fe_2B phase was identified in pure α -iron (Davis et al. 1998). Boron ion implantation of AISI M2 high-speed steel resulted in formation of Fe_2B and Fe_3B phases (Davis et al. 1998) or thin layers, consisting of boron film as well as precipitations of FeB and Fe_2B iron borides (Uglov et al. 2002). However, the produced microstructures weren't shown sufficiently in order to evaluate their quality.

The general characterization of selected processes of beam line boron ion implantation (BLBII) of non-ferrous materials was presented in Table 5.11. Titanium and its alloys as well as nickel-based alloys were hardly ever implanted with boron. It was difficult to describe the trends in this treatment because of the small number of literature data. The simple ion implantation (SII) was applied in order to form the hardened surface layer on these alloys. Boron ion implantation of titanium resulted in the formation of TiB_2 and TiB borides (Soltani-Farshi et al. 1998). Whereas TiB_2 phase was identified in implanted VT8M titanium wrought alloy (Shulov 1994). After boron ion implantation of Inconel[®] 718-alloy (Shulov 1994), only CrB and TiB_2 borides were detected. However, the produced microstructures weren't shown. So, it would be difficult to evaluate the usability of beam line boron ion implantation of such materials during formation of surface layers.

Beam line boron ion implantation by ion beam intermixing (IBI) was also used in order to improve the hardness and tribological properties of TiAlN coating (Zhu et al. 2002) or, together with silicon ion implantation, to improve the resistance to high-temperature corrosion of TiN coating (Werner et al. 2003).

In general, the effects of BLBII processes of both iron alloys and non-ferrous alloys were incomparable to the boride layers produced using the other methods of boriding which were described up to now. It would be difficult to produce the compact, relative thick, hard and wear resistant boride layers, operating at high load conditions, with the use of beam line boron ion implantation. Probably, this could be the reason why there were so few data in the literature regarding such applications of this process in the last decade.

In recent years, BLBII process was more commonly used during fabrication of Si-based semiconductor devices, Si(n) based solar cells' fabrication, obtaining p-type doping of diamond and graphene or diamond optical elements (DOEs) on a polished surface of synthetic diamond, generating the superconductivity on diamond as well as improving some properties of polymers (see Table 5.11). The boron-doped diamond was also produced by Ynsa et al. (2017) using modified technique, called *high energy ion implantation (HEII)*. Such applications represented the current trends in beam line boron ion implantation.

5.2.2 Plasma Immersion Boron Ion Implantation

Plasma immersion ion implantation (PI³) was initially developed in order to replace conventional beam line ion implantation (BLII) for some application cases (Ensinger 1996). As it was mentioned above, BLII process often used the plasma as the ion source, i.e. as a reservoir from which ions were extracted and accelerated as an ion beam. The plasma was in the significant distance from the target. During PI³ process, instead of using a remote plasma, the workpieces were immersed into the plasma. Such a method could eliminate the line-of-sight problem of beam line ion implantation where the workpiece of complex shape or the ion beam had to be manipulated to obtain the uniform implantation of the entire surface of substrate material.

The main features of PI³ processes, particularly in comparison to beam line ion implantation, were as follows (Ensinger 1996):

- no ion mass separation, as a consequence, multiple ion implantation was observed, i.e. all the ionized species were implanted,
- no ion beam manipulation, i.e. beam transport optics or beam scanning system etc. wasn't required,
- non line-of-sight, i.e. implantation of workpieces with complex shape was possible, and process time was independent of workpiece dimensions and implanted surface area,
- relatively easy handling of large and heavy workpieces,
- relatively high gas pressure and high dose rates ($10^{16}/\text{cm}^2 \text{ s}$),
- ion energies from tens of eV to 10^5 eV, i.e. limited compared to the technically important range of beam line ion implantation,
- not strictly mono-energetic process, mainly depending on gas pressure and pulse shape,

- limited thermodynamic restrictions, and basically, low process temperatures in accordance with typical beam line ion implantation,
- simpler and cheaper equipment than that used for the conventional ion implantation,
- a possibility of integration of the process in production line as cluster tool (important for semiconductor industry),
- compatibility with other plasma techniques, e.g. plasma assisted chemical vapor deposition (PACVD);
- a possibility of applying the multiple processes by simultaneous implantation, deposition or etching,
- difficult in situ dose monitoring,
- generation of secondary electrons which reduced efficiency and lead to X-ray formation.

The two modes of ion energies could be used during PI^3 processes (Ensinger 1996): **low-energy mode** at low bias voltage, causing a shallow implantation and **high-energy mode** at bias pulse higher than -100 kV, corresponding to the BLII process in the medium range of energy. Too high ion energies could increase the probability of arcing and generation of intense X-rays with energies enough to penetrate through vacuum chamber walls. Ensinger (1996) reported that the ionic species could be produced using gaseous plasma-forming source materials (gaseous species), e.g. N_2 , O_2 , BF_3 or using the species vaporized from the surface of a solid precursor. The distribution of ion energies and angles of ion incidence depended on the gas pressure. The two regimes of gas pressure were applied: **low pressure** and **high pressure** (Ensinger 1996). During the low pressure regime the PI^3 process was collision-less, and the distribution of angles of ion incidence was narrow, i.e. the effects of the implantation (e.g. implantation profiles) were similar to those-characteristic of BLII. The gas pressure above 0.1 Pa was characteristic of the high pressure regime. In this case, the ions were scattered during displacement through the plasma sheath. The disadvantage consisted in a broad energy distribution, i.e. the beam lost its mono-energetic nature. As a consequence, the obtained depth profile was quite different from the profile observed during BLII process. The larger angular distribution could be an advantage if the shape of treated workpiece was more complex.

The PI^3 process was schematically presented in Fig. 5.14 (Ensinger 1996). After the implanted workpiece had been biased to a negative high voltage, the electrons, moving much faster than ions, were repelled from its surface (Fig. 5.14a). The ion matrix sheath was formed around the workpiece, and the ions were accelerated toward the workpiece surface in the electrical field (Fig. 5.14b). The plasma sheath expanded until a steady-state conditions were reached or, in the case of pulse biasing, until the high voltage was switched off (Fig. 5.14c).

The main equipment, required for **plasma immersion boron ion implantation (PIBII)**, was similar to that applied during plasma gas boriding and consisted of: tubular reactor, plasma generator, gas cylinder with boron gas precursor (boron trifluoride BF_3 or diborane B_2H_6) as a source of ions, off-gas washer (gas scrubber),

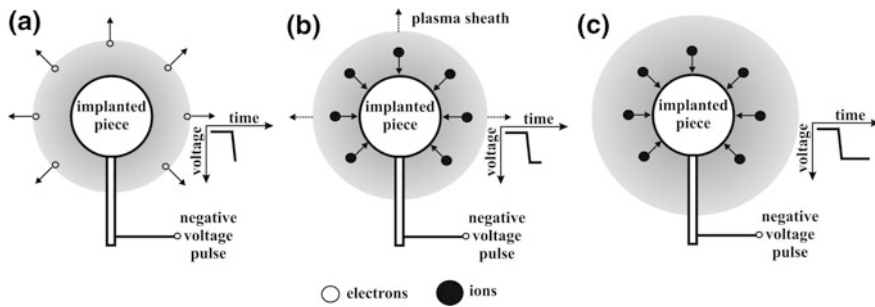


Fig. 5.14 Development of the plasma sheath during PI^3 process (Ensinger 1996 with permission): applying the high voltage pulse and repelling the electrons (a), forming the plasma sheath by the ions which were left back and accelerating the ions towards the implanted piece (b), expanding the plasma sheath (c)

vacuum pump, temperature control and measurement system. The plasma could be generated by different techniques, e.g. DC glow discharge using a DC power supply or pulsed DC generator as well as microwave or radio frequency (rf) excitation. The selected techniques of PIBII processes were represented in Fig. 5.15. At the beginning, a thermionically assisted DC glow discharge was used for PI^3 processes (Conrad 1987; Conrad et al. 1987) because of the simplicity and cheap cost of this method. In case of PIBII, such a process could be carried out according to the Fig. 5.15a. However, its use turned out to be inadvisable if the corrosive gases were used for plasma generation. Additionally, this method could cause contaminations of the implanted material. Therefore, it was applied rather for implantation of nitrogen ions (Kholmetskii et al. 2003; Mukherjee et al. 2007; Ueda et al. 2016, 2017) than boron ions. Although the capacitively coupled rf excitation was also relatively simple, the contaminations from electrode sputtering could appear in this case. For this reason, the electrode-less inductively coupled rf excitation was more appropriate, taking into account a low degree of contamination as well as a large volume and uniformity of the generated plasma (Ensinger 1996). Schematic representation of this technique, mostly used for plasma immersion boron ion implantation, was shown in Fig. 5.15b. In this case, the device was often equipped with Langmuir probe in order to determine the plasma density, the plasma potential and the electron temperature versus the discharge parameters (rf power, gas pressure, magnetic field in the source) as well as in energy-selective mass spectrometer to estimate the ratio of each ion species in the plasma (Kaepelin et al. 2002). The rf-excited plasma systems have been also reported to be better than the glow-discharge systems because of their higher ion densities for higher throughput, lower charging effect, and possibility of the use of lower working pressure and implant energy (Qin and McTeer 2007). The electrode-less microwave excitation also resulted in acceptable contaminations, being predominantly used in electron cyclotron resonance (ECR) mode (Mizuno et al. 1988). The additional advantage of this method was a relatively high ion density at low gas pressure. However, it was rarely applied for boron ion implantation.

The major difference between BLBII and PIBII processes was the absence of ion mass separation. It resulted in implantation of all the positive ions, generated in the plasma, into the target (Ensinger 1996; Coig et al. 2016). If the boron trifluoride (BF_3) was used as the plasma source, the possible ions generated were as follows: $\text{BF}_{x<3}^+$, B^+ , F^+ . Kaepelin et al. (2002) reported that the molecular decomposition of BF_3 depended on the rf power. BF_3^+ ions occurred only in traces ($<0.1\%$). The percentage of BF_2^+ ranged from 85 to 95%. BF^+ ions were represented in the range of 2–12%. Whereas B^+ ions obtained the percentage between 0 and 2%. The increase in the rf power resulted in a higher percentage of BF^+ and B^+ ions. Simultaneously, the percentage of BF_2^+ was diminished (Kaepelin et al. 2002). The use of diborane (B_2H_6) as a plasma source caused a formation of $\text{B}_2\text{H}_{x<6}^+$, B^+ , BH_x^+ positive ions (Milési et al. 2017), generated by ionization or dissociation–ionization. The mixture of diborane and hydrogen ($\text{B}_2\text{H}_6 + \text{H}_2$) was also used as the plasma source during plasma immersion boron ion implantation (Qin and McTeer 2007). In this case, such positive ions as $\text{B}_2\text{H}_{x<6}^+$, B^+ , BH_x^+ , H^+ and H_2^+ were generated. Qin and McTeer (2007) indicated that such a plasma also contained the radical species, formed by excitation or dissociation (i.e. $\text{B}_2\text{H}_{x<6}^*$, B^* , BH_x^*). However, these radicals contributed only to the possible deposition. Diborane diluted with hydrogen in a ratio of 7.5:92.5 created the advantageous conditions for minimizing deposition without sacrificing the boron dose rate.

The general characterization of selected processes of plasma immersion boron ion implantation (PIBII) was shown in Table 5.12, taking into account the available literature data regarding ion source, the ions generated by plasma, scheme of the method in Fig. 5.15, type of implanter, ion energy, ion dose, time of the treatment, pressure, voltage and type of plasma generator.

However, many authors didn't report the full data regarding the used methods and parameters of PIBII process. Missing data in the description of the individual processes have been marked as unknown (abbreviation: unk). In recent years, PIBII process was used rather during fabrication of Si-based semiconductor devices, than

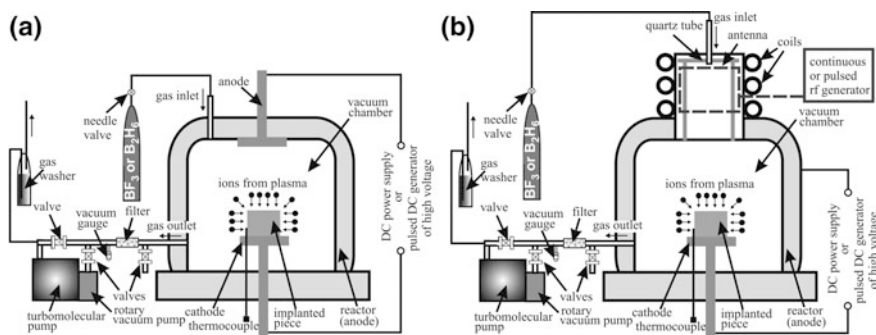


Fig. 5.15 Schematic representation of the selected techniques of plasma immersion boron ion implantation: using a thermionically assisted DC glow discharge (a), using an electrode-less inductively coupled rf excitation (b)

Table 5.12 General characterization of selected processes of plasma immersion boron ion implantation

Type of material	Ion source/ions generated by plasma/scheme of the method/type of implanter	Ion energy (keV)/dose (ions/cm ²)/time (s)/pressure (Pa)/voltage (kV)/plasma generator	References
Si	BF ₃ /BF _{x<3} ⁺ , B ⁺ , F ⁺ /Fig. 5.15b/PULSION [®] ion implanter developed by IBS	6.5/10 ¹⁵ –10 ¹⁷ /unk/unk/unk/continuous or pulsed rf generator	Burenkov et al. (2011)
n-type PERT Si solar cells	BF ₃ or B ₂ H ₆ /BF _{x<3} ⁺ , B ⁺ , F ⁺ or B ₂ H _{x<6} ⁺ , B ⁺ , BH _x ⁺ /Fig. 5.15b/PULSION [®] ion implanter	10/10 ¹⁵ /unk/unk/unk/pulsed rf generator	Coig et al. (2016)
	PIBII/B ₂ H ₆ /B ₂ H _{x<6} ⁺ , B ⁺ , BH _x ⁺ /Fig. 5.15b/PULSION [®] ion implanter	unk/unk/unk/0.01–1/unk/pulsed rf generator	Lerat et al. (2016)
	BF ₃ /BF _{x<3} ⁺ , B ⁺ , F ⁺ /Fig. 5.15b/PULSION [®] ion implanter	unk/10 ¹⁶ /unk/50–1000/unk/pulsed rf generator	Lanterne et al. (2016)
	BF ₃ or B ₂ H ₆ /BF _{x<3} ⁺ , B ⁺ , F ⁺ or B ₂ H _{x<6} ⁺ , B ⁺ , BH _x ⁺ /Fig. 5.15b/PULSION [®] ion implanter	10/3 × 10 ¹⁵ /unk/unk/unk/pulsed rf generator	Milési et al. (2017)
n-type Si wafers	7.5% B ₂ H ₆ + 92.5% H ₂ /B ₂ H _{x<6} ⁺ , B ⁺ , BH _x ⁺ , H ⁺ , H ₂ ⁺ /Fig. 5.15b/unknown implanter	unk/5 × 10 ¹⁵ –2 × 10 ¹⁶ /unk/0.8/4–8/pulsed rf generator	Qin and McTeer (2007)
	PIBII/BF ₃ /BF _{x<3} ⁺ , B ⁺ , F ⁺ /unknown scheme of the method and implanter	unk/5 × 10 ¹⁵ /unk/unk/10/unknown plasma generator	Essa et al. (2014)
	BF ₃ or B ₂ H ₆ /BF _{x<3} ⁺ , B ⁺ , F ⁺ or B ₂ H _{x<6} ⁺ , B ⁺ , BH _x ⁺ /Fig. 5.15b/PULSION [®] ion implanter	unk/6 × 10 ¹⁵ /unk/unk/1/continuous or pulsed rf generator	Vervisch et al. (2009)
	PIBII/BF ₃ /BF _{x<3} ⁺ , B ⁺ , F ⁺ /Fig. 5.15b/unknown implanter	unk/2.4 × 10 ¹⁵ –3.5 × 10 ¹⁵ /2.5–3.5/0.11/1–5/pulsed rf generator	Shao et al. (1997)
p-type Si wafers	BF ₃ /BF _{x<3} ⁺ , B ⁺ , F ⁺ /Fig. 5.15b/unknown implanter	unk/2.4 × 10 ¹⁵ –3.5 × 10 ¹⁵ /2.5–3.5/0.11/1–5/pulsed rf generator	Shao et al. (1997)

during implantation of metallic materials. The n-type passivated emitter rear totally diffused (PERT) Si solar cells, n-type or p-type Si wafers were commonly produced using PIBII (see Table 5.12). Such applications indicated the current trends in plasma immersion boron ion implantation. The predominant method of plasma generation consisted in the electrode-less inductively coupled rf excitation because of the advantages, mentioned above. Both BF₃ (Shao et al. 1997; Vervisch et al. 2009; Burenkov et al. 2011; Essa et al. 2014; Coig et al. 2016; Lanterne et al. 2016; Milési et al. 2017) and B₂H₆ (Qin and McTeer 2007; Vervisch et al. 2009; Coig et al. 2016; Lerat et al. 2016; Milési et al. 2017) were applied as the plasma source. It would be difficult to characterize the typical parameters of PIBII processes because of the lack of detailed data in many cases.

PI³ processes were also combined with deposition technique. It often required the special device in which plasma immersion ion implantation could be carried out in combination with an rf sputter deposition or triode DC sputter deposition (Ensinger et al. 1999). Such processes, called *plasma immersion ion implantation and deposition (PIIID)*, were often carried out in order to produce the coatings, containing boron. The thin boron films, deposited on Si wafers by electron beam evaporation of B chunks, were subjected to PI³ in plasmas of methane or toluene (Ensinger et al. 2007). As a consequence, the boron carbide film was produced. TiBN nanocomposite multilayer was also formed on Si wafers and 9Cr18Mo steel by a PIIID process (Lü et al. 2017). B₄C coatings were synthesized on steel substrate using PIIID in the mixture of diborane, helium and acetylene (B₂H₆, He and C₂H₂) in order to provide wear resistance and wetting resistance to molten aluminum (Nastasi et al. 2001).

5.3 High-Energy Techniques of Boriding

High-energy techniques were often applied in order to produce the surface layers of advantageous properties. Hard, wear and corrosion resistant surface layers or coatings could be produced using these methods. In general, any of the elements might be introduced into the surface or deposited on the surface of metal alloys, causing the modification of their chemical and phase composition as well as properties. Surface alloying with boron and formation of boride coatings by typical thermal spraying, detonation spraying and cladding were classified as the most important high-energy techniques of boriding (Fig. 2.1).

5.3.1 Surface Alloying with Boron

The term “alloying” was used in a very wide meaning by Burakowski and Wierzchoń (1998) in order to unify the terminology. It included all the techniques of introduction of alloying elements into the material such as: mechanical alloying, being mechanical mixing of materials in the form of powders, followed by their sintering; alloying by metallurgical or laser remelting, being hydrodynamic mixing of materials, of which at least one was in a liquid state or, finally, diffusion alloying (well-known as diffusion saturation), consisting in diffusion of one material into the other in the solid state.

In this section, the processes of *surface alloying with boron*, comprising laser surface alloying, plasma surface alloying and electron beam surface alloying, were described taking into account their importance in the formation of boride layers.

5.3.1.1 Laser Surface Alloying with Boron

The most important laser techniques in surface engineering could be divided into the four main types of laser treatment (Burakowski and Wierzchoń 1998): *remelting-free techniques*, *remelting techniques*, *evaporation techniques* and the *special techniques for the formation of thin and hard coatings*. Their simplified classification was shown in Fig. 5.16. Remelting-free techniques were represented by surface annealing, tempering or preheating, surface hardening and surface cleaning. Remelting techniques included surface remelting, surface alloying and cladding. The most commonly used evaporation techniques were as follows: pure evaporation, detonation hardening and ablation cleaning. The thin and hard coatings could be formed by the fusion alloying in gas method, pure vapor deposition, pyrolytic and photochemical methods as well as by chemical methods, e.g. laser-assisted chemical vapor deposition (LACVD). *Laser surface alloying* had a special importance for the formation of boride layers. Therefore, this process was marked in Fig. 5.16 with the box drawn in a broken line.

Laser irradiation, propagating in different media, was subjected to the laws of reflection, refraction, polarization and absorption. The power of laser beam P_0 , reaching the material surface, included the power reflected from the surface, the power lost as a result of the convection and the power absorbed by material (Kusiński 2000):

$$P_0 = P_{abs} + P_{refl} + P_{conv} \quad (5.34)$$

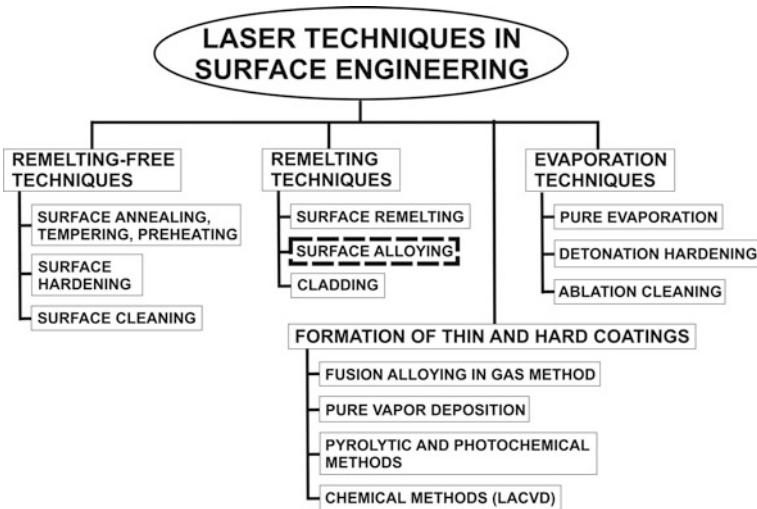


Fig. 5.16 Simplified classification of the most important laser techniques in surface engineering inspired by Burakowski and Wierzchoń (1998)

where: P_{abs} is absorbed power, P_{refl} is reflected power and P_{conv} is power lost by convection.

The scheme of action of laser irradiation on the surface of semi-infinite material was shown in Fig. 5.17 based on Kusiński (2000). The three components of laser beam power P_0 were marked with the same dark gray color. The phenomena outside and inside material were distinguished. The effectiveness of laser heat treatment depended to a high degree on the absorptivity of material surface. If the power lost by convection was negligible, the total absorbed laser beam power could be expressed as (Kawasumi 1981):

$$P_{abs} = A_p \cdot P_0 \quad (5.35)$$

where: A_p is absorption coefficient of irradiated material.

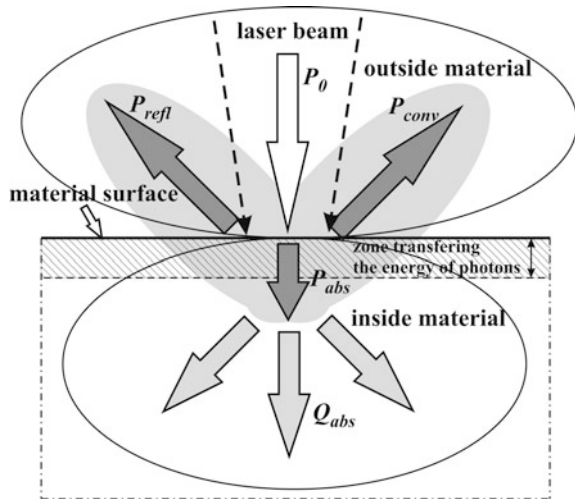
The total heat, absorbed per unit of material surface, could be calculated as follows (Kusiński 2000):

$$Q_{abs} = P_{abs} \cdot t \quad (5.36)$$

where: t is a time of action of laser irradiation.

Laser surface alloying (LSA) consisted in simultaneous remelting and mixing of **alloying material** and **alloyed material** (substrate). The action of the laser beam and its pressure brought both alloying material and substrate to melt (Burakowski and Wierzchoń 1998). The molten pool of material was formed. The melting point of the alloying material should be higher than the melting point of the substrate because of the risk of evaporation of alloying material before the substrate material will be heated. Makuch et al. (2015) reported that the convection and vortex motions strongly influenced the microstructure of laser-alloyed layers. With the remelting, alloying and alloyed materials were mixed, and the alloying material

Fig. 5.17 Scheme of the action of laser irradiation on the material surface inspired by Kusiński (2000)



partially or totally dissolved in the substrate material. After resolidification of this mixture, the microstructure and chemical composition of re-melted zone was quite different compared to that of the substrate. According to the other literature data (Gladush and Smurov 2011), the vortices appeared in the material if the laser beam power exceeded 17 W. The velocity of convection and vortex motions was higher at the increased laser beam power or power density. Close to the re-melted surface, the velocity of the liquid material was non-uniform. It corresponded to the vortical nature of the flow. The maximal velocity was observed in the vortex center. At the higher laser beam power, the flow velocity increased and the vortex motions shifted from the center of laser track to the adjacent areas. Burakowski and Wierzchoń (1998) reported that at the interface between solid (substrate material) and liquid (re-melted zone), a very thin diffusion zone (not exceeding 10 μm) could usually be observed. It resulted from the diffusion by narrow canals of the molten phase along solid grain boundaries and grain blocks or could be a consequence of the local deformations (in the case of displacement of atoms by dislocations).

There was a wide range of elements or their compounds for LSA because it was relatively easy to introduce them into the surface of the alloyed material (Lyakhovich et al. 1985). The alloying materials, most commonly used, were classified by Burakowski and Wierzchoń (1998) as well as by Kusiński (2000). They were as follows: non-metallic elements such as carbon, nitrogen, silicon, boron; metals such as Co, Cr, Mn, Nb, Ni, Mo, W, Ta, V or their alloys; compounds (mainly carbides) of infusible metals such as TiC, NbC, VC, TaC, WC or alloys of these metals (e.g. Co–W, Cr–Ti, C–Cr–Mn, Al–Cr–C–W, Ni–Cr, Cr–Ni–B, stellite and superalloys) as well as gases such as commercially pure nitrogen or acetylene. Laser surface alloying with carbon, nitrogen, silicon or boron was often called *laser carburizing*, *laser nitriding*, *laser siliconizing* and *laser boriding*, respectively (Kusiński 2000). Taking into account *laser surface alloying with boron* (i.e. laser boriding), powder of amorphous boron as well as the powders made of the compounds, containing boron (e.g. borax $\text{Na}_2\text{B}_4\text{O}_7$, boron oxide B_2O_3 , boron carbide B_4C , boron nitride BN or metal borides such as CrB, VB_2 and TaB_2), were used as the most common alloying materials.

Depending on the method of introducing the alloying material into the molten pool, the LSA process could be carried out using the two techniques, called *remelting* and *fusion* (Thiemann et al. 1990; Burakowski and Wierzchoń 1998; Kusiński 2000; Dobrzański and Dobrzańska-Danikiewicz 2011). They were shown in Fig. 5.18 in case of producing the single laser tracks.

LSA by remelting was a two-stage process, consisting in prior deposition of coating with the alloying material on the alloyed material (substrate) and subsequent remelting of this coating together with the surface layer of the alloyed material (Fig. 5.18a). The thickness of the re-melted surface layer was usually at least equal to the thickness of a deposited coating with alloying material. The process started with remelting of the alloying material and was continued by propagation of this remelting into the surface layer of alloyed material. The alloying material was often completely dissolved in the substrate (Burakowski and

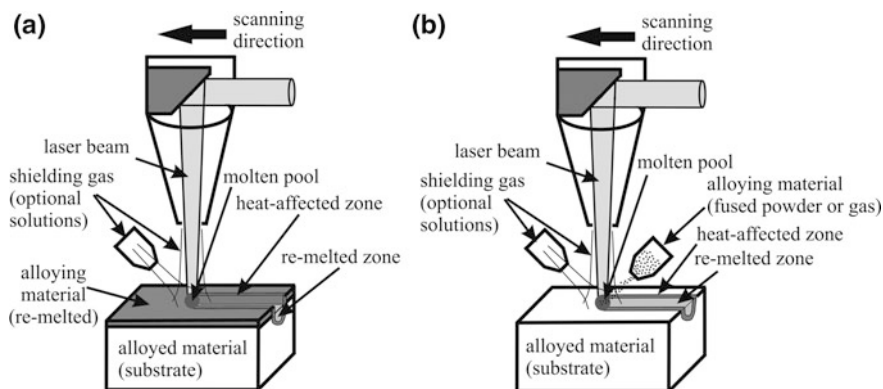


Fig. 5.18 Schematic representation of the techniques of laser surface alloying with the formation of single laser tracks on a flat surface: remelting (a), fusion (b)

Wierzchoń 1998). Such a process was also called *laser surface alloying with predeposited coatings* (Riabkina-Fishman and Zahavi 1996).

The course of laser surface alloying with the use of remelting process was shown in Fig. 5.19. During the first stage of the process, a coating with alloying material was deposited on the cleaned surface of alloyed material (Fig. 5.19a). The alloying material could be deposited on the substrate using different techniques (Burakowski and Wierzchoń 1998): painting, covering by adhesive powders or pastes (containing alloying elements, boron carbides, tungsten and titanium carbides, metal borides, amorphous boron or borax), spraying of suspensions, thermal spraying (flame, plasma, arc or detonation), vapor deposition, electrodeposition, thin foil, plates, rods or wires. Sometimes, the alloying material could be introduced into the substrate using the typical thermochemical treatment, resulting in formation of diffusion layer (e.g. diffusion boriding). The thickness of the deposited coating usually ranged from several to more than 100 μm . The laser irradiation of the adequate laser beam power (P_0), falling on the treated surface (Fig. 5.19b), was mainly absorbed (P_{abs}), partially reflected (P_{refl}) and partially lost by convection (P_{conv}). The absorbed heat depended on: the absorption coefficients of the alloying material and the substrate, the wavelength of the laser beam, the laser beam power density and exposure time (scanning speed of the laser beam). The absorptivity of the surface could be increased using one of the following methods: surface roughening, surface oxidation, preheating of the treated material, or applying a dark mat coating on the surface. If the alloying material consisted of the paste containing amorphous boron and niobium (Makuch et al. 2015), the deposited coating was dark brown and matt, and the increase of absorptivity was unnecessary. During laser treatment, the photons were absorbed by electrons of the treated material. As a consequence, the energy of these electrons increased and they interacted with the crystalline lattice of treated material causing its heating (Burakowski and Wierzchoń 1998; Kusiński 2000; Steen and Mazumder 2010). During laser heating,

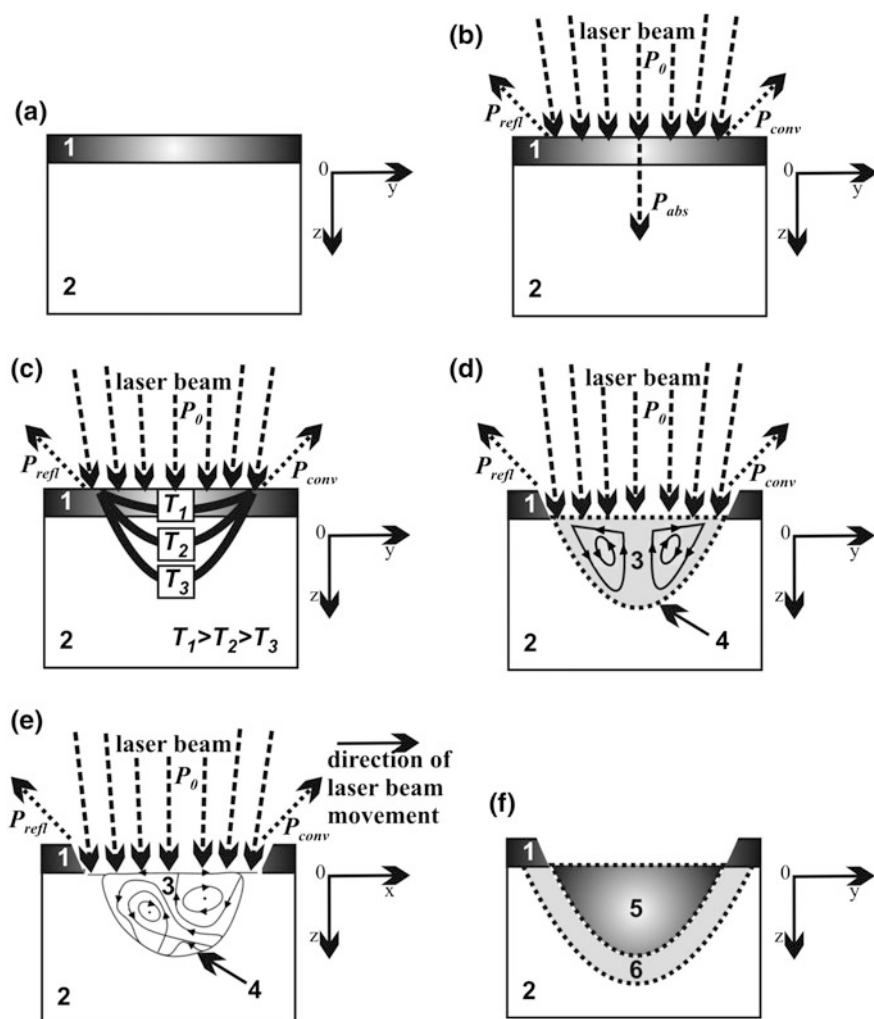


Fig. 5.19 Course of LSA by remelting: deposition of coating with alloying material on the surface of alloyed material (a), action of laser beam on alloying material and substrate (b), temperature distribution in the laser-processed layer (c), convection and vortex motions in molten pool in zOy section (d), convection and vortex motions in molten pool in zOx section (e), resolidification of the laser-processed layer (f); 1—alloying material; 2—alloyed material (substrate); 3—liquid molten pool; 4—liquid-solid interface; 5—re-melted (laser-processed) zone (MZ); 6—heat-affected zone (HAZ); T_1, T_2, T_3 —temperatures in the laser-processed layer; zOy —section perpendicular to direction of laser beam movement; zOx —section parallel to this direction

the highest temperature was obtained in the thin layer close to the surface (Fig. 5.19c). Below, the electrons with higher energy caused the transfer of heat to the colder areas of material. If the temperature was higher than all the melting points of alloying elements and substrate material, the molten pool appeared.

The redistribution of alloying elements in a molten pool depended on laser processing parameters, thermal properties of the treated materials and the presence of gravitational motion and convection.

The intensive mixing in molten pool was described by Cunningham (1964) and Liu (1990). It occurred due to convection, vortex and gravitational motions, and resulted in a flash at the surface of molten pool. The convection and vortex motions both in section zOy perpendicular to direction of laser beam movement (Fig. 5.19d) and in section zOx parallel to this direction (Fig. 5.19e) were primarily responsible for mixing, and therefore, they influenced the chemical and phase composition of the laser re-melted zone (MZ). The intensity of the mixing and transport of alloying elements in the molten pool also depended on the temperature gradient. After the end of laser irradiation, the liquid material coagulated (Fig. 5.19f). During the resolidification process, the new phases often appeared. They were characterized by different microstructure and properties in comparison with alloying elements and alloyed substrate. The high cooling rate caused the formation of alloyed layer with dendritic or cellular microstructure during resolidification. Simultaneously, the heat-affected zone (HAZ) could occur below the laser-alloyed layer as a consequence of remelting-free heat treatment. This zone could also influence the microstructure and properties of this part of the substrate.

Whereas **LSA by fusion** was a single stage process, in which the molten pool of the alloyed material was produced by a laser beam and simultaneously the alloying material (in the form of powder, paste or gas) was introduced into this molten pool (Fig. 5.18b). This method was also called **laser alloying using direct powder injection** (Riabkina-Fishman and Zahavi 1996). The alloying material was completely or partially soluble in the alloyed material. In order to carry out laser surface alloying by fusion, lasers should operate in continuous mode because the alloying material could be introduced to the molten pool only during laser heating, and during break between pulses it would be impossible (Burakowski and Wierchoń 1998). The course of laser surface alloying with the use of fusion process was presented in Fig. 5.20, taking into account convection, vortex and gravitational motions in re-melted zone. The surface of alloyed material should be only adequately cleaned (Fig. 5.20a). Like in the case of LSA by remelting, the laser beam power (P_0) was mainly absorbed (P_{abs}), partially reflected (P_{refl}) and partially lost by convection (P_{conv}). Simultaneously, the alloying material was provided as a powder (Fig. 5.20b). The temperature distribution was shown in Fig. 5.20c. The molten pool appeared after the temperature exceeded the melting point of substrate material. The laser processing parameters, thermal properties of the treated material and alloying material as well as the presence of convection, vortex and gravitational motions influenced the redistribution of alloying elements in a molten pool. The intensive mixing of the alloying material with alloyed material resulted from convection and vortex motions in section zOy (Fig. 5.20d) as well as in section zOx (Fig. 5.20e). The chemical and phase composition of the alloyed surface was modified, often resulting in the formation of new phases. After resolidification (Fig. 5.20f), the re-melted (alloyed) zone (MZ) was accompanied by HAZ.

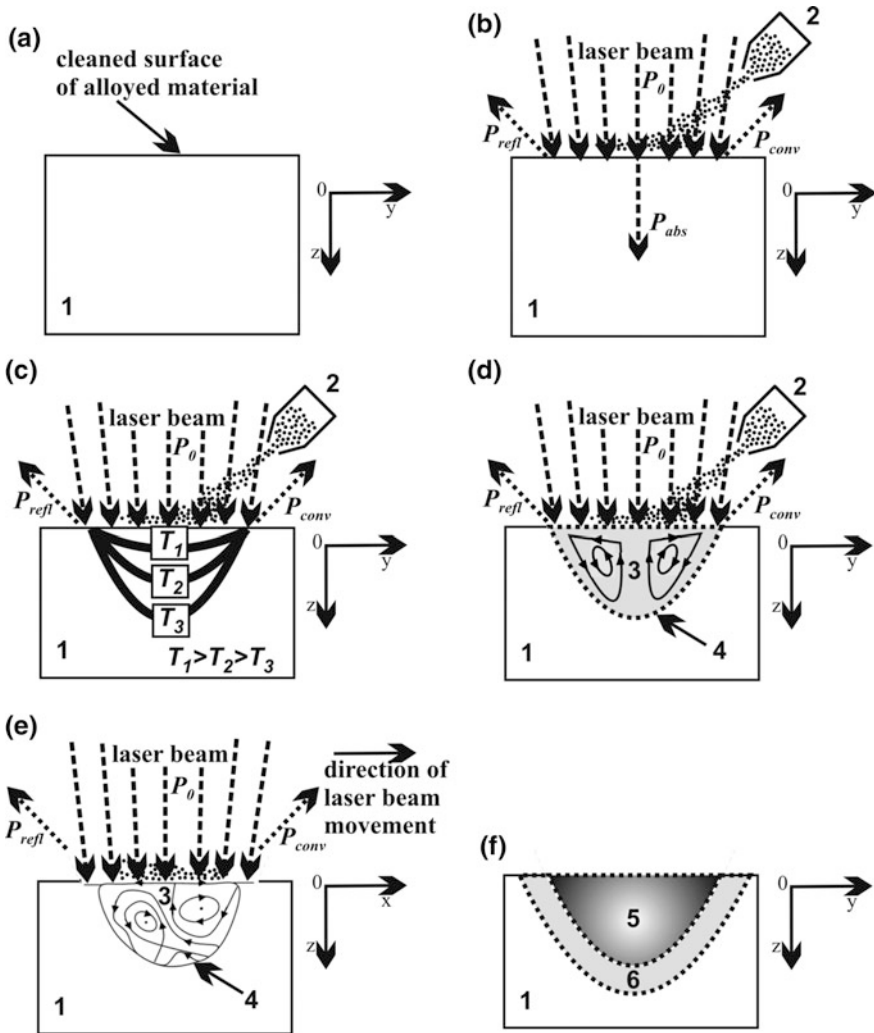


Fig. 5.20 Course of LSA by fusion: cleaned surface of alloyed material prior to the treatment (a), action of laser beam on the substrate with fusion of alloying material (b), temperature distribution in the laser-alloyed layer (c), convection and vortex motions in molten pool in $z0y$ section (d), convection and vortex motions in molten pool in $z0x$ section (e), resolidification of the laser-alloyed layer (f); 1—alloyed material (substrate); 2—alloying material; 3—liquid molten pool; 4—liquid-solid interface; 5—re-melted (laser-alloyed) zone (MZ); 6—heat-affected zone (HAZ); T_1, T_2, T_3 —temperatures in the laser-alloyed layer; $z0y$ —section perpendicular to direction of laser beam movement; $z0x$ —section parallel to this direction

The similar method was applied during **laser cladding** (Riabkina-Fishman and Zahavi 1996). However, laser cladding differed from the laser surface alloying, taking into account the depth of the re-melted surface layer of substrate material.

Laser cladding was a hardfacing process that used a high-powered laser beam to melt the introduced material (usually powder) and a thin layer of the substrate. The process resulted in a pore- and crack-free coating with low dilution that was perfectly bonded to the substrate (Vilar 1999). Laser cladding limited substrate melting to a minimum depth in order to provide a good fusion bonding between the laser clad coating and the substrate. Hence, the composition and properties were determined primarily by the cladding material (Riabkina-Fishman and Zahavi 1996).

Usually, there was a need to produce the laser-alloyed layer on the larger areas than those resulted from the single laser track formation. In this case, the multiple laser tracks were formed, easing conditions for the industrial applications of LSA processes. The schematic representations of such a treatment were presented in Figs. 5.21 and 5.22 for flat and cylindrical laser-alloyed surface of substrate material, respectively. The lines limiting the size of the treated object after and prior to LSA were approximately the same.

The LSA process required the use of the lasers, which were characterized by an adequately high laser beam power. Therefore, the most commonly used lasers during laser surface alloying were as follows: molecular CO₂ lasers, solid-state Nd:YAG lasers and semiconductor lasers, also called diode lasers. The emitted radiation could be continuous with laser beam power ranging from several tens of microwatts to several tens of kilowatts or pulsed in the form of single pulses or series of pulses with frequency of repetition from several Hz to several tens of MHz (Burakowski and Wierzchoń 1998). The shape of a laser beam on its cross-section has been usually circular or rectangular.

Laser beam power (P) and exposure time of radiation were recognized as the main laser processing parameters. During laser treatment, laser beam should be moved relative to the treated surface. This relative speed of the laser beam, indirectly representing the exposure time, has often been called scanning rate (v_l). The intensity distribution of the laser beam in the cross and longitudinal section to the

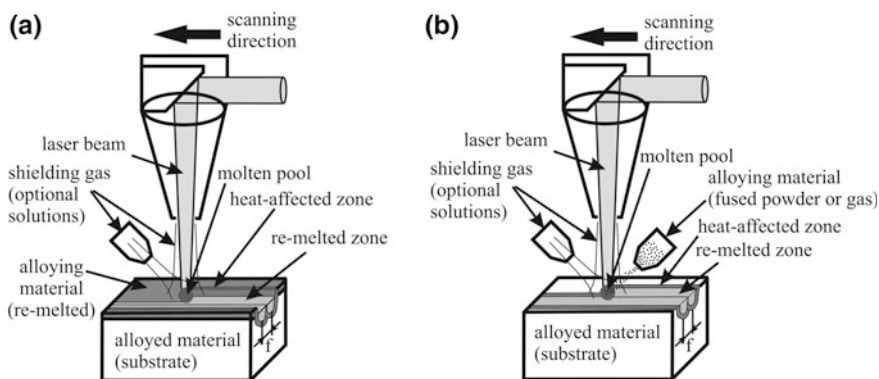


Fig. 5.21 Schematic representation of the techniques of laser surface alloying with the formation of multiple laser tracks on a flat surface: remelting (a), fusion (b); f —distance between axes of adjacent laser tracks

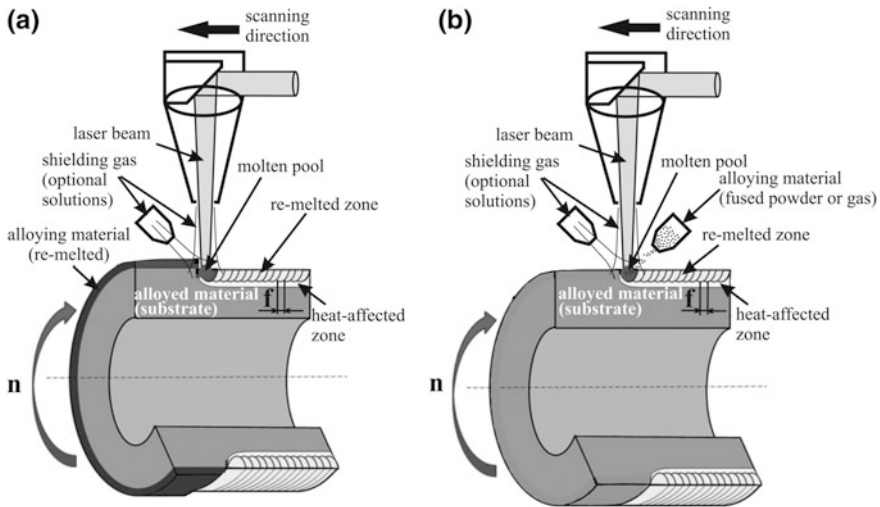


Fig. 5.22 Schematic representation of the techniques of laser surface alloying with the formation of multiple laser tracks on a cylindrical surface: remelting (a), fusion (b); f —distance between axes of adjacent laser tracks; n —rotational speed

beam axis was also very important. It was described as the **transverse electro-magnetic (TEM) mode** of the laser beam. The two most important modes for CO₂ lasers were the basic TEM₀₀ mode and TEM_{01*} mode (TRUMPF Technical information 2007). The TEM₀₀ mode was well-known as Gaussian mode. The greatest intensity was observed in the axis of laser beam, and its intensity distribution corresponded to the Gaussian normal distribution. The TEM_{01*} mode, the so-called doughnut mode, was a special case consisting of a superposition of two TEM₀₁ modes, rotated at 90° with respect to one another. The irradiance profiles of TEM₀₀ and TEM_{01*} modes were shown in Fig. 5.23 in two mutually perpendicular planes. The use of both TEM₀₀ and TEM_{01*} mode caused that the effect of laser action did not depend on the direction of laser beam tracking. Whereas this direction would strongly influence the shape of the laser tracks, produced with the use of TEM₀₁ mode (Fig. 5.23b). TEM_{01*} mode could be formed with radial or azimuthal polarization (Niziev and Nesterov 1999). However, the mode with azimuthal polarization had no practical importance because of the low absorption coefficient.

The influence of TEM_{01*} mode and its irradiance profile on the effects of laser remelting was shown in Fig. 5.24 in case of formation of single laser track (Kulka et al. 2013c) and multiple laser tracks (Kulka et al. 2013b). The radial dependence of irradiance was presented in Fig. 5.24a. The projection of the toroidal irradiance profile on the laser-modified surface was shown in Fig. 5.24b, and the microstructure of the produced laser tracks—in Fig. 5.24c.

If the single laser track was produced (see Fig. 5.24), the obtained microstructure resulted from the laser beam power (P) and scanning rate (v_l). The laser beam

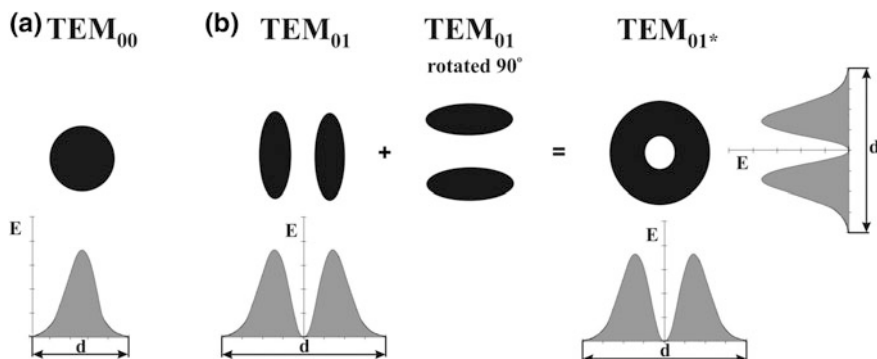


Fig. 5.23 Schematic representation of the irradiance profiles for the selected laser beams: Gaussian TEM_{00} mode (a), doughnut TEM_{01*} mode as superposition of two TEM_{01} modes (b); d —laser beam diameter; E —irradiance

was moved relative to the treated surface and it resulted in the single laser track formation. The dimensions of the laser track (depth and width of re-melted zone as well as heat-affected zone) depended on laser processing parameters. The toroidal irradiance profile also influenced the shape and the dimensions of laser track. The material was subjected to the maximal values of irradiance twice in the axis of a track. That was why the maximal depths of MZ and HAZ were obtained in this region (Makuch et al. 2015). The total width of the laser track (b), i.e. width of HAZ, has been often less than the laser beam diameter (d) because of the short exposure time during the relative motion of laser beam and the treated surface. It also resulted from the irradiance profile of a laser beam. The low irradiance in a distance greater than 0.66 mm from the axis of laser beam caused the material heating to a relatively low temperature. Therefore, the effects of laser modification could be invisible in the microstructure, if the distance from the axis of a laser beam was greater than 0.66 mm (Kulka et al. 2013c).

The formation of multiple laser tracks as a consequence of the use of TEM_{01*} mode during laser remelting was also shown in Fig. 5.24 (Kulka et al. 2013b). In this case, the laser head should be also moved without action towards the direction parallel to scanning direction. The size of this shift corresponded to the distance between the axes of adjacent laser tracks (f) and additionally influenced the obtained microstructure and the dimensions of laser tracks.

Some regions of the material were subjected to the action of laser beam again. The adjacent laser tracks overlapped, and their overlapping (O) has been often given by literature data. However, the method of calculation wasn't usually reported. Probably, the given values of overlapping could take into account the effects of laser modification, i.e. the width of re-melted zone.

Hence, there was a need to formulate the equation in which the value of overlapping would depend on laser processing parameters only. Such an equation was proposed by Makuch et al. (2014):

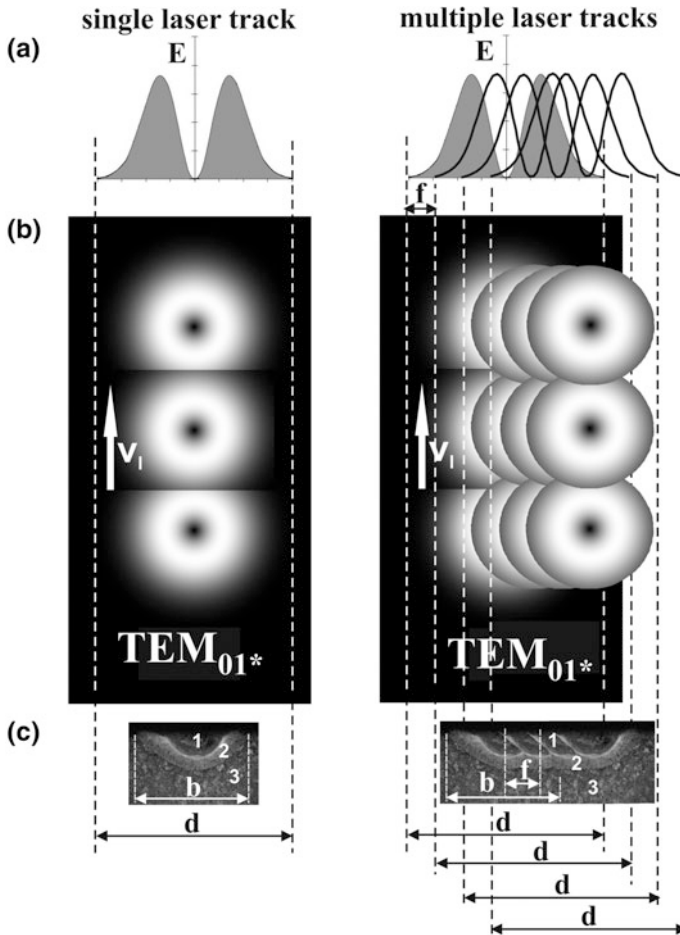


Fig. 5.24 Influence of the TEM_{01*} mode and its irradiance profile on the effects of laser remelting during formation of single track (Kulka et al. 2013c with permission) and multiple laser tracks (Kulka et al. 2013b with permission): radial dependence of irradiance (a), projection of irradiance profile on the laser-modified surface (b), image of the produced laser tracks (c); d —laser beam diameter; b —width of a single laser track; E —irradiance; f —distance between axes of adjacent laser tracks; 1—MZ; 2—HAZ; 3—substrate material

$$O = \frac{d-f}{d} \times 100\% \quad (5.37)$$

where: d is the laser beam diameter (mm), and f is the distance between the axes of adjacent laser tracks (mm).

The formation of the multiple laser tracks during the LSA process required the use of the appropriate device performing the laser head movement relative to the treated surface. In case of flat surface (Figs. 5.18 and 5.21), the movement of laser

head in two perpendicular directions sufficed. The cylindrical surface (Fig. 5.22) was usually rotated about its own axis, and the laser head was moved along a pitch-surface generator. Such motions could be implemented using turning lathe. The laser tracks were arranged as a helix. It was shown in Fig. 5.25. The rotational speed (n) of the laser-alloyed workpiece as well as feed rate (v_f) of laser head influenced the important laser processing parameters such as scanning rate (v_l) and overlapping (O). The angular speed (ω) and the tangential speed (v_t) of the laser-alloyed cylindrical surface could be expressed as (Kulka et al. 2014a):

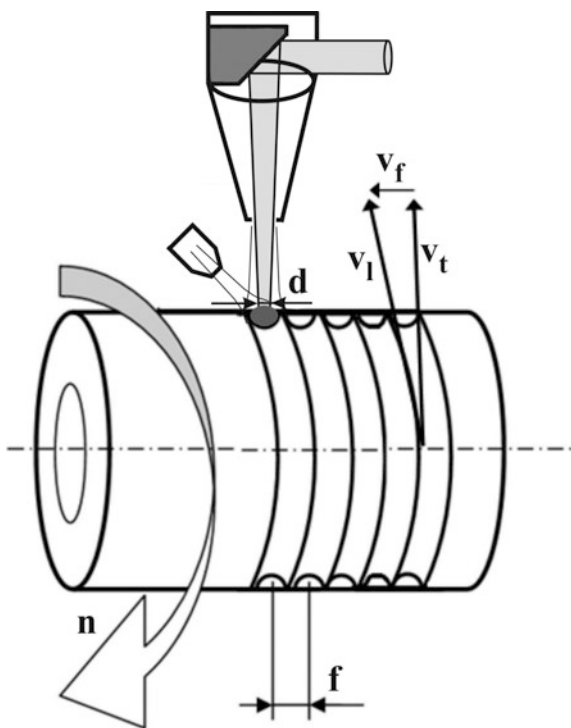
$$\omega = 2 \cdot \pi \cdot n \quad (5.38)$$

$$v_t = \omega \cdot \frac{D}{2} = 2 \cdot \pi \cdot n \cdot \frac{D}{2} \left(\frac{m}{min} \right) \quad (5.39)$$

where: n is rotational speed (min^{-1}), D is external diameter of the workpiece (m).

The distance between the axes of adjacent laser tracks (f) resulted directly from the feed rate. If lathe was used to carry out the motions of the cylindrical workpiece and laser head, rate of feed (v_f) was usually expressed in millimeters per revolution. It could be converted to meters per minute, according to the relationship:

Fig. 5.25 Method of formation of multiple laser tracks on the cylindrical surface; d —laser beam diameter; v_f —feed rate; v_l —scanning rate; v_t —tangential speed; n —rotational speed; f —distance between the axes of adjacent laser tracks



$$v_f \left(\frac{m}{min} \right) = v_f \left(\frac{m}{rev} \right) \cdot n \left(\frac{rev}{min} \right) \quad (5.40)$$

Scanning rate v_l was calculated as a resultant speed of v_t and v_f (Fig. 5.25) according to the equation (Kulka et al. 2014a):

$$v_l = \sqrt{v_t^2 + v_f^2} \left(\frac{m}{min} \right) \quad (5.41)$$

The commonly used values of feed rate (v_f) were relatively low compared to tangential speed (v_t). As a consequence, the scanning rate (v_l) depended mainly on the tangential speed (v_t) on the external surface of the workpiece, that is, on the rotational speed (n) and diameter (D) of the laser-alloyed cylindrical surface.

Summarizing, the main parameters of the LSA with boron using remelting were as follows: type of alloying material, i.e. boron source (powder or paste), thickness of the coating with boron source (μm), mode of laser beam, laser beam power P (kW), laser beam diameter d (mm), average irradiance E (kW/cm²) or power density q (kW/cm²), scanning rate of laser beam v_l (m/min), overlapping O (%) and type of shielding gas. Average irradiance resulted directly from the laser beam power and the surface of laser beam, incident on the alloying material. In case of the circular laser beam, its surface depended on its diameter. If the emitted radiation was pulsed, the pulse power, pulse duration and frequency of pulse generating were additional important parameters of laser processing (Avril et al. 2006).

The coating with alloying material (boron source) was usually prepared in the form of a paste or suspension. Its thickness ranged from 18 to 600 μm . An aqueous suspension of amorphous boron powder was applied by Lyakhovich et al. (1985). Amorphous boron powder was also placed on the surface of alloyed material using a binder, containing an adhesive and acetone (Lysenko et al. 1991, 1995; Safonov et al. 1998). Amorphous boron or boron nitride (h-BN) powders were mixed with ethanol and collodion by Avril et al. (2006). Sometimes, the mixture of amorphous boron powder, water-glass and distilled water was used in order to prepare a paste coating (Wiśniewski and Pertek 2009; Paczkowska et al. 2010; Kulka et al. 2013c, 2015). The powders, containing amorphous boron and nickel (Tian et al. 2005a) or amorphous boron and, optionally, graphite, titanium or RE oxides (Tian et al. 2006a, b, 2009) were blended with diluted sodium silicate solution. The paste coating was often prepared using a mixture of amorphous boron powder and diluted polyvinyl alcohol solution (Tian et al. 2008; Kulka et al. 2013b, 2014a, b, 2016; Makuch et al. 2014; Piasecki et al. 2016). Polyvinyl alcohol was also used as a binder, if alloying material consisted of more components, e.g. amorphous B and Ti powders (Tian et al. 2008), amorphous B and graphite powders (Makuch et al. 2014), amorphous B and niobium powders (Makuch et al. 2015) or powders, containing amorphous B and CaF₂ or BaF₂ self lubricating addition (Piasecki et al. 2016, 2017) as well as in case of the use of BN powder (Senthil Selvan et al. 1999). BN and graphite powders (Filip et al. 2006) or TaB₂ + graphite powders (Filip 2008) were mixed with water. The powders, containing B + TiN + Si + Ni or

B + Ti, were blended with diluted polyethylene solution (Tian et al. 2005b; Tian 2010). The paste coating was usually dried before laser remelting. The alloying material very rarely consisted of the powders only. The substrate was coated directly with amorphous boron powder (Tayal and Mukherjee 1994; Berjeza et al. 1995), B_2O_3 + Fe–B powders (Morimoto et al. 2009) or B_4C + Cr powders (Postnikov and Tagirov 1994). The B, B_4C or h-BN powders could be also sprayed onto the alloyed material (Guo et al. 2011).

The main parameters of the LSA with boron using fusion were similar to those mentioned in the case of remelting. Only instead of the thickness of the coating with boron source, the powder feed rate (expressed in g/min) was used as an important laser processing parameter. The fused powder was blown into the molten pool using a carrier gas of an adequate flow rate (l/min) and usually consisted of boron carbide B_4C , chromium boride CrB or vanadium boride VB_2 (Major 1996) as well as of high-melting boride phase with nickel (Podchernyaeva 1997).

The general characterization of selected processes of LSA of iron alloys with boron was presented in Tables 5.13, 5.14 and 5.15, taking into account the main laser processing parameters, i.e. boron source, thickness of the coating with boron source or powder feed rate, mode of laser beam, laser beam power, laser beam diameter, average irradiance, scanning rate of laser beam, overlapping and type of shielding gas, as well as the type of the laser, shape of the alloyed surface and scheme of the method in Figs. 5.18, 5.21 or 5.22. Carbon steels, low- and high-alloy steels, cast carbon steels, cast irons and carburized steels were successfully subjected to LSA with boron. The process of remelting seemed to be most widely used method of laser surface alloying with boron. Both flat and cylindrical surfaces were successfully laser-alloyed with boron. CO_2 lasers of continuous emitted radiation have been used most often. The use of solid-state lasers (e.g. Nd: YAG laser or other) was less common (Tayal and Mukherjee 1994; Podchernyaeva 1997; Avril et al. 2006) like the pulsed radiation (Lakhtin et al. 1985; Avril et al. 2006). The mode of laser beam was rarely given by literature data. It could be only indicate that TEM_{01*} mode was often used in the case of CO_2 lasers (Wiśniewski and Pertek 2009; Paczkowska et al. 2010; Kulka et al. 2013c, 2015, 2016; Piasecki et al. 2016, 2017). The wide range of laser beam power P was applied (from 0.2 to 3 kW), as well as the range of scanning rate v_l (0.12–5.76 m/min). The reason for such a situation was that the same effect of laser action could be obtained using the relatively low laser beam power and long exposure time (low scanning rate) as well as using high laser beam power at short exposure duration (high scanning rate). The laser beam of cylindrical shape was usually applied, and the laser beam diameter d ranged from 1.29 to 6 mm. As a consequence of the laser beam power P and the laser beam diameter d used, the calculated average irradiance E obtained the values in the range of 3.54–990 kW/cm². However, rejecting the extreme values used by Lyakhovich et al. (1985) and by Safonov (1998), the irradiance ranged from 7.13 to 104 kW/cm². Whereas the most commonly used values were equal to 12.5–57.93 kW/cm². The shape of the laser beam was rectangular very rarely (Morimoto et al. 2009), resulting in irradiance from 53.75 to 65.7 kW/cm². In the case of producing the multiple laser tracks, their overlapping had a significant importance

Table 5.13 General characterization of selected processes of laser surface alloying of iron alloys with boron. Part I

Type of alloyed material	Boron source (alloying material)/thickness of the coating (μm) or powder feed rate (g/min) and carrier gas flow rate (l/min)/type of the laser/ mode of laser beam/ shape of alloyed surface/ scheme of the method	Laser beam power (kW)/ laser beam diameter (mm)/average irradiance (kW/cm^2)/scanning rate (m/min)/overlapping (%) /shielding gas	References
Low-carbon steels	Amorphous boron/180–380/Nd:YAG laser/ unknown/flat/Fig. 5.21a	0.2/1.89/7.13/0.12/ unknown/unknown	Tayal and Mukherjee (1994)
Medium-carbon steels	Amorphous boron/150–500/ CO_2 laser/unknown/ flat/Fig. 5.18a	unknown/unknown/28–990/0.12–0.6/single laser tracks/unknown	Lyakhovich et al. (1985)
	Amorphous boron/30/ CO_2 laser/unknown/flat/ Fig. 5.18a	unknown/unknown/20/ 3/single laser tracks/ argon	Lysenko et al. (1991)
	Amorphous boron/50/ CO_2 laser/unknown/flat/ Fig. 5.21a	unknown/unknown/ 12.5/unknown/ unknown/unknown	Lysenko et al. (1995)
	B_4C , CrB or VB_2 / unknown/ CO_2 laser/ unknown/flat/Fig. 5.21b	unknown/unknown/ unknown/unknown/ unknown/inert gas	Major (1996)
	high-melting boride phase with nickel/ unknown/ CO_2 laser or LTN-103 solid-state laser/unknown/flat/ Fig. 5.21b	unknown/unknown/104 (CO_2 laser) or 22.3 (solid-state laser)/0.16–1/unknown/inert gas	Podchernyaeva (1997)
	20–50% B_2O_3 + Fe–B/ 300–600/direct diode laser/unknown/flat/ Fig. 5.21a	0.225–0.275/ 0.23 $\times$ 1.82/53.75–65.7/unknown/ unknown/unknown	Morimoto et al. (2009)
High-carbon steels	Amorphous boron/50/ CO_2 laser/unknown/flat/ Fig. 5.21a	unknown/unknown/ 12.5/unknown/ unknown/unknown	Lysenko et al. (1995)
Low-alloy steels	Amorphous boron/ unknown/Kvant-16 pulsed laser/unknown/ flat/Fig. 5.18a	data not available	Lakhtin et al. (1985)
	Amorphous boron/20–140/Spectra Physics 973 CO_2 laser/unknown/flat/ Fig. 5.21a	1–3/2–6/3.54–95.49/ 0.15–0.825/unknown/ unknown	Safonov (1998)

Table 5.14 General characterization of selected processes of laser surface alloying of iron alloys with boron. Part II

Type of alloyed material	Boron source (alloying material)/thickness of the coating (μm) or powder feed rate (g/min) and carrier gas flow rate (l/min)/type of the laser/mode of laser beam/shape of alloyed surface/scheme of the method	Laser beam power (kW)/laser beam diameter (mm)/average irradiance (kW/cm ²)/scanning rate (m/min)/overlapping (%) /shielding gas	References
Low-alloy steels	Amorphous boron/40/TRUMPF TLF 2600 CO ₂ laser/TEM ₀₁ */cylindrical/ Fig. 5.18a	0.91–1.3/2/28.97–41.38/0.17–5.76/single laser tracks/unknown	Wiśniewski and Pertek (2009)
	Amorphous boron/40/TRUMPF TLF 2600 CO ₂ laser/TEM ₀₁ */cylindrical/ Fig. 5.22a	1.17/2/37.24/3.84/62.5 ^a /without shielding gas	Kulka et al. (2013c)
	Amorphous boron or amorphous boron + CaF ₂ (mass ratio 10:1)/60/TRUMPF TLF 2600 CO ₂ laser/TEM ₀₁ */cylindrical/ Fig. 5.22a	1.17/2/37.24/2.88/86 ^a /argon	Piasecki et al. (2016)
	Amorphous boron + CaF ₂ or BaF ₂ (mass ratio 5:1)/100/TRUMPF TLF 2600 CO ₂ laser/TEM ₀₁ */cylindrical/ Fig. 5.22a	1.43/2/45.52/2.88/86 ^a /argon	Piasecki et al. (2017)
High-alloy steels	Amorphous boron/30/CO ₂ laser/unknown/flat/ Fig. 5.18a	unknown/unknown/20/3/single laser tracks/argon	Lysenko et al. (1991)
	Amorphous boron/50/CO ₂ laser/unknown/flat/ Fig. 5.21a	unknown/unknown/12.5/unknown/unknown/unknown	Lysenko et al. (1995)
	Amorphous boron/20–140/Spectra Physics CO ₂ laser/unknown/flat/ Fig. 5.21a	1–3/2–6/3.54–95.49/0.15–0.825/unknown/unknown	Safonov (1998)
	Amorphous boron or boron nitride (h-BN)/18–20/pulsed Nd:YAG laser/unknown/flat/ Fig. 5.21a	0.36–0.37/1.26/28.87–29.67/0.228/60.3 ^a /argon	Avril et al. (2006)
	Amorphous boron/200–230/TRUMPF TLF 2600 CO ₂ laser/TEM ₀₁ */cylindrical/ Fig. 5.22a	1.43–1.82/2/45.52–57.93/2.88/86 ^a /argon	Kulka et al. (2016)

^aCalculated using Eq. (5.37)

Table 5.15 General characterization of selected processes of laser surface alloying of iron alloys with boron. Part III

Type of alloyed material	Boron source (alloying material)/thickness of the coating (μm) or powder feed rate (g/min) and carrier gas flow rate (l/min)/type of the laser/mode of laser beam/shape of alloyed surface/scheme of the method	Laser beam power (kW)/laser beam diameter (mm)/average irradiance (kW/cm^2)/scanning rate (m/min)/overlapping (%) /shielding gas	References
Cast carbon steel	High-melting boride phase with nickel/unknown/ CO_2 laser or LTN-103 solid-state laser/unknown/flat/Fig. 5.21b	Unknown/unknown/104 (CO_2 laser) or 22.3 (solid-state laser)/0.16–1/unknown/inert gas	Podchernyaeva (1997)
Nodular cast iron	Amorphous boron/40/TRUMPF TLF 2600 CO_2 laser/TEM ₀₁ */flat/Fig. 5.18a	Unknown/4/2.4–20/unknown/single laser tracks/unknown	Paczkowska et al. (2010)
Carburized low-alloy steel	Amorphous boron/40/TRUMPF TLF 2600 CO_2 laser/TEM ₀₁ */cylindrical/ Fig. 5.22a	1.17/2/37.24/3.84/62.5 ^a /without shielding gas	Kulka et al. (2015)

^aCalculated using Eq. (5.37)

in order to obtain the uniform thickness of the re-melted (i.e. laser-alloyed) zone and homogeneous microstructure. However, the values of overlapping was often not given. Only the processes of LSA with boron, carried out by the group of Poznan University of Technology (Kulka et al. 2013c, 2015, 2016; Piasecki et al. 2016, 2017), were characterized using the values of overlapping, calculated according to Eq. (5.37). Based on the data, reported by Avril et al. (2006), it was also possible to calculate overlapping using the same equation. Overlapping usually ranged from 60.3 (Avril et al. 2006) to 86% (Kulka et al. 2016). The higher values resulted in the formation of the laser-alloyed boride layer of more uniform thickness. Argon was usually applied as shielding gas during LSA of iron alloys with boron by means of remelting. LSA with boron by fusion was hardly ever used in order to produce boride layers on iron alloys (Major 1996; Podchernyaeva 1997). Boron carbide B_4C , vanadium borides VB_2 or chromium borides CrB (Major 1996) as well as high-melting boride phase with nickel (Podchernyaeva 1997) were used as an alloying powder which was introduced into the molten pool by inert gas.

The position of the focal point of laser beam also influenced the effects of the laser surface alloying with boron (Fig. 5.26). Many authors omitted this position in their publications. The laser-treated surface was usually located before the focal point (Fig. 5.26a). Although the position of laser-treated surface behind the focal point (defocused laser beam—Fig. 5.26b) resulted in more wasted energy, such a treatment avoided the adverse influence of the evaporated alloying material on the

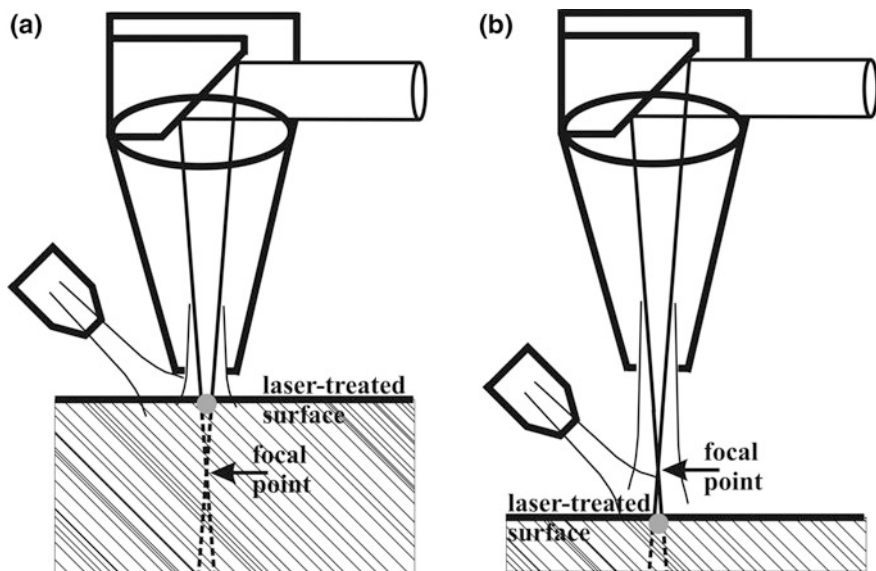


Fig. 5.26 Position of the laser-treated surface in relation to the focal point of laser beam: focused laser beam—the laser-treated surface before the focal point (a); defocused laser beam—the laser-treated surface behind the focal point (b)

focusing mirror (Kulka et al. 2013c, 2015, 2016; Piasecki et al. 2016, 2017). The laser beam diameter was controlled with the use of light-sensitive paper (Kulka et al. 2013c).

LSA of iron alloys with boron provided the composite microstructure of re-melted zone (MZ), in which the hard ceramic phases, especially iron borides, occurred in an iron-based matrix. MZ became the laser-alloyed zone with boron. It was described in detail by Lyakhovich et al. (1985) as well as by Molian and Rajasekhara (1986). The MZ usually consisted of eutectic mixture of iron borides ($\text{FeB} + \text{Fe}_2\text{B}$) and Fe_α phase (Tayal and Mukherjee 1994; Podchernyaeva 1997; Morimoto et al. 2009). Sometimes FeB phase didn't occur in re-melted zone (Lysenko et al. 1991, 1995; Kulka et al. 2013c). As a consequence of segregation of boron during resolidification, iron richer Fe_3B phase was also identified in MZ (Lakhtin et al. 1985; Safonov 1998; Paczkowska et al. 2010; Kulka et al. 2013c, 2015; Piasecki et al. 2016, 2017). In medium- and high-carbon steels as well as in low-alloy steels, borocementite $\text{Fe}_3(\text{C},\text{B})$ also appeared in laser-alloyed zone (Lysenko et al. 1991, 1995; Podchernyaeva 1997; Paczkowska et al. 2010; Piasecki et al. 2016, 2017). Whereas laser alloying of high-alloy steels could result in the additional formation of $\text{M}_{23}(\text{C},\text{B})_6$ borocarbides (Lysenko et al. 1991, 1995; Safonov 1998; Avril et al. 2006; Kulka et al. 2016) as well as Cr_2B or Ni_2B borides in the case of high concentration of chromium and nickel in substrate material (Kulka et al. 2016). If alloying material included calcium fluoride CaF_2 or barium

fluoride BaF_2 , these self-lubricating additions were also identified in the re-melted zone (Piasecki et al. 2016, 2017).

The iron-based matrix could be sometimes quenched due to the high cooling rate. It resulted in the formation of martensite, which was usually identified as Fe_α phase. As a consequence, the microstructure of MZ consisted of eutectic mixture of borides and martensite (Kulka et al. 2015; Piasecki et al. 2016). The fine-grained iron borides were located in martensitic matrix. In case of laser-borided austenitic steel, the matrix was composed of the soft FeCrNiC_γ phase, i.e. alloyed austenite (Lysenko et al. 1991, 1995; Kulka et al. 2016). Some authors (Lyakhovich et al. 1985; Piasecki et al. 2016) reported the possible zonation of the MZ. It resulted in the formation of the zone with only borides' mixture close to the surface, and the eutectic mixture appeared at larger depth.

Below the MZ (i.e. laser-alloyed zone with boron), the heat-affected zone (HAZ) was usually formed (Lyakhovich et al. 1987). Its microstructure depended on the cooling rate in this area and could contain the martensite, bainite or even pearlite. The presence of HAZ diminished a hardness gradient between the MZ and substrate material. HAZ wasn't visible in microstructure after LSA of austenitic steel with boron (Kulka et al. 2016) because an austenitic structure could not be hardened, irrespective of cooling rate obtained during laser heat treatment. Therefore, the HAZ and the substrate didn't differ in microstructure from each other.

The general characterization of selected processes of LSA of non-ferrous alloys with boron was shown in Tables 5.16 and 5.17, taking into account the same parameters of laser processing as it was mentioned previously. Titanium and its alloys as well as nickel alloys became the most popular non-ferrous materials, subjected to laser surface alloying with boron. The difficulties in the use of typical thermochemical methods of boriding (caused by easy passivation of the surface) were the reason for the great interest in the laser boriding of titanium alloys. Whereas the laser boriding of nickel alloys resulted in the easy formation of boride layer which was uniform in respect of the thickness and free of defects such as cracks or gas pores.

Many features of LSA of non-ferrous alloys with boron were similar to those-mentioned in the case of iron alloys. The remelting process was also the predominant LSA method of the considered materials with boron, and CO_2 lasers were also applied most commonly. Like for iron alloys, the laser beam was usually characterized by circular shape, and the mode of a laser beam (TEM_{01*}) was only given by the group of Poznan University of Technology (Kulka et al. 2013b, 2014a, b; Makuch et al. 2014, 2015) and by Senthil Selvan et al. (1999). The ranges of laser beam diameter ($d = 1\text{--}4$ mm), laser beam power ($P = 0.5\text{--}2.5$ kW) and scanning rate ($v_l = 0.05\text{--}2.88$ m/min) were diminished compared to laser boriding or iron alloys. However, they were still wide because of the possibilities of obtaining the same effects of laser action at various combinations of the mentioned parameters. As a consequence, the calculated average irradiance E usually ranged from 7.07 to 62.07 kW/cm². Only if the laser beam diameter was diminished to

Table 5.16 General characterization of selected processes of laser surface alloying of non-ferrous alloys with boron. Part I

Type of alloyed material	Boron source (alloying material)/ thickness of the coating (μm) or powder feed rate (g/min) and carrier gas flow rate (l/min)/type of the laser/mode of laser beam/ shape of alloyed surface/scheme of the method	Laser beam power (kW)/laser beam diameter (mm)/average irradiance (kW/cm^2)/scanning rate (m/min)/overlapping (%) / shielding gas	References
Pure titanium	Amorphous boron and nickel (mass ratio 1:1)/500/ CO_2 laser/ unknown/flat/Fig. 5.21a	1.2/4/9.55/0.05–0.39/30 ^b /argon	Tian et al. (2005a)
	TiN + B + Si + Ni (mass ratio 2:1:1:2)/500/ CO_2 laser/unknown/ flat/Fig. 5.21a	1.2/4/9.55/0.05–0.2/25 ^b /argon	Tian et al. (2005b)
	B + Ti (mass ratio 1:1) or B + Ce_2O_3 + Y_2O_3 + Ti (2:1:1:4)/500/ CO_2 laser/ unknown/flat/Fig. 5.21a	unknown/3/unknown/0.21/ unknown/argon	Tian et al. (2006b)
	B, B_4C or hexagonal BN/400 (B), 50 (B_4C) or 250 (hBN)/ CO_2 laser/unknown/flat/Fig. 5.21a	0.5–1.5/3/7.07–21.22/0.25–1.5/ 50 ^b /argon	Guo et al. (2011)
	Amorphous boron/250/TRUMPF TLF 2600 CO_2 laser/TEM ₀₁ */ cylindrical/Fig. 5.22a	1.56–1.95/2/49.66–62.07/2.88/ 86 ^a /argon	Kulka et al. (2014a)
	Amorphous boron or amorphous boron + graphite (mass ratio 3.2:1)/250 or 210/TRUMPF TLF 2600 CO_2 laser/TEM ₀₁ */ cylindrical/Fig. 5.22a	1.56–1.95/2/49.66–62.07/2.88/ 86 ^a /argon	Makuch et al. (2014)
Titanium alloys	25–75% B_4C + Cr/unknown/ Kvant-15 pulsed laser/unknown/ flat/Fig. 5.18a	data not available	Postnikov and Tagirov (1994)
	Amorphous boron/unknown/ CO_2 laser/unknown/flat/Fig. 5.18a	1/unknown/unknown/0.5–2/ single laser tracks/unknown	Berjeza et al. (1995)
	BN/100/ CO_2 laser/TEM ₀₁ */flat/ Fig. 5.18a	1.5–2.5/1/190.99–318.31/0.5/ single laser tracks/argon	Senthil Selvan et al. (1999)

^aCalculated using Eq. (5.37)^bMethod of calculation was not given

1 mm, the average irradiance increased to 190.99–318.31 kW/cm^2 (Senthil Selvan et al. 1999). Overlapping of the multiple laser tracks (O) was more common given. The values of O were marked with superscript “a” if they were calculated using Eq. (5.37). However, sometimes the method of calculations was not reported. In this case, the values of overlapping were marked with superscript “b”. Based on

Table 5.17 General characterization of selected processes of laser surface alloying of non-ferrous alloys with boron. Part II

Type of alloyed material	Boron source (alloying material)/ thickness of the coating (μm) or powder feed rate (g/min) and carrier gas flow rate (l/min)/type of the laser/mode of laser beam/shape of alloyed surface/scheme of the method	Laser beam power (kW)/laser beam diameter (mm)/average irradiance (kW/cm^2)/ scanning rate (m/min)/ overlapping (%) /shielding gas	References
Titanium alloys	BN + graphite (volume ratio 1:1)/ 200–300/ CO_2 laser/unknown/flat/ Fig. 5.18a	1/3/14.15/0.6/single laser tracks/nitrogen	Filip et al. (2006)
	Boron + graphite (mass ratio 2:1, 1:1 or 1:2)/500/ CO_2 laser/unknown/flat/ Fig. 5.21a	1.2/4/9.55/0.12–0.27/40 ^b / argon	Tian et al. (2006a)
	Boron + graphite + Ti (mass ratio 1:1:2), B + Ti (1:1), B + graphite + Ce_2O_3 + Y_2O_3 + Ti (1:1:1:1:4) or B + Ce_2O_3 + Y_2O_3 + Ti (2:1:1:4)/ 500/ CO_2 laser/unknown/flat/ Fig. 5.21a	Unknown/3/unknown/0.21/ unknown/argon	Tian et al. (2006b)
	Boron or B + Ti (mass ratio 1:4 or 1:8)/500/ CO_2 laser/unknown/flat/ Fig. 5.21a	1.2/3/16.98/0.21/50 ^b /argon	Tian et al. (2008)
	TaB_2 + graphite (volume ratio 1:1)/ 100–300/ CO_2 laser/unknown/flat/ Fig. 5.21a	1/2/31.83/0.48–1.02/50 ^b / argon	Filip (2008)
	B + Ti (mass ratio 1:2 or 1:8)/300–500/ CO_2 laser/unknown/flat/ Fig. 5.21a	1.2/2/38.2/0.18–0.54/50 ^b / argon	Tian et al. (2009) and Tian (2010)
Nickel alloys	Amorphous boron/230/TRUMPF TLF 2600 CO_2 laser/ TEM_{01*} / cylindrical/ Fig. 5.22a	1.56–1.95/2/49.66–62.07/ 2.88/86 ^a /argon	Kulka et al. (2013b, 2014b)
	Amorphous boron + Nb (mass ratio 1:1)/200/TRUMPF TLF 2600 CO_2 laser/ TEM_{01*} /cylindrical/ Fig. 5.22a	1.56/2/49.66/2.88/86 ^a /argon	Makuch et al. (2015)

^aCalculated using Eq. (5.37)^bMethod of calculation was not given

all the data, overlapping of the laser tracks ranged from 25 (Tian et al. 2005b) to 86% (Kulka et al. 2013b, 2014a, b; Makuch et al. 2014, 2015). Shielding gas (usually argon) was commonly used during LSA of non-ferrous materials with boron.

The composite microstructure of commercially pure titanium (Cp–Ti), subjected to laser boriding using only amorphous boron or the mixture of amorphous boron and titanium as alloying material, consisted mostly of the hard titanium borides

(TiB₂ and TiB) in a soft titanium matrix (Tian et al. 2006b; Guo et al. 2011; Kulka et al. 2014a). The traces of titanium oxides (TiO₂, Ti₃O or Ti₂O₃) were also observed in the laser re-melted zone because of the insufficient protection by shielding gas. In the case of the cylindrical surface of the substrate material, it was difficult to avoid oxidizing. The cylindrical surface of the workpiece was rotated relatively quickly during laser treatment. Therefore, the heated surface was not sufficiently protected for oxidation because of the limited time of the shielding gas impact (Kulka et al. 2014a). The results of X-ray diffraction usually indicated the presence of Ti_α phase in the matrix, and didn't provide the information about the occurrence of Ti_{α'} phase (martensite). It was difficult to distinguish this phase from Ti_α by XRD because of the same crystal structure (hexagonal) and slightly different lattice parameters. However, the presence of the martensitic phase was reported by some authors (Kulka et al. 2014a; Makuch et al. 2014). Makuch et al. (2014) characterized the composite microstructure of laser-alloyed Cp–Ti with boron as stick-like titanium borides (TiB₂ + TiB) among the eutectic mixture of TiB whiskers and martensite (Ti_{α'}). If the alloying material contained, in addition to boron, other elements (such as C, N, Si or Ni), in the microstructure of the re-melted zone appeared titanium carbides TiC (Tian et al. 2006b; Guo et al. 2011; Makuch et al. 2014), titanium nitrides TiN (Guo et al. 2011) and other intermetallic phases or interstitial compounds: TiNi (Tian et al. 2005a), Ti₆Ni₆Si₇, TiNiSi and Ni₂B (Tian et al. 2005b). Laser-borided titanium alloys were characterized by similar microstructure. The hard titanium borides, mainly TiB (Postnikov and Tagirov 1994; Senthil Selvan et al. 1999; Filip et al. 2006; Tian et al. 2006a, b, 2008, 2009; Filip (2008); Tian 2010) and TiB₂ (Tian et al. 2006b, 2008, 2009), were identified in soft titanium matrix. Sometimes, other titanium borides were observed in MZ, e.g. Ti₃B₄ (Postnikov and Tagirov 1994; Senthil Selvan et al. 1999) or Ti₂B₅ (Postnikov and Tagirov 1994).

As an alloying material, not only amorphous boron was commonly used. Therefore, titanium carbides TiC (Postnikov and Tagirov 1994; Filip et al. 2006; Tian et al. 2006a, b; Filip 2008) as well as titanium nitrides TiN (Filip et al. 2006) or Ti₂N (Senthil Selvan et al. 1999) often appeared in the laser-alloyed titanium alloys. The presence of the Ti_{α'} martensitic phase in the matrix was also reported by some authors (Filip et al. 2006; Filip 2008), and the formation of eutectic mixture of TiB whiskers and martensite was confirmed. Ti_β phase was also identified in the titanium matrix (Filip et al. 2006; Filip 2008; Tian 2010).

In the HAZ, below MZ, the presence of titanium martensite (Ti_{α'}-phase) was probable (Filip et al. 2006; Kulka et al. 2014a).

The composite microstructure was also characteristic of laser-borided layers produced on Ni-based alloys. The re-melted zone contained hard nickel borides (Ni₃B, Ni₂B) and chromium borides (Cr₂B, CrB) as well as soft Ni–Cr–Fe phase (γ phase), i.e. substitutional solid solution of chromium and iron in nickel (Kulka et al. 2013b, 2014b). If niobium was added to alloying material, niobium borides (NbB₂, NbB) also appeared in laser-alloyed zone (Makuch et al. 2015). Kulka et al. (2013b) reported the possible zonation of the re-melted zone after LSA with boron as it was previously observed for iron alloys. Close to the surface, the compact zone of

borides occurred, and the soft Ni–Cr–Fe matrix appeared only at larger depth. HAZ revealed the negligibly refined microstructure in comparison with base material (Kulka et al. 2013b).

According to the previous considerations, the coating with boron (as alloying material) could be produced by means of the diffusion boriding. The process of diffusion boriding followed by laser remelting could be also classified as laser surface alloying with boron. The general characterization of such processes was shown in Table 5.18, taking into account the similar parameters of laser processing as it was analyzed for typical LSA with boron. In this case, diffusion borided layer of a suitable thickness (40–100 μm) became the coating with alloying material. Laser remelting of the borided layer was applied mainly for iron alloys. Borided low-carbon steel (Gopalakrishnan et al. 2001) as well as borided low-alloy steel (Pertek and Kulka 2003; Kulka and Pertek 2003) contained FeB and Fe_2B iron borides and was successfully laser re-melted. Laser remelting was also carried out after hybrid treatment, e.g. boronickelizing (Bartkowska and Pertek 2014; Bartkowska et al. 2015) or borochromizing (Bartkowska et al. 2012). In these cases, the diffusion borided layer consisted of iron borides and nickel borides or chromium borides. Borocarburing (Kulka and Pertek 2004, 2007; Kulka et al. 2012) was also the hybrid process, subjected to laser surface modification. However, such a treatment was rather similar to laser cladding because the borided layer wasn't re-melted together with the substrate. Laser treatment caused only modification of the morphology of iron borides, produced by diffusion process on carburized steel.

The microstructure of laser re-melted borided layers was similar to that-obtained as a consequence of the typical LSA with boron and revealed the features of composite layer. The eutectic mixture of iron borides and martensite was characteristic of such microstructure. Iron borides FeB (Kulka and Pertek 2003), Fe_2B (Gopalakrishnan et al. 2001; Kulka and Pertek 2003) as well as non-equilibrium Fe_3B phase (Gopalakrishnan et al. 2001; Kulka and Pertek 2003) were located in a martensitic matrix. If the boriding process was followed by nickel plating (boronickelizing), laser remelting resulted in the formation of eutectic mixture of iron borides (Fe_2B , Fe_3B), nickel borides (Ni_3B , Ni_2B , Ni_4B_3) and Fe–Ni martensite (Bartkowska and Pertek 2014; Bartkowska et al. 2015). The re-melted borochromized layer (Bartkowska et al. 2012) probably contained iron borides, chromium borides and Fe–Cr martensite. The laser modification of borocarbured layers (Kulka and Pertek 2004, 2007; Kulka et al. 2012) caused only the changes in the morphology of iron borides FeB and Fe_2B without remelting of the substrate (carburized steel).

The main advantages of the laser surface alloying with boron were as follows: possibility to produce boride layers in a wide range of thickness (significantly exceeding the thickness of the diffusion boride layers), relatively short duration compared to diffusion processes, obtaining a fine-crystalline microstructure and hardness profile of the more gradual decrease towards the substrate material (alloyed material), local heating and lower risk of thermal deformation, possibility of treating the surfaces of complex shape, possibility of partial treatment of the surface, precise control of the laser beam, elimination of cooling media, easy

Table 5.18 General characterization of selected processes of laser remelting of diffusion borided iron alloys

Type of material	Boron source (alloying material)/thickness of the boride layer (μm)/type of the laser/mode of laser beam/shape of alloyed surface/scheme of the method	Laser beam power (kW)/laser beam diameter (mm)/average irradiance (kW/ cm^2)/scanning rate (m/min)/overlapping (%) /shielding gas	References
Borided low-carbon steel	Iron borides FeB + Fe ₂ B/40/ CO_2 laser/unknown/flat/Fig. 5.18a	0.15–0.25/1.5/8.49–14.15/0.24/single laser tracks/argon	Gopalakrishnan et al. (2001)
Borided low-alloy steel	Iron borides FeB + Fe ₂ B/100/TRUMPF TLF 2600 CO_2 laser/TEM _{01*} /cylindrical/Fig. 5.22a	0.78–1.56/2/24.83–49.66/0.17–2.88/single laser tracks/argon	Pertek and Kulka (2003)
	Iron borides FeB + Fe ₂ B/100/TRUMPF TLF 2600 CO_2 laser/TEM _{01*} /cylindrical/Fig. 5.22a	1.17/2/37.24/2.88/86 ^a /argon	Kulka and Pertek (2003)
Boronickelized medium-carbon steel	Nickel borides Ni ₃ B, Ni ₄ B ₃ , NiB and iron borides FeB, Fe ₂ B/90/TRUMPF TLF 2600 CO_2 laser/TEM _{01*} /cylindrical/Fig. 5.22a	1.04/2/33.1/2.88/75 ^a /argon	Bartkowska and Pertek (2014)
	Nickel borides Ni ₃ B, Ni ₄ B ₃ , NiB and iron borides FeB, Fe ₂ B/100/TRUMPF TLF 2600 CO_2 laser/TEM _{01*} /cylindrical/Fig. 5.22a	1.3/2/41.38/1.12/75 ^a /argon	Bartkowska et al. (2015)
Borochromized medium-carbon steel	Iron borides FeB, Fe ₂ B and chromium borides/unknown/TRUMPF TLF 2600 CO_2 laser/TEM _{01*} /cylindrical/Fig. 5.22a	1.3/2/41.38/0.67–2.012/75 ^a /argon	Bartkowska et al. (2012)
Borocarbured low-alloy steel ^b	Iron borides FeB + Fe ₂ B/65/TRUMPF TLF 2600 CO_2 laser/TEM _{01*} /cylindrical/Fig. 5.22a	0.65/2/20.69/3.84/72 ^a /argon	Kulka and Pertek (2004)
	Iron borides FeB + Fe ₂ B/65/TRUMPF TLF 2600 CO_2 laser/TEM _{01*} /cylindrical/Fig. 5.22a	0.78/2/24.83/2.88/72 ^a /argon	Kulka and Pertek (2007) and Kulka et al. (2012)

^aCalculated using Eq. (5.37)^bProcess rather similar to laser cladding

automation of the process and its integration into production lines, environmental performance of the process as well as its energy- and material-saving. High cost of equipment, possibility of cracks in the subsurface, slightly worse cohesion compared to diffusion borided layers or greater roughness and waviness of the treated surface were the main disadvantages of the laser-alloyed layers with boron.

5.3.1.2 Electron Beam Surface Alloying with Boron

The electron beam techniques in surface engineering were very similar to laser techniques. Depending on the combination of main parameters, i.e. power density of electron beam q and its exposure time t (time of heating), the possible treatment was as follows: heating, remelting and evaporation (after reaching the boiling point) of the treated material. It well corresponded to the previously described laser techniques.

Based on the proposed simplified classification, electron beam techniques could be divided into the three main types: *remelting-free techniques*, *remelting techniques* and *evaporation techniques* (Fig. 5.27) which were comparable to the laser techniques. Surface annealing and tempering as well as surface hardening were classified as remelting-free techniques. Remelting techniques consisted of surface remelting, surface alloying or cladding. The detonation hardening represented the most commonly used evaporation technique. Electron beam surface alloying (EBSA) was marked in Fig. 5.27 with the box drawn in a broken line because of its special importance for the formation of boride layers.

The stream of electrons, practically applied after shaping into a beam and after suitable deflection, has been called *electron beam* (Burakowski and Wierchoń 1998). The two sources of electrical energy were necessary in order to generate an electron beam. The first source enabled the emission of electrons from the emitter (cathode). Whereas the second source was used to accelerate the electrons. Both

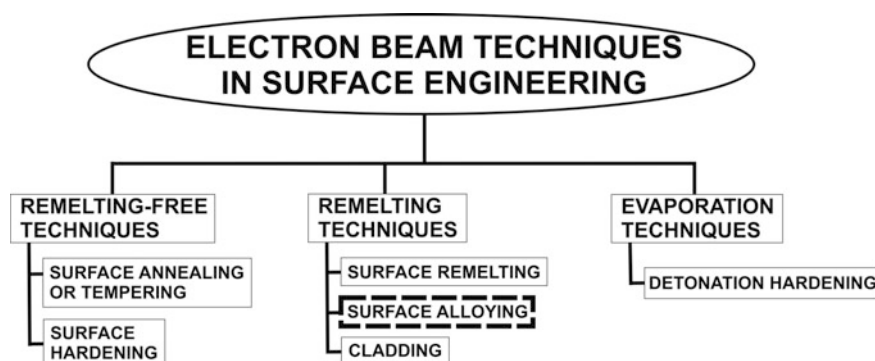


Fig. 5.27 Simplified classification of the most important electron beam techniques in surface engineering

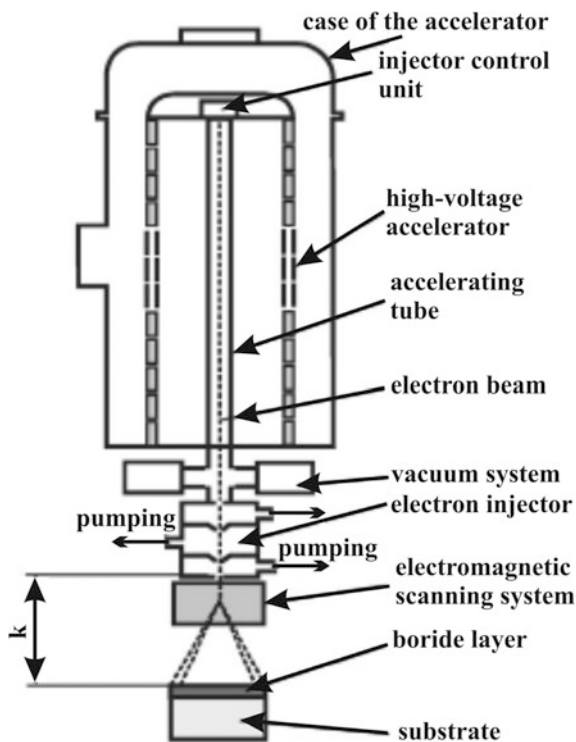
sources became the main components of the *electron gun*, which was applied as the principal functional element of the electron beam heater.

The details of design of *electron beam heaters* were described by Burakowski and Wierzchoń (1998). They distinguished the two types of electron guns, depending on the emitter used. *Thermal emission gun* (also called thermoemissive gun) consisted of thermal emission cathode (called thermo-cathode), a control electrode and an anode and was the most commonly used type of gun. Both metal thermo-cathodes (tungsten or tantalum) and non-metal thermo-cathodes (lanthanum hexaboride LaB_6 , sometimes doped with barium hexaboride BaB_6) were often used in this case. The direct glowing thermo-cathode (using resistance heating) as well as its indirect glowing (using bombardment by electrons emitted from an additional thermo-cathode and accelerated by the electric field) were applied. Whereas *plasma emission guns* (also called plasma-emissive guns) could work as plasma cathode guns or cold cathode guns. In plasma cathode guns, plasma was generated by glow discharge in nitrogen, argon, helium, hydrogen or methane and became a direct emitter. In the case of cold cathode guns, plasma was the indirect emitter of electrons.

Electron beam heaters usually contained the four functional systems (Burakowski and Wierzchoń 1998) responsible for: *generation of electron beam* (including the electron gun), *formation of electron beam* (focusing, acceleration), *control of the electron beam* (deflection) and the *use of electron beam* (rotating table or x-y stage with the workpiece). They usually worked in a pulse mode and their power ranged from 10^3 to 10^5 W in order to modify properties of the surface layers and coatings. Accelerating voltage has been usually within the range of 0.1–23 MV (Frey and Kienel 1987). In order to accelerate an electron obtained as a consequence of thermal emission or glow discharge, it was necessary to create conditions, which ensured the maximal free path for that electron. The longer the free path of electron, the higher the electron energy could be reached. Electrons could impart their energy to the gas particles upon collisions with them. In this case, the electron beam could disperse. Therefore, vacuum (in general, the reduced pressure) became an essential functional feature of electron beam heater equipment. The maximal pressure (minimal vacuum) in electron beam heaters was equal to several Pa. Soft vacuum (down to 133 Pa) was easier to obtain and to maintain. However, it had usually an undesirable effect on the equipment life and might lead to a breakdown of the interelectrode space, owing to the ionization of residual gases. For this reason, high vacuum was most commonly used. The typical values of the pressure ranged from 10^{-3} to 10^{-6} Pa (Oczko 1988). Hence, the use of electron beam in order to heat the workpiece was usually carried out in a vacuum chamber. However, the heating by electron beam was also possible in air. The simplified scheme of the ELV-6 electron accelerator providing electron beam extraction into air (Bataev et al. 2013) was shown in Fig. 5.28.

The electron beam could be generated and delivered to the workpiece either as *continuous beam* or as *pulsed beam*. Usually, the pulses were short, and their duration ranged from 10^{-9} to 10^{-4} s. The shape of the laser beam, depending on the geometry of its cross-section, was classified by Burakowski and Wierzchoń (1998)

Fig. 5.28 Simplified scheme of the ELV-6 electron accelerator providing electron beam extraction into air in order to produce boride layer (Bataev et al. 2013 with permission); k —distance from the outlet window to the workpiece



as: point, line, ring and surface. **Point beam** had a circular shape of minimal diameter 0.5 nm and could be continuous or pulsed. **Linear beam** was usually continuous and could obtain a length up to several tens millimeters with the width similar to the diameter of point beam. The diameter and thickness of pulsed **ring-shaped beam** depended on the technological process. **Surface beams** were usually pulsed and were generated in the form of a circle of rectangle with dimensions up to several tens of millimeters. The power density (q) could be calculated as the electron beam power (P), divided by the surface of its cross-section. The profile of power density in the beam cross-section was not constant. Usually, it was characterized by at least one maximum, being similar to a normal Gaussian curve.

In practice, the combined action of electron beam movement and motions of the workpiece (linear or rotational movement) was responsible for the formation of so-called **pattern**, representing the electron beam tracks on the surface of workpiece. Depending on the method of heating and scanning, Burakowski and Wierzchoń (1998) distinguished five types of patterns: **scanned electron beam (SEB)**, **swept line electron beam (SLEB)**, **pulsed electron beam (PEBeam)**, **island** (island-surface) and **custom shaped**. Some of them could be useful for electron beam surface alloying.

The character of interaction of the electron beam with the workpiece didn't depend on the type of electron beam and method of scanning. The electrons of the

beam could be subjected to partial absorption, partial reflection and partial transmission (Burakowski and Wierzchoń 1998). They could generate secondary electron emission from the bombarded workpiece or X-ray and gamma radiation. The bombarding electrons could also cause ionization or excitement of some atoms. Their energy and the nature of bombarded material influenced the proportions of the phenomena observed. In general, the kinetic energy of bombarding electrons was transformed into other forms of energy. During thermal processes, the most energy of electrons was converted into thermal energy. Such processes were especially interesting in relation to their utilization in surface engineering (Burakowski and Wierzchoń 1998).

Electron beam surface alloying (EBSA), like the process of laser surface alloying (LSA), could be described as simultaneous remelting and mixing of alloying material and alloyed material (substrate). The action of the electron beam and its pressure brought both alloying material and substrate to melt. During EBSA, the saturation of surface layers by alloying elements was carried out at suitable power density and heating time (Burakowski and Wierzchoń 1998). Alloying elements were partially or totally dissolved in the substrate material. Like in the case of LSA, **remelting** and **fusion** were the two main techniques of EBSA. Although they were very similar to the corresponding methods of LSA, described above, some of their features were different. The most common techniques of electron beam surface alloying were shown in Fig. 5.29.

Remelting was the first technique of EBSA, consisting of the two stages: deposition of coating with alloying material on the surface of substrate (alloyed material) and remelting of this coating together with the substrate to a certain depth. The coating could be deposited on the substrate using various methods (e.g. by electrolysis or thermal spray) and was either compact and sealed (e.g. as foil, strip or electroplating) or porous (e.g. in the form of paste or powder). As a consequence of the remelting of both alloying and alloyed materials, they were mixed, and the alloying material partially or totally dissolved in the substrate (alloyed material).

Pulsed electron beam, scanned electron beam and swept line electron beam were known as the most commonly used types of patterns during electron beam surface alloying. They were described in detail by Burakowski and Wierzchoń (1998). **Pulsed electron beam (PEBeam)** was a type of pattern (Fig. 5.29a), in which a point beam with a constant or changeable diameter heated the successive points of workpiece with alloying material. This point beam changed its position by leaps with a leap time of e.g. 10 μs and remained fixed at each successive spot for a duration of e.g. 20 μs . When the larger surface (exceeding several cm^2) was treated, the additional movement of the workpiece was necessary. **Scanned electron beam (SEB)** was a pattern (Fig. 5.29b), in which a point electron beam was also used. However, the beam could be both continuous and pulsed. Point beam scanned the workpiece with a definite frequency (usually above 1 kHz) in a direction transverse to linear tracking or rotation. The scanning amplitude could be constant or variable. The pattern, called **swept line electron beam (SLEB)**, was produced with the use of a linear, continuous electron beam with constant and controlled thickness (Fig. 5.29c). During such a treatment, a strip of the surface of workpiece with

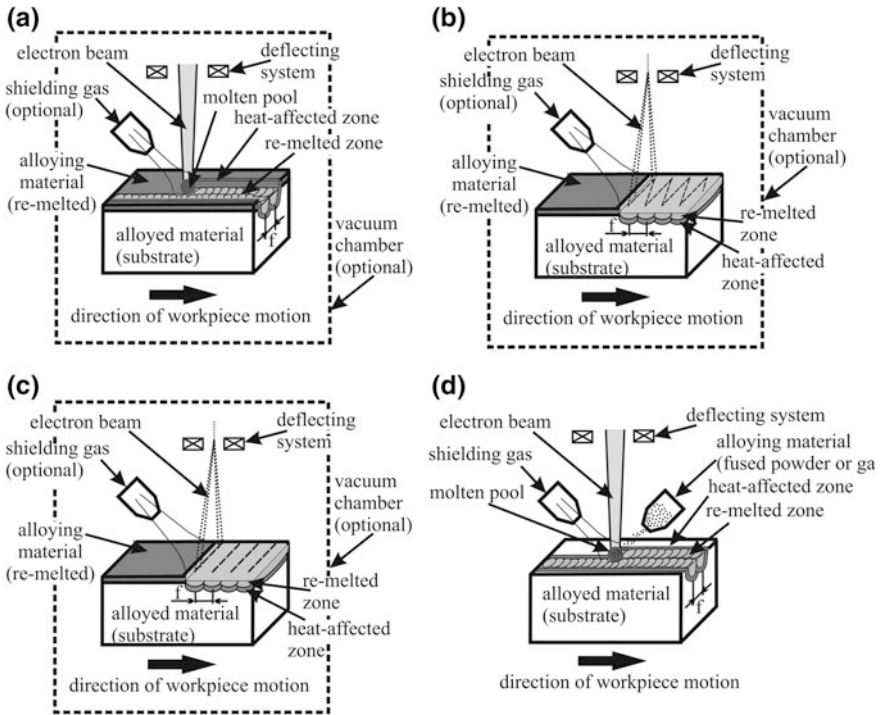


Fig. 5.29 Schematic representation of the techniques of electron beam surface alloying with the formation of multiple laser tracks on a flat surface: remelting by pulsed electron beam (a), remelting by scanned electron beam (b), remelting by swept line electron beam (c), fusion by pulsed electron beam (d); f —distance between axes of adjacent electron beam tracks. *Remark: Methods in (a), (c) and (d) could be also carried out on a cylindrical surface; electron beam cladding could be carried out using the similar methods*

alloying material was heated, and the workpiece was moved in the transverse direction to the electron beam. The workpiece could be located in the vacuum chamber. It is optionally proposed in Figs. 5.29a–c. In this case, the surface of workpiece was sufficiently protected against oxidation, and the free path of electrons could be longer, resulting in higher energy of the electron beam. Recently, the non-vacuum EBSA was also carried out (Bataev et al. 2012, 2013). Although the use of shielding gas seemed to be necessary in this case, such protection of the workpiece against oxidation wasn't usually applied. The delivery of shielding gas to the area of electron beam action could result in the imparting of energy of electrons to the gas particles upon collisions with them. As a consequence, the electron beam could disperse. Hence, shielding gas couldn't be delivered directly into the area of electron beam action (i.e. into molten pool), and the use of shielding gas was optional. Only the resolidified electron beam tracks could be protected by shielding gas during their cooling.

Fusion was the EBSA process, in which delivery of alloying material and remelting was carried out simultaneously. Like in the case of laser surface alloying, the solid particles of alloying material were injected or the gas molecules were blown into the molten pool of the substrate (alloyed material). Like during remelting, the alloying material was partially or totally dissolved in the substrate and these two materials were mixed. It was characteristic of EBSA by fusion, that the process couldn't proceed in a vacuum chamber because of the possible removal of the alloying material from this chamber by vacuum pump. Hence, only non-vacuum process would be acceptable.

Electron beam surface alloying with boron, also called **electron beam boriding (EBB)**, consisted in the simultaneous remelting and mixing of alloying material, containing boron, and alloyed material (substrate). The process could be carried out using both remelting and fusion.

The main parameters of the electron beam surface alloying with boron using remelting were similar to those mentioned for LSA with boron: type of alloying material, i.e. boron source (powder or paste), thickness of the coating with boron source (μm), electron beam power P_{eb} (kW), electron beam diameter d_{eb} (mm) or other its dimensions, power density q_{eb} (kW/cm^2), scanning rate of electron beam v_{eb} (m/min), overlapping O (%) and type of shielding gas. Sometimes, instead of the electron beam power, the accelerating voltage U_{eb} (V) and beam current I_{eb} (A) were reported (Novakova et al. 2004; Dasheev et al. 2015). Then, the power of continuous electron beam P_{ceb} could be calculated using equation (Burakowski and Wierzchoń 1998):

$$P_{ceb} = U_{ceb} \cdot I_{ceb} \quad (5.42)$$

where: U_{ceb} is accelerating voltage of continuous beam (V), and I_{ceb} is current of continuous beam (A).

During the electron beam heating with the use of continuous electron beam, the time of heating (i.e. exposure time) was usually controlled by scanning rate of electron beam (v_{eb}). It depended mainly on the rate of the workpiece motions (linear or rotational movement). The control of the exposure time could be also implemented by the selection of the frequency and amplitude of beam deflection.

If the pulsed electron beam was applied, the power of pulsed beam, pulse duration and pulse frequency became the important parameters of EBSA process. Then, the power of pulsed electron beam P_{peb} could be expressed as (Burakowski and Wierzchoń 1998):

$$P_{peb} = U_{peb} \cdot I_{peb} \cdot t_p \cdot f_p \quad (5.43)$$

where: U_{peb} is accelerating voltage of pulsed beam (V), I_{peb} is the current of pulsed beam (A), t_p is the pulse duration (s), and f_p is pulse frequency (s^{-1}).

Power density resulted directly from the electron beam power and the surface of electron beam, acting on the alloying material. In case of the point (circular) beam, its surface depended on its diameter. Additionally, the distribution of power density

in the beam cross-section has been usually not constant, taking a shape similar to a normal Gaussian curve. Hence, the average power density q_{eb} could be calculated using the similar equation as that applied for laser beam power density:

$$q_{eb} = \frac{4 \cdot P_{eb}}{\pi \cdot d_{eb}^2} (\text{kW/cm}^2) \quad (5.44)$$

where: P_{eb} (equal to P_{ceb} or P_{peb}) is the electron beam power (kW), d_{eb} is the electron beam diameter (cm).

Rykalin et al. (1985) used the equivalent notation:

$$q_{eb} = \frac{4 \cdot U_{eb} \cdot I_{eb}}{\pi \cdot d_{eb}^2} (\text{kW/cm}^2) \quad (5.45)$$

where: U_{eb} (equal to U_{ceb} or U_{peb}) is accelerating voltage of electron beam (V), I_{eb} (equal to I_{ceb} or I_{peb}) is beam current (A), d_{eb} is the electron beam diameter (cm).

However, in some cases the another formula was used (Burakowski and Wierzchoń 1998):

$$q_{eb} = \frac{P_{eb}}{d_{eb}^2} (\text{kW/cm}^2) \quad (5.46)$$

Sometimes, instead of electron beam power or power density, energy of the beam and the beam current was given. Electron beam energy was usually stated in MeV (million electron volts), and electron beam current in mA (Euh et al. 2001; Bataev et al. 2012, 2013). The energy of the beam was responsible for the penetration ability of the beam. Electrons with more energy will penetrate deeper into and through the workpiece. The power of the electron beam could be calculated by multiplying the energy (eV) and beam current (A).

The main parameters of the EBSA with boron using fusion could be similar to those indicated for remelting process. The only difference would be the powder feed rate (expressed in g/min), used instead of the thickness of the coating with boron source, as well as and the carrier gas flow rate (l/min). However, it was difficult to find such processes in literature data. It led to a conclusion that this method had to be applied very rarely.

During EBSA with boron using remelting, the coating with alloyed material (boron source) was usually prepared in the form of a paste or suspension. The diffusion borided layers was also very often subjected to the action of electron beam. Boron carbide B_4C or amorphous boron was blended with an organic binder, consisting of a solution of BF-6 adhesive in acetone with ratio 1:10 (Sizov et al. 1999, 2001; Dasheev et al. 2015; Dasheev and Smirnyagina 2017). The alloyed material (substrate) was coated with such a paste of the thickness about 1 mm. The powders of amorphous boron or 94% pure boron were mixed with a flux (MgF_2) in a 1:1 ratio and then poured on the surface of alloyed material using 0.2 g of powder mixture onto 1 cm^2 (Bataev et al. 2012, 2013). The thickness of such an alloying

material ranged from 500 to 1000 μm , depending on the number of poured coatings (one, two or three coatings). Sometimes, the alloying material consisted of powder mixture of oxide (V_2O_3 or Fe_2O_3), boron-containing component (amorphous boron) and carbon (charcoal). Such a powder mixture was blended in a 1:1 ratio with an organic binder, containing a solution of BF-6 adhesive in acetone with ratio 1:10 (Milonov et al. 2015). TiB_2 powder, mixed with a flux (CaF_2) in a 1.5:1 ratio, as well as a $\text{TiB}_2 + \text{MoB} + \text{CaF}_2$ powder mixture (with ratio 1.5:1.5:2) could be used as alloying material, which was deposited on the surface of titanium alloy and then pressed with a load of 300 N (Euh et al. 2001). Plasma sprayed hexagonal boron nitride (Al8Si20BN) was applied as an alloying material during EBSA of pure titanium (Utu et al. 2007). $\text{Fe}_2\text{O}_3 + \text{B}+\text{C}$ powder mixture with ratio 1:1:3 or 1:2:3, mixed with an organic binder, was used in order to initiate the self-propagating high-temperature synthesis (SHS), which was accompanied by the high heat release as a consequence of highly concentrated energy flux (about 20 keV) and was followed by electron beam treatment (Dasheev et al. 2015; Dasheev and Smirnyagina 2017). In order to obtain boride layers of refractory metals on the surface of high-carbon steel by means of electron beam treatment, the two various methods were used (Sizov et al. 1999). The first one used the mixture of tungsten and nickel borides $\text{W}_2\text{B}_5 + \text{Ni}_2\text{B}$ as alloying material. The second method resulted in the simultaneous synthesis of W_2B_5 , CrB_2 , VB_2 and TiB_2 borides on the surface of steel workpieces as a consequence of reduction of oxides (WO_3 , Cr_2O_3 , V_2O_3 or TiO_2) by mixtures of boron carbide B_4C and carbon or boric acid H_3BO_3 and carbon. The alloying material was also produced by powder-pack boriding which resulted in a formation of iron borides of a thickness from 50 to 100 μm (Sizov 2003; Novakova et al. 2004; Dasheev et al. 2015). TiB_2 borides, produced by powder-pack boriding under reduced pressure on the surface of carbon steels, were coated with the powder mixture, consisting of boron oxide B_2O_3 , boron-containing component and carbon (Smirnyagina et al. 2002). Such an alloying material was subjected to electron beam treatment.

The general characterization of selected processes of EBSA with boron was presented in Tables 5.19, 5.20, 5.21 and 5.22, taking into account the main parameters of the process, i.e. boron source, thickness of the paste coating with boron source or boride layer, electron beam power, electron beam diameter or its other dimensions, power density, scanning rate of electron beam, overlapping and type of shielding gas or pressure in vacuum chamber as well as the type of electron beam heater, type of electron gun, type of beam (pulsed or continuous), shape of the alloyed surface and scheme of the method in Fig. 5.29. Low-, medium- and high-carbon steels were most commonly subjected to EBSA with boron. Titanium alloys were also surface alloyed with boron using electron beam. The process of remelting was most widely used method of electron beam boriding. The boride layers were usually produced on the flat surfaces.

The type of electron beam heater was often not given. However, many authors used the device, described as EPA-60-04.2 axial thermoemissive electron gun with BUEL control block and V-TPE-2-30k-2U KhL4 high-voltage rectifier (Sizov et al. 1999, 2001; Smirnyagina et al. 2002; Sizov 2003; Novakova et al. 2004; Milonov et al. 2015).

Table 5.19 General characterization of selected processes of electron beam surface alloying with boron. Part I

Type of alloyed material	Boron source (alloying material)/thickness of the paste coating or boride layer (μm)/type of the electron beam heater/type of the electron gun/pulsed or continuous beam/shape of the alloyed surface/scheme of the method	Electron beam power (kW)/ electron beam diameter (mm) or its size/power density (kW/cm^2)/scanning rate (m/min)/overlapping (%) /shielding gas or pressure in vacuum chamber (Pa)	References
Low-carbon steels	B ₄ C or amorphous B/1000/EPA-60-04.2 axial electron gun, BUEL control block and V-TPE-2-30k-2U KhL4 high-voltage rectifier/thermoemissive gun/continuous/flat/Fig. 5.29a, b, or c—vacuum process	0.15–0.30/unknown/unknown/unknown/ 2×10^{-3}	Sizov et al. (1999)
	Iron borides produced by powder-pack boriding/80–90/EPA-60-04.2 axial electron gun, BUEL control block and V-TPE-2-30k-2U KhL4 high-voltage rectifier/thermoemissive gun/continuous/flat/Fig. 5.29a, b, or c—vacuum process	0.22/unknown/unknown/unknown/unknown/ 10^{-3} – 10^{-5}	Novakova et al. (2004)
	94% pure boron and MgF ₂ as flux with ratio 1:1/500–1000, 0.2 g of powder onto 1 cm ² /ELV-6 electron accelerator/unknown/pulsed/flat/Fig. 5.29b—non-vacuum process	5.6/10/7.13/0.6/unknown/without shielding gas	Bataev et al. (2012)
	Amorphous B and MgF ₂ as flux with unknown ratio/500–1000, 0.2 g of powder onto 1 cm ² /ELV-6 electron accelerator/unknown/pulsed/flat/Fig. 5.29b—non-vacuum process	33.6/unknown/unknown/0.6/unknown/without shielding gas	Bataev et al. (2013)
	B ₄ C or amorphous B/1000/unknown/thermoemissive gun/continuous/flat/unknown—vacuum process	0.25–0.45/unknown/unknown/unknown/ 2×10^{-3}	Dasheev et al. (2015) and Dasheev and Smirnyagina (2017)

Table 5.20 General characterization of selected processes of electron beam surface alloying with boron. Part II

Type of alloyed material	Boron source (alloying material)/thickness of the paste coating or boride layer (μm)/type of the electron beam heater/type of the electron gun/pulsed or continuous beam/shape of the alloyed surface/scheme of the method	Electron beam power (kW)/electron beam diameter (mm) or its size/power density (kW/cm^2)/scanning rate (m/min)/overlapping (%) /shielding gas or pressure in vacuum chamber (Pa)	References
Low-carbon steels	$\text{Fe}_2\text{O}_3 + \text{B} + \text{C}$ powder with ratio 1:1:3 or 1:2:3/unknown/unknown/thermoemissive gun/continuous/flat/unknown—vacuum process, SHS followed by EBBSA	0.25–0.45/unknown/unknown/unknown/ 2×10^{-3}	Dasheev et al. (2015) and Dasheev and Smirnyagina (2017)
Medium-carbon steels	B_4C or amorphous B/1000/EPA-60-04.2 axial electron gun, BUEL control block and V-TPE-2-30k-2U KhL4 high-voltage rectifier/thermoemissive gun/continuous/flat/Fig. 5.29a, b, or c—vacuum process	0.15–0.30/unknown/unknown/unknown/ 2×10^{-3}	Sizov et al. (1999) and Sizov et al. (2001)
	Iron borides produced by powder-pack boriding/50/EPA-60-04.2 axial electron gun, BUEL control block and V-TPE-2-30k-2U KhL4 high-voltage rectifier/thermoemissive gun/continuous/flat/Fig. 5.29a, b, or c—vacuum process	Unknown/unknown/29/unknown/unknown/ 2×10^{-3}	Sizov (2003)
	B_4C or amorphous B/1000/unknown/thermoemissive gun/continuous/unknown/unknown—vacuum process	0.25–0.45/unknown/unknown/unknown/ 2×10^{-3}	Dasheev et al. (2015) and Dasheev and Smirnyagina (2017)
	Iron borides produced by powder-pack boriding/70–100/unknown/thermoemissive gun/continuous/unknown/unknown—vacuum process	0.22/unknown/unknown/unknown/unknown/ 2×10^{-3}	Dasheev et al. (2015)

Table 5.21 General characterization of selected processes of electron beam surface alloying with boron. Part III

Type of alloyed material	Boron source (alloying material)/thickness of the paste coating or boride layer (μm)/type of the electron beam heater/type of the electron gun/pulsed or continuous beam/shape of the alloyed surface/scheme of the method	Electron beam power (kW)/electron beam diameter (mm) or its size/power density (kW/ cm^2)/scanning rate (m/min)/overlapping (%) / shielding gas or pressure in vacuum chamber (Pa)	References
Medium-carbon steels	$\text{Fe}_2\text{O}_3 + \text{B} + \text{C}$ powder with ratio 1:1:3 or 1:2:3/ unknown/unknown/thermoemissive gun/continuous/flat/unknown—vacuum process, SHS followed by EBSA	0.25–0.45/unknown/unknown/unknown/ 2×10^{-3}	Dashev et al. (2015) and Dashev and Smirnyagina (2017)
High-carbon steels	B_4C or amorphous B or $\text{W}_2\text{B}_5 + \text{Ni}_2\text{B}$ or $\text{B}_4\text{C} + \text{C}$ + oxide (WO_3 , V_2O_5 , Cr_2O_3 or TiO_2) or $\text{H}_3\text{BO}_3 + \text{C}$ + oxide (WO_3 , V_2O_5 , Cr_2O_3 or TiO_2)/1000 (for B_4C or boron), unknown for the other powders/ EPA-60-04.2 axial electron gun, BUEL control block and V-TPE-2-30k-2U KhL4 high-voltage rectifier/thermoemissive gun/continuous/flat/Fig. 5.29a, b, or c—vacuum process	0.15–0.30/unknown/unknown/unknown/ 2×10^{-3}	Sizov et al. (1999)
	TiB_2 borides produced by powder-pack boriding under reduced pressure, coated with B_2O_3 + boron-containing component + carbon/ unknown/EPA-60-04.2 axial electron gun, BUEL control block and V-TPE-2-30k-2U KhL4 high-voltage rectifier/thermoemissive gun/continuous/flat/Fig. 5.29a, b, or c—vacuum process	0.15–0.30/unknown/unknown/unknown/ 2×10^{-3}	Smirnyagina et al. (2002)

Table 5.22 General characterization of selected processes of electron beam surface alloying with boron. Part IV

Type of alloyed material	Boron source (alloying material)/thickness of the paste coating or boride layer (μm)/type of the electron beam heater/type of the electron gun/pulsed or continuous beam/shape of the alloyed surface/scheme of the method	Electron beam power (kW)/electron beam diameter (mm) or its size/power density (kW/cm^2)/scanning rate (m/min)/overlapping (%) /shielding gas or pressure in vacuum chamber (Pa)	References
High-carbon steels	Amorphous B + charcoal + V_2O_5 + Fe_2O_3 /unknown/EPA-60-04.2 axial electron gun, BUEL control block and V-TPE-2-30k-2U KhL4 high-voltage rectifier/thermoemissive gun/pulsed or continuous/flat/Fig. 5.29a, b, or c—vacuum process	0.15–0.30/unknown/22–28/unknown/unknown/ 2×10^{-3}	Milonov et al. (2015)
Titanium and its alloys	TiB_2 + CaF_2 with ratio 1.5:1 or TiB_2 + MoB + CaF_2 with ratio 1.5:1.5:2/unknown/ELV-6 electron accelerator/unknown/continuous/flat/Fig. 5.29a—non-vacuum process	36.4/11.5/35.04/1.47/unknown/without shielding gas	Euh et al. (2001)
	hexagonal boron nitride ($\text{Al}_8\text{Si}_{20}\text{BN}$) plasma sprayed/100–150/EBW700/3–60 electron beam heater/unknown/continuous/flat/Fig. 5.29b—vacuum process	0.9/unknown/unknown/0.15–0.30/unknown/unknown pressure	Utu et al. (2007)

ELV-6 electron accelerator, produced by the Budker Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Science, was also applied (Euh et al. 2001; Bataev et al. 2012, 2013). Sometimes, only the use of thermoemissive electron gun was reported (Dasheev et al. 2015; Dasheev and Smirnyagina 2017). The electron beam was usually delivered to the treated material continuously. The short pulses with an adequate frequency were used during remelting by scanned electron beam (Bataev et al. 2012, 2013). The wide range of electron beam power P_{eb} was applied (from 0.15 to even 36.4 kW). In case of the processes, carried out at relatively low beam power (0.15–0.45 kW), the electron beam diameter or the beam dimensions were usually not given. Hence, the valuation of the power density q_{eb} was difficult. The available data (Sizov 2003) suggested the values of about a few tens kW/cm^2 . If the significantly higher electron beam power (5.6–36.4 kW) was applied, the diameter of electron beam was usually reported (Euh et al. 2001; Bataev et al. 2012, 2013) and was relatively large (10–11.5 mm). It caused that power density ranged from 7.13 to $35.04 \text{ kW}/\text{cm}^2$ and its values were comparable to those used at lower electron beam power. The values of

scanning rate v_{eb} were also often omitted. Based on the available literature data they varied between 0.6 and 1.47 m/min. The values of overlapping were usually not reported. The process of EBSA with boron was carried out either under reduced pressure (in a vacuum chamber) or as a non-vacuum process. The shielding gas wasn't used during non-vacuum processes because of the possible transfer of energy of electrons to the gas particles and dispersion of the electron beam. The utilization of the electron beam outside the vacuum chamber required its high power (Euh et al. 2001; Bataev et al. 2012, 2013). Only such an electron beam could leave the vacuum chamber and could carry out the considered treatment in air atmosphere.

EBSA of iron alloys with boron provided the composite microstructure, which was similar to that formed as a consequence of LSA process to a certain degree. The boundary between the re-melted zone (electron beam-alloyed zone) and the substrate (alloyed material) was clearly visible. The alloyed zone, produced by the electron beam remelting of the paste coating with amorphous boron or boron carbide B_4C together with the steel substrate, contained FeB and Fe_2B borides, cementite Fe_3C and Fe_α phase (Sizov et al. 1999; Dasheev et al. 2015; Dasheev and Smirnyagina 2017). If the boron carbide was used as boron source, the precipitates of borides were round, and the alloyed zone contained mainly Fe_2B iron borides. Whereas the use of amorphous boron as alloying material resulted in the predominant percentage of FeB phase in the alloyed zone, and the borides took the rhombic, prismatic and dendritic shape. Sizov et al. (1999) reported the possible formation of an eutectic mixture of iron borides and Fe_α phase in the re-melted zone (MZ). The phase analysis after EBSA with boron by remelting using the mixture of boron and MgF_2 flux as alloying material (Bataev et al. 2012, 2013) provided very interesting results. The phase composition was studied at different depths of the alloyed zone. If the single coating with alloying material was poured on the steel substrate, the phase analysis revealed the presence of FeB, Fe_2B and Fe_α phases at the depth of 100 μm . Fe_2B and Fe_α were identified at the depth of 300 μm , and only Fe_α phase was observed at the depth of 600 mm. The two coatings with alloying material, poured on the substrate, resulted in the formation of FeB, Fe_2B and Fe_α phases up to the depth of 300 μm . In the distance of 600 μm from the surface, Fe_2B borides and Fe_α phase were revealed. If the steel substrate was three times coated with alloying material, containing boron and MgF_2 flux, the phase composition of the alloyed zone didn't change at the considered depths. FeB and Fe_2B borides as well as Fe_α phase were observed at all the investigated depths. Bataev et al. (2012) reported the gradient microstructure of the alloyed zone, depending on the shape of precipitations of iron borides. Bataev et al. (2013) suggested the evolution of this microstructure from the hypereutectic mixture of borides and Fe_α close to the surface, through the eutectic mixture until the hypoeutectic mixture close to the end of alloyed zone. If the alloying material consisted of amorphous boron, charcoal and V_2O_3 oxide (Milonov et al. 2015), the alloyed zone contained Fe-V $_\alpha$ phase and vanadium borides V_3B_4 . The presence of VB_2 borides wasn't excluded. The use of alloying material, containing W_2B_5

tungsten borides, resulted in formation of Fe_α , Fe_3C and W_2B_5 phases in alloyed zone of high carbon steel (Sizov et al. 1999). If the reduction of oxides (WO_3 , Cr_2O_3 , V_2O_5 or TiO_2) by mixtures of boron carbide B_4C and carbon or boric acid H_3BO_3 and carbon was used in order to produce the boride layer by EBSA (Sizov et al. 1999), the alloyed zone consisted mainly of borides W_2B_5 , CrB_2 , VB_2 and TiB_2 . Sometimes, EBSA with boron was preceded by the self-propagating high-temperature synthesis (SHS). The highly concentrated energy flux (about 20 keV) released a high amount of heat and initiated SHS process on the surface of steels coated by $\text{Fe}_2\text{O}_3 + \text{B} + \text{C}$ powder mixture with ratio 1:1:3 or 1:2:3 (Dasheev et al. 2015; Dasheev and Smirnyagina 2017). The microstructure after EBSA depended on the mixing ratio of powder components and consisted mainly of FeB and Fe_α or Fe_2B and Fe_α , for the ratio of components 1:1:3 and 1:2:3, respectively.

Iron borides ($\text{FeB} + \text{Fe}_2\text{B}$), produced on the steel surface by diffusion boriding, also became the alloying material, subjected to electron beam treatment (Sizov 2003; Novakova et al. 2004; Dasheev et al. 2015). As a consequence of powder-pack boriding, the microstructure consisted mainly of FeB , Fe_2B and Fe_3B borides. However, the presence of solid solution $\text{Fe}_{1-x}\text{B}_x$ (with $x < 0.4$) and quasiamorphous solid solution $\text{Fe}_{1-x}\text{B}_x$ (with $x > 0.4$) was also reported. The electron beam treatment caused changes in this microstructure regarding the shape and size of borides as well as phase composition (Sizov 2003; Novakova et al. 2004). However, the modified microstructure differed from that characteristic of the typical remelting. The amount of Fe_2B phase was significantly increased. Whereas the percentage of the other phases, containing boron, lessened considerably. The radiation-stimulated diffusion of boron atoms into the layer and probable sputtering of a part of boron atoms from the surface were the reason for this microstructure modification.

TiB_2 borides were also synthesized on the surface of carbon steel by powder-pack boriding. The formation of TiB_2 phase resulted from the interaction between titanium oxide TiO_2 , various boron sources (boron carbide B_4C , boron or boron oxide B_2O_3) and carbon under reduced pressure. Before the electron beam treatment, the diffusion borided surface was coated with the powder mixture, containing boron oxide B_2O_3 , boron source and carbon (Smirnyagina et al. 2002). TiB_2 was the predominant phase after such a hybrid treatment. However, the produced microstructure wasn't studied in detail.

The use of TiB_2 powder as alloying material, mixed with a flux (CaF_2), resulted in the formation of primary TiB borides with eutectic mixture of TiB and Ti_α (or Ti_β) in the re-melted zone of titanium alloy (Euh et al. 2001). The appropriate addition of MoB to the alloying material made the formation of the surface alloyed materials of various properties possible by controlling the kind, size, and percentage of TiB borides and matrix (Euh et al. 2001). Titanium boride Ti_3B_4 in Ti_α matrix appeared in the re-melted zone of pure titanium subjected to EBSA process. Boron was characterized by a higher reactivity compared to nitrogen. Hence, it was able to react faster with titanium. Whereas nitrogen was evaporated during the process.

Although the heat-affected zone (HAZ) could be visible below re-melted zone (MZ), it wasn't characterized in detail in the case of EBSA of steels with boron.

Przybyłowicz (2000) reported that the use of vacuum, i.e. reduced pressure during electron beam treatment, provided the excellent protection against oxidation causing good degassing of the depth of fusion. However, such a treatment reduced significantly the cooling rate. It could be the reason for the rarely observed HAZ as well as for the absence of literature reports regarding the presence of martensite in steels subjected to EBSA with boron. The HAZ and the substrate (alloyed material) could not differ in microstructure from each other. Taking into account the analyzed literature data, only Euh et al. (2001) reported the presence of HAZ after electron beam surface alloying of titanium alloy with boron. They identified Ti_2 martensite in the heat-affected zone.

The main advantages of the electron beam surface alloying with boron were similar to those indicated for LSA with boron: possibility to produce boride layers in a wide range of thickness (significantly exceeding the thickness of the diffusion boride layers), relatively short duration compared to diffusion processes, obtaining a fine-crystalline microstructure and hardness profile of the more gradual decrease towards the substrate material, local heating and elimination of deformations and dimensional changes, possibility of treating fragments of surfaces of complex shape, precise control of the electron beam, elimination of cooling media, easy automation of the process, environmental performance of the process as well as low energy and material consumption. Among disadvantages, the main of them were as follows: high investment cost of equipment, limitation of application to selected shapes and relatively small dimensions, the predominant necessity of using reduced pressure (vacuum chamber), impossibility of the suitable protection against oxidation during non-vacuum treatment, and, if the accelerating voltage was high (about 150 kV), the necessity of protection against X-ray radiation.

5.3.1.3 Plasma Surface Alloying with Boron

Plasma surface alloying (PSA) used a constricted high-energy plasma arc between a non-consumable electrode and the base material as a heat source in order to remelt and mix the alloying material together with alloyed material (substrate). The process wasn't commonly used up to now. Hence, PSA wasn't widely represented in the literature data. However, plasma surface alloying became very interesting alternative for other high-energy techniques of alloying, such as laser surface alloying or electron beam surface alloying, because of its simplicity, the possible use of the typical welding devices and their relatively low cost in comparison with lasers or electron beam heaters. Additionally, the PSA processes were recently used in biomedical applications (Miklaszewski and Jurczyk 2011; Miklaszewski et al. 2011, 2012, 2013; Kaczmarek et al. 2016). This technique was also called *plasma transferred arc (PTA) surfacing* (Bourithis et al. 2002; Bourithis and Papadimitriou 2003).

The typical equipment, used for PSA, corresponded to the plasma arc welding (PAW) equipment and consisted of: cylinders with plasma and shielding gases, power source, plasma console, water cooler, plasma torch and controller of plasma

torch movement (Bourithis et al. 2002). By analogy to LSA and EBSA processes, the PSA could be carried out using the two well-described above methods: **remelting** (Bourithis et al. 2002; Miklaszewski and Jurczyk 2011) or **fusion**. Their schematic representations were depicted in Fig. 5.30. During PSA process, at least the two gas streams were used: **plasma gas**, also called **primary gas** (Kim et al. 1999a), which flowed surrounding the tungsten electrode and which created a column of the plasma arc and **shielding gas**, used to protect molten pool against oxidation. Sometimes, an **extra shielding gas** was additionally applied in order to complete elimination of possible atmospheric contamination during the process (Miklaszewski et al. 2011, 2013; Kaczmarek et al. 2016). In the case of PSA by fusion, alloying material was introduced into the molten pool by a **carrier gas**.

Plasma surface alloying with boron consisted in simultaneous remelting and mixing of alloying material, containing boron, and alloyed material. The main operation parameters of PSA with boron by remelting were as follows: type of alloying material, i.e. boron source (powder or paste), thickness of the coating with boron source (μm), voltage U (V), current I (A), diameter of tungsten electrode d_{te} (mm), nozzle diameter (tip diameter) corresponding to the diameter of plasma arc column d_p (mm), scanning rate of plasma torch v_p (m/min), overlapping of multiple plasma tracks O (%), type of plasma gas and shielding gas as well as their flow rate Q (l/min). Overlapping could be calculated using the equation similar to that reported for laser surface alloying with boron (5.37), based on the tip diameter d_p and lateral (transverse) step (mm) corresponding to the distance between the axes of adjacent plasma tracks f (see Fig. 5.30):

$$O = \frac{d_p - f}{d_p} \times 100\% \quad (5.47)$$

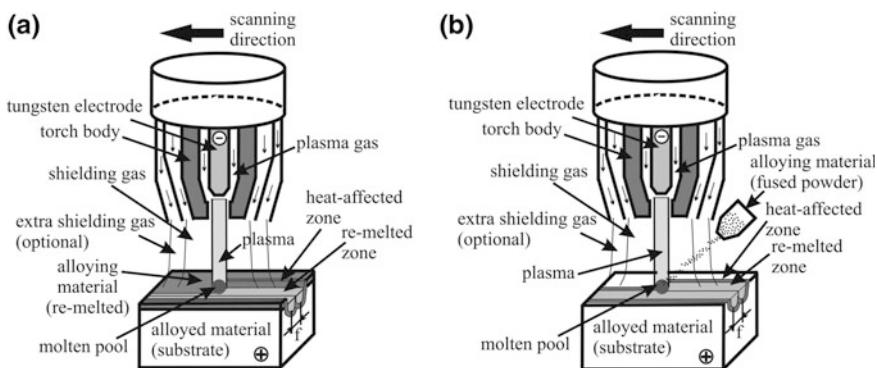


Fig. 5.30 Schematic representation of the techniques of plasma surface alloying with the formation of multiple laser tracks on a flat surface by remelting (a) inspired by Bourithis et al. (2002) and by Miklaszewski et al. (2013) and by fusion (b); f —distance between axes of adjacent plasma tracks

where: d_p is diameter of plasma arc column, corresponding to the tip (nozzle) diameter (mm), and f is the distance between the axes of adjacent plasma tracks, corresponding to the lateral (transverse) step (mm).

Like for LSA and EBSA processes using remelting, the coating with alloyed material (boron source) was usually prepared in the form of a paste or suspension. However, the thickness of this coating was usually not given. Taking into consideration the selected works, only Bourithis et al. (2002) reported the use of the coatings with alloying material of a thickness in the range of 160–500 μm . Some authors provided information about the mass of powder mixture per the unit of the surface (Bourithis and Papadimitriou 2003; Darabara et al. 2007). Usually, the coating contained 0.07–0.13 g of powder onto 1 cm^2 . The starting powders consisted of both pure boron and compounds, containing boron. Sometimes, the mixture of these boron sources was applied. Bourithis et al. (2002) used the suspension, which was prepared by mixing 99% pure boron powder (325 mesh, i.e. $<44 \mu\text{m}$) with ethanol and was pasted on the surface of alloyed material (low-carbon steel). Then, the workpieces with paste coatings were heated at 60 $^{\circ}\text{C}$ (333 K) for drying. The same preparation of alloying material was applied by Bourithis and Papadimitriou (2003, 2005, 2009) as well as, in the case of plasma-alloyed high-carbon steel, by Iakovou et al. (2002). CrB_2 and TiB_2 borides were the most commonly used compounds, containing boron, during PSA with boron by remelting. The mixture of 99% pure CrB_2 powder (325 mesh, i.e. $<44 \mu\text{m}$) with alcohol was used by Bourithis and Papadimitriou (2003, 2005, 2009) as a paste, which coated the substrate surface. The workpieces were then dried at 60 $^{\circ}\text{C}$ (333 K). TiB_2 powder (grain size: 10 μm) was also blended with alcohol in order to be coated on the surface of low-carbon steel (Darabara et al. 2007, 2008). The powders, containing the titanium borides (TiB_2) and 99% pure boron with various ratios, were mixed with alcohol and were applied as alloying material (Darabara et al. 2007). Ti–B nano- and micropowders became the alloying material during PSA of pure titanium with boron (Miklaszewski and Jurczyk 2011; Miklaszewski et al. 2011, 2012, 2013; Kaczmarek et al. 2016). The starting powders consisted of the mixture of Ti and B powders of grain size <45 . The content of boron powder was equal to 2 or 10 wt%. The powders were mixed in the glove box and poured into the vial. The nanopowders were prepared by mechanical alloying (MA) for 48 h under Ar atmosphere. Ti–B micropowders were produced by ball-milling (BM) from the same starting powders (Miklaszewski et al. 2013). The prepared powders of the same, defined amount, were blended with water-glass. Sometimes, non beta stabilizing elements were added to this mixture in order to protect from high ductility decrease and possible cracks in the produced layers (Miklaszewski et al. 2011).

The parameters of the PSA with boron using fusion would be similar to those characteristic of remelting process. The powder feed rate (g/min) would be only indicated instead of the thickness of the coating with boron source, and the powder would be blown up into the molten pool using an inert carrier gas of an adequate flow rate (l/min). However, it was difficult to find PSA by fusion in literature data. Hence, only PSA with boron by remelting could be analyzed.

The general characterization of selected processes of plasma surface alloying with boron was presented in Tables 5.23 and 5.24, taking into account the main parameters of the process, i.e. boron source, thickness of the paste coating with boron source (for remelting) or powder feed rate with flow rate of carrier gas (for fusion), arc voltage and current, diameter of tungsten electrode, tip (nozzle) diameter, scanning rate of plasma torch, overlapping, type of plasma gas and its flow rate, type of shielding gas and its rate, type of extra shielding gas and its flow rate as well as the type of welding device, shape of the alloyed surface and scheme of the method in Fig. 5.30. Low- and high-carbon steels (Table 5.23) as well as pure titanium (Table 5.24) were most commonly subjected to PSA with boron. It was easy to indicate PSA by remelting as the predominant method of such surface alloying. In general, it was difficult to find PSA by fusion in literature data. The flat surfaces were usually alloyed with boron. The type of welding device was often not given. Pure titanium was subjected to PSA with boron using microplasma EWM 50 equipment with PHB 50 welding torch (Miklaszewski and Jurczyk 2011;

Table 5.23 General characterization of selected processes of plasma surface alloying of iron alloys with boron

Type of alloyed material	Boron source (alloying material)/thickness of the coating (μm), or mass of powder onto the unit of surface (g/cm^2)/type of the welding device/shape of the alloyed surface/scheme of the method	Voltage (V)/current (A)/diameter of tungsten electrode (mm)/tip diameter (mm)/scanning rate (m/min)/overlapping (%) /plasma gas, its flow rate (l/min)/shielding gas, its flow rate (l/min)/extra shielding gas, its flow rate (l/min)	References
Low-carbon steels	99% pure boron powder/160–500 (μm)/unknown/flat/ Fig. 5.30a	Unknown/80/2.4/2.36/0.12/34 ^a /Ar, 1/Ar, 9/not used	Bourithis et al. (2002)
	99% pure boron or CrB_2 powders/unknown, 0.07 g/cm^2 (B) or 0.2 g/cm^2 (Cr_2B)/unknown/flat/ Fig. 5.30a	Unknown/80/2.4/2.36/0.12/34 ^a /Ar, 1/Ar, 9/not used	Bourithis and Papadimitriou (2003, 2005, 2009)
	TiB_2 or $\text{TiB}_2 + 1.3\text{--}3.6\%$ B powders/unknown, 0.07–0.13 g/cm^2 /PWH-3A plasma torch/flat/ Fig. 5.30a	Unknown/80/2.4/2.36/0.12/0.84 ^a /Ar, 0.7/Ar, 7.1/not used	Darabara et al. (2007)
	TiB_2 powder/unknown, 0.13 g/cm^2 /PWH-3A plasma torch/flat/ Fig. 5.30a	Unknown/80/2.4/2.36/0.12/0.84 ^a /95% Ar + 5% N_2 , 0.7/95% Ar + 5% N_2 , 7.1/not used	Darabara et al. (2008)
High-carbon steels	99% pure boron powder/unknown/unknown/flat—once, twice or three times treated/ Fig. 5.30a	Unknown/70/2.4/2.06/0.18/24 ^a /Ar, 0.5/Ar, 9.4/not used	Iakovou et al. (2002)

^aCalculated using Eq. (5.47)

Table 5.24 General characterization of selected processes of plasma surface alloying of pure titanium with boron

Type of alloyed material	Boron source (alloying material)/thickness of the coating (μm), or mass of powder onto the unit of surface (g/cm^2)/type of the welding device/shape of the alloyed surface/scheme of the method	Voltage (V)/Current (A)/diameter of tungsten electrode (mm)/tip diameter (mm)/scanning rate (m/min)/overlapping (%) /plasma gas, its flow rate (l/min)/shielding gas, its flow rate (l/min)/extra shielding gas, its flow rate (l/min)	References
Pure titanium	Ti–B nanopowders with 2 and 10% B (98% pure)/unknown/microplasma EWM 50 equipment with PHB 50 welding torch/flat/Fig. 5.30a	Unknown/unknown/unknown/unknown/Ar, Unknown/50% Ar + 50% He, unknown/not used	Miklaszewski and Jurczyk (2011)
	Ti–B nanopowders with 2 and 10% B (98% pure) and non beta stabilizing elements/unknown/microplasma EWM 50 equipment with PHB 50 welding torch/flat/Fig. 5.30a	10/28/unknown/1.6/0.036/unknown/Ar, 0.1/50% Ar + 50% He, 10/Ar, 10	Miklaszewski et al. (2011)
	Ti–B nanopowders with 2 and 10% B (98% pure)/unknown/microplasma EWM 50 equipment with PHB 50 welding torch/flat/Fig. 5.30a	Unknown parameters	Miklaszewski et al. (2012)
	Ti–B nano- and micropowders with 10% B (98% pure)/unknown/microplasma EWM 50 equipment with PHB 50 welding torch/flat/Fig. 5.30a	10/28/unknown/1.6/0.036/unknown/Ar, 0.1/50% Ar + 50% He, 10/Ar, 10	Miklaszewski et al. (2013)
	Ti–B nanopowders with 2% and 10% B (98% pure)/unknown/microplasma EWM 50 equipment with PHB 50 welding torch/flat/Fig. 5.30a	Unknown/unknown/unknown/unknown/Ar, unknown/50% Ar + 50% He, unknown/Ar, unknown	Kaczmarek et al. (2016)

Miklaszewski et al. 2011, 2012, 2013; Kaczmarek et al. 2016). Sometimes (Darabara et al. 2007, 2008), only the type of plasma torch was given (e.g. PWH-3A plasma torch). Arc voltage was rarely reported. Its value (10 V) was given only by Miklaszewski et al. (2011, 2013). The arc current ranged from 28 to 80 A. It could be observed that the arc current strongly depended on the alloyed material. The relatively low its value (28 A) was characteristic of the PSA of pure titanium with boron (Miklaszewski et al. 2011, 2013). If the iron alloys was selected as the substrate material (Bourithis et al. 2002; Iakovou et al. 2002; Bourithis and Papadimitriou 2003, 2005, 2009; Darabara et al. 2007, 2008), the

current was significantly higher (70–80 A). Although many authors didn't report the diameter of tungsten electrode, the available data indicated its value of 2.4 mm in case of PSA of iron alloys. The nozzle (tip) diameter, corresponding to the diameter of plasma arc column, was usually strongly related to the diameter of tungsten electrode. Their values were the same or differed slightly. Scanning rate of plasma torch was usually given and obtained the values from 0.036 to 0.18 m/min. Overlapping was often omitted. Based on the available data, its values varied in a wide range (between 0.84 and 34%). The types of plasma gas as well as shielding gas were usually given. The use of pure argon predominated. The mixture of argon and nitrogen (95% Ar + 5% N₂) was used as both plasma and shielding gas by Darabara et al. (2008) in order to achieve the absorption of nitrogen in the alloyed layer. Whereas the mixture of argon and helium (50% Ar + 50% He), used as a shielding gas, changed the penetration profile of heat and improved reaction on the surface (Miklaszewski and Jurczyk 2011; Miklaszewski et al. 2011). The flow rate of plasma gas ranged from 0.1 to 1 l/min, and was lower than that of shielding gas (7.1–10 l/min). Extra shielding gas was applied sporadically, obtaining the flow rate of 10 l/min (Miklaszewski et al. 2011, 2013).

Plasma surface alloying with boron provided the composite microstructure comparable to that obtained as a consequence of LSA and EBSA with boron. Usually, the microstructure consisted of hard borides in softer iron-based matrix. The alloyed zone, produced by the plasma surface remelting of the paste coating with amorphous boron together with the low-carbon steel substrate, contained FeB and Fe₂B borides in Fe_α matrix (Bourithis et al. 2002; Bourithis and Papadimitriou 2003, 2005, 2009). The phase composition depended on the thickness of coating with boron. If this thickness increased, the microstructure evolved from the Fe_α phase and eutectic mixture, through the Fe₂B borides and eutectic mixture up to FeB + Fe₂B borides and eutectic mixture (Bourithis et al. 2002). Iakovou et al. (2002) reported that the eutectic mixture of martensite and Fe₂B borides occurred after PSA of high-carbon steel using amorphous boron as alloying material. The use of coating with Cr₂B powder as a boron source resulted in the formation of the re-melted (alloyed) zone with eutectic mixture of Fe_α solid solution and Fe₂B phase (Bourithis and Papadimitriou 2003, 2005). In this case, instead of Fe₂B borides, the complex (Cr_x, Fe_{1-x})₂B borides could appear (Bourithis and Papadimitriou 2009).

Remelting of the coating with TiB₂ powder caused the occurrence of eutectic mixture of Fe_α and TiB₂ phases with precipitates of TiB₂ borides and Ti(C, N) carbonitrides in alloyed zone of low-carbon steel (Darabara et al. 2007, 2008). If the paste coating with TiB₂ + B powders was used, the eutectic mixture consisted of Fe_α, TiB₂ and Fe₂B phases. The precipitates of TiB₂ borides and Ti(C, N) carbonitrides as well as, at higher boron contents in alloying material, Fe₂B borides were also observed (Darabara et al. 2007).

The use of the coating with Ti–B nanopowders during PSA of pure titanium resulted in the formation of re-melted zone with hard TiB borides, highly dispersed in the soft Ti_α-based matrix (Miklaszewski and Jurczyk 2011; Miklaszewski et al. 2011, 2012, 2013; Kaczmarek et al. 2016). If the Ti–B micropowder was applied as alloying material, TiB₂ borides also appeared in the alloyed layer. Ti–B

nanopowders simplified the reaction during plasma alloying process and strongly reduced or even eliminated the possibility of gas pores' formation. Additionally, they accelerated TiB phase nucleation and caused its high dispersion and structure refinement. The zonation of the plasma-alloyed layer was visible. Precipitates of TiB borides occurred close to the surface in the form of needle-shaped whiskers. The very fine microstructure was observed in this region. Whereas the coarse microstructure was identified at higher depth of the layer because of the longer heat outflow from this section of the layer (Miklaszewski et al. 2011).

The main advantages of the plasma surface alloying with boron were comparable to those described for other techniques of surface alloying (LSA or EBSA): wide range of thickness of produced layers (the thickness often significantly exceeded the thickness of the diffusion borided layers), relatively short duration of the process in comparison with diffusion boriding, a fine-crystalline microstructure of boride layers, hardness profile of the gradual decrease towards the substrate, local heating and possibility to eliminate the deformations and dimensional changes, possibility of layer formation on the selected fragments of surfaces of complex shape, precise control of the plasma arc column, elimination of the use of cooling media, easy automation, environmental performance of the process as well as relatively low energy and material consumption. Additionally, the simplicity of PSA with boron was its important advantage compared to LSA and EBSA processes. The possible cracks or gas pores, greater roughness and waviness of the treated surface should be specified as the disadvantages of the plasma-alloyed layers.

5.3.2 Formation of Boride Coatings

Contrary to the typical *superficial layer* (top layer), which was characteristic of all the materials, the *surface layer* was well-known as the effect of deliberate action, i.e. was produced using specific techniques. Based on the terminology, proposed by Burakowski and Wierzchoń (1998), the two main types of *surface layers* could be distinguished: *technological superficial layers* and *coatings*. In general, the surface layers could be produced by various techniques, which could be classified as: *decremental*, *non-decremental* and *incremental methods*.

Decremental techniques resulted in decreasing the dimensions of the treated object, e.g. machining, burnishing or etching. *Non-decremental techniques* didn't cause the substantial change in the dimensions of the treated object, e.g. diffusion methods, ion implantation or surface alloying. As a consequence of *incremental techniques*, the significant increase in the dimensions of the treated object was observed, e.g. electroplating, painting or thermal spraying. The differences between these techniques were shown in Fig. 5.31. Decremental (Fig. 5.31b) and non-decremental (Fig. 5.31c) surface treatment of medium carbon steel resulted in the formation of technological superficial layers. They could be produced using polishing or boriding, respectively. Whereas coatings were deposited on top of the medium-carbon steel with a superficial layer using incremental surface treatment

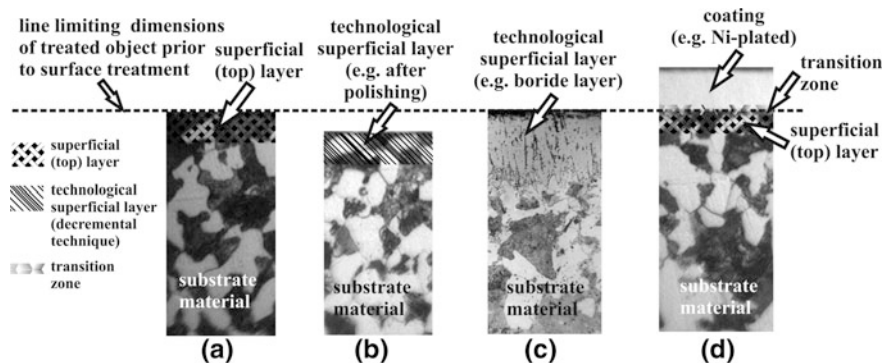


Fig. 5.31 Schematic representation of the dimensions of object made of medium-carbon steel: prior to the surface treatment (a), after decremental surface treatment (b), after non-decremental surface treatment (c) and after incremental surface treatment (d)

(Fig. 5.31d), e.g. nickel plating. The transition zone usually appeared between the coating and the substrate.

All the techniques of boriding, described up to now in the present work, resulted in formation of technological superficial layers, briefly called layers, which were produced by non-decremental techniques. If the layer contained metal borides, it was called **boride layer**. The coatings could be fabricated using different manufacturing techniques, such as: chemical deposition, painting, enameling, electroplating, cladding, thermal spraying, detonation treatment, CVD and PVD techniques, PLD (pulsed laser deposition), hot dip metallization or sol-gel techniques.

Cladding processes (laser, electron beam or plasma cladding) as well as the techniques of spraying (thermal or detonation spraying) represented the most commonly used and the most effective high-energy techniques of producing the **boride coatings**. Therefore, they were described in this section. During typical thermal or detonation spraying, the substrate wasn't subjected to re-melting. The process of cladding was similar to surface alloying, taking into account the main operating parameters and the techniques. However, melting of the substrate was limited to a minimum depth just to provide a good fusion bonding between the clad coating and the substrate. The phase composition and properties were determined primarily by the clad material.

5.3.2.1 Thermally Sprayed Boride Coatings

Thermal spraying techniques were well-known processes of formation of coatings, in which re-melted or only heated and strong softened material was sprayed onto a substrate surface. The feedstock (spraying material) as a coating precursor was usually heated by electrical (plasma or arc) or chemical means (combustion flame).

Hence, the main methods of thermal spraying were as follows (Dobrzański and Dobrzańska-Danikiewicz 2011; Fauchais et al. 2014): **flame spraying (FS)**, **high-velocity oxy-fuel (HVOF) flame spraying**, **wire arc spraying (WAS)** and **plasma spraying (PS)**. Schematic representations of these techniques were depicted in Fig. 5.32.

Flame spraying, also known as **oxy/acetylene combustion spraying** was the thermal spraying technique developed about 100 years ago. The method used the basic principles of a welding torch with the addition of a high velocity air stream to deposit molten particles of feedstock onto the substrate material (Dobrzański and Dobrzańska-Danikiewicz 2011). The material of coating (spraying material) could be delivered either a wire or powder form (Fig. 5.32a). A gas flame of a temperature about 3000 °C (3273 K) became the heat source which was used to melt the thermal spray material. The molten particles were then propelled towards the surface to be sprayed. Compressed air was often used on the wire flame spray in order to atomize the molten particles and to propel them towards the substrate. If the powder flame spray was used, the metal or ceramic powder particles were softened by the flame. Next, this powder was sprayed onto the substrate surface through the nozzle using the gas flame. The flame-sprayed coatings were often fused after being fabricated in order to enhance bond strength and coating density.

High-velocity oxy-fuel (HVOF) flame spraying process was developed during the 1980s. It consisted in continuous combustion of oxygen and liquid or gaseous fuel, e.g. aviation petrol, propane, propylene or hydrogen. The powder was usually used as a feedstock. The molten particles were transferred by the supersonic stream of hot gas and hit the substrate with high kinetic energy. Although the HVOF system used the basic principle of combustion, the HVOF gun produced higher flame temperatures and higher velocities of molten particles. As a consequence, the increase in the coating density and improvement of its adhesion to the substrate occurred. The typical HVOF thermal spray system consisted of a combustion chamber, a Laval nozzle and a barrel (Fig. 5.32b). Sometimes, the separate mixing chamber was used in order to mix oxygen and fuel (Fig. 5.32c). The other version of the HVOF system used additionally air of a suitable pressure (Fig. 5.32d). The combustion gases of high pressure and high temperature were produced by the reaction of oxygen and fuel in the combustion chamber. Then, they were accelerated to supersonic velocity through the Laval nozzle, which could be characterized as a duct of convergent divergent area.

Wire arc spraying was a method of thermal spraying, which utilized the same principles employed in wire arc welding systems. The feedstock (coating material) was delivered into the spray gun in the form of two consumable metal wires (Fig. 5.32c). Cored wires, containing the adequate powder, were often used. The wires were electrically charged, and then contacted creating an arc (Dobrzański and Dobrzańska-Danikiewicz 2011). The molten particles of the wires were then atomized and propelled towards the substrate using a high velocity air stream and, this way, they were sprayed onto the substrate material. This technique was also known as **twin wire arc spraying (TWAS)**.

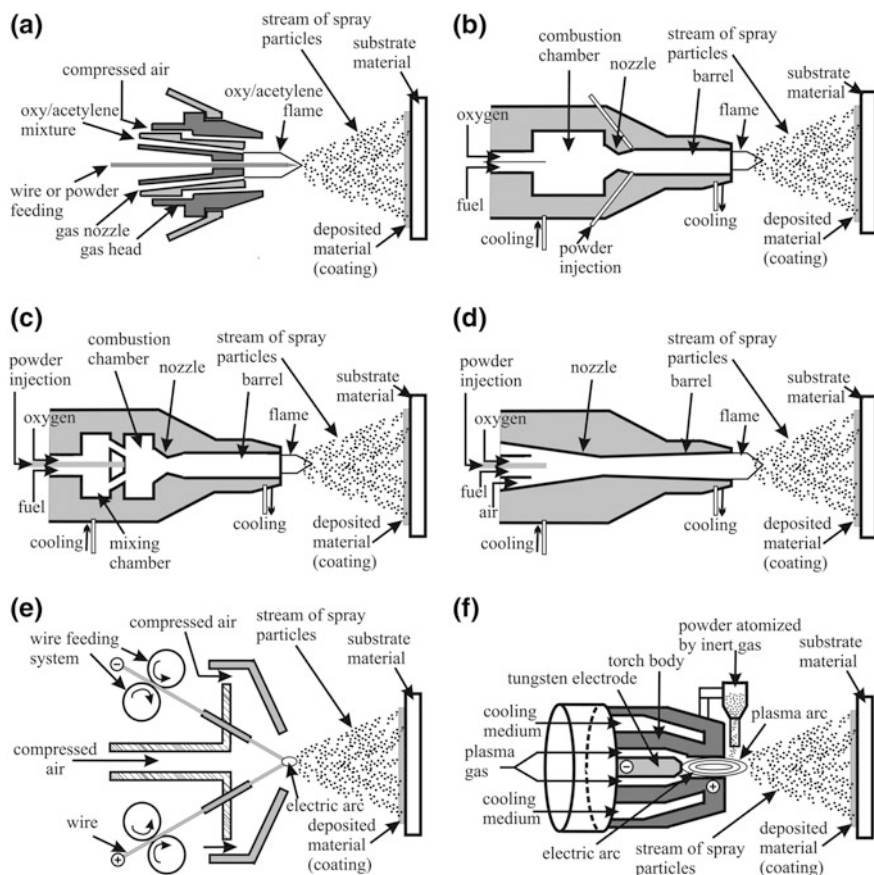


Fig. 5.32 Schematic representation of the most commonly used techniques of thermal spraying: flame spraying (a), three variants of HVOF flame spraying (b), (c) and (d), wire arc spraying (e) and plasma spraying (f); (a), (e) and (f) inspired by Dobrzański and Dobrzańska-Danikiewicz (2011), (b) used by Li and Christofides (2004), (c) used by Horlock et al. (2002) and (d) used by Li et al. (2005). Remark: The process of plasma spraying could be also carried out in vacuum chamber or in chamber with inert gas

Plasma spraying (non-transferred arc) was a process, in which the material to be deposited (feedstock) was introduced into the plasma jet, produced by a plasma torch (Fig. 5.32d). Plasma was produced in an electric arc, glowing between a non-consumable electrode (cathode) and a nozzle (anode). Inert gases were usually used as a plasma gas. The powder was applied as the typical feedstock, which was atomized and injected with inert gas. Sometimes, it was a liquid, suspension or wire. The coating material was melted and propelled towards the substrate. Its molten particles flattened on the substrate, rapidly solidified and formed a deposit.

Thermal spraying was often used in order to fabricate coatings with borides. During such processes, the feedstock (spraying material) contained an amount of

boron and metallic elements. The produced boride coatings have been rarely composed of only metal borides. The composite microstructure with the limited percentage of borides was usually formed. In the present work, only some characteristic processes of thermal spraying with boron were analyzed.

Flame spraying with boron was relatively rarely applied. The powder, containing boron, was usually specially prepared and used as a feedstock. Co–Cr–W–B–Si–Ni gas atomized self-fluxing powder (known as FP-160M Co-based powder) with boron content of about 3 wt% was used to prepare the feedstock, sprayed onto the surface of low-carbon steel by Sakata et al. (2007). XRD of the prepared powder revealed the presence of Co_2B and Cr_2B borides as well as of Co_α phase. Ma et al. (2011) used the raw powder composed of 32% FeB, 48% Mo and 20% Fe (wt%) in order to deposit the coating with borides on low-carbon steel. Such a powder was mixed in planetary ball-mill for 5 and 15 h. Then, the powder was sieved, pelletized, sintered in a vacuum furnace at 900 °C (1173 K), crushed and sieved once again. After sintering, the phase analysis revealed the presence of FeB, Fe_2B , Mo_2FeB_2 , Mo and Fe phases. Whereas Ni–Cr–Fe–Si–B or Ni–Cr–Fe–Si–B–WC powders with boron content in the range of 3.1–3.3 wt% were applied by Rachidi et al. (2017). The similar feedstock (Ni–Cr–Fe–Si–B powder with 3.9 wt% B) was flame sprayed onto the copper surface (Sharma and Majumdar 2012). Phase analysis by X-ray diffraction showed the presence of Ni_3B , Si and Ni_γ phases in such a feedstock. Nd–Fe–B gas atomized powder was sprayed onto the surface of Al-based alloy (Gan and Berndt 2011).

The main parameters of FS with boron, reported by literature data, were as follows: type of feedstock (containing boron), powder feed rate (g/min), oxygen (O_2) pressure (kPa) and its flow rate (l/min), acetylene (C_2H_2) pressure (kPa) and its flow rate (l/min), distance of torch tip from the substrate material (mm), also called spraying distance, torch scanning speed (m/min), also called traverse speed, feed pitch distance (mm/pass) as well as preheating or post spray temperature (°C). Air pressure (kPa) was an optional parameter. Preheating was carried out to avoid cracks' formation. Whereas post spray heat treatment was carried out in order to improve the bonding strength as well as to increase the density and hardness of the coating because of the elimination of some pores.

The selected processes of flame spraying with boron were compared in Table 5.25, taking into account the parameters mentioned above as well as the type of the spraying device, shape of the sprayed surface and scheme of the method in Fig. 5.32. Some of the parameters were omitted by the authors in their works. The powder feed rate in the range of 40–120 g/min was given only by Sharma and Majumdar (2012) as well as by Gan and Berndt (2011). Oxygen pressure ranged from 207 to 361.9 kPa with its flow rate between 41.67 and 45 l/min. Whereas acetylene pressure was lower (103–117.6 kPa) with a flow rate in the range of 25–55 l/min. Spraying distance (distance of torch tip from the substrate) reached values in a wide range of 30–200 mm. Torch scanning speed ranged from 0.1 to 16 m/min. Feed pitch distance (15 mm/pass) was reported only by Sakata et al. (2007), and air with pressure of 276 kPa was used only by Gan and Berndt (2011). Preheating at 300 °C (573 K) was applied only by Ma et al. (2011). Whereas post

Table 5.25 General characterization of selected processes of flame spraying with boron

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min)/type of the spraying device/shape of the sprayed surface/scheme of the method/optional air pressure (kPa)	Oxygen pressure (kPa), its flow rate (l/min)/acetylene pressure (kPa), its flow rate (l/min)/distance of torch tip from substrate (mm)/torch scanning speed (m/min)/feed pitch distance (mm/pass)/preheating temperature (°C)/post spray temperature (°C)	References
Low-carbon steels	Co ₂ B–Cr ₂ B–Co _α powder prepared using FP-160M (Co–Cr–W–B–Si–Ni) gas atomized self-fluxing powder/unknown/TeroDyn system 3000, Eutectic device/flat/Fig. 5.32a	361.9, 41.67/103.4, 25/200/16/15/without preheating/1105–1145	Sakata et al. (2007)
	FeB–Fe ₂ B–Mo ₂ FeB ₂ –Mo–Fe powder (prepared using 32% FeB + 48% Mo + 20% Fe raw powder)/unknown/QT-E2000-7/H flame spray gun/flat/Fig. 5.32a	294, unknown/117.6, unknown/30/0.1/unknown/300/1000	Ma et al. (2011)
	Ni–Cr–Fe–Si–B or Ni–Cr–Fe–Si–B–WC powder/unknown/SuperJet-Eutalloy, Castolin Eutectic torch/flat/Fig. 5.32a	Unknown parameters	Rachidi et al. (2017)
Copper	Ni ₃ B–Si–Ni _γ powder (prepared using Ni–Cr–Fe–Si–B powder)/40/PowderJet-86 device/flat/Fig. 5.32a	225.06, 45/110.03, 55/unknown/unknown/unknown/without preheating/without post spray heat treatment	Sharma and Majumdar (2012)
Aluminium alloys	Nd–Fe–B gas atomized amorphous powder/54–120/Metco 6P II oxy-acetylene spray torch/flat/Fig. 5.32a/276	207, unknown/103, unknown/100–200/unknown/unknown/without preheating/without post spray heat treatment	Gan and Berndt (2011)

spray heat treatment was carried out by Sakata et al. (2007) at 1000–1145 °C (1273–1418 K) in Ar atmosphere or vacuum furnace.

Flame spraying with boron usually resulted in the formation of a composite microstructure which was composed of hard borides and softer metallic phases. Co_α phase as well as Co₂B and Cr₂B borides were identified after flame spraying with FP-160M Co-based powder (Sakata et al. 2007). If the sprayed powder consisted of FeB, Fe₂B, Mo₂FeB₂, Mo and Fe phases (Ma et al. 2011), the flame spraying resulted in the formation of a coating, containing hard Mo₂FeB₂ phase in Fe_α matrix. Additionally, the presence of oxides (Fe₂O₃ and FeO) was reported. If Ni₃B, Si and Ni_γ phases were identified in a feedstock (Sharma and Majumdar 2012), the phase analysis of the deposited coating revealed Ni₃B borides among Ni_{2.9}Cr_{0.7}Fe_{0.36} and Ni_γ phases. Gan and Berndt (2011) didn't provide the phase composition of the coating.

HVOF flame spraying with boron has been intensively developed in the last two decades. Such a process was used more often than the typical flame spraying. The typical Fe–Cr–B or Fe–Cr–Ni–B gas atomized powders, commercially available as Armacor M and Armacor 16, were sprayed onto the surface of low-carbon steel by Kim et al. (1999a, b). The spherical grains with size in the range of 40–85 or 5–35 μm were characteristic of Armacor M and Armacor 16 feedstock powders, respectively. The phases, identified in Armacor 16 powder, were as follows: Fe_α , Fe_γ , $\text{Cr}_{1.65}\text{Fe}_{0.35}\text{B}_{0.96}$ and Cr_2B . Whereas Armacor M contained only Fe_α , Fe_γ and $\text{Cr}_{1.65}\text{Fe}_{0.35}\text{B}_{0.96}$ phases. Fe–Mn–Cr–Si powder was mixed with B or Ni + B powders and used as sprayed material by Sucharski et al. (2015). The specific chemical composition of Fe–Mn–Cr–Si alloy was not given because of not completed patent rights before publication. The powders were sieved and particles with diameters up to 63 μm were applied in order to spray onto the substrate made of low-carbon steel. The feedstock powder, composed of Cr_{23}C_6 , Cr_3NiB_6 , Ni_5Si_2 and NiCrFe phases, was prepared using 67.5Ni–16Cr–0.5Si–3.5B–3Mo–3Cu–4Fe–0.8C (wt%) Tafa's powder 1275H by Shrestha et al. (2001) in order to deposit the coating on the surface of medium-carbon steel. The commercial MoB/CoCr (DTS-B49-45/15) or MoB/NiCr (DTS-B43-45/15) powders were HVOF sprayed on the surface of SKD61 tool steel by Khan et al. (2011). The phase analysis of MoB/CoCr powder revealed the presence of CoMoB and CoMo_2B phases. Whereas MoB/NiCr powder consisted of MoB, Mo_2B_5 , and $\text{Cr}_2\text{Ni}_3\text{B}_6$ borides as well as Ni_γ and Cr_3Ni_2 phases. The Fe–44.7Cr–5.8B–1.98 Si (wt%) powder with trace amounts of C, Mn and S was produced by gas atomization in an argon atmosphere and then dried at 100 °C (373 K) by Wu et al. (2006, 2007, 2009). The phase composition of this powder, used for HVOF spraying of high-alloy steel, was as follows: $\text{Fe}(\text{Cr})_\alpha$, FeB, Fe_2B , Fe_3B , CrB and Cr_2B . The Ni-based Ni–17Cr–5.8Fe–4.9Si–3.9B (wt%) powder was sprayed onto the surface of copper or high-alloy steel by Sharma and Majumdar (2012, 2013, 2014, 2015). The phase analysis of feedstock revealed the presence of Ni_3B , Si and Ni_γ phases. A commercially available Ni–Cr–B–Si powder (labelled PA 101HV) of nominal composition Ni–15.3Cr–3.1B–4.8Si–4.2Fe–0.6 C (wt%) and particle size of about 44 μm was applied for HVOF spraying of Ni- and Fe-based superalloys (Sidhu et al. 2006).

Sometimes, the procedure of feedstock preparation was more complicated. Fe–17.9B–0.4C–1.6Si–0.3Al (wt%) ferroboration based powder as well as the mixture of this powder with 20 wt% Ni was applied by Ozdemir et al. (2014) in order to spray them and deposit the coating on low-carbon steel. The particles of ferroboration powder were sieved into about 20 μm size. Afterwards, the powders were subjected to high-energy ball milling. It could facilitate the deposition due to the increase in the internal energy of feedstock. Powder of SAF2507 superduplex alloy was modified by the addition of 3 wt% B using a Fe–16.5 wt% B alloy in order to prepare the sprayed material for HVOF flame spraying of low-carbon steel (Berger et al. 2017). At first, such powders were produced by a spray forming process. Then, some of them were subjected to a high-energy ball milling. The commercial raw powders of TiB_2 , Ni and Cr were used for preparation of the sprayed material by Zhao et al. (2018). Such powders were mixed with a composition of 60 wt%

TiB₂, 32 wt% Ni and 8 wt% Cr. Then, the slurry was prepared with addition of deionized water and a small amount of dispersant and organic binder. Afterwards, the slurry was milled in a planetary mill for several hours and then spray-dried using an atomization spraying drier. The as-sprayed TiB₂-40NiCr (wt%) powder was sintered at 1230 °C (1503 K) in a tubular furnace under argon atmosphere and sieved in the range of 20–45 µm for HVOF spraying of medium-carbon steel. The phase composition of this powder was as follows: TiB₂, CrB, Ni₂B and Ni₇. Mizuno and Kitamura (2007) prepared the prototype of commercial MoB/CoCr (DTS-B49-45/15) powder using fine powders of molybdenum boride, chromium boride, and cobalt-based alloy (Co-30 wt% Cr-4 wt% W-1.2 wt% C) as raw materials. The raw powders were mixed, milled in a solvent by ball milling and agglomerated using spray drier. Then, the agglomerated powder was sintered at more than 1000 °C (1273 K) in an inert atmosphere in order to produce the borides of Co-Mo-B system by a chemical reaction of cobalt-based alloy and metal borides. MoB/CoCr powder, prepared this way, contained mainly double borides: CoMoB and CoMo₂B₂ and was sprayed onto the surface of high-alloy steel. The raw powders of iron, chromium and amorphous boron, mixed in a suitable ratio, were subjected to self-propagating high-temperature synthesis (SHS) by Jones et al. (2001). The SHS reaction was carried out in a glove chamber under argon atmosphere in order to minimize oxidation. The SHS compacts were crushed and then sieved. The particles with diameters in the range of 15–45 µm were applied in order to spray onto the surface of low-carbon steel. SHS process was also used by Horlock et al. (2002) and Lotfi et al. (2003) to prepare the HVOF sprayed material. The raw material consisted of titanium, amorphous boron and Ni-20 wt% Cr powders. These powders were mixed in a ratio which resulted in an adequate final composition. As a consequence of SHS reaction, the feedstock powders contained 35 or 60 wt% of Ni-20 wt% Cr and 65 or 40 wt% of TiB₂, respectively. Fe₅₇Cr₉Nb₁₃B₂₁ (at.%) gas atomized powder was subjected to high-energy ball milling by Guo et al. (2016) in order to prepare the feedstock powder for spraying of high-alloy steel. As a consequence, chemical homogeneous particles with size ranging between 20 and 53 µm were produced. Koga et al. (2017) used the same procedure to form the feedstock powder based on Fe₆₀Cr₈Nb₈B₂₄ (at.%) alloy. Nanostructured powders Fe₇₅Si₁₅B₁₀ and Fe_{73.5}Si_{13.5}B₉Nb₃Cu₁ (at.%) were obtained by mechanical alloying and used in order to deposit the coating on copper by HVOF spraying (Alleg et al. 2010, 2015). The phase analysis of the final feedstock powders revealed the presence of Fe₂B boride and Fe(Si, B)_x-type solid solution with crystallite sizes up to 11 nm. Pougoum et al. (2016a, b) and Taillon et al. (2016) prepared the sprayed material from Fe₃Al, Ti and BN powders with various ratios. They were subjected to high-energy ball milling and applied in order to produce the coatings on high-alloy steel.

The main operating parameters of HVOF spraying with boron, indicated by literature data, were as follows: type of feedstock containing boron (i.e. spraying material), powder feed rate (g/min or rpm), type of carrier gas and its flow rate (l/min), oxygen (O₂) pressure (kPa) and its flow rate (l/min), type of fuel, fuel pressure (kPa) and its flow rate (l/min), combustion pressure (kPa), distance of torch

tip from the substrate material (mm), also called spraying distance, torch scanning speed (m/min), scanning step (mm), number of passes as well as post spray temperature ($^{\circ}\text{C}$). Air pressure (kPa) and its flow rate (l/min) were the optional parameters, if the spraying device corresponded to that presented in Fig. 5.32d. The aim of the post spray heat treatment was to improve the bonding strength as well as to increase the density of coating because of the elimination of some pores. Such treatment also influenced the microstructure and hardness of the coating. The preheating process wasn't usually applied. At least, there were no data regarding the use of preheating in the analyzed works.

The selected processes of HVOF flame spraying with boron were compared in Tables 5.26, 5.27, 5.28, 5.29 and 5.30, taking into account the parameters specified above as well as the type of the spraying device, shape of the sprayed surface and scheme of the method in Fig. 5.32. Both iron alloys (e.g. low-carbon, medium-carbon and high-alloy steels or Fe-based superalloys) and non-ferrous materials (copper, Ni-based superalloys) were successfully subjected to HVOF flame spraying with boron. Not always the type of the spraying device was given. However, JP-5000 (Praxair/Tafa) HVOF system with the use of kerosene as fuel was applied most commonly (Kim et al. 1999a, b; Shrestha et al. 2001; Wu et al. 2006, 2007, 2009; Mizuno and Kitamura 2007; Ozdemir et al. 2014; Zhao et al. 2018). Pougoum et al. (2016a, b) and Taillon et al. (2016) used the next generation of this system, known as JP-8500 (Praxair/Tafa). These systems corresponded to the Fig. 5.32b. According to Tafa[®] HP/HVOF brochure, spark plug was used for ignition. The feedstock powder was injected behind the combustion chamber in a region of the relatively low flame temperature. It resulted in a decreased degree of phase transformations (Fauchais et al. 2014). The same effect was observed when the flame temperature was diminished by cooling air (Fig. 5.32d) as in the DiamondJet 2700 HVOF gun with the use of propylene (C_3H_6) as fuel (Sucharski et al. 2015). Such solution was also used in HIPOJET-2100 HVOF system by Sidhu et al. (2006) and Khan et al. (2011) using LPG (liquefied petroleum gas) or kerosene as fuel, respectively, as well as in the next generation of this system (HIPOJET-2700) by Sharma and Majumdar (2012, 2013, 2014, 2015) with the use of LPG as fuel. If the hydrogen (H_2) was used as a fuel, the UTP Top Gun HVOF system was usually applied (Jones et al. 2001; Horlock et al. 2002; Lotfi et al. 2003). In this case, the feedstock powder was injected directly into the combustion chamber (Fig. 5.32c) where the highest flame temperature occurred. It caused the increase in the degree of phase transformations because of the significant amount of heat transferred to the powder particles (Fauchais et al. 2014). Alleg et al. (2010, 2015) used methane (CH_4) as fuel and CDS 8944 HVOF gun in order to deposit the coating by HVOF spraying.

Some of the operating parameters were not given by the authors in the analyzed works. The powder feed rate was most commonly given in g/min. During HVOF flame spraying with boron, its values ranged from 8 to 45 g/min based on the available literature data. When the JP-5000 (Praxair/Tafa) HVOF system was used, the powder feed rate was often expressed in rpm (rotations per minute). It resulted from the use of the special powder feeder which operated on a volumetric principle.

Table 5.26 General characterization of selected processes of HVOF flame spraying with boron. Part I

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min or rpm)/carrier gas, its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method/optional air pressure (kPa) and its flow rate (l/min)	Oxygen pressure (kPa)/oxygen flow rate (l/min)/type of fuel and its pressure (kPa)/fuel flow rate (l/min)/combustion pressure (kPa)/distance of torch tip from substrate (mm)/torch scanning speed (m/min)/scanning step (mm)/number of passes/post spray temperature (°C)	References
Low-carbon steels	Fe–Cr–B based gas atomized powders with Fe _α , Fe _γ , Cr _{1.65} Fe _{0.35} B _{0.96} and optional Cr ₂ B/150–300 (rpm)/unknown, 10.85–12.27/JP-5000 Tafa HVOF system/flat/ Fig. 5.32b	1447.9/849.51–920.3/kerosene, 779.11–1172.11/0.38–0.44/668.79/350/unknown/unknown/unknown/700–1000	Kim et al. (1999a, b)
	Fe + Cr + Ti + B powder, mixed in a ratio which resulted in formation of Fe + + Cr + TiB ₂ SHS feedstock powder/unknown/N ₂ , 21/UTP Top Gun HVOF system/flat/Fig. 5.32c	Unknown/236/H ₂ , unknown/599/unknown/203/0.3/unknown/20/without post spray heat treatment	Jones et al. (2001)
	Ti + B + Ni-20 wt.% Cr powder, mixed in a ratio resulting in formation of 35 wt.% (Ni-20 wt.% Cr) + 65 wt.% TiB ₂ SHS feed-stock powder/17 (g/min)/N ₂ , 18/UTP Top Gun HVOF system/flat/ Fig. 5.32c	Unknown/210/H ₂ , unknown/624/unknown/203/0.3/unknown/24/without post spray heat treatment	Horlock et al. (2002)
	Ti + B + Ni-20 wt.% Cr powder, mixed in a ratio re-sulting in formation of 35–60 wt.% (Ni-20 wt.% Cr) + 40–65 wt.% TiB ₂ SHS feedstock powder/16.8 (g/min)/N ₂ , 18/UTP Top Gun HVOF system/flat/Fig. 5.32c	Unknown/210/H ₂ , unknown/624/unknown/203/0.3/unknown/28/without post spray heat treatment	Lotfi et al. (2003)

In this case, the powder feed rate was controlled by the speed of a pickup wheel. During operation of the feeder, holes in the wheel filled up with powder which was delivered to the gun by gravity, carrier gas and rotation of the wheel. The important advantage of such type of powder feeder was lack of sensitivity to the gun back-pressure. The powder feed rate, given in this way, reached the values in a wide range of 5.5–300 rpm (Kim et al. 1999a, b; Wu et al. 2006, 2007, 2009; Pougoum

Table 5.27 General characterization of selected processes of HVOF flame spraying with boron. Part II

Type of substrate material	Feedstock containing boron (spraying material)/ powder feed rate (g/min or rpm)/carrier gas, its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method/optional air pressure (kPa) and its flow rate (l/min)	Oxygen pressure (kPa)/ oxygen flow rate (l/min)/ type of fuel and its pressure (kPa)/fuel flow rate (l/min)/ combustion pressure (kPa)/ distance of torch tip from substrate (mm)/torch scanning speed (m/min)/ scanning step (mm)/ number of passes/post spray temperature (°C)	References
Low-carbon steels	Fe–17.9B–0.4C–1.6Si–0.3 Al (wt%) powder or its mixture with 20 wt% Ni/ unknown/unknown, unknown/JP-5000 (Praxair/Tafa) HVOF system/flat/Fig. 5.32b	Unknown parameters	Ozdemir et al. (2014)
	Fe–Mn–Cr–Si + B or Fe–Mn–Cr–Si + Ni + B gas atomized powder/35–45 (g/min)/N ₂ , 60/Diamond Jet 2700 HVOF gun/flat/ Fig. 5.32d/517, 317	1034/265.4/propylene (C ₃ H ₆), 689/unknown/ unknown/unknown/ unknown/without post spray heat treatment	Sucharski et al. (2015)
	Powder of SAF2507 superduplex alloy modified by the addition of 3 wt% B using a Fe–16.5 wt% B alloy/6.8 (rpm)/unknown, 565.8/unknown/ cylindrical/Fig. 5.32b or 5.32c	880/52,500/kerosene, 680/ 0.32/630/330/0.03/10/5/ without post spray heat treatment	Berger et al. (2017)
Medium-carbon steels	Cr ₂₃ C ₆ –Cr ₃ NiB ₆ –Ni ₅ Si ₂ –NiCrFe powder prepared using 67.5Ni–16Cr–0.5Si–3.5B–3Mo–3Cu–4Fe–0.8C (wt%)—Tafa's powder 1275H/unknown/ unknown, unknown/ JP-5000 (Praxair/Tafa) HVOF system/flat/ Fig. 5.32b	Unknown/unknown/ kerosene, unknown/ unknown/unknown/ unknown/unknown/ unknown/unknown/1050–1150	Shrestha et al. (2001)

et al. 2016a, b; Taillon et al. 2016; Berger et al. 2017). The feedstock powder was injected using an inert carrier gas. Nitrogen with a flow rate in the range of 10.85–60 l/min was most often used as a carrier gas in various HVOF systems, e.g. in UTP TOP Gun HVOF system (Jones et al. 2001; Horlock et al. 2002; Lotfi et al.

Table 5.28 General characterization of selected processes of HVOF flame spraying with boron. Part III

Type of substrate material	Feedstock containing boron (spraying material)/ powder feed rate (g/min or rpm)/carrier gas, its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method/optional air pressure (kPa) and its flow rate (l/min)	Oxygen pressure (kPa)/ oxygen flow rate (l/min)/ type of fuel and its pressure (kPa)/fuel flow rate (l/min)/ combustion pressure (kPa)/ distance of torch tip from substrate (mm)/torch scanning speed (m/min)/ scanning step (mm)/ number of passes/post spray temperature (°C)	References
Medium-carbon steels	60TiB ₂ –40NiCr (wt%) powder with TiB ₂ , CrB, Ni ₂ B and Ni ₃ , prepared using TiB ₂ –Ni–Cr powder/ 35–40 (g/min)/N ₂ , 16.7/ JP-5000 (Praxair/Tafa) HVOF system/flat/ Fig. 5.32b	Unknown/unknown/ kerosene, 680/unknown/ unknown/355/0.03/10/5/ without post spray heat treatment	Zhao et al. (2018)
High-alloy steels	MoB/CoCr (DTS-B49-45/ 15) powder of phase composition: CoMo ₂ B ₂ + CoMoB/ unknown/unknown, unknown/JP-5000 (Praxair/Tafa) HVOF system/flat/ Fig. 5.32b	Unknown/893/kerosene, unknown/0.32/unknown/ 380/unknown/unknown/ unknown/without post spray heat treatment	Mizuno and Kitamura (2007)
	Fe(Cr) _x –FeB–Fe ₂ B–Fe ₃ B–CrB–Cr ₂ B powder prepared using Fe–44.7Cr–5.8B–1.98 Si (wt%) powder with trace amounts of C, Mn, S/8 (g/min), 5.5 (rpm)/Ar, 10.5/JP-5000 (Praxair/Tafa) HVOF system/flat/ Fig. 5.32b	Unknown/755/kerosene, unknown/0.3/unknown/ 330/unknown/unknown/ 15/without post spray heat treatment	Wu et al. (2006, 2007, 2009)
	MoB/CoCr (DTS-B49-45/ 15) or MoB/NiCr (DTS-B43-45/15) powder/ unknown/N ₂ , 10.85/ HIPOJET-2100 HVOF system/flat/ Fig. 5.32d/ unknown, unknown	Unknown/802.31–939.17/ kerosene, unknown/0.45–0.53/unknown/380/ unknown/unknown/ unknown/without post spray heat treatment	Khan et al. (2011)

2003), JP-5000 (Praxair/Tafa) HVOF system (Zhao et al. 2018), HIPOJET-2100 HVOF system (Khan et al. 2011), DiamondJet 2700 HVOF gun (Sucharski et al. 2015) or CDS 8944 HVOF system (Alleg et al. 2010, 2015). Argon was more rarely applied with a flow rate of 10.5 l/min (Wu et al. 2006, 2007, 2009) or with

Table 5.29 General characterization of selected processes of HVOF flame spraying with boron. Part IV

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min or rpm)/carrier gas, its flow rate (l/min)/type of the spraying device/Shape of the sprayed surface/scheme of the method/optional air pressure (kPa) and its flow rate (l/min)	Oxygen pressure (kPa)/oxygen flow rate (l/min)/type of fuel and its pressure (kPa)/fuel flow rate (l/min)/combustion pressure (kPa)/distance of torch tip from substrate (mm)/torch scanning speed (m/min)/scanning step (mm)/number of passes/post spray temperature (°C)	References
High-alloy steels	Ni ₃ B–Si–Ni ₇ powder (prepared using Ni–Cr–Fe–Si–B powder)/40 (g/min)/unknown, unknown/HIPO-JET-2700 HVOF system/flat/Fig. 5.32d/unknown, unknown	1000/260/LPG (liquefied petroleum gas), 700/60/unknown/unknown/0.6/unknown/unknown/without post spray heat treatment	Sharma and Majumdar (2013)
	Ni ₃ B–Si–Ni ₇ powder (prepared using Ni–Cr–Fe–Si–B powder)/25 (g/min)/unknown, unknown/HIPO-JET-2700 HVOF system/flat/Fig. 5.32d/unknown, unknown	1000/250/LPG (liquefied petroleum gas), 700/60/unknown/unknown/unknown/unknown/without post spray heat treatment	Sharma and Majumdar (2014, 2015)
	30–100 Fe ₃ Al + 0–41 Ti + 0–35 BN (wt%) or (Fe ₃ Al) ₃₀ Ti ₃₅ BN ₃₅ (at.%) powders/150–300 (rpm)/unknown, 10.85–12.27/JP-8500 (Praxair/Tafa) HVOF system/flat/Fig. 5.32b	Unknown/897/kerosene, unknown/0.39/710/380/6/10/10–15/without post spray heat treatment	Pougoum et al. (2016a, b) and Taillon et al. (2016)
	Fe ₅₇ Cr ₉ Nb ₁₃ B ₂₁ (at.%) gas atomized powder/unknown/Ar, unknown/unknown/flat/Fig. 5.32b or c	Unknown/897/kerosene, unknown/0.37/unknown/330/30/15/1/without post spray heat treatment	Guo et al. (2016)
	Fe ₆₀ Cr ₈ Nb ₈ B ₂₄ (at.%) gas atomized powder/unknown/Ar, unknown/unknown/cylindrical/Fig. 5.32b or c	Unknown/896.8/kerosene, unknown/0.37/unknown/330.2/30/10/5/without post spray heat treatment	Koga et al. (2017)

unknown flow rate (Guo et al. 2016). Oxygen pressure was rarely given, and ranged from 880 to 1447.9 kPa. The flow rate of oxygen strongly depended on the type of fuel obtaining values in the range of 755–920.3 l/min in case of the use of kerosene as a fuel. If LPG (liquefied petroleum gas), hydrogen (H₂), propylene (C₃H₆) and methane (CH₄) were used as a fuel, oxygen flow rate was diminished to 250–260,

Table 5.30 General characterization of selected processes of HVOF flame spraying with boron. Part V

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min or rpm)/carrier gas, its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method/optional air pressure (kPa) and its flow rate (l/min)	Oxygen pressure (kPa)/oxygen flow rate (l/min)/type of fuel and its pressure (kPa)/fuel flow rate (l/min)/combustion pressure (kPa)/distance of torch tip from substrate (mm)/torch scanning speed (m/min)/scanning step (mm)/number of passes/post spray temperature (°C)	References
Copper	Fe ₇₅ Si ₁₅ B ₁₀ (at.%) nano-structured powder/35 (g/min)/N ₂ , 20/CDS 8944 HVOF gun/flat/Fig. 5.32b or c	Unknown/350/methane (CH ₄), unknown/145/unknown/300/3/12/10–30/without post spray heat treatment	Alleg et al. (2010)
	Ni ₃ B–Si–Ni _γ powder (prepared using Ni–Cr–Fe–Si–B powder)/40 (g/min)/unknown, unknown/HIPO-JET-2700 HVOF system/flat/Fig. 5.32d/unknown, unknown	1000/260/LPG (liquefied petroleum gas), 700/60/unknown/unknown/unknown/unknown/unknown/without post spray heat treatment	Sharma and Majumdar (2012)
	Fe _{73.5} Si _{13.5} B ₉ Nb ₃ Cu ₁ (at. %) nanostructured powder/35 (g/min)/N ₂ , 20/CDS 8944 HVOF gun/flat/Fig. 5.32b or c	Unknown/350/methane (CH ₄), unknown/145/unknown/300/3/12/10–30/without post spray heat treatment	Alleg et al. (2015)
Ni- and Fe-based super-alloys	commercial Ni–Cr–B–Si powder (PA 101HV) of nominal composition Ni–15.3Cr–3.1B–4.8 Si–4.2 Fe–0.6 C (wt%)/unknown/unknown, unknown/HIPOJET-2100 HVOF system/flat/Fig. 5.32d/588.40, 900	784.53/250/LPG (liquefied petroleum gas), 588.40/60/unknown/200/unknown/un-known/unknown/without post spray heat treatment	Sidhu et al. (2006)

210–236, 265.4 and 350 l/min, respectively. Berger et al. (2017) applied the very high flow rate of oxygen, which differed significantly from the other values (52,500 l/min). Kerosene pressure ranged from 680 to 1172.11 kPa. Whereas its flow rate obtained the values of 0.32–0.53 l/min. The flow rate of the other fuels was higher, obtaining 60, 145 and 599–624 l/min for LPG, methane and hydrogen, respectively. Combustion pressure was reported only if kerosene was a fuel. Its value was equal to 668.79 (Kim et al. 1999a, b), 630 (Berger et al. 2017) or 710 kPa (Pougoum et al. 2016a, b; Taillon et al. 2016). Air pressure and its flow rate became the optional parameters which were characteristic of the variant of

HVOF spraying shown in Fig. 5.32d. However, only Sucharski et al. (2015) reported these parameters (517 kPa and 317 l/min). Spraying distance, i.e. the distance of torch tip from the substrate material, ranged from 200 to 380 mm for all the selected processes of HVOF flame spraying with boron. The relatively wide range of torch scanning speed was reported (0.03–30 m/min). Scanning step, i.e. distance between the adjacent passes of torch, was usually equal to 10–15 mm. Whereas the number of passes obtained the values of 1–30. In general, the deposited coatings were not subjected to heat treatment. Only the coatings produced by Kim et al. (1999a, b) and Shrestha et al. (2001) were heat-treated in a vacuum furnace at 700–1000 °C (973–1273 K) and at 1050–1150 °C (1323–1423 K), respectively. All the values of operating parameters based on the data reported in the analyzed works. All the variants of HVOF flame spraying (Fig. 5.32b–d) were quite often used in order to deposit the coatings using the feedstock containing boron.

The HVOF sprayed boride coatings were composed of a composite microstructure, in which the hard ceramic phases (including borides) occurred in the softer metallic matrix. The as-sprayed coating, produced by Kim et al. (1999a, b) using Armacor 16 powder, contained Fe_α solid solution, $\text{Cr}_{1.65}\text{Fe}_{0.35}\text{B}_{0.96}$ borides as well as Fe_3O_4 oxides. The oxide inclusions contained a large amount of B and Si. The post spray treatment at 1000 °C (1273 K) modified this phase composition this way that oxides were almost eliminated and Fe_γ appeared. Whereas HVOF spraying with Armacor M resulted in the formation of hard $\text{Cr}_{1.65}\text{Fe}_{0.35}\text{B}_{0.96}$ and Cr_2B borides in a soft Fe_α solid solution. In general, the post spray treatment at 1000 °C (1273 K) didn't influence this phase composition. The coatings, produced by Jones et al. (2001), contained the hard TiB_2 phase among $\text{Fe}(\text{Cr})_\alpha$ and Si phases, FeTi intermetallic phase as well as FeTiO_3 and Ti_2O_3 oxides. More borides appeared after HVOF spraying with TiB_2 + Ni-20 wt% Cr SHS feedstock powder (Horlock et al. 2002; Lotfi et al. 2003). The phase analysis of the as-sprayed coatings revealed TiB_2 , TiB and Ni_2B borides among Ni solid solution as well as NiTiO_3 and Ti_2O_3 oxides. After HVOF spraying with ferroboron powder, the relatively thin coating (10–15 μm) consisted of FeB iron borides (Ozdemir et al. 2014). The mixture of this ferroboron with 20 wt% of Ni powder, used as a feedstock, resulted in the formation of thicker coating with FeB , Fe_2B and Ni_4B_3 borides in a soft Fe_α and Ni_γ matrix. The boron and iron oxides were also identified. The coatings, produced by Sucharski et al. (2015), optimized the parameters of HVOF spraying with a mixture of Fe–Mn–Cr–Si powder with B or Ni + B powders, taking into account the porosity and the presence of oxides. The detailed phase composition of the coatings wasn't analyzed. The coatings, HVOF sprayed with SAF2507 superduplex alloy modified by the addition of 3 wt% B, contained Fe_3B and $(\text{Fe},\text{Cr})_2\text{B}$ borides as well as the typical phases in duplex steels: ferrite FeCr_α and austenite FeCrNi_γ (Berger et al. 2017). If the feedstock powder was characterized by a relatively fine particles, an amount of $(\text{Fe},\text{Ni})_3\text{O}_4$ oxides was also observed. If the feedstock powder was composed of Cr_{23}C_6 , Cr_3NiB_6 , Ni_5Si_2 and NiCrFe phases (Shrestha et al. 2001), the as-sprayed coating didn't contain borides. They appeared after post spray heat treatment, consisting in the vacuum fusion between the liquidus and solidus states

(1050–1150 °C, i.e. 1323–1423 K). The sharp coating/substrate interface was modified because of the significant interfacial diffusion in this region. The porosity of the coating was reduced. The phase analysis by XRD revealed the hard phases to be carbides (Cr_{23}C_6) and borides (Cr_3NiB_6 , FeMo_2B_2 , and Fe_2MoB_4) as well as the soft NiCrFe phase to be a matrix. If $\text{TiB}_2 + \text{CrB} + \text{Ni}_2\text{B} + \text{Ni}$ powder was used as a feedstock (Zhao et al. 2018), the fabricated coating contained all these phases as well as a small amount of Ti_2O_3 oxides. The coating, produced with MoB/NiCr powder, contained MoB, Mo_2B_5 and $\text{Cr}_2\text{Ni}_3\text{B}_6$ borides as well as Ni_γ , Cr_α , MoNi_4 and Cr_3Ni_2 phases (Khan et al. 2011). The HVOF sprayed coating with MoB/CoCr powder consisted of the same borides which were identified in the feedstock, i.e. $\text{CoMo}_2\text{B}_2 + \text{CoMoB}$ (Khan et al. 2011). The deposition of the same MoB/CoCr feedstock by Mizuno and Kitamura (2007) resulted probably in the formation of coating of similar phase composition. The coating, fabricated by Wu et al. (2006, 2007, 2009), contained all the phases which were identified in prepared feedstock powder, i.e. FeB, Fe_2B , Fe_3B , CrB and Cr_2B borides occurred in a $\text{Fe}(\text{Cr})_\alpha$ -based matrix. If the feedstock powder contained Ni_3B , Si and Ni_γ phases, the phase composition of coating was as follows: Ni_3B and Cr_2B borides among Ni_γ matrix (Sharma and Majumdar 2012, 2013, 2014, 2015). If the sprayed material was prepared from Fe_3Al , Ti and BN powders with various ratios, the coating contained TiB_2 and Fe_2B borides, TiN nitrides and Fe_3Al phase (Pougoum et al. 2016a). Whereas the use of the mixture of only Fe_3Al and BN powders as feedstock (Pougoum et al. 2016b) resulted in the formation of Fe_2B borides, AlN nitrides and Fe_3Al phase in the produced coating. The borides wasn't identified in the coating, fabricated by HVOF spraying with $(\text{Fe}_3\text{Al})_{30}\text{Ti}_{35}\text{BN}_{35}$ (at.%) powder (Taillon et al. 2016). In this case, the coating contained mainly TiN nitrides and Fe_3Al phase. The FeNbB , Fe_2B , FeB and $(\text{Fe,Cr,Nb})_3\text{B}_2$ borides in the Fe_α -matrix were identified in the coating, deposited using $\text{Fe}_{57}\text{Cr}_9\text{Nb}_{13}\text{B}_{21}$ (at.%) powder (Guo et al. 2016). The $\text{Fe}_{60}\text{Cr}_8\text{Nb}_8\text{B}_{24}$ (at.%) feedstock powder, HVOF sprayed by Koga et al. (2017), caused the formation of coating with Fe_2B and FeNbB borides among Fe_α phase. The microstructure of the coatings, produced using the nanostructured $\text{Fe}_{75}\text{Si}_{15}\text{B}_{10}$ and $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ (at.%) powders, consisted of Fe_2B borides and amorphous $\text{Fe}(\text{Si}, \text{B})_\alpha$ phase, being similar to the phase composition of the feedstock (Alleg et al. 2010, 2015).

Wire arc spraying with boron was hardly ever applied, like the typical flame spraying. The feedstock was composed of cored wires filled with powders, containing boron. The commercially produced boride-rich Alpha 1800 cored wires were used as a feedstock by Amushahi et al. (2010) in order to form arc-sprayed coating on low-carbon steel. The filled powder contained mainly Fe and 6.1–9.5 wt % B. Wang et al. (2015c) used a self-developed FeTi/CrB composite cored wires or a commercial product, i.e. Fe–17Cr–5Ni–B (wt%) stainless amorphous metal (SH-SAM) cored wires. The steel sheath of FeTi/CrB wire was made of 08F high quality low-carbon strip. The filled powder was composed of 40% Fe–Ti powder, 58% Cr–B powder and 2% other powder. The flux-cored wire with a chemical composition of Fe–0.7C–2Mn–1Si–2Ni–4.5B (wt%) was used during wire arc spraying of Hardox 450 steel by Gromov et al. (2017). The core wires for arc

spraying of stainless steel were fabricated using metal flat strips (Dallaire and Levert 1992; Dallaire et al. 1995). The strips, made of 304 stainless steel or Nickel 200, were shaped to form a U-shape into which the Fe–Ti + B powders were introduced. The stainless steel was also arc-sprayed with the use of self-designed Fe-based cored wires (Fe–Ni–Cr–B–Si–Nb–W) as a feedstock (Lin et al. 2014a, b, 2015). The SHS 7170 cored wires were applied during twin wire arc spraying of Ti6Al4V alloy with or without thin boride layer of thickness 70–100 μm (Mann et al. 2011). SHS 7170 was Fe-based alloy with a nanoscale microstructure, containing up to 26 wt% Cr and 5 wt% B. The boride layer occurred between Ti6Al4V alloy and TWAS SHS 7170 coating in order to overcome the thermal mismatch and to improve the diffusion between Ti6Al4V alloy and the coating.

The main operating parameters of WAS with boron, partially reported as well as partially omitted by literature data, would be as follows: type of feedstock, i.e. cored wires with filler powders containing boron (spraying material), wire diameter (mm), wire feed rate (m/min), spraying voltage (V), spraying current (A), compressed air (or other gas) pressure (kPa), distance of gun tip from the substrate material (mm), i.e. spraying distance or stand-off distance, gun scanning speed (m/min), i.e. gun traverse speed, scanning step (mm), number of passes as well as preheating or post spray temperature ($^{\circ}\text{C}$).

The selected processes of wire arc spraying with boron were characterized in Tables 5.31 and 5.32, taking into account the parameters mentioned above as well as the type of the spraying device, shape of the sprayed surface and scheme of the method in Fig. 5.32. However, the indicated parameters were not always reported by the authors in their works.

The analyzed works showed the possibility of successful deposition of wire arc-sprayed boride coatings on the surface of low-carbon or high-alloy steels as well as titanium alloys. The type of spraying device was usually given. Amushahi et al. (2010) deposited the coating on low-carbon steel using Mogul A4P electric arc machine. CMD-AS1620 instrument was applied by Wang et al. (2015c) to spray the coating onto low-carbon steel. Whereas Gromov et al. (2017) sprayed the coating on the same type of material using the typical MIG/MAG arc welding device with an automatic feed of cored wire. Dallaire and Levert (1992) and Dallaire et al. (1995) fabricated the coating on stainless steels with the use of Miller BP 400 Arc Spray System. Mann et al. (2011) used the Hobart Tafa TWAS 9000 system during formation of coatings on titanium alloy. Lin et al. (2014a, b, 2015) didn't specify the type of spraying device. They only reported the use of self-designed twin wire arc gun system with a gun mounted to a robot wrist. The available literature data indicated that the wire diameter ranged from 1.6 to 2 mm. The wire feed rate was reported only by Linn et al. (2015). Its value was equal to 2.7 m/min. Spraying voltage obtained the values in the range of 27–39 V. Whereas the wide range of spraying current (100–300 A) was used. Compressed air was usually applied as atomizing gas. The values of its pressure were between 500 and 700 kPa. However, sometimes air was replaced by argon (Dallaire and Levert 1992; Dallaire et al. 1995) with a pressure of 380 or 600 kPa in order to avoid the oxidation of reagents or reaction products. Although the heat capacity and conductivity of argon was

Table 5.31 General characterization of selected processes of wire arc spraying with boron. Part I

Type of substrate material	Feedstock—cored wires with filler powders containing boron (spraying material)/ wire diameter (mm)/wire feed rate (m/min)/type of the spraying device/shape of the sprayed surface/scheme of the method	Spraying voltage (V)/ spraying current (A)/ compressed air (or other gas) pressure (kPa)/distance of gun tip from substrate (mm)/ scanning speed (m/min)/ scanning step (mm)/number of passes/preheating temperature (°C)/post spray temperature (°C)	References
Low-carbon steels	Commercially produced boride-rich Alpha 1800 cored wires/1.6/unknown/ Mogul A4P electric arc machine/flat/Fig. 5.32e	32/200/550/unknown/ unknown/unknown/ unknown/150/without post spray heat treatment	Amushahi et al. (2010)
	Self-developed FeTi/CrB composite cored wires or Fe–17Cr–5Ni–B (wt%) stainless amorphous metal cored wires/2/unknown/ CMD-AS1620 instrument/ flat/Fig. 5.32e	37/120–160/500/180/ unknown/unknown/ unknown/without preheating/without post spray heat treatment	Wang et al. (2015c)
	Flux-cored wire with a chemical composition of Fe–0.7C–2Mn–1Si–2Ni–4.5B (wt%)/unknown/unknown/ MIG/MAG arc welding/ Fig. 5.32e	30–35/250–300/unknown (98% Ar + 2% CO ₂)/ unknown/unknown/ unknown/unknown/without preheating/without post spray heat treatment	Gromov et al. (2017)

lower than air, it protected the synthesized products against solidification before their impact with the substrate surface (Dallaire and Levert 1992). The relatively low pressure of argon (380 kPa) caused the accumulation of a large pool of molten material at the tip of the electrode. It ensured a relatively large reaction zone as well as good mixing. Gromov et al. (2017) used the mixture of argon (98%) and CO₂ (2%) of unknown pressure. Distance of gun tip from substrate (i.e. stand-off distance) usually ranged from 150 to 200 mm. Unfortunately, scanning step and number of passes were not reported in the considered works. The wire arc spraying with boron was usually carried out without preheating of the substrate material. Preheating up to 150 °C (423 K) was applied only by Amushahi et al. (2010). The post spray heat treatment was also rarely used. The coating was post annealed by Linn et al. (2014a, b, 2015) at the temperature of 450–650 °C (723–923 K).

Like the previous methods of spraying, WAS with boron resulted in the formation of composite coatings with hard ceramic phases (including borides) among the soft metallic matrix. Fe_α phase as well as FeB and Fe₂B borides were identified in the produced coating by Amushahi et al. (2010). In some areas of the coating, eutectic mixture of Fe₂B and Fe_α was observed. Because of the use of air, oxides

Table 5.32 General characterization of selected processes of wire arc spraying with boron. Part II

Type of substrate material	Feedstock—cored wires with filler powders containing boron (spraying material)/ wire diameter (mm)/wire feed rate (m/min)/type of the spraying device/shape of the sprayed surface/scheme of the method	Spraying voltage (V)/ spraying current (A)/ compressed air (or other gas) pressure (kPa)/distance of gun tip from substrate (mm)/ scanning speed (m/min)/ scanning step (mm)/number of passes/preheating temperature (°C)/post spray temperature (°C)	References
High-alloy steels	304 stainless steel-based or Nickel 200-based cored wires filled with Fe–Ti and B powders/1.6/unknown/Miller BP 400 Arc Spray System/ flat/Fig. 5.32e	27–39/170/380 (argon)/150/ unknown/unknown/ unknown/without preheating/ without post spray heat treatment	Dallaire and Levert (1992)
	304 stainless steel-based cored wires filled with Fe–Ti and B powders/1.6–1.75/ unknown/Miller BP 400 Arc Spray System/flat/Fig. 5.32e	27/100/600 (air or argon)/ 150/unknown/unknown/ unknown/without preheating/ without post spray heat treatment	Dallaire et al. (1995)
	Self-designed Fe-based cored wires (Fe–Ni–Cr–B–Si–Nb–W)/2/2.7/twin wire arc gun system with a gun mounted to a robot wrist/flat/Fig. 5.32e	36/120/700/200/6/unknown/ unknown/without preheating/ 450–650	Lin et al. (2014a, b, 2015)
Titanium alloys	SHS 7170 cored wires/1.6/ unknown/Hobart Tafa TWAS 9000 system/flat/Fig. 5.32e	33/200/522.48/unknown/ unknown/unknown/ unknown/without preheating/ without post spray heat treatment	Mann et al. (2011)

also became a part of the coating. Iron borides (FeB , Fe_2B , Fe_3B) and chromium borides (CrB , Cr_5B_3) occurred in a soft FeCr matrix after wire arc spraying with the use of a self-developed FeTi/CrB composite cored wires (Wang et al. 2015c). FeO and CrO oxides also appeared in such coating. The use of Fe-17Cr-5Ni-B (wt%) stainless amorphous metal cored wires as sprayed material by the same authors resulted in producing the coating with FeB , CrB , $\text{Fe}_3\text{Ni}_3\text{B}$ and $\text{Cr}_2\text{Ni}_3\text{B}_6$ borides as well as Ni_3Fe phase among the softer FeCr matrix in a presence of Fe_2O_3 and Cr_2O_3 oxides. The self-designed Fe-based cored wires ($\text{Fe-Ni-Cr-B-Si-Nb-W}$) were used by Lin et al. (2014a, b, 2015) in order to produce the coating which was composed of almost amorphous phase. Only post heat treatment at 650 °C (923 K) resulted in crystallization of Fe(Cr)_α , Fe_3B and Fe_{23}B_6 phases (Lin et al. 2014b). The phase composition of the TWAS SHS 7170 coating wasn't provided by Mann et al. (2011). It was only reported that without boride layer it wasn't possible to bond this coating to Ti6Al4V alloy. The presence of boride layer helped

to overcome the thermal mismatch between TWAS SHS 7170 coating and the substrate material. Wire arc spraying using 304 stainless steel-based sheath of cored wires (filled with ferrotitanium and boron powders) resulted in the formation of the coatings, containing up to 26% of TiB_2 borides (Dallaire and Levert 1992). TiB_2 could be provided by the reaction of the ferrotitanium alloy with boron at 1080 °C (1353 K). The XRD pattern of the reaction products revealed the presence of TiB_2 and iron as well as titanium and some oxides. Both air and argon were used as atomizing gas. Air was more efficient than argon in fabricating the coatings of high wear resistance. However, argon was preferable due to protection against oxidation. The oxides, occurring within coating, could impair the corrosion properties (Dallaire et al. 1995). The use of Nickel 200-based sheath of cored wires was inadvisable because of the large difference between the melting point of nickel and the temperature to initiate the reaction of ferrotitanium with boron (Dallaire and Levert 1992). After WAS of flux-cored wire with a chemical composition of Fe–0.7C–2Mn–1Si–2Ni–4.5B (wt%), the microstructure of the deposited coating consisted of eutectic mixture of Fe_2B iron borides and Fe_α phase (Gromov et al. 2017). The Fe_α phase had often the structure characteristic of batch martensite. The use of 98% Ar + 2% CO_2 gas mixture protected the coating against oxidation.

Plasma spraying with boron (non-transferred arc) was carried out in the two ways. The typical process under atmospheric pressure was called **atmospheric (or air) plasma spraying (APS) with boron** (Dikici and Ozdemir 2012; Culha et al. 2014). However, it could also proceed in a vacuum chamber under reduced pressure. Such a process, called **vacuum plasma spraying (VPS) with boron** was applied relatively rarely (Galvanetto et al. 2006; Lin 2012).

The powders, containing boron, were used as a feedstock during APS processes. Fe-based amorphous powder with a composition of Fe–28Cr–3.1B–2Cu–1Si–17Ni–3.3Mo–8.4 Co (wt%) was applied by Lu et al. (2011) in order to produce the coating on the surface of low-carbon steel. Umanskii et al. (2015) fabricated the sprayed coating on the same type of steel using the mixture of Ni-based powder of composition Ni–16Cr–3.2Si–2.7B–0.75C–<5Fe (wt%) with TiB_2 powder. The starting components were mixed with alcohol at a ratio of 80 wt% Ni-based powder and 20 wt% TiB_2 . Then, they were pressed and sintered in a vacuum furnace at 1100 °C (1373 K) for 30 min. The produced sinter was ground and powdered into the adequate particle-size fraction for plasma spraying. The feedstock, subjected to APS of medium-carbon steel by Wang et al. (2015b), was composed of 60 wt% TiB_2 + 40 wt% NiCr powder. Storozhenko et al. (2017) applied the TiB_2 + (Fe–13 wt% Mo) powders to spray the coating onto the surface of high-carbon steel. They were prepared by powder metallurgy techniques. The starting powders, i.e. titanium diboride, Fe and Mo, were mixed in a planetary mill for 3 h in acetone. Then, the charge was pressed and sintered at 1450–1500 °C (1723–1773 K) in a vacuum furnace. The sintered material was mechanically crushed and sieved. The percentage of metallic phase (Fe–Mo) ranged from 20 to 80 wt%. The very complex feedstock, consisting of 60(Ni–Co–Cr–Al–Y) + 24ZrB₂ + 16B₄C (wt%) powders, was applied by Huang et al. (2014). Ferrobore powder with a composition of Fe–18.8B–0.2C–0.5Si–0.8Al (wt%) was atmospheric plasma-sprayed onto the surface

of die cast Al-alloy (Dikici and Ozdemir 2012; Culha et al. 2014). Dikici and Ozdemir (2012) also used the mixture of this powder with 5 wt% of hexagonal boron nitride (h-BN) as a solid lubricant. Such composite powders (ferroboron + h-BN) were fabricated by spray drying and post-sintering. The gas atomized neodymium-iron-boron (Nd-Fe-B) alloy was applied as a feedstock during APS of Al-alloy (Gan et al. 2013). Boron was incorporated into a Ca-Si system in order to prepare $\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$ (at.%) ceramic powder (B-CS powder) for atmospheric plasma spraying of pure titanium (Lu et al. 2016). Sodium carbonate CaCO_3 , silicon dioxide SiO_2 and boron oxide B_2O_3 were used as raw materials. At first, they were blended and milled in an Al_2O_3 mortar for 2 h. Then, such a mixture was calcined in alumina crucible at 1420 °C (1693 K). The mixture, containing 85 wt% of Ti6Al4V alloy powder and 15 wt% of hexagonal boron nitride (h-BN), was also used as a feedstock in order to deposit the plasma-sprayed coating on pure titanium (Anand et al. 2017). The unknown substrate was coated by APS using the feedstock, containing the powders of ferrotitanium (Fe-Ti), boron and nickel (Dallaire and Champagne 1984; Dallaire 1992). Vacuum plasma-sprayed coating was fabricated on medium-carbon steel using Fe_2B powder or the mixture of FeB and Fe_α powders (Galvanetto et al. 2006). B_4C powder became a feedstock during VPS of pure aluminum (Lin 2013).

The main operating parameters of atmospheric plasma spraying (APS) with boron were also only partially reported by literature data. They were as follows: type of feedstock, i.e. powder containing boron (sprayed material), powder feed rate (g/min), type of carrier gas and its flow rate (l/min), arc voltage (V), arc current (A), type of primary gas, its pressure (kPa) and its flow rate (l/min), type of secondary gas, its pressure (kPa) and its flow rate (l/min), distance of gun tip from the substrate material (mm), i.e. spraying distance or stand-off distance, gun scanning speed (m/min), i.e. gun traverse speed, scanning step (mm), number of passes as well as post spray temperature (°C). The same parameters were characteristic of vacuum plasma spraying (VPS) with boron. Chamber pressure (Pa) was the only additional parameter.

The general characterization of selected processes of atmospheric plasma spraying with boron was shown in Tables 5.33, 5.34 and 5.35, taking into account the parameters specified above as well as the type of the spraying device, shape of the sprayed surface and scheme of the method in Fig. 5.32. Whereas the Table 5.36 characterized the two typical processes of vacuum plasma spraying with boron. However, some operating parameters were often omitted by the authors in their works. Because of that, sometimes it was difficult to determine the most commonly used parameters.

The selected works showed the possibility of successful deposition of atmospheric plasma-sprayed boride coatings on the surface of low-, medium- and high-carbon steels, high-alloy steels as well as pure titanium. Unfortunately, sometimes the authors didn't report the substrate material (Dallaire 1992; Dallaire and Champagne 1984). It could only suppose that the coatings were deposited onto pure titanium surface. The two examples of vacuum plasma spraying focused on the use of medium-carbon steel and pure aluminum as a substrate material. The type of

Table 5.33 General characterization of selected processes of atmospheric plasma spraying with boron. Part I

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min)/carrier gas, its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method	Arc voltage (V)/Arc current (A)/primary gas, its pressure (kPa), its flow rate (l/min)/secondary gas, its pressure (kPa), its flow rate (l/min)/distance of gun tip from substrate (mm)/scanning speed (m/min)/scanning step (mm)/number of passes/post spray temperature (°C)	References
Low-carbon steels	Fe-based amorphous powder with a composition of Fe–28Cr–3.1B–2Cu–1Si–17Ni–3.3Mo–8.4 Co (wt%)/21.3/Ar, 7.1/Praxair/Tafa 3710 plasma spraying system with SG-100 gun/flat/Fig. 5.32f	48/900/Ar, unknown, 44.8/He, unknown, 27.8/110/6/3.2/unknown/without post spray heat treatment	Lu et al. (2011)
	Ni-based Ni–16Cr–3.2Si–2.7B–0.75C–<5Fe (wt%) powder mixed with 20 wt% of TiB ₂ powder/unknown/unknown, unknown/UPU-3D-M plasma spray coating machine fitted with 15VB manipulator camera/flat/Fig. 5.32f	65/450/Ar, unknown, unknown/H ₂ , unknown, unknown/150–160/unknown/unknown/unknown/without post spray heat treatment	Umanskii et al. (2015)
Medium-carbon steels	60 wt% TiB ₂ + 40 wt% NiCr powder/unknown/unknown, unknown/9MB Metco gun/flat/Fig. 5.32f	Unknown/550/Ar, unknown, 40/H ₂ , unknown, 10/100/unknown/unknown/unknown/without post spray heat treatment	Wang et al. (2015b)
High-carbon steels	TiB ₂ + (Fe-13 wt% Mo) powders with 20, 40, 60, and 80 wt% of the metallic phase/unknown/unknown, unknown/UPU-3D-M plasma spray coating machine fitted with 15VB manipulator camera/flat/Fig. 5.32f	60–70/500–550/Ar, unknown, unknown/H ₂ , unknown, unknown/150–160/unknown/unknown/unknown/without post spray heat treatment	Storozhenko et al. (2015)

spraying device was not always reported. Lu et al. (2011) deposited the plasma-sprayed coating on low-carbon steel using Praxair/Tafa 3710 plasma spraying system with SG-100 gun. The UPU-3D-M plasma spray coating machine fitted with 15VB manipulator camera was used by Umanskii et al. (2015) and by Storozhenko et al. (2017) in order to form a coating on low-carbon and high-carbon steel, respectively. The devices, provided by Sulzer Metco Inc. (now Oerlikon

Table 5.34 General characterization of selected processes of atmospheric plasma spraying with boron. Part II

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min)/carrier gas, its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method	Arc voltage (V)/Arc current (A)/primary gas, its pressure (kPa), its flow rate (l/min)/secondary gas, its pressure (kPa), its flow rate (l/min)/distance of gun tip from substrate (mm)/scanning speed (m/min)/scanning step (mm)/number of passes/post spray temperature (°C)	References
High-alloy steels	60(Ni–Co–Cr–Al–Y) + + 24ZrB ₂ + 16B ₄ C (wt%) powder/35/N ₂ , unknown/APS-2000K plasma spraying system/flat/Fig. 5.32f	70/500/Ar, 600, 35/H ₂ , 650, 2/130/unknown/unknown/unknown/without post spray heat treatment	Huang et al. (2014)
Aluminium alloys	Ferroboration Fe–18.8B–0.2C–0.5Si–0.8Al (wt%) powder or ferroboration + h-BN powders/69/Ar, 7.2/unknown/flat/Fig. 5.32f	50/80–100, 500/Ar, unknown, 47.4/H ₂ , unknown, 0.144/100/unknown/unknown/unknown/without post spray heat treatment	Dikici and Ozdemir (2012)
	Ferroboration Fe–18.8B–0.2C–0.5Si–0.8Al (wt%) powder/unknown/unknown, unknown/unknown/flat/Fig. 5.32f	Unknown parameters, only post spray temperature 450–550 °C was given	Culha et al. (2014)
	Nd–Fe–B powders/30/Ar, 16.52/unknown/flat/Fig. 5.32f	40/750/Ar, unknown, 42.48/He, unknown, 23.6/100–300/unknown/unknown/unknown/without post spray heat treatment	Gan et al. (2013)
Pure titanium	Ca ₁₁ Si ₄ B ₂ O ₂₂ (at.%) B-CS ceramic powder/24/Ar, 4/F4-MB Sulzer Metco plasma spraying system/flat/Fig. 5.32f	60/650/Ar, unknown, 40/H ₂ , unknown, 10/100/unknown/unknown/un-known/without post spray heat treatment	Lu et al. (2016)
	Ti6Al4V alloy + h-BN powders/20/unknown, unknown/9MC Sulzer Metco spray system/flat/Fig. 5.32f	Unknown/unknown/unknown/unknown/150/unknown/unknown/unknown/without post spray heat treatment	Anand et al. (2017)

Metco), were commonly applied. Wang et al. (2015b) fabricated the coating using 9MB Metco plasma spray gun. The F4-MB and 9MC Sulzer Metco plasma spraying systems were used by Lu et al. (2016) and Anand et al. (2017), respectively, for atmospheric plasma spraying of pure titanium surface. Whereas the APS-2000K plasma spraying system was applied during APS of high-alloy steel

Table 5.35 General characterization of selected processes of atmospheric plasma spraying with boron. Part III

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min)/carrier gas, its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method	Arc voltage (V)/Arc current (A)/primary gas, its pressure (kPa), its flow rate (l/min)/secondary gas, its pressure (kPa), its flow rate (l/min)/distance of gun tip from substrate (mm)/scanning speed (m/min)/scanning step (mm)/number of passes/post spray temperature (°C)	References
Unknown (probably pure Ti)	54(Fe–Ti) + 14.6B + 30.8 Ni (wt%) powders/unknown/unknown, unknown/unknown/flat/Fig. 5.32f	Unknown parameters	Dallaire and Champagne (1984)
	Fe–Ti + B + Ni powders/unknown/unknown, unknown/unknown/flat/ Fig. 5.32f	Unknown parameters	Dallaire (1992)

Table 5.36 General characterization of selected processes of vacuum plasma spraying with boron

Type of substrate material	Feedstock containing boron (spraying material)/ powder feed rate (g/min)/ carrier gas, its flow rate (l/min)/type of the spraying device/shape of the alloyed surface/scheme of the method/chamber pressure (Pa)	Arc voltage (V)/Arc current (A)/primary gas, its pressure (kPa), its flow rate (l/min)/secondary gas, its pressure (kPa), its flow rate (l/min)/distance of gun tip from substrate (mm)/ scanning speed (m/min)/ scanning step (mm)/ number of passes/post spray temperature (°C)	References
Medium-carbon steels	Fe ₂ B or FeB + Fe _x powders/45/unknown, unknown/unknown/flat/ Fig. 5.32f in vacuum chamber/6	Unknown/unknown/Ar, unknown, unknown/H ₂ , unknown, unknown/270/12/unknown/unknown/ without post spray heat treatment	Galvanetto et al. (2006)
Pure aluminium	B ₄ C powder/16.67/Ar, unknown/A-3000 vacuum plasma spraying system with ABB IRB-L6-type robot and F4-VB spray gun/flat/Fig. 5.32f in vacuum chamber/6.5–8.0	Unknown/650–680/Ar, unknown, 30–45/H ₂ , unknown, 10.5–15/150–300/unknown/unknown/ unknown/without post spray heat treatment	Lin (2013)

(Huang et al. 2014). Lin (2013) used A-3000 vacuum plasma spraying system with ABB IRB-L6-type robot and F4-VB spray gun in order to produce the boride coating on the pure aluminum surface. The other authors (Dallaire 1992; Dallaire and Champagne 1984; Galvanetto et al. 2006; Dikici and Ozdemir 2012; Culha et al. 2014; Gan et al. 2013) omitted the type of spraying device in their publications. The available literature data indicated that the powder feed rate ranged from 16.67 to 69 g/min. Although the literature data were incomplete in this regard, argon seemed to be the most commonly used carrier gas (Lu et al. 2011, 2016; Dikici and Ozdemir 2012; Lin 2013). Only Huang et al. (2014) applied nitrogen as a carrier gas. The flow rate of carrier gas has even more rarely been given. Its values for argon were in the range of 4–7.2 l/min. Taking into account the available data, arc voltage obtained the values in the range of 48–70 V. Whereas the range of arc current ranged from 450 to 900 A. Argon with a flow rate of 30–47.4 l/min was commonly applied as a primary gas. Its pressure (600 kPa) was reported only by Huang et al. (2014). Hydrogen was predominantly used as secondary gas with a flow rate in the range of 0.144–10 l/min. Only Lu et al. (2011) and Gan et al. (2013) applied helium. Its flow rate was higher, obtaining the values from 23.6 to 27.8 l/min. The pressure of secondary gas (650 kPa) was given only by Huang et al. (2014). The distance of gun tip from the substrate material (also called spraying distance or stand-off distance) ranged from 100 to 300 mm. The gun scanning speed (gun traverse speed) was reported only by Galvanetto et al. (2006) and Lu et al. (2011). They used the speed of 12 or 6 m/min, respectively. The scanning step (3.2 mm) was provided only in one case (Lu et al. 2011). Whereas the number of passes was not given in the analyzed works. The post spray treatment at temperatures of 450–550 °C (723–823 K) was applied only by Culha et al. (2014).

The composite microstructure, composed of hard ceramic phases (including borides) among the soft metallic matrix, has been usually characteristic of the plasma-sprayed coating. The chromium and iron borides (CrB_2 , Cr_2B , Fe_7B) as well as FeSi_2 and SiO_2 phases occurred in $\text{Fe}(\text{Cr})_x$ -based matrix after APS with the use of Fe-based amorphous powder with chromium and boron as a feedstock (Lu et al. 2011). Atmospheric plasma spraying of the mixture of NiCrSiB and TiB_2 powders onto the surface of low-carbon steel resulted in formation of coating, composed of chromium borides and titanium diborides (TiB_2) among the soft Ni-based solid solution (Umanskii et al. 2015). The microstructure of atmospheric plasma-sprayed coating, produced using the $\text{NiCr} + \text{TiB}_2$ powder, consisted of hard TiB_2 borides and soft NiCr matrix (Wang et al. 2015b). The formation of composite coatings with multiphase structure, consisting of ductile iron-based metallic phase and reinforcing boride phases was observed as a consequence of APS using $\text{TiB}_2 + \text{FeMo}$ powders as a feedstock (Storozhenko et al. 2017). Huang et al. (2014) fabricated the coating in which CrB_2 and ZrB_2 borides together with B_4C and $\text{Ni}_3\text{Co}_3\text{Al}_{14}$ phases occurred in NiCoCr matrix. Because of the chemical composition of ferroboron, used by Dikici and Ozdemir (2012) as well as by Culha et al. (2014) as a feedstock, only FeB borides or FeB and h-BN phases (without softer metallic phase) were identified in the atmospheric plasma-sprayed coatings onto Al-alloy. The post spray heat treatment of such a coating (Culha et al. 2014)

resulted in smoother and improved microstructure, that is, decrease in pore size and coating densification. The phase composition of the coating, fabricated by Gan et al. (2013) with the use of Nd–Fe–B powder as a feedstock, wasn't provided. The authors indicated only dark Fe-rich and light Nd-rich phases among unmelted, semi-melted and resolidified particles which were unidentified. The phase analysis of the coating, fabricated by Lu et al. (2016), didn't reveal the borides in microstructure. Orthorhombic $\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$ phase as well as $\text{Ca}_3\text{B}_2\text{O}_6$ and Ca_2SiO_4 phases were identified in the coating. Titanium borides (TiB), titanium dioxides (TiO_2) and $\text{Ti}_{0.76}\text{N}$ phase were observed in Ti_α -based matrix after APS of pure titanium with the use of $\text{Ti6Al4V} + \text{h-BN}$ powders as a feedstock (Anand et al. 2017). The use of feedstock, containing the powders of ferrotitanium (Fe–Ti), boron and nickel (Dallaire and Champagne 1984; Dallaire 1992), resulted in the formation of the atmospheric plasma-sprayed coating which was composed of TiB_2 borides in FeNi matrix. The phase composition of the coating, produced by vacuum plasma spraying of medium-carbon steel (Galvanetto et al. 2006) depended on the powder used as a feedstock. If Fe_2B powder was used, the same Fe_2B iron borides occurred in the microstructure. Whereas the use of the mixture of FeB and Fe_α powders resulted in the formation of FeB and Fe_3B borides among the Fe_α -based matrix. Probably, the use of boron carbide as a feedstock during VPS process caused the formation of B_4C coating on the surface of pure aluminum. However, the phase analysis wasn't reported by the authors.

Because of the great diversity of applied techniques and feedstocks, it was difficult to indicate the trends in thermal spraying with boron. Both the simple techniques, i.e. flame spraying and wire arc spraying, and the more complicated techniques (HVOF flame spraying and plasma spraying) were used in order to produce the boride coatings. The number of available publications indicated a slight advantage of more complicated techniques over the simple ones.

Fauchais et al. (2014) accurately characterized advantages and limitations of each technique. The important disadvantage of thermal spraying was partial loss of spraying material. The percentage of spraying material, used for producing the coatings, was called deposition efficiency. The main advantages of flame spraying (FS) were its simplicity and low cost of the treatment. Among the limitations, the main were as follows: high porosity and low adhesion of the produced coatings, in-flight oxidation of the powder as well as the necessary of cooling the substrate and coating during spraying. The use of self-fluxing alloys, containing Si and B, was advisable because they could be used as deoxidizers. The post spray treatment improved the bonding strength and increased the density and hardness of the coating because of the elimination of some pores (Fauchais et al. 2014). The very high-velocity gas streams, thanks to a convergent–divergent nozzle following the combustion chamber, relatively low porosity and good adhesion of coatings became the main advantages of the HVOF flame spraying technique. However, in-flight oxidation of the powder could be also observed. Hence, the current trends indicated the tendency to increase the velocity of particles and reduce their temperatures in order to limit their oxidation (Fauchais et al. 2014). The spray rates and deposition efficiency of wire arc spraying (WAS) were higher than most other techniques. As a

consequence, it became one of the most economical techniques, as long as the feedstock could be prepared in the form of wires or cored wires. The content of oxides was rather high. The oxidation level could be reduced by the use of nitrogen instead of air as atomizing gas. However, this way the technique became more expensive (Fauchais et al. 2014). The air plasma-sprayed (APS) coatings were characterized by a relatively low content of oxides, low porosity and good adhesion of boride coatings. When oxidation became a problem, the feedstock powder could be sprayed only in vacuum chamber (VPS) or in inert atmosphere (e.g. chamber filled with argon). The last technique was called *inert atmosphere plasma spraying (IAPS)*. Both VPS and IAPS technique provided the significant reduction of oxidation. However, the equipment was more complex than that of the other techniques. Hence, these techniques were the most expensive of all the other spraying processes. The important advantage of VPS technique was the possibility to remove the oxides from the substrate material by a plasma transferred arc etching the surface of the substrate prior to coating deposition (Fauchais et al. 2014).

The surface of the substrate material should be properly prepared before the thermal spraying. Without this special preparation of the surface the coating could be characterized by many defects which led to its failure. The quality of coating adhesion was strongly related to the cleanliness, roughness, and sometimes the proper machining for optimal coating performance. The kind of surface preparation depended on the nature of coating material and the substrate material and influenced the bonding strength. The techniques of surface preparation were described by Fauchais et al. (2014) in detail.

5.3.2.2 Detonation-Sprayed Boride Coatings

Detonation gun spraying (DGS) was often classified as a type of thermal spraying (Fauchais et al. 2014). Hermanek (2001) described DGS process as a variation of thermal spraying in which the controlled explosion of a mixture of inflammable gas (fuel) and oxygen was applied in order to melt the powdered coating material (spraying material) and propel its towards the surface of substrate material. However, sometimes detonation gun spraying was distinguished from the typical techniques of thermal spraying because of its special features. The essence of the detonation gun spraying was the use of explosive energy of combustion of gas mixture in order to heat the powder particles and to provide them the required kinetic energy (Dobrzański and Dobrzańska-Danikiewicz 2011). The delivery of powdered spraying material before a detonation wave was a reason for its entrainment by the combustion products which gave speed the powder particles and raised their temperature. As a consequence, the two-phase stream consisting of gas phase (detonation products) and powder particles was formed (Babul 2011). The velocity of the detonation wave depended on the composition of the gas mixture used. It usually ranged from 1000 to 3000 m/s, being several times higher than the speed of sound in these mixtures (Kadyrov and Kadyrov 1995).

In recent years, the techniques of DGS (see Fig. 5.33) were intensively developed. The main component of a typical valve device (Fig. 5.33a) was a barrel in which the formation two-phase stream consisting of gas detonation products and spraying material (powder particles) occurred. The other important components were as follows: combustion chamber together with detonation chamber, feeder of powdered spraying material, systems for the delivery of the explosive gas mixture and inert gas with an optional special gas mixing chamber, and ignition system. The explosive gas mixture was prepared and introduced into the combustion and detonation chamber with the use of special valves (Babul 2011). The mechanical or electromagnetic valves were located between the systems for the delivery of gases and the mixing chamber as well as between the mixing chamber and combustion chamber. They were used in order to ensure a controlled and periodic flow rate of oxygen-inflammable gas mixture into the detonation chamber, to prevent detonations from moving outwards from the detonation chamber through the inlet, and to provide a sufficient time for mixing of gas fuel with oxygen (Kharlamov and Kharlamov 2013). Sometimes, the separate gas mixing chamber wasn't applied. In this case, the combined mixing, combustion and detonation chambers were used. During a simple cycle of the spray stream formation, the successive stages occurred in order of: fill of the barrel with explosive gas mixture with simultaneous powder feeding, injection of nitrogen to prevent backfiring, initiation of ignition of the explosive gas mixture, formation of the spray stream, including the acceleration of particles in detonation wave and their heating by the detonation products, outflow of the spray stream from the barrel, purging of the barrel by nitrogen (Kadyrov and Kadyrov 1995; Babul 2011). The detonation wave had a tendency to propagate in all directions, including the propagation towards the gas delivery system. It created the hazard of an explosion. Such an effect was called backfiring. Hence, the nitrogen was used as a buffer gas (also called phlegmatizing agent) in order to solve this problem. Nitrogen separated the successive portions of the gas fuel from one another and protected against the propagation of detonation wave into the gas delivery system (Kadyrov and Kadyrov 1995).

The new generation of DGS devices consisted in the use of a valveless technique (Fig. 5.33b, c). The main feature distinguishing this technique from the previously used, was the elimination of valve systems. The continuous or intermittent delivery of propellants (gas fuel and oxidizer) to the detonation chamber was carried out without using mechanical valves (Kharlamov and Kharlamov 2013). Instead of them, the phenomena related to dynamic gas flow from areas of different pressure were used. The valve systems were replaced with the system of direct delivery of gases (Babul 2011). Some technical solutions of the valveless detonation gun spraying were patented by Babul (1994). The technique was intensively developed through the next two decades (Bojar and Senderowski 2006; Babul 2011). The suitable shape of the mixing chamber and the combustion chamber enabled to eliminate valves. After ignition, the process of the detonation combustion of gases caused that the pressure of detonation wave significantly exceeded the pressure of the delivered gases. As a consequence, the detonation products retreated towards the gas delivery system. The pressure of detonation wave violently reduced.

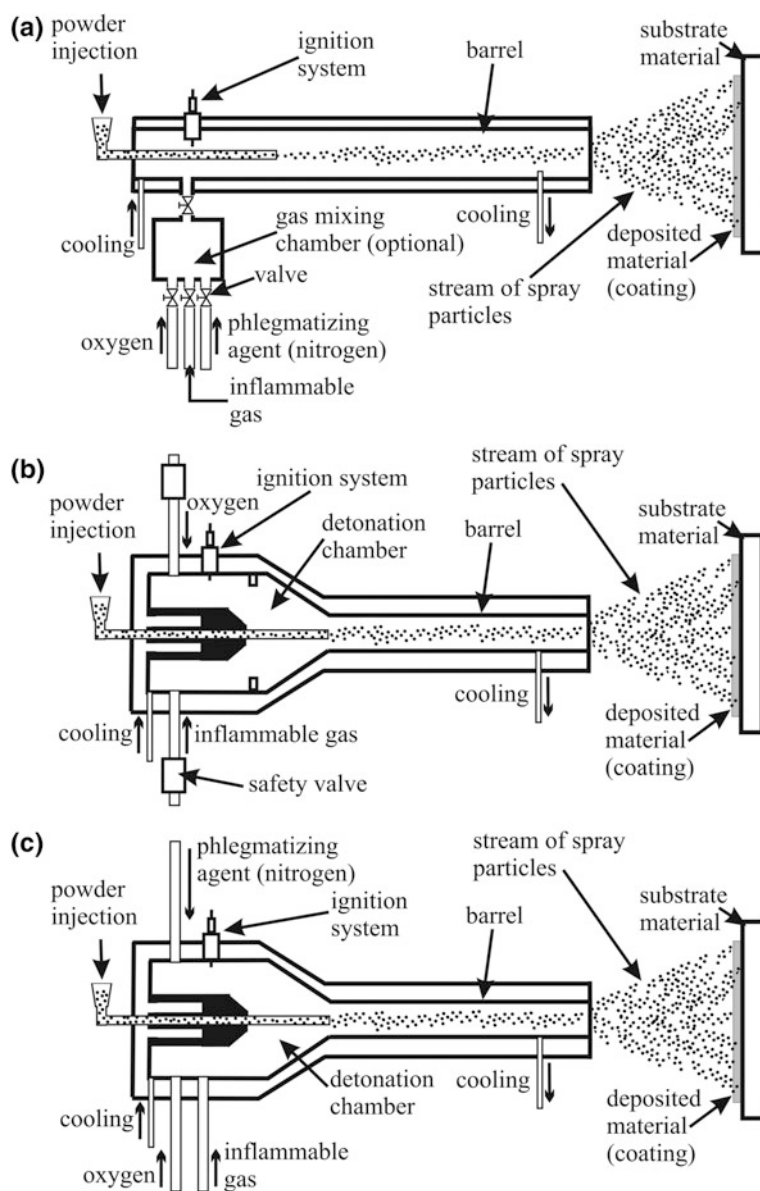


Fig. 5.33 Schematic representation of the most commonly used variants of detonation gun spraying: according to Kadyrov and Kadyrov (1995) with the use of valve technique (a), according to Babul (1994, 2011) with the use of valveless technique (b), according to Bojar and Senderowski (2006) with the use of valveless technique (c)

Whereas the pressure of the delivered gases was still the same. Therefore, these gases filled the mixing chamber again. Properly selected the diameters of the gas pipes and placed on them suppressors of a detonation wave protected the system against uncontrolled gas explosion (Babul 2011).

Detonation gun spraying (DGS) with boron consisted in the delivery of powdered spraying material, containing boron, before a detonation wave in order to heat the powder particles and to provide them the required kinetic energy by detonation combustion products. Like in case of the other spraying techniques, the diversity of applicable powders with boron was also characteristic of DGS processes. The feedstock, prepared from Fe–Cr–B alloy powder with a composition of 56.28Fe–24.22Cr–3.04B–8.68Ni–4.59Mo–<2Si–<2 others (wt%), contained Cr_2B and $\text{Cr}_{1.65}\text{Fe}_{0.35}\text{B}_{0.96}$ phases as well as Fe–Cr solid solution (Jin et al. 1999). Yang et al. (2001) used the two types of powders with boron, varying in the size of particles. The fine powder was composed of αMoB , βMoB and MoB_2 phases. Whereas the coarse powder contained βMoB and MoB_2 . The composite powders were applied as a feedstock by Podchernyaeva et al. (2010). The starting materials were mixed in a vibratory mill in acetone and then sintered at 1400 °C (1673 K) in a vacuum chamber. The obtained sinters were ground and sieved to separate the particles of TiCrB_2 –30FeCr or $(\text{AlN}–\text{ZrB}_2–\text{ZrSi}_2)$ –35NiCr (wt%) powder. Babul (2011) used Ni–Cr–Si–B alloy powder with a composition of 70Ni–16Cr–4Si–4B–4Fe–2C (wt%) in order to fabricate detonation-sprayed boride coatings. 80Ni–20Cr (wt%) alloy powder as well as Ni or stainless steel powders were mixed with B and Al powders by Kadyrov et al. (1985) in order to prepare the proper composite feedstock.

Aksenov et al. (1991) prepared the powders by diffusion saturation of nickel or nichrome with boron and aluminum. As a consequence, the feedstock was composed of Ni or Ni–Cr with nickel and chromium borides (Ni_3B , Cr_2B) as well as Al_3Ni and αAlB_{12} phases at grain boundaries. The powder, containing Mo_2CoB_2 , CrB, MoB and MoCoB phases, was prepared by Lv et al. (2010) from commercially available MoB–CoCr alloy powder with a composition of Mo–8B–22.5Co–19.4Cr (wt%). The commercial ferrobore powder with a composition of Fe–18.4B–0.32C–0.34Si–0.003S–0.02P–0.08Al (wt%) was used by Shankar et al. (2010) in order to produce detonation-sprayed coating. The FeB was a predominant phase of this powder. Besides, small amounts of Fe_2B , Fe_5PB_2 and Fe_2AlB_2 phases were also observed. Tillmann et al. (2014) separately injected Al powder and B_4C powder into the detonation chamber. Olikier et al. (2009) fabricated the powder with phase composition as follows: TiB, TiB_2 , TiAl, Ti_2Al and Ti_2O . It was prepared from Ti–50Al–25B (wt%) by mechanical alloying in a planetary-ball mill.

Based on the available literature data, the main operating parameters of detonation gun spraying (DGS) with boron were as follows: type of feedstock, i.e. powder containing boron (sprayed material), powder feed rate (g/min or rpm), type of carrier gas, its pressure (kPa) and its flow rate (l/min), oxygen pressure (kPa) and its flow rate (l/min) of, type of inflammable gas, its pressure (kPa) and flow rate (l/min), type of buffer (phlegmatizing) gas, its pressure (kPa) and flow rate (l/min), ratio of oxygen to inflammable gas, distance of gun tip from the substrate material (mm), i.e. spraying distance or stand-off distance as well as frequency of spraying

(Hz), also called firing rate or ignition frequency. However, as it was noticed previously for the other thermal spraying processes, many of these parameters weren't reported by literature data.

The general characterization of selected processes of detonation spraying with boron was shown in Tables 5.37, 5.38 and 5.39, taking into account the available parameters specified above as well as the type of the spraying device, shape of the sprayed surface and scheme of the technique in Fig. 5.33. The type of device was not always provided by authors of publications. Perun-S detonation spray gun (Aksenov et al. 1991; Podchernyaeva et al. 2010) and Dnepr detonation spray gun (Aksenov et al. 1991; Oliker et al. 2009) became the most popular devices representing the valve technique. Ukrainian GEMENOH D-gun spraying device was used by Lv et al. (2010). Whereas Yang et al. (2001) mentioned only that they applied Ukrainian detonation spray gun, and Shankar et al. (2010) reported the use of computer controlled D-Gun spray system. In case of valveless technique, Polish SAT98 detonation spray gun, produced by T Surface Advance Technology (Polish company), was quite commonly used (Babul 2011; Tillmann et al. 2014).

The powder feed rate was often omitted by the authors of selected works. Only Yang et al. (2001) and Tillmann et al. (2014) reported the values of powder feed rate: 80 g/min and 0.3–0.5 rpm, respectively. The type of carrier gas, used during the powder feeding, was also rarely given. Nitrogen was used as a carrier gas by Podchernyaeva et al. (2010), Babul (2011) and Tillmann et al. (2014). Oliker et al. (2009) used compressed air, argon or nitrogen alternately. The pressure of carrier gas (0.5 kPa) was given only by Babul (2011). Whereas its flow rate (10–15 l/min) was mentioned only by Tillmann et al. (2014). The detonation-sprayed boride coatings were usually sprayed onto the flat surface of substrate material. Oxygen pressure (48 kPa) was reported only by Babul (2011), and the flow rate of oxygen (30 l/min) by Tillmann et al. (2014). Acetylene (C_2H_2) was often used as an inflammable component of the gas mixture (Jin et al. 1999; Yang et al. 2001; Oliker et al. 2009; Lv et al. 2010). Propane-butane mixture (C_3H_8 – C_4H_{10}) was an equally popular inflammable gas (Aksenov et al. 1991; Podchernyaeva et al. 2010; Babul 2011). The mixture of propane-butane and oxygen was sometimes diluted with air (Aksenov et al. 1991). Tillmann et al. (2014) applied propane as a component of gas mixture. The use of nitrogen as a buffer gas (phlegmatizing agent) was reported by Yang et al. (2001), Oliker et al. (2009) and Lv et al. (2010) without data regarding its pressure or flow rate. The ratio of oxygen to the inflammable gas strongly depended on the type of gas used. In case of the use of acetylene, this ratio ranged from 1.1 to 1.5. If propane-butane was applied as inflammable gas, the values of this ratio were significantly higher (in the range of 4–10). Spraying distance was not always given. Based on the available data, its values varied between 90 and 150 mm. The most commonly reported frequency of spraying (also called firing rate or ignition frequency) was equal to 3–6.6 Hz.

The microstructure of the detonation-sprayed boride coatings usually contained the hard particles, including borides, in a metallic matrix. The coatings, as-sprayed on the low-carbon steel, were composed of a Cr-rich boride phases (Cr_2B and $Cr_{1.65}Fe_{0.35}B_{0.96}$) and Fe–Cr solid solution matrix phase (Jin et al. 1999). It

Table 5.37 General characterization of selected processes of detonation spraying with boron. Part I

Type of substrate material	Feedstock containing boron (spraying material)/ powder feed rate (g/min or rpm)/carrier gas, its pressure (kPa), its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method	Oxygen pressure (kPa), its flow rate (l/min)/ inflammable gas, its pressure (kPa), its flow rate (l/min)/buffer gas, its pressure (kPa), its flow rate (l/min)/ratio of oxygen to inflammable gas/distance of gun tip from substrate (mm)/frequency of spraying (Hz)	References
Low-carbon steels	(Fe–Cr)–Cr _{1.65} Fe _{0.35} B _{0.96} –Cr ₂ B powder prepared from Fe–Cr–B alloy powder with a composition of 56.28Fe–24.22Cr–3.04B–8.68Ni–4.59Mo–<2Si–<2others (wt%)/ unknown/unknown, unknown, unknown/ unknown/flat/probably, Fig. 5.33a	Unknown, unknown/ acetylene (C ₂ H ₂), unknown, unknown/ unknown, unknown, unknown/1.11:1/90/4	Jin et al. (1999)
	αMoB–βMoB–MoB ₂ fine powder or βMoB–MoB ₂ coarse powder/80 (g/min)/ unknown, unknown, unknown/Ukrainian detonation gun spray/flat/ probably, Fig. 5.33a	Unknown, unknown/ acetylene (C ₂ H ₂), unknown, unknown/ nitrogen (N ₂), unknown, unknown/from 1.1:1 to 1.35:1/unknown/unknown	Yang et al. (2001)
Medium-carbon steels	TiCrB ₂ –30FeCr or (AlN–ZrB ₂ –ZrSi ₂)–35NiCr (wt %) composite powders/ unknown/nitrogen (N ₂), unknown, unknown/ Perun-S detonation gun spray/flat/Fig. 5.33a	Unknown, unknown/ propane-butane (C ₃ H ₈ –C ₄ H ₁₀), unknown, unknown/unknown, unknown, unknown/4:1/ 110/6.6	Podchernyaeva et al. (2010)
	Ni–Cr–Si–B alloy powder with a composition of 70Ni–16Cr–4Si–4B–4Fe–2C (wt%)/unknown/ nitrogen (N ₂), 0.5, unknown/SAT98 detonation spray gun/flat/ Fig. 5.33b	48, unknown/ propane-butane (C ₃ H ₈ –C ₄ H ₁₀), 10, unknown/ unknown, unknown, unknown/unknown/ unknown/unknown	Babul (2011)

Table 5.38 General characterization of selected processes of detonation spraying with boron. Part II

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min or rpm)/carrier gas, its pressure (kPa), its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method	Oxygen pressure (kPa), its flow rate (l/min)/inflammable gas, its pressure (kPa), its flow rate (l/min)/buffer gas, its pressure (kPa), its flow rate (l/min)/ratio of oxygen to inflammable gas/distance of gun tip from substrate (mm)/frequency of spraying (Hz)	References
Low-alloy steels	80Ni–20Cr (wt%) alloy, Ni, or stainless steel powders with B and Al/unknown/unknown, unknown, unknown/unknown/flat/Fig. 5.33a	Unknown parameters	Kadyrov et al. (1985)
High-alloy steels	(Ni or Ni–Cr)–Ni ₃ B–CrB–Al ₃ Ni– α AlB ₁₂ powder/unknown/unknown, unknown, unknown/Perun-S or Dnepr detonation gun spray/flat/Fig. 5.33a	Unknown, unknown/propane-butane (C ₃ H ₈ –C ₄ H ₁₀), unknown, unknown/unknown, unknown, unknown/unknown/unknown (also diluted with air)	Aksenov et al. (1991)
	Mo ₂ CoB ₂ –CrB–MoB–MoCoB powder prepared from MoB–CoCr alloy powder with a composition of Mo–8B–22.5Co–19.4Cr (wt %)/30–84 (g/min)/unknown, unknown, unknown/Ukrainian GEMENOH D-gun spraying system/flat/Fig. 5.33a without separate mixing chamber	Unknown, unknown/acetylene (C ₂ H ₂), unknown, unknown/nitrogen (N ₂), unknown, unknown/1.2:1/100/4–6	Lv et al. (2010)
	commercial ferroboron powder with a composition of Fe–18.4B–0.32C–0.34Si–0.003S–0.02P–0.08Al (wt%)/unknown/unknown, unknown, unknown/computer controlled D-Gun spray system/flat/Fig. 5.33a	Unknown parameters	Shankar et al. (2010)

corresponded to the phase composition of the feedstock. Sometimes, an FeCr₂O₄ spinel-type oxide also appeared in such a coating. The main phases, identified in the coatings by Yang et al. (2001) on the same substrate material, were as follows: molybdenum borides MoB and Mo₂B, and metallic Mo matrix. They differed from the phases of feedstock powders with MoB as a primary phase. The reaction of

Table 5.39 General characterization of selected processes of detonation spraying with boron. Part III

Type of substrate material	Feedstock containing boron (spraying material)/powder feed rate (g/min or rpm)/carrier gas, its pressure (kPa), its flow rate (l/min)/type of the spraying device/shape of the sprayed surface/scheme of the method	Oxygen pressure (kPa), its flow rate (l/min)/inflammable gas, its pressure (kPa), its flow rate (l/min)/buffer gas, its pressure (kPa), its flow rate (l/min)/ratio of oxygen to inflammable gas/distance of gun tip from substrate (mm)/frequency of spraying (Hz)	References
Aluminum alloys	Al powder and B ₄ C powder separately injected into the detonation chamber/0.3–0.5 (rpm)/nitrogen (N ₂), unknown, 10–15/SAT98 detonation spray gun/flat/ Fig. 5.33b	Unknown, 30/propane (C ₃ H ₈), unknown, 3/ unknown, unknown, unknown/10:1/150/3	Tillmann et al. (2014)
Titanium alloys	(Ni or Ni–Cr)–Ni ₃ B–CrB–Al ₃ Ni– α AlB ₁₂ powder/ unknown/unknown, unknown, unknown/Perun-S or Dnepr detonation gun spray/flat/ Fig. 5.33a	Unknown, unknown/ propane-butane (C ₃ H ₈ –C ₄ H ₁₀), unknown, unknown/ unknown, unknown, unknown/unknown/ unknown/unknown (gas mixture also diluted with air)	Aksenov et al. (1991)
Unknown (probably Al- or Ti-alloy)	TiB–TiB ₂ –TiAl–Ti ₂ Al–Ti ₂ O powder prepared from Ti–50Al–25B (wt%) powder/ unknown/compressed air or argon or nitrogen, unknown, unknown/Dnepr-5MA gas detonation gun spray/flat/ Fig. 5.33a	Unknown, unknown/ acetylene (C ₂ H ₂), unknown, unknown/nitrogen (N ₂), unknown, unknown/1.5:1/ unknown/unknown	Oliker et al. (2009)

deboronization between the detonation gases and the MoB powder was the reason for the formation of Mo and Mo₂B phases. The main phases (TiCrB₂ borides and Fe–Cr) of the feedstock remained in the detonation-sprayed coating, produced on the surface of medium-carbon steel (Podchernyaeva et al. 2010). The metal binder was only partially oxidized and an amount of FeCr₂O₄ phase was identified in the coating. The gradient microstructure of the coating was observed after DGS with the use of (AlN–ZrB₂–ZrSi₂)–35NiCr (wt%) powder as a feedstock (Podchernyaeva et al. 2010). The outer zone was composed mainly of ZrB₂ phase and mullites (3Al₂O₃ · 2SiO₂) among Ni–Cr matrix. The next zone contained mullites and Ni–Cr matrix. The part of coating close to the substrate consisted of a mixture of ZrB₂ with Ni–Cr solid solution and mullites. The phase analysis also revealed the presence of AlN, ZrSi₂, SiC and NiCr₂O₄ phases. The detonation spraying of medium carbon steel with Ni–Cr–Si–B alloy powder as a feedstock resulted in the formation of (Fe,Ni)₃B borides among the Ni-based solid solution

(Babul 2011). The detailed phase composition of the detonation-sprayed coatings, fabricated by Kadyrov et al. (1985) as well as by Aksenov et al. (1991), wasn't provided. The binary borides (CrB and MoB) occurred in the ternary matrix phases (Mo_2CoB_2 and MoCoB) after DGS of high-alloy steel (Lv et al. 2010). Although Shankar et al. (2010) didn't analyze the phase composition of the produced coatings, it was obvious that FeB iron borides predominated in the microstructure. Al-based matrix with boron carbide (B_4C) particles were observed in the detonation-sprayed coating onto the surface of Al-alloy (Tillmann et al. 2014). The phase composition of detonation coatings, produced by Olikier et al. (2009) from Ti–Al–B powder, depended on the carrier gas used. The composite coating sprayed with argon consisted of TiB and TiB_2 borides in intermetallic matrix (TiAl and TiAl_3 phases). If nitrogen was used as a carrier gas, the coating contained borides (TiB and TiB_2), nitrides (TiN and AlN) as well as AlTi_2 in a metallic matrix (Al and Ti phases). The use of air as a carrier gas resulted in formation of coating which was composed of TiB and TiB_2 borides, TiAl, Al_3Ti and Ti_2AlN phases as well as of Ti_2O and Al_2TiO_3 oxides.

The very high velocity of the detonation wave was the main advantage of DGS process. This velocity varied between 1000 and 3000 m/s, depending on the composition of the gas mixture, and was several times higher than the speed of sound in these mixtures (Kadyrov and Kadyrov 1995; Fauchais et al. 2014). The produced coatings were also extremely hard, dense, and tightly bonded to the substrate material (Fauchais et al. 2014). They were also characterized by low porosity (below 1 vol%) and high deposition efficiency (around 90%). However, detonation spraying had also disadvantages. The process was the noisiest (more than 145 dBA) of all the thermal spraying processes. The powder flow rates were limited to the range of 1–2 kg/h. The substrate material together with the sprayed coating should be cooled during spraying (Fauchais et al. 2014). The surface of the substrate required the special preparation.

5.3.2.3 Cladding with Boron

Cladding with boron differed from the surface alloying with boron, taking into account the depth of the re-melted surface layer of substrate material. During cladding, the introduced material (usually powder) was re-melted together with only a thin layer of the substrate material. The process resulted in a formation of a pore- and crack-free coating that should be perfectly bonded to the substrate (Vilar 1999). Cladding process limited substrate melting to a minimum depth just to provide a good fusion bonding between the clad coating and the substrate. Therefore, the composition and properties of the coating depended primarily on the cladding material (Riabkina-Fishman and Zahavi 1996).

Sometimes, it was difficult to detect the difference between surface alloying and cladding. In the present work, the basic criteria to qualify the process as surface alloying, or cladding were as follows: phase composition of the layer/coating, especially, the presence or absence of elements from the substrate in the identified

phases as well as the hardness profile, especially, at the interface with substrate material. If the hardness gradually diminished towards the end of the re-melted zone, and its gradient at the interface of re-melted zone and the substrate was relatively small, the process was classified as surface alloying. Whereas the constant hardness through the entire re-melted zone and its sharp decrease at the interface with substrate material was characteristic of clad coating. The thickness of the deposited coatings often obtained up to a few millimeters and was significantly higher compared to the surface alloyed layers. The important factor which helped to distinguish cladding from surface alloying were also the positions of the lines limiting the dimensions of the treated object (substrate material) before and after the process. In case of cladding, the line limiting the dimensions of the substrate before the process was below the line, which limited dimensions after this treatment. Whereas surface alloying was characterized by approximately the same positions of the lines limiting the dimensions of the treated object before and after the process.

Plasma cladding (PC) used a constricted high-energy plasma arc between a non-consumable electrode and the base material as a heat source in order to remelt cladding material with its limited mixing with the substrate. The process became a very interesting alternative for laser cladding because of its simplicity, the possible use of the typical welding devices and their relatively low cost in comparison with lasers. This technique was also called **plasma transferred arc (PTA)** process (Kim et al. 1999a).

The typical equipment, used for PC, corresponded to the plasma arc welding (PAW) equipment and didn't differ from the equipment for plasma surface alloying, mentioned previously. By analogy to PSA process, plasma cladding could be carried out using the two well-described above methods: **remelting** or **fusion** (Kim et al. 1999a, 2001; Gurumoorthy et al. 2007). Like during plasma surface alloying, the two gas streams were used: **plasma gas**, also called **primary gas** (Kim et al. 1999a), and **shielding gas**. Plasma gas flowed surrounding the tungsten electrode and created a column of the plasma arc. Whereas shielding gas was used in order to protect the molten pool and cladding material against oxidation. If plasma cladding was carried out by fusion, cladding material was delivered into the molten pool by a **carrier gas** (Kim et al. 1999a).

Plasma cladding with boron consisted in simultaneous remelting of the cladding material, containing boron, and a thin surface layer of the substrate material. The schematic representations of PC with boron by remelting and fusion were shown in Fig. 5.34 and corresponded to the methods of PSA (Fig. 5.30). The only difference was that the line limiting the dimensions of the substrate before the surface treatment was below the line, which limited dimensions after this treatment (compare Figs. 5.30 and 5.34).

The main operation parameters of plasma cladding with boron by remelting could be similar to those-reported for plasma surface alloying: type of cladding material, i.e. boron source (powder or paste), thickness of the coating with boron source (μm), voltage U (V), current I (A), diameter of tungsten electrode d_{te} (mm), nozzle diameter (tip diameter) corresponding to the diameter of plasma arc column d_p (mm), scanning rate of plasma torch v_p (m/min), overlapping of multiple plasma

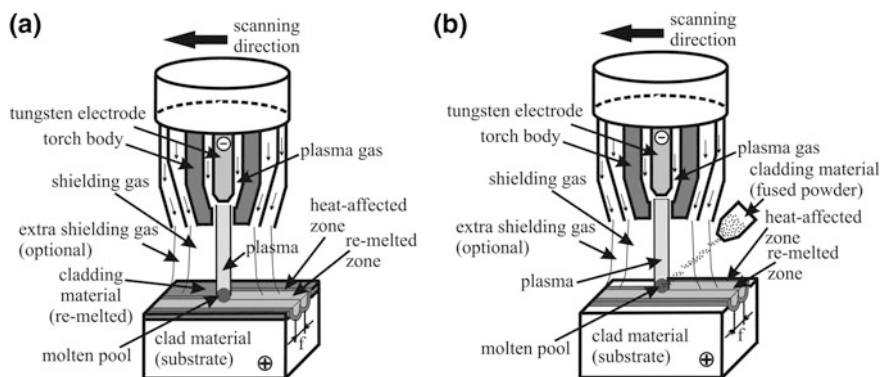


Fig. 5.34 Schematic representation of the techniques of plasma cladding with the formation of multiple laser tracks on a flat surface: remelting (a) and fusion (b); f —distance between axes of adjacent plasma tracks

tracks O (%), type of plasma gas and shielding gas as well as their flow rate Q (l/min). Overlapping could be calculated using the Eq. 5.47 which was shown for plasma surface alloying process. However, it was difficult to find PC with boron by remelting in literature data. At least, PC by fusion was the predominant method of such cladding with boron. Therefore, only this process will be further analyzed.

The parameters of the PC with boron using fusion well corresponded to those-characteristic of remelting process. Instead of the thickness of the coating with boron source, the powder feed rate (g/min) should be only taken into account. The type of an inert carrier gas and its flow rate (l/min) were the additional operating parameters. In the considered works, the powder feed rate ranged from 8 to 90 g/min, and the flow rate of inert gas was in the range of 1.3–5 l/min. The type of carrier gas (Ar) was provided only by Sigolo et al. (2016). Sometimes, the powder feed rate was expressed in rpm, i.e. rotations per minute (Kim et al. 1999a, 2001). It resulted from the use of a special system of powder delivery, which was described previously. Kim et al. (1999a, 2001) also reported the additional parameters of plasma torch movement, such as oscillation speed (cm/s) or oscillation width (mm). However, these parameters weren't explained precisely. As cladding material, the powder mixtures, containing usually a limited content of boron, were applied. Fe–Cr–B or Fe–Cr–Ni–B gas atomized powders, commercially available as Armacor M or C, were used by Kim et al. (1999a, 2001) during PC of low-carbon or low-alloy steel by fusion. These powders were characterized by spherical grains with size in the range of 40–85 or 106–180 μm and contained mainly Fe_α and $\text{Cr}_{1.65}\text{Fe}_{0.35}\text{B}_{0.96}$ (Armacor M) or Fe_γ and Cr_2B (Armacor C) phases. Sigolo et al. (2016) used atomized powders of boron-modified supermartensitic and superduplex stainless steels in order to produce the coating on low-alloy steel. The atomization of powders was carried out under N_2 atmosphere in a close-coupled atomizer. Ni-based powders were often applied during PC of high-alloy steels by fusion. A hardfacing alloy corresponding to AWS NiCr–B was used by Gurumoorthy et al.

(2007) as cladding material. Ni–Cr–Si–B powders were introduced into the molten pool of stainless steel by Sudha et al. (2008) and Liyange et al. (2010) during plasma cladding processes. Da Silva and D'Oliveira (2016, 2017) used the atomized Ni–Cr–Si–B–C powders with increased carbon content. Powders of fer-roalloys (Fe–B, Fe–Ti and Fe–W) with various ratios were used as a cladding material by Teker et al. (2013). In the case of PC using fusion, the substrate materials were often preheated up to 100–300 °C (373–573 K) to avoid cracks' formation.

The general characterization of selected processes of plasma cladding with boron was presented in Tables 5.40 and 5.41, taking into account the main parameters of the process, i.e. boron source, thickness of the paste coating with boron source (for remelting) or powder feed rate with flow rate of carrier gas (for fusion), arc voltage and current, diameter of tungsten electrode, tip (nozzle) diameter, scanning rate of plasma torch, overlapping, type of plasma gas and its flow rate, type of shielding gas and its rate, type of extra shielding gas and its flow rate as well as the type of welding device, shape of the clad surface and scheme of the method in Fig. 5.34. Low-carbon, low-alloy and high-alloy steels (see Tables 5.40 and 5.41) were successfully subjected to PC with boron. The coating with boron was usually produced on the flat surfaces. The type of welding device was often not given. Some processes were carried out with the use of Handy Plasma Depo 200 welding

Table 5.40 General characterization of selected processes of plasma cladding of iron alloys with boron. Part I

Type of substrate material	Boron source (cladding material)/thickness of the coating (μm) or powder feed rate (g/min or rpm) and carrier gas flow rate (l/min)/type of the welding device/shape of the clad surface/scheme of the method	Voltage (V)/Current (A)/diameter of tungsten electrode (mm)/tip diameter (mm)/scanning rate (m/min)/overlapping (%) /plasma gas, its flow rate (l/min)/shielding gas, its flow rate (l/min)	References
Low-carbon steels	Fe–Cr–B gas atomized powder/ 16 (rpm) and 5 (l/min)/Handy Plasma Depo 200 welding device/flat/Fig. 5.34b	Unknown/160/unknown/ unknown/0.08/unknown/ unknown, 1.5/unknown, 25	Kim et al. (1999a)
Low-alloy steels	Fe–Cr–B or Fe–Cr–Ni–B gas atomized powder/15 (rpm) and 4 (l/min)/Handy Plasma Depo 200 welding device/flat/ Fig. 5.34b	Unknown/180/unknown/ unknown/0.08/unknown/ unknown, 1.2/unknown, 25	Kim et al. (2001)
	atomized powders of boron-modified supermartensitic and superduplex stainless steels/8 (g/min) and 1.3 (l/min)/ unknown/flat/Fig. 5.34b	Unknown/100/unknown/ unknown/0.1/40 ^a /Ar, 1.2/Ar, 13.5	Sigolo et al. (2016)

^aMethod of calculation was not given

Table 5.41 General characterization of selected processes of plasma cladding of iron alloys with boron. Part II

Type of substrate material	Boron source (cladding material)/Thickness of the coating (μm) or powder feed rate (g/min or rpm) and carrier gas flow rate (l/min)/type of the welding device/shape of the clad surface/scheme of the method	Voltage (V)/Current (A)/diameter of tungsten electrode (mm)/tip diameter (mm)/scanning rate (m/min)/overlapping (%) /plasma gas, its flow rate (l/min)/shielding gas, its flow rate (l/min)	References
High-alloy steels	AWS NiCr-B powder/30 (g/min) and 3.5 (l/min)/unknown/flat/Fig. 5.34b	unknown/140/unknown/unknown/0.08/unknown/unknown, 4/unknown, 12	Gurumoorthy et al. (2007)
	Ni-Cr-Si-B powder/30 (g/min) and 4 (l/min)/unknown/flat/Fig. 5.34b	24/150/4/unknown/unknown/unknown/unknown, 3/Ar, 12	Sudha et al. (2008)
	Ni-Cr-Si-B powder/25 (g/min)/unknown/flat/Fig. 5.34b	25/140–150/unknown/unknown/0.036/unknown/unknown/Ar, 12	Liyange et al. (2010)
	Fe-B + Fe-Ti + Fe-W powder with various ratios/90 (g/min)/unknown/flat/Fig. 5.34b	Unknown/130/3.2/3.2/0.01/unknown/unknown, 0.8/Ar, 20	Teker et al. (2013)
	Ni-Cr-Si-B-C atomized powder/17 (g/min) and 0.8 (l/min)/PTA Starweld 300 device with Excalibur plasma torch/flat/Fig. 5.34b	Unknown/180/3.2/3.2/0.06/unknown/unknown, 2/Ar, 15	Da Silva and D'Oliveira (2016, 2017)

device from Matsumoto Kikai Co Ltd. (Kim et al. 1999a, 2001). Da Silva and D'Oliveira (2016, 2017) used PTA Starweld 300 device with Excalibur plasma torch. Arc voltage was rarely reported. Based on the available data, the values of voltage ranged from 24 to 25 V. The increase in arc voltage resulted probably in the higher values of arc current. The values of arc current ranged from 100 to 180 A, being significantly higher than those characteristic of plasma surface alloying with boron (28–80 A). Probably, it could be also related to the method of treatment.

The processes of PC with boron were usually carried out by fusion. Whereas remelting was the predominant method of PSA with boron. Although many authors didn't report the diameter of tungsten electrode, the available data indicated its value in the range of 3.2–4 mm. The nozzle (tip) diameter, corresponding to the diameter of plasma arc column, was usually strongly related to the diameter of tungsten electrode. Their values were the same or differed slightly. Scanning rate of plasma torch was usually given and obtained the values from 0.01 to 0.1 m/min. Overlapping was often omitted. The value of 40% was reported only by Sigolo et al. (2016). However, the method of calculation was not given. The types of plasma gas and shielding gas were not always given. However, argon was usually

used as plasma and shielding gas. The flow rate of plasma gas ranged from 0.8 to 4 l/min, and was lower than that of shielding gas (12–25 l/min).

Like for the PSA of iron alloys with boron, the hard precipitates of borides in softer iron-based matrix were also observed after PC with boron by fusion. Cr_2B and $\text{Cr}_{1.65}\text{Fe}_{0.35}\text{B}_{0.96}$ borides in Fe_α -based matrix were identified in re-melted zone of plasma-clad low-carbon steel by fusion with the use of Fe–Cr–B powders (Kim et al. 1999a, 2001). It was possible that $\text{Cr}_{1.65}\text{Fe}_{0.35}\text{B}_{0.96}$ phase corresponded to the complex $(\text{Cr,Fe})_2\text{B}$ borides. Powder of boron-modified supermartensitic stainless steel, introduced into the molten pool of low-alloy steel, resulted in the formation of M_2B borides ($\text{M}=\text{Fe, Cr, Mo}$) among low-carbon martensite in the coating (Sigolo et al. 2016). The similar M_2B phase was identified by Sigolo et al. (2016) in an austenitic or ferritic matrix if the powder of boron-modified superduplex stainless steel was used as a cladding material.

Nickel-based powders with boron were often used during PC by fusion in order to produce the coatings on the surface of high-alloy steels, especially stainless steels. After fusion of AWS NiCr–B powder into the surface of austenitic steel, Cr_7B_3 and Cr_5B_3 chromium borides as well as $(\text{Ni,Fe})_3\text{B}$ complex borides were identified by Gurumoorthy et al. (2007). Together with Cr_7C_3 carbides, these borides occurred in a soft Ni_γ matrix. Sudha et al. (2008) reported the presence of Cr_2B borides and carbides (Cr_3C_2 or Cr_7C_3) in the coating which was deposited on stainless steel during PC by fusion with the use of Ni–Cr–Si–B powder. The similar powder was applied as clad material by Liyange et al. (2010). The microstructure of coating consisted of borides (CrB and Ni_3B), carbides (Cr_3C_2 and Cr_7C_3) and silicides (Ni_3Si) in the soft Ni_γ matrix. Chromium borides (CrB , Cr_5B_3), nickel borides (Ni_4B_3 , Ni_2B , Ni_3B), nickel silicides (Ni_3Si) and carbides (Cr_7C_3) appeared among the soft Ni_γ phase after the fusion of Ni–Cr–Si–B–C powder into the surface of stainless steel (Da Silva and D'Oliveira 2016, 2017). Powders of Fe–B and Fe–Ti ferroalloys, used during PC of stainless steel by fusion, modified the microstructure on the surface this way that iron borides (Fe_2B and Fe_3B) and titanium borides (TiB_2) were identified in Fe_α matrix. If the powder contained additionally Fe–W ferroalloy, tungsten borides WB_2 also appeared in the deposited coating (Tekler et al. 2013).

Laser cladding (LC) used a high-energy laser beam as a heat source in order to remelt cladding material with its limited mixing with the substrate material.

The action of the laser beam and its pressure brought cladding material and the limited thickness of the substrate to melt. The typical equipment, used for PC, corresponded to the laser surface alloying equipment, mentioned previously. Like LSA, PSA and PC processes, laser cladding could be also carried out using the two techniques: **remelting** (Chen et al. 2008a; Masanta et al. 2009) or **fusion** (Majumdar and Li 2010; Hemmati et al. 2013).

Laser cladding with boron consisted in simultaneous remelting of the cladding material, containing boron, and a thin surface layer of the substrate material. The schematic representations of LC with boron by remelting and fusion were shown in Figs. 5.35 and 5.36 for the flat or cylindrical surface of substrate material, respectively. These techniques corresponded to the techniques of LSA (Figs. 5.21

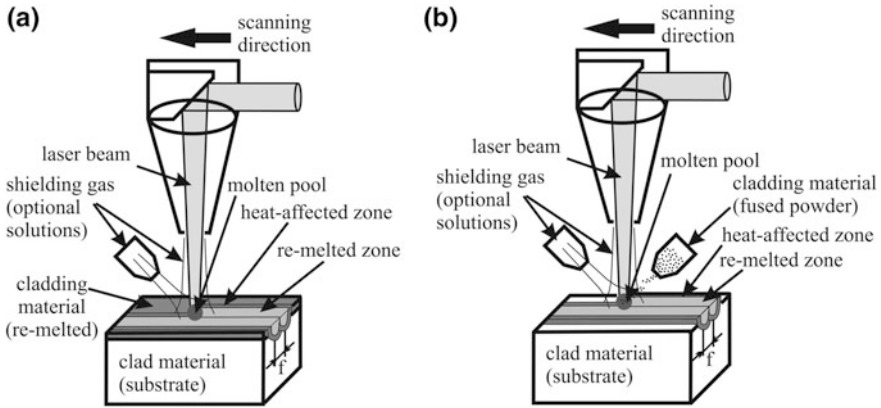


Fig. 5.35 Schematic representation of the techniques of laser cladding with the formation of multiple laser tracks on a flat surface: remelting (a) and fusion (b); f —distance between axes of adjacent plasma tracks

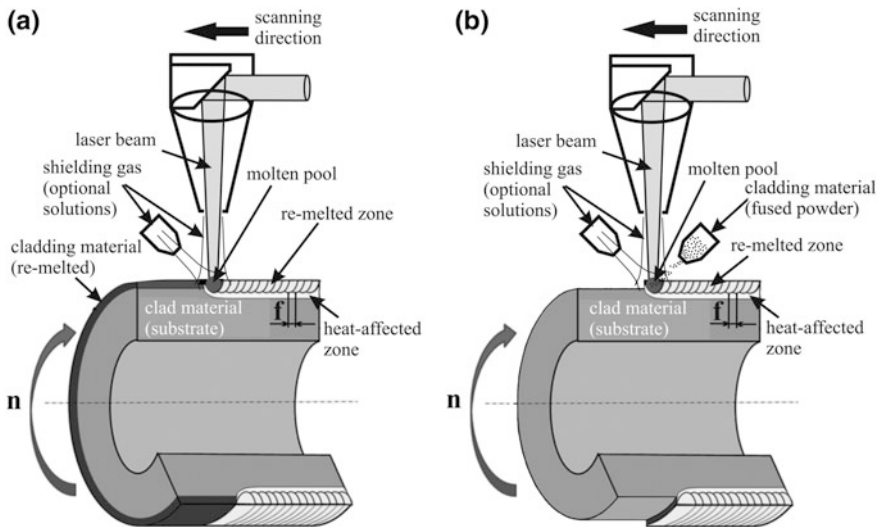


Fig. 5.36 Schematic representation of the techniques of laser cladding with the formation of multiple laser tracks on a cylindrical surface: remelting (a) and fusion (b); f —distance between axes of adjacent plasma tracks

and 5.22). However, the line limiting the dimensions of the treated object before the laser cladding was below the line, which limited dimensions after this treatment (compare Figs. 5.35 and 5.21 or Figs. 5.36 and 5.22). Whereas during laser surface alloying the lines limiting the dimensions of the object before and after process were approximately the same. In general, it was the main difference between LSA and PC processes.

The main operation parameters of LC with boron by remelting corresponded to those reported for laser surface alloying: type of cladding material, i.e. boron source (powder or paste), thickness of the coating with boron source (μm), mode of laser beam, laser beam power P (kW), laser beam diameter d (mm), average irradiance E (kW/cm^2) or power density q (kW/cm^2), scanning rate of laser beam v_l (m/min), overlapping O (%) and type of shielding gas. Average irradiance could be calculated based on the laser beam power and the surface of laser beam, incident on the treated surface. Overlapping could be calculated using the Eq. 5.37 which was formulated for laser surface alloying process.

It was characteristic of laser-clad boride coatings by remelting that the thickness of re-melted zone was usually comparable to the thickness of preplaced coating with cladding material or slightly thinner. Whereas laser surface alloyed layers were characterized by the higher thickness of re-melted zone compared to the thickness of preplaced coatings with alloying material. Sometimes, the coating with cladding material (boron source) was prepared in the form of a paste or suspension. The powder, containing TiO_2 , B_4C and Al, was used by Masanta et al. (2009) during laser cladding by remelting in order to produce the boride coating on the low-carbon steel. This powder mixture was blended in acetone with the help of a magnetic stirrer. An amount of polyurethane-based adhesive was also added. Wu et al. (2015) used the 10Cr–90(Mo + Ni + B) (wt%) powder mixture with the ratio of Mo, Ni and B powder corresponded to that of stoichiometric Mo_2NiB_2 phase. The powder was blended with an organic binder, and then coated onto the Ni layer, thermally sprayed on a low-carbon steel substrate. However, during laser cladding by remelting, the cladding material often consisted of the powders only. The Fe–Cr–Co–Ni–Si–B high entropy alloy powder was obtained by mechanically mixing commercial ferrosilicon powder, ferroboration powder and pure element powders including Fe, Ni, Cr and Co (Shu et al. 2018). Chen et al. (2008a) used Ni–Cr–B–Si powder or its mixture with WC–12Co (wt%) powder as a cladding material. These powder mixtures were preplaced on the surface of low-carbon steel. The titanium alloy was coated directly with B_4C + Ti–8Al–1Mo–1V powder mixture (Wang et al. 2013c). The thickness of the preplaced paste coating or powder coating with cladding material (containing boron) ranged from only 85 up to even 1200 μm .

The main parameters of the laser cladding with boron by fusion corresponded to those characteristic of remelting process. Only instead of the thickness of the coating with boron source, the powder feed rate (g/min), the type of a carrier gas and its flow rate (l/min) were the optional operating parameters. Like in case of PC processes, the powder mixtures, applying as a cladding material, usually contained metallic elements and a limited content of boron. Hemmati et al. (2013) applied Ni–Cr–B–Si–C powder or its mixture with Nb (2–10 wt%) to form the laser-clad boride coating on the low-carbon steel. The mixture of Ni–Cr–B–Si and WC powders was used by Deschuyteneer et al. (2015) during LC of the same substrate by fusion. Makarov et al. (2017) as well as Soboleva et al. (2018) fused Ni–Cr–B–Si powder into the surface of low-carbon steel in order to produce the laser-clad coatings. The powder mixture of titanium and 2 wt% B was used as a feedstock by Majumdar and Li (2010) during laser

cladding of Ti-alloy. The powder feed rate ranged from 0.96 to 25 g/min. Whereas the flow rate of carrier gas was not given in the analyzed works.

The general characterization of selected processes of laser cladding with boron was shown in Tables 5.42 and 5.43, taking into account the main parameters of the process, i.e. boron source (cladding material), thickness of the paste coating with boron source (for remelting) or powder feed rate with flow rate of carrier gas (for fusion), mode of laser beam, laser beam power, laser beam diameter, average irradiance or power density, scanning rate of laser beam, overlapping and type of shielding gas as well as the type of laser, shape of the clad surface and scheme of the method in Figs. 5.35 and 5.36. The process of laser cladding with boron was usually carried out on the flat surface of the substrate material. Low-carbon steel was most commonly subjected to laser cladding with boron. Laser-clad boride coatings were also successfully produced on the flat surface of medium-carbon steel or titanium alloys. The type of laser, used for LC with boron, was not always reported. However, the CO₂ laser was the predominant device (Chen et al. 2008a; Masanta et al. 2009; Wang et al. 2013c; Wu et al. 2015; Makarov et al. 2017; Soboleva et al. 2018). Besides, the Nd:YAG laser (Deschuyteneer et al. 2015), fiber laser (Hemmati et al. 2013) or diode lasers (Majumdar and Li 2010; Deschuyteneer et al. 2015) were also applied. The mode of the laser beam was omitted by authors of the selected works. The laser beam power varied in a wide range of 0.467–2.5 kW or of 0.8–1.6 kW for LC with boron by remelting or by fusion, respectively. It depended on the type of cladding material as well as the substrate material, and was related to the laser beam diameter or spot size of the laser beam. The diameter of a laser beam ranged from 1.5 to 4 mm (Chen et al. 2008a; Wang et al. 2013c; Deschuyteneer et al. 2015; Shu et al. 2018). The rectangular spot of the laser beam was also often used with a size of 6 mm × 1.5 mm (Wu et al. 2015; Makarov et al. 2017; Soboleva et al. 2018) or 3.5 mm × 2 mm (Majumdar and Li 2010). The elliptical shaped laser beam with major axis of 10 mm and minor axis of 2.5 mm was applied by Masanta et al. (2009). The size of the laser beam and its power influenced the average irradiance which varied between 11.94 and 29.89 kW/cm² for laser-clad coatings by remelting. In case of the fusion technique, the average irradiance ranged from 10 to 50.93 kW/cm². The scanning rate during laser cladding with boron by remelting obtained the values in the range of 0.09–0.6 m/min. Whereas the scanning rate during the fusion varied between 0.006 to 1.2 m/min. Overlapping was rarely given, obtaining the values from 17 to 60%. However, the method of calculation was never provided. Argon was predominantly used as a shielding gas.

The process of laser cladding with boron usually provided the composite microstructure, containing the hard metal borides among the soft metallic matrix. Masanta et al. (2009) confirmed the presence of TiB and TiB₂ titanium borides, TiC titanium carbides, TiAl₃ intermetallic phase as well as Ti–B–C phase and Al₂O₃ oxides in laser-clad coating which was produced on the surface of low-carbon steel by remelting. The same technique of LC with boron, carried out on the same substrate using another boron source, resulted in the formation of Mo₂NiB₂ and Fe₃O₄ among (Fe,Ni)_γ solid solution (Wu et al. 2015).

Table 5.42 General characterization of selected processes of laser cladding with boron. Part I

Type of alloyed material	Boron source (cladding material)/ thickness of the coating (μm) or powder feed rate (g/min) and carrier gas flow rate (l/min)/type of the laser/mode of laser beam/shape of clad surface/scheme of the method	Laser beam power (kW)/laser beam diameter (mm)/average irradiance (kW/cm^2)/scanning rate (m/min)/overlapping (%) /shielding gas	References
Low-carbon steels	$\text{TiO}_2 + \text{B}_4\text{C} + \text{Al}$ powder/85/ CO_2 laser/unknown/flat/Fig. 5.35a	2.5/elliptical shaped laser beam (major axis 10 mm; minor axis 2.5 mm)/12.73/0.15–0.6/unknown/unknown	Masanta et al. (2009)
	Ni–Cr–B–Si–C powder or its mixture with Nb (2–10 wt. %)/ unknown/IPG fiber laser/unknown/flat/Fig. 5.35b	0.8–0.9/unknown/unknown/0.3/single tracks or 33° /argon	Hemmati et al. (2013)
	Ni–Cr–B–Si + WC powder/12 or 25 (g/min), unknown/Nd:YAG laser or high-power diode laser (HPDL)/ unknown/flat/Fig. 5.35b	0.7–0.9 (Nd:YAG), 1.5 (HPDL)/1.5 (Nd: YAG), 4 (HPDL)/39.61–50.93 (Nd: YAG), 11.94 (HPDL)/1.2 (Nd: YAG), 1 (HPDL)/unknown/argon	Deschuyteneer et al. (2015)
	10Cr–90(Mo + Ni + B) (wt. %)/ powder/1000/ CO_2 laser/unknown/flat/Fig. 5.35a	2.5/spot size of $6 \text{ mm} \times 1.5 \text{ mm}$ /27.78/0.09/17 $^\circ$ /argon	Wu et al. (2015)
	Ni–Cr–B–Si powder/2.9–4.9 (g/min), unknown/ CO_2 laser/unknown/flat/Fig. 5.35b	1.4–1.6/spot size of $6 \text{ mm} \times 1.5 \text{ mm}$ /15.56–17.78/0.16–0.18/unknown/unknown	Makarov et al. (2017)
	Fe–Cr–Co–Ni–Si–B high entropy alloy powder/100–150/unknown/ unknown/flat/Fig. 5.35a	0.467/2.5/29.89/0.1/30 $^\circ$ /argon	Shu et al. (2018)
	Ni–Cr–B–Si powder/2.9–3.8 (g/min), unknown/ CO_2 laser/unknown/flat/Fig. 5.35b	1.4–1.6/spot size of $6 \text{ mm} \times 1.5 \text{ mm}$ /15.56–17.78/0.16/unknown/unknown	Soboleva et al. (2018)

^aMethod of calculation was not given

Table 5.43 General characterization of selected processes of laser cladding with boron. Part II

Type of alloyed material	Boron source (cladding material)/thickness of the coating (μm) or powder feed rate (g/min) and carrier gas flow rate (l/min)/type of the laser/mode of laser beam/shape of clad surface/scheme of the method	Laser beam power (kW)/laser beam diameter (mm)/average irradiance (kW/cm ²)/scanning rate (m/min)/overlapping (%) /shielding gas	References
Medium-carbon steels	Ni–Cr–B–Si powder or its mixture with WC–12Co (wt.%) powder (mass ratio 7:3)/1100–1200/CO ₂ laser/unknown/flat/Fig. 5.35a	1.6/4/12.73/0.24/unknown/nitrogen	Chen et al. (2008a)
Titanium alloys	Ti–2 wt.% B powder/0.96 (g/min), unknown/Diode laser/unknown/flat/Fig. 5.35b	0.7–0.9/spot size of 3.5 mm $\times$ 2 mm/10–12.86/0.006/unknown/argon	Majumdar and Li (2010)
	B ₄ C + Ti–8Al–1Mo–1V powder (mass ratio 1:39)/800/CO ₂ laser/unknown/flat/Fig. 5.35a	1.5–2/4/11.94–15.92/0.12–0.24/60 ^a /argon	Wang et al. (2013c)

^aMethod of calculation was not given

Chen et al. (2008a) fabricated the laser-clad coating on medium carbon steel by remelting with a phase composition as follows: unspecified metal borides of general formula M_3B , WC and $M_{23}C_6$ carbides and Ni_γ based solid solution. The composite coating, formed on titanium alloy using the same technique, was composed of TiB borides, TiC carbides and Ti_α , titanium martensite (Wang et al. 2013c). In spite of the boron presence in cladding material, the metal borides were not always identified in the coating which was laser-clad by remelting (Shu et al. 2018).

The composite microstructure was also characteristic of laser-clad coatings which were obtained by the fusion technique. Hemmati et al. (2013) revealed the presence of CrB and Cr_5B_3 chromium borides among Ni-based solid solution and Ni–B–Si eutectics in the coating clad on the low-carbon steel. Ni_3B and CrB borides as well as $Ni_{31}Si_{12}$ and Ni_3Fe phases occurred in the Ni_γ matrix after laser cladding of the same substrate with the use of another cladding material (Deschuyteneer et al. 2015). The laser-clad coatings, produced on low-carbon steel using Ni–Cr–B–Si feedstock powder, were composed of CrB borides, $Cr_{23}C_6$ and Cr_7C_3 carbides (depending on the amount of carbon in cladding material) among Ni_γ solid solution and Ni_γ + Ni_3B eutectic mixture (Makarov et al. 2017; Soboleva et al. 2018). The microstructure of the coating, fabricated by fusion on the titanium alloy, consisted of fine dispersed of titanium boride (TiB) in the Ti_α + TiB eutectic mixture (Majumdar and Li 2010).

The main advantages of the plasma or laser cladding with boron were similar to those mentioned for the techniques of surface alloying (LSA, EB-SA of PSA): wide range of thickness of produced coatings (the thickness often significantly exceeded the thickness of the typical diffusion borided layers), shorter duration of the process compared to diffusion boriding, a fine-crystalline microstructure of boride coatings, possibility of coating formation only on the selected surfaces of treated object, precise control of the plasma arc column or laser beam, easy automation, environmental performance of the process as well as relatively low energy and material consumption. The possible cracks or gas pores, greater roughness and waviness of the treated surface should be specified as the main disadvantages of the clad boride coatings. Additionally, the hardness profiles through the coatings were not as advantageous as those obtained by surface alloying because of the sharp decrease of hardness at the interface with substrate material. Although the local heating didn't cause the essential deformations of the treated object, its dimensional changes could be appreciable because of the incremental nature of these techniques. The simplicity and relatively low cost of plasma cladding was its important advantage compared to laser cladding process.

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Chapter 6

Developmental Prospects of Boriding



Abstract All the types of microstructure of surface layers with boron were classified. The boriding techniques, resulting in the formation of these types of microstructure, were specified. The developmental prospects of the boriding process were formulated by indicating the most attractive techniques, taking into account their most important features and possibility of their use for boriding of a wide range of materials.

6.1 Classification of Surface Layers with Boron in Respect of Microstructure

According to the terminology, implemented by Burakowski and Wierchoń (1999), the *surface layers with boron* could be produced with the use of both *non-decremental techniques* and *incremental techniques*. The classification of the surface layers with boron in respect of the types of their microstructure was shown in Fig. 6.1.

The incremental techniques provided the *boride coatings*. Based on the literature data, the two types of boride coatings were produced using various techniques: *composite boride coatings* and *single-phase boride coatings*. The composite boride coatings usually contained the hard metal borides among the soft metallic matrix. Whereas the single-phase boride coating were produced relatively rarely. They were composed of one type of metal borides. The most commonly used boriding techniques which resulted in the formation of boride coatings were as follows:

- *thermal spraying with boron*, including *flame spraying (FS)*, *high-velocity oxy-fuel (HVOF) flame spraying*, *twin wire arc spraying (TWAS)*, *atmospheric plasma spraying (APS)* and *vacuum plasma spraying (VPS)*,
- *detonation gun spraying (DGS) with boron* as a special variation of thermal spraying with the controlled explosion of a mixture of inflammable gas and oxygen,
- *cladding with boron*, including *laser cladding (LC)* and *plasma cladding (PC)*.

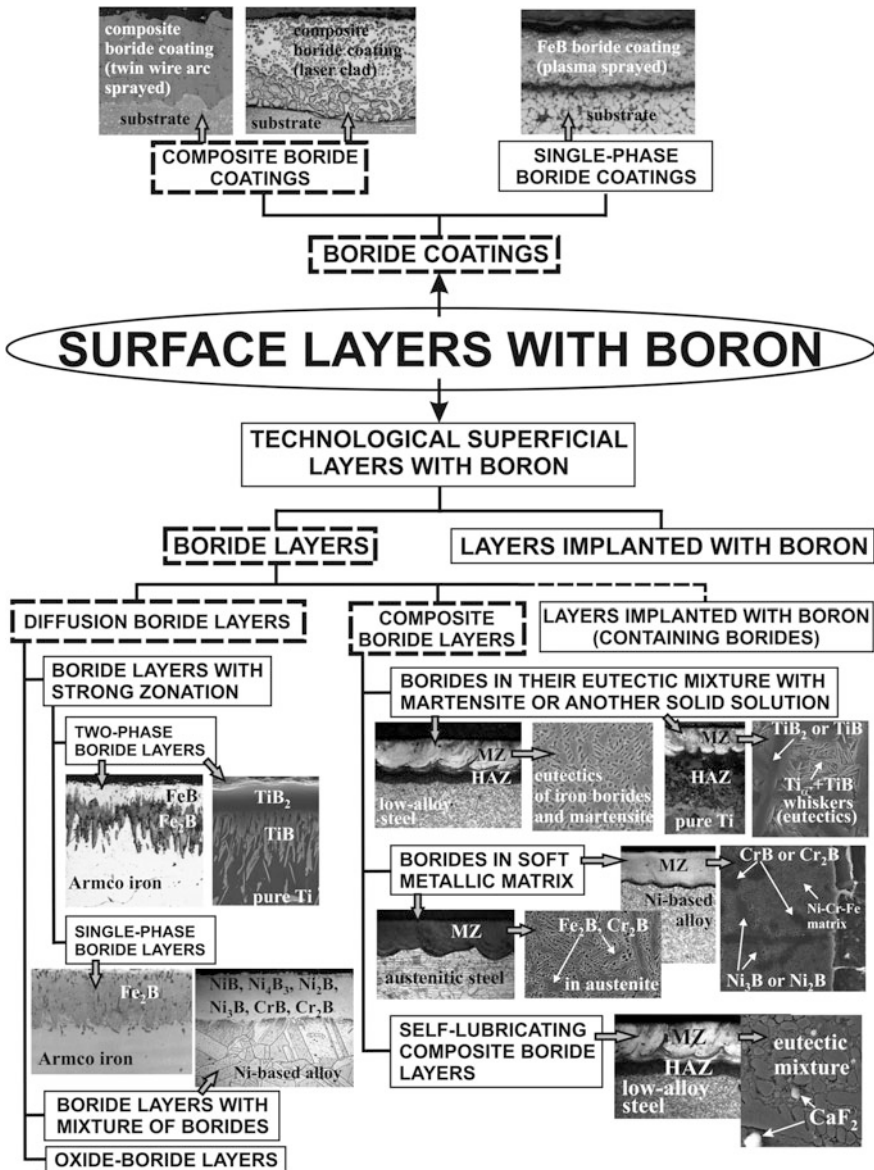


Fig. 6.1 Classification of surface layers with boron in respect of the microstructure. All the examples of microstructure have been unpublished yet

Although the microstructure of boride coatings will be analyzed in detail in the second part of the series, entitled *Current Trends in Boriding: Microstructure*, some examples of composite boride coatings (twin wire arc sprayed and laser clad) as well as single-phase boride coatings (plasma sprayed) were shown in Fig. 6.1 based on Wypych (2012).

The non-decremental techniques of boriding led to the formation of *technological superficial layers with boron*. Among them, the *boride layers* and the *layers implanted with boron* were specified. The *layers implanted with boron* were usually characterized by amorphous microstructure without metal borides. They could be produced using the two techniques:

- *beam line boron ion implantation (BLBII)*,
- *plasma immersion boron ion implantation (PIBII)*.

The three types of *boride layers* could be produced: *diffusion boride layers*, *composite boride layers* and *layers implanted with boron* (containing metal borides).

The *layers implanted with boron* could contain metal borides under certain technological conditions. In general, transformation of amorphous state of the implanted region into a crystalline one required the additional heat treatment such as annealing process (Ballhause and Wolf 1989). Besides, the amorphous borides could be transformed into metastable or stable crystalline borides after exceeding the certain critical ion dose which depended on the temperature (Reuther et al. 1988). Hence, the relatively high ion dose, high beam current density and elevated temperature of the implantation process as well as annealing after ion implantation favored the formation of metal borides. Such conditions were most commonly met during *beam line boron ion implantation (BLBII)*. However, the obtained layers were very thin, and percentage of borides in the microstructure was still small (Shulov 1994; Davis et al. 1998; Soltani-Farshi et al. 1998; Uglov et al. 2002; Kholmetskii et al. 2003).

The *diffusion boride layers* were formed as *boride layers with strong zonation*, *boride layers with a mixture of borides* and more rarely as *oxide-boride layers*. It was characteristic of the boride layers with strong zonation that the individual metal borides occurred in separate zones in a specific order from the surface according to the decreasing boron content. Each zone was composed of other boride, and the zones were separated by a distinct interface. The interface between the separate zones as well as between the last zone and the substrate could be a needle-like (saw-tooth), e.g. for borided pure iron, low- and medium-carbon steels and cobalt alloys, or smooth, e.g. for borided high-carbon and high-alloy steels. Sometimes, the borides took the shape of characteristic whiskers as it was observed for TiB phase in borided titanium and its alloys.

The *two-phase boride layers* and *single-phase boride layers* were known as the most often produced boride layers with characteristic zonation. The two-phase boride layers consisted of the two separate zones with various types of borides. The single-phase boride layers contained only one type of boride. Some examples of two-phase and single-phase boride layers were shown in Fig. 6.1. The two-phase boride layer, produced by gas boriding on Armco iron, was composed of FeB and Fe₂B zones with the interfaces of the needle-like nature (Kulka et al. 2013a). Whereas the plasma paste boriding of pure titanium resulted in the formation of compact TiB₂ zone and a zone with TiB whiskers (Makuch et al. 2017).

The single-phase Fe_2B layer, shown in Fig. 6.1, could be produced by gas boriding and diffusion annealing (Pertek 2001).

All the thermochemical techniques of boriding could result in the formation of two-phase boride layers, that is:

- *powder-pack boriding (P-PB)*,
- *paste boriding (PB)*,
- *boriding in chloride, fluoride or carbonate salt baths using reducers with boron*,
- *boriding in molten borate baths using reducers with boron*,
- *boriding in molten borate baths using reducers without boron*,
- *electrochemical boriding (EB) in molten salt baths*,
- *boriding in fluidized bed (BFB)*,
- *gas boriding (GB) with the use of boron halides*,
- *gas boriding (GB) with the use of boranes*.

The physical techniques which provided the two-phase boride layers were limited to the techniques under glow discharge conditions, that is:

- *plasma gas boriding (PGB)*,
- *plasma paste boriding (PPB)*,
- *cathode plasma electrolytic boriding (PEB)*,
- *spark plasma sintering boriding (SPSB)*,
- *double glow plasma surface alloying (DGPSA) with boron*,

The formation of single-phase boride layers wasn't so easy. Usually, it was possible under certain conditions. In the case of thermochemical techniques, these conditions were as follows:

- *powder-pack boriding (P-PB)* required the use of the boriding agent of special composition and the adequate selection of parameters of boriding or an additional heat treatment after boriding, i.e. diffusion annealing process (DAP),
- *paste boriding (PB)* often resulted in the formation of single-phase boride layers because of the limited boron supply by the atmosphere; probably, the thickness of the paste with boron source and its composition was also important,
- *boriding in chloride, fluoride or carbonate salt baths using reducers with boron* could also provide the single-phase boride layer at a special molten bath composition as well as the adequate selection of process parameters,
- *boriding in molten borate baths using reducers with boron* also required an adequate bath composition and parameters of boriding in order to form single-phase boride layers,
- *boriding in molten borate baths using reducers without boron* usually provided the single-phase boride layer if the SiC was used as a reducer,
- *electrochemical boriding (EB) in molten salt baths* required the adequate selection of boriding parameters and bath composition or the use of additional phase homogenization process in which the borided objects were left in the same molten bath without any polarization for an adequate time,

- ***boriding in fluidized bed (BFB)*** provided the single-phase boride layers with the use of an adequate bed composition as well as at adequate process parameters,
- ***gas boriding (GB) with the use of boron trichloride*** could form the single-phase boride layers only with the use of an additional heat treatment after boriding, i.e. diffusion annealing process (DAP),
- ***gas boriding (GB) with the use of boron trifluoride*** required the use of an adequate solid boriding agent or reducing the activity of boron during the second stage of process,
- ***gas boriding (GB) under reduced pressure with the use of amine triethyl borane complex*** provided the thin single-phase boride layers of unsatisfactory quality, and the reason for the obtained phase composition wasn't studied,
- ***gas boriding (GB) under H_2 atmosphere using the amorphous boron coating*** could also result in the formation of single-phase boride layer; however, the reasons for such a situation wasn't provided.

The general guidelines for producing the single-phase boride layers by the physical methods of boriding under glow discharge conditions were as follows:

- ***plasma gas boriding (PGB)*** required the use of limited content of boron trichloride or diborane in boriding atmosphere; single-phase layers were also formed using trimethyl borate or triethyl borane as a boron source in boriding atmosphere,
- ***plasma paste boriding (PPB)*** didn't provide the single-phase boride layers based on the analyzed literature data; however, it would be probable with the use of limited boron supply by the atmosphere, i.e. the thin paste coating with boron and its adequate composition,
- ***spark plasma sintering boriding (SPSB)*** caused the formation of single-phase boride layer on the pure tungsten or on pure molybdenum.

The formation of single-phase boride layers wasn't reported with the use of ***cathode plasma electrolytic boriding (PEB)*** or ***double glow plasma surface alloying (DGPSA) with boron***. However, it couldn't be ruled out under certain conditions which were unknown. It should be noticed that the single-phase boride layers, especially in the case of iron alloys, could often be produced using the diffusion annealing process (DAP) of two-phase boride layers which were formed by all the thermochemical as well as physical techniques of boriding.

The ***boride layers with strong zonation*** were also fabricated as ***gradient boride layers*** which were characterized by a changeable microstructure towards the substrate (Kulka 2009). They weren't listed as separate layers because of the same needle-like or smooth nature, depending on the carbon concentration or concentration of alloying elements. The occurrence of the transition zone between the boride layer and the substrate material was the only difference. Such layers were produced using the complex processes which consisted in carburizing or carbonitriding of steels followed by gas boriding. Such two-stage processes, called ***borocarburing*** (Kulka and Pertek 2003b) or ***borocarbonitriding*** (Kulka and Pertek 2003c), usually resulted in the

formation of two-phase $\text{FeB} + \text{Fe}_2\text{B}$ layers on the carburized or carbonitrided steel substrate. The simultaneous saturation with boron and other elements, such as carbon, nitrogen or sulfur, was possible using plasma electrolytic processes which also resulted in the formation of gradient boride layers. The ***cathode plasma electrolytic borocarburing (PEB/C)*** of low-carbon steel provided the microstructure, consisting of the three zones (Wang et al. 2013a, b): loose top layer which was easy to remove by polishing, a single-phase Fe_2B boride layer and the transition layer which was composed of cementite (Fe_3C) and ferrite (Fe_α). The similar process, carried out on high-alloy steel (Taheri et al. 2007), resulted in the formation of the two zones: two-phase $\text{FeB} + \text{Fe}_2\text{B}$ zone of more smooth nature and carburized zone of unknown phase composition. The microstructure after ***cathode plasma electrolytic borocarbonitriding (PEB/C/N)*** wasn't studied in detail (Taheri et al. 2007). It was composed of the two-phase $\text{FeB} + \text{Fe}_2\text{B}$ boride zone and borocarbonitrided zone. Whereas ***cathode plasma electrolytic boronitriding (PEB/N)*** provided the two-phase $\text{FeB} + \text{Fe}_2\text{B}$ boride zone close to the surface and nitrided zone of unknown composition below (Taheri et al. 2007).

Boride layers with mixture of borides was usually produced as a consequence of boriding of pure nickel or Ni-based alloys. Based on the analyzed literature data, the boriding techniques which provided such a microstructure of boride layers were as follows:

- ***powder-pack boriding (P-PB)***,
- ***paste boriding (PB)***,
- ***electrochemical boriding (EB)***,
- ***boriding in fluidized bed (BFB)***,
- ***gas boriding (GB)***,
- ***plasma gas boriding (PGB)***,
- ***plasma paste boriding (PPB)***.

Although some authors tried to reveal the characteristic zonation, the produced boride layers were rather composed of the mixture of nickel borides, e.g. in the case of borided pure nickel. The boride layer, formed on Ni-based alloys, contained either the mixture of nickel borides or the mixture of nickel and chromium borides depending on the boriding technique. It was usually difficult to form chromium borides. The powder-pack boriding or electrochemical boriding of Ni-based alloys didn't result in the formation of chromium borides. In the first case, the boron source, exhausting with increasing the time, was a reason for such a situation. Whereas during electrochemical boriding, the relatively short duration of the process avoided producing the chromium borides. They appeared in the borides' mixture without a slightest doubt only after gas boriding in spite of the relatively short duration because of the permanent supplementing the boron source (Makuch et al. 2015). Such a microstructure was shown in Fig. 6.1. Lou et al. (2009) reported the presence of nickel and chromium borides after paste boriding of Ni-based alloy. Probably, the mixture of nickel and chromium borides could also occur in the case

of plasma gas boriding or plasma paste boriding (Frąckowiak et al. 2018) of nickel alloys under certain condition, e.g. using the relatively high temperature and long duration of the process.

Oxide-boride layers were fabricated mainly as a consequence of **anode plasma electrolytic boriding (PEB)** of iron alloys. Such a layer consisted of the two characteristic zones (Kusmanov et al. 2016): top oxide zone (containing iron oxides) and so-called boride-martensite zone, which was composed of FeB and Fe₂B borides, martensite and retained austenite and was located below the oxide zone. The **anode plasma electrolytic borocarburing (PEB/C)** provided the microstructure, consisting of the zones as follows: top oxide zone with Fe₃O₄ phase, FeB boride zone and diffusion zone, which was composed of martensite and retained austenite (Kusmanov et al. 2017). After **anode plasma electrolytic saturation with boron, carbon, nitrogen and sulfur (PEB/C/N/S)**, the top oxide zone was followed by the diffusion zone in which the borides coexisted with martensite and retained austenite (Kusmanov et al. 2015).

The microstructure of **composite boride layers** consisted of hard metal borides in the softer metallic matrix. The three types of **composite boride layers** were distinguished: layers in which **borides in their eutectic mixture with martensite or another solid solution** occurred, layers which were composed of **borides in soft metallic matrix** as well as **self-lubricating composite boride layers**. The basis for such a distinction was microstructure of the re-melted zone (MZ), i.e. alloyed layer of substrate material. All these composite boride layers could be produced using the described techniques of surface alloying with boron:

- **laser surface alloying (LSA) with boron** (laser boriding),
- **electron beam surface alloying (EBSA) with boron** (electron beam boriding),
- **plasma surface alloying (PSA) with boron**.

The microstructure of the MZ was composed of **borides in their eutectic mixture with martensite** under certain conditions. First, the substrate material had to be able to create a martensitic phase. Secondly, the cooling rate of the MZ should be sufficiently high. Such conditions were possible to meet in the case of ferrous alloys as well as titanium and its alloys. Hence, the laser-borided steel was characterized by the re-melted zone, which was composed of eutectic mixture of FeB, Fe₂B and Fe₃B iron borides and martensite (Piasecki et al. 2016). Such a microstructure was shown in Fig. 6.1. The iron richer Fe₃B phase appeared because of the segregation of boron during re-melting. If the steel contained a high carbon concentration, borocementite Fe₃(C,B) could appear in MZ. The re-melted zone revealed a certain zonation. The compact boride zone occurred close to the surface, and the percentage of eutectic mixture of borides and martensite increased towards the substrate. The characteristic stick-like microstructure of titanium borides (TiB and TiB₂) among eutectic mixture of TiB whiskers and Ti_α, titanium martensite (see Fig. 6.1) appeared in MZ of the laser-borided commercially pure titanium (Makuch et al. 2014). It was characteristic of the composite boride layers with eutectics of borides and martensite that the heat-affected zone (HAZ) was clearly distinguished because of the influence of the

quick heating and cooling on the microstructure of substrate material below the MZ. In the case of steels, martensite, bainite, sorbite or even pearlite could occur in the HAZ, depending on the cooling rate in this region (Piasecki et al. 2016). The HAZ of laser-borided titanium or its alloys could contain titanium martensite (Filip et al. 2006; Kulka et al. 2014).

If the diffusion boride layers, produced on steels, were subjected to laser re-melting, the microstructure didn't differ from that obtained using laser surface alloying with boron. The eutectic mixture of FeB, Fe₂B and Fe₃B iron borides with martensite was characteristic of the MZ, and the heat-affected zone was also clearly visible below (Kulka and Pertek 2003a).

In all the cases, mentioned above, the microstructure of the HAZ strongly differed from the substrate material. Hence, such layers could be also classified as **gradient boride layers** (Kulka 2009) which weren't listed as separate layers because of the same composite nature of re-melted zone like in the case of typical laser surface alloying.

The very similar microstructures were detected after electron beam surface alloying (EBSA) with boron. The only difference consisted in the absence of martensitic phases in MZ because of the diminished cooling rate under reduced pressure. Therefore, the microstructure of re-melted zone consisted of **borides in their eutectic mixture with another solid solution**. The MZ of steels usually contained the eutectic mixture of iron borides and Fe_α phase. Bataev et al. (2013) reported the evolution of the microstructure of MZ from the top zone with hypereutectic mixture, through the eutectics until the hypoeutectic mixture of iron borides and Fe_α. EBSA of titanium and its alloys with boron often resulted in formation of primary TiB borides in the eutectic mixture of TiB and Ti_α (or Ti_β) phase (Euh et al. 2001). The use of reduced pressure Although the HAZ has been usually visible below the MZ, its phase composition wasn't studied in detail. Only Euh et al. (2001) reported the presence of titanium martensite (Ti_{α'}) in HAZ after EBSA of titanium alloy with boron.

Plasma surface alloying with boron also didn't provide the martensitic phases in MZ, probably because of the insufficient cooling rate. PSA of steels with boron resulted usually in the formation of iron borides (FeB and Fe₂B) in their eutectic mixture with Fe_α solid solution (Bourithis et al. 2002). The use of the coating with Ti-B nanopowders caused the formation of the MZ with highly dispersed and hard TiB borides in the soft Ti_α-based matrix after PSA of pure titanium with boron (Miklaszewski et al. 2013). Although the presence of eutectic mixture wasn't mentioned, the obtained microstructure was very similar to the eutectics reported after laser surface alloying of pure titanium with boron (Makuch et al. 2014). Therefore, the re-melted zone was probably composed of eutectic mixture of TiB whiskers and Ti_α phase. The HAZ was also clearly visible below the MZ (Miklaszewski et al. 2013). However, its phase composition wasn't analyzed.

Taking into account the absence of martensitic phases after EBSA and PSA of steels and titanium alloys with boron, the produced composite boride layers could be

also classified as **borides in soft metallic matrix**. However, the evident presence of eutectic mixture of borides with a solid solution decided to classify these layers as layers in which the borides occurred in their eutectic mixture. Besides, the hardening of metallic matrix (especially in the case of PSA with boron) would be possible with a proper processing parameters, and the distinction of martensitic phases ($\text{Fe}_{\alpha'}$ or $\text{Ti}_{\alpha'}$) from the Fe_{α} and Ti_{α} solid solutions has been difficult based on XRD.

The **borides in soft metallic matrix** constituted the composite boride layers which were produced without the possibility of hardening the metallic matrix. In this case, the surface layer was usually limited to re-melted zone (MZ) which was surface alloyed with boron. Although the heat-affected zone occurred, its microstructure didn't differ from the substrate material in respect of phase composition. Such a situation was observed in the case of surface alloying of nickel alloys (Kulka et al. 2013b) as well as austenitic steel (Kulka et al. 2016) with boron (see Fig. 6.1). The re-melted zone of laser-alloyed Ni-based alloys with boron consisted of the hard nickel and chromium borides (Ni_3B , Ni_2B , Cr_2B and CrB) among the soft Ni–Cr–Fe matrix, i.e. substitutional solid solution of Cr and Fe in Ni (Kulka et al. 2013b). A certain zonation of the MZ was visible. Close to the surface, the compact boride zone occurred. Whereas the mixture of borides and soft metallic phase (Ni–Cr–Fe) appeared at larger depth, and its percentage increased towards the substrate. The composite boride layer, produced by LSA of austenitic steel with boron, resulted in the formation of the hard ceramic phases, such as Fe_2B , $(\text{FeCr})_2\text{B}$ and $(\text{Fe}, \text{Ni})_2\text{B}$ borides as well as $\text{M}_{23}(\text{B}, \text{C})_6$ boro-carbides among the soft $\text{FeCrNiC}\gamma$ austenitic matrix (Kulka et al. 2016). Irrespective of the cooling rate during laser treatment, the austenitic structure couldn't be hardened. Hence, the austenite occurred in the MZ, and the HAZ and the substrate material didn't differ in microstructure from each other.

The **self-lubricating composite boride layers** were specified as the last type of composite boride layers. They differed from the two other types of composite boride layers only by the presence of the self-lubricating additions, e.g. calcium fluoride CaF_2 (Piasecki et al. 2016; Mikołajczak et al. 2016) or barium fluoride BaF_2 (Piasecki et al. 2017), in the MZ. Such layers were produced using **laser surface alloying (LSA) with boron and self-lubricating addition**. It was possible to form the self-lubricating composite boride layers both with borides in their eutectic mixture (Piasecki et al. 2016, 2017) and with borides in soft austenitic matrix (Mikołajczak et al. 2016). The phase composition of re-melted zone, excluding the presence of self-lubricating additive, was typical of the laser surface alloyed layers with boron (see Fig. 6.1). During laser alloying, the particles of CaF_2 or BaF_2 were partially melted and vaporized, partially melted and re-solidified, and some of them weren't subject to these transformations and stayed in the unchanged shape. The heat-affected zone occurred or not in self-lubricating composite boride layers, depending on the possibility of hardening the substrate material and the obtained cooling rate.

6.2 Indications for the Use of Boriding Techniques

The boriding techniques, described in the present work, provided the two types of surface layers with boron: *boride coatings* and *technological superficial layers with boron* among which the *boride layers* gained exceptional importance (see Fig. 6.1). The selection of the most important boriding techniques in respect of their developmental prospects wasn't easy because of their variety and sometimes because of no data, regarding the essential process parameters. However, among them there were the techniques that were intensively developed in recent years and could indicate clearly the trends in boriding.

The need to produce boride layers of high hardness and high wear resistance at relatively high corrosion resistance was recognized as the main reason for the application of various boriding techniques. As the techniques that set trends in boriding which provided the formation of such boride layers, the following have been selected:

- *powder-pack boriding (P-PB) using commercial powder mixtures based on B4C* because of its simplicity, good processability, reproducibility of the powder composition, repeatability of the effects of boriding, cost effectiveness, good repeatability of the effects of boriding and relatively high quality of the boride layers produced on the surface of various materials,
- *electrochemical boriding (EB) in borate baths* (especially in borax baths) because of the possibility of the use of lower temperature and significantly shorter duration in order to form boride layers on the surface of various materials compared to many other methods, good repeatability of the effects of boriding and relatively high quality of the boride layers,
- *gas boriding (GB) using boron trichloride BCl₃* because of the precise control of boron trichloride supply and, as a consequence, constant chemical composition of the boriding atmosphere which was continuously provided to the borided materials resulting in the relatively short duration of the process, good repeatability of the effects of boriding and relatively high quality of the boride layers, easy automation of the process,
- *gas boriding (GB) using boranes* (diborane, trimethyl borane, triethyl borane) because of the possibility of precise control of boron source supply and obtaining the boriding atmosphere with constant chemical composition as well as because of the very probable possibility of the formation of boride layers on the surface of high-alloy steels and titanium alloys, easy automation of the process,
- *plasma gas boriding (PGB)* because of the reduction of the process temperature and the decreased percentage of toxic gases in the atmosphere compared to the typical gas boriding as well as because of the possibility of the use of sputtering in order to remove the atoms of impurities from the treated surface during the first stage of the process (without boron source supply) and, as a consequence, the possibility of the formation of boride layers on the surface of stainless steels

and titanium alloys which were easily subjected to passivation as well as easy automation of the process,

- **plasma paste boriding (PPB)** because of its simplicity as well as the advantages typical of PGB processes, i.e. diminished process temperature and percentage of toxic gases or the possibility of boriding of stainless steels or titanium alloys, good repeatability of the effects of boriding and relatively high quality of the boride layers,
- **cathode plasma electrolytic boriding (PEB)** because of the short process duration which was comparable to the duration of electrochemical boriding,
- **double glow plasma surface alloying (DGPSA) with boron** as the environmental friendly process,
- **laser surface alloying (LSA) with boron** because of the possibility to produce boride layers in a wide range of thickness (significantly exceeding the thickness of the diffusion boride layers), relatively short duration compared to diffusion processes, obtaining a fine-crystalline microstructure and hardness profile of the more gradual decrease towards the substrate material (alloyed material), local heating and lower risk of thermal deformation, possibility of treating the surfaces of complex shape, possibility of partial treatment of the surface, precise control of the laser beam, elimination of cooling media, repeatability of the effects of boriding and relatively high quality of the composite boride layers, easy automation of the process and its integration into production lines, environmental performance of the process as well as its energy- and material-saving,
- **plasma surface alloying (PSA) with boron** because of its simplicity compared to LSA with boron, precise control of the plasma arc column and the same advantages which were mentioned above for LSA with boron regarding the obtained thickness, process duration, fine-crystalline microstructure, hardness profile, risk of thermal deformation, shape of the treated surface, partial treatment of the surface, cooling media, repeatability of the effects of boriding, quality of the composite boride layers, automation of the process, environmental performance of the process as well as energy or material consumption.

A wide range of the possible borided materials including both iron alloys and non-ferrous alloys was characteristic of all these techniques. It was shown in Table 6.1, where the recommended use of the selected techniques (confirmed by the high quality of boride layers) regarding the selected materials was marked as „ $\sqrt{\sqrt{}}$ ”, the possible use as „ $\sqrt{}$ ”, and the inadvisable use as „–“. A statement has been prepared based only on the analyzed literature data. Hence, the list was probably incomplete because not taking into account some data which could be essential. However, it indicated the main trends in the formation of boride layers in respect of the used techniques and borided materials. Among these methods, gas boriding (GB) using boranes was relatively rarely represented in literature data. The precise control of boron source supply was possible only in the case of the use of diborane. However, if this boron source would be mixed with moist air, it could easily form the explosive mixtures. Whereas applying the trimethyl borane, triethyl borane or borane triethyl amine complex would require the precise control of their addition to

Table 6.1 Possibilities of the boride layers' formation in different materials using the most important boriding techniques

Boriding technique resulted in boride layers' formation	Iron alloys				Non-ferrous alloys					
	Pure iron	Carbon steels	Low-alloy steels	High-alloy steels (including stainless steels)	Cast irons	Cast steels	Titanium and its alloys	Nickel and its alloys	Cobalt and its alloys	Other non-ferrous materials
Powder-pack boriding (P-PB) using commercial powders*	✓	✓✓	✓✓	✓✓	✓✓	✓	✓	✓✓	✓✓	✓✓
Electrochemical boriding (EB) in borate baths	✓✓	✓✓	✓	✓✓	✓	✓	✓✓	✓✓	✓	✓✓
Gas boriding (GB) using boron trichloride BCl ₃	✓✓	✓✓	✓✓	–	✓	✓	–	✓✓	✓	✓
Gas boriding (GB) using boranes	✓	✓✓	✓	✓	✓	✓	✓	✓	✓	✓
Plasma gas boriding (PGB)	✓✓	✓✓	✓✓	✓✓	✓	✓	✓✓	✓✓	✓	✓
Plasma paste boriding (PPB)	✓	✓✓	✓✓	✓✓	✓	✓	✓✓	✓✓	✓	✓
Cathode plasma electrolytic boriding (PEB)	✓	✓✓	✓✓	✓	✓	✓	✓	✓	✓	✓
Double glow plasma surface alloying (DGPSA) with boron	✓	✓	✓✓	✓	✓	✓	✓✓	✓	✓	✓
Laser surface alloying (LSA) with boron	✓	✓✓	✓✓	✓✓	✓✓	✓	✓✓	✓✓	✓	✓
Plasma surface alloying (PSA) with boron	✓	✓✓	✓	✓	✓	✓	✓✓	✓	✓	✓

✓✓ recommended use; ✓ possible use; – inadvisable use; * EKABOR®I, EKABOR®II, EKABOR®III, EKABOR®HM, EKABOR®Ni, DURBORID®G

✓✓ recommended use; ✓ possible use; – inadvisable use; * EKABOR[®] I, EKABOR[®] II, EKABOR[®] III, EKABOR[®] HM, EKABOR[®] Ni, DURBORID[®] G

boriding atmosphere based on the relationship between their vapor pressure and evaporation temperature. However, this technique seemed to be very interesting because of the possible formation of boride layers on austenitic steels or titanium alloys, i.e. materials which were easy subjected to passivation. Although cathode plasma electrolytic boriding (PEB) and double glow plasma surface alloying (DGPSA) with boron were also relatively rarely applied, these techniques were classified as important because of the short duration and environmental performance, respectively.

The other techniques were recognized as the less developmental in the formation of wear and corrosion resistant boride layers, e.g.:

- ***powder-pack boriding (P-PB) using amorphous boron as a boron source*** because of the reduced effectiveness of the process as a consequence of the formation of compounds of B with oxygen or nitrogen,
- ***powder-pack boriding (P-PB) using ferroboration as a boron source*** because of the relatively long duration of the process and worsening the layer quality as a consequence of contamination of the powder by silicon and aluminum,
- ***powder-pack boriding (P-PB) using metalothermic technique*** because of the difficult control of the exothermic reaction of boron oxide with aluminum and the limited repeatability of the process,
- ***powder-pack boriding (P-PB) in electrically conductive powder*** because of the difficulties in the control of temperature which had to be below the melting point of the substrate material,
- ***paste boriding (PB)*** because of the difficulties in the control of the paste thickness and need to use a special and complicated procedure of coating with this paste as well as a need to use protective atmosphere,
- ***boriding in chloride, fluoride or carbonate molten salt baths using reducers with boron*** because of the special and complicated procedure of salt bath preparation, the tendency to separation of the bath components which were characterized by significantly different densities as well as a need to supplement the bath with spent reducing agents,
- ***boriding in molten borate baths using reducers with or without boron*** because of the similar reasons as were mentioned for the previous boriding process,
- ***boriding in hydrous electrolytes*** because of no representation of this technique in literature data in recent years,
- ***boriding in fluidized bed (BFB)*** because of the difficulties in control the gas velocity which should be higher than the critical velocity of fluidization and problems with repeatability of the produced layers,
- ***gas boriding (GB) under reduced pressure with the use of amine triethyl borane complex*** because of the unsatisfactory quality of the boride layers,
- ***gas boriding (GB) under H_2 atmosphere using the amorphous boron coating*** because of the humble representation of this technique in literature data,
- ***anode plasma electrolytic boriding (PEB)*** because of the formation of the oxides on the top surface of layer,

- **spark plasma sintering boriding (SPSB)** because of the difficulties in cleaning the treated objects after the process,
- **electron beam surface alloying (EBSA) with boron** because of the relatively high cost of devices and the limited dimensions of the treated objects during the treatment under reduced pressure.

Among the boriding techniques which resulted in the formation of the technological superficial layers with boron, the **beam line boron ion implantation (BLBII)** and **plasma immersion boron ion implantation (PIBII)** should be mentioned. They provided the **layers implanted with boron**. Their main application consisted in the doping of silicon with boron in order to fabricate semiconductor devices or solar cells. The use of these techniques to produce the boride layers (containing borides) was marginal and didn't result in the acceptable quality of such layers.

The **boride coatings** were usually produced in order to improve the hardness, and wear resistance of the coated materials with acceptable corrosion resistance. As the techniques that set trends in boriding which provided the formation of such boride coatings, the following have been selected:

- **high-velocity oxy-fuel (HVOF) flame spraying with boron** because of the very high-velocity gas streams, thanks to a convergent–divergent nozzle following the combustion chamber as well as the relatively low porosity and good adhesion of boride coatings,
- **plasma spraying (PS) with boron** because of a relatively low content of oxides even after **atmospheric plasma spraying (APS)**, the sufficient protection against oxidation during **vacuum plasma spraying (VPS)** and **inert atmosphere plasma spraying (IAPS)**, the possibility to remove the oxides from the substrate material by a plasma transferred arc etching the surface of the substrate prior to coating deposition (in the case of VPS) as well as low porosity and good adhesion of boride coatings,
- **detonation gun spraying (DGS) with boron** because of the very high velocity of the detonation wave and formation of extremely hard and dense boride coatings which were tightly bonded to the substrate material and were characterized by a low porosity,
- **laser cladding (LC) with boron** because of the similar advantages which were listed in the case of laser surface alloying (LSA) with boron,
- **plasma cladding (PC) with boron** because of the similar advantages which were listed in the case of plasma surface alloying (PSA) with boron.

In general, the boride coatings could be fabricated (under certain conditions) on all the alloys including both iron alloys and non-ferrous alloys. It was shown in Table 6.2, where the recommended use of the selected techniques (confirmed by the high quality of boride coatings) regarding the selected materials was marked as „√√” and the possible use as „√”.

Table 6.2 Possibilities of the boride coatings' formation in different materials using the most important boriding techniques

Boriding technique resulted in boride coatings' formation	Iron alloys			Non-ferrous alloys						Other non-ferrous materials
	Pure iron	Carbon steels	Low-alloy steels	High-alloy steels (including stainless steels)	Fe-based super alloys	Titanium and its alloys	Nickel and its alloys	Aluminum and its alloys	Copper and its alloys	
High-velocity oxy-fuel (HVOF) flame spraying with boron	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Plasma spraying (PS) with boron	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Detonation gun spraying (DGS) with boron	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Laser cladding (LC) with boron	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Plasma cladding (PC) with boron	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

✓ recommended use; ✓ possible use

Although the other techniques of boride coatings' formation (e.g. *flame spraying* or *wire arc spraying with boron*) were characterized by some advantages, they were recognized as less prospective, mainly because of the limited number of publications in recent years.

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Curriculum Vitae



Michal Kulka, Ph.D. D.Sc.,
Associate Professor
Poznan University of Technology
Institute of Materials Science and Engineering
Division of Metal Science and Surface Engineering
pl. M. Skłodowskiej-Curie 5
60-965 Poznan, Poland
e-mail: michal.kulka@put.poznan.pl

Education

Sep 2010–Sep 2010 **Lodz University of Technology**
Ph.D. D.Sc., Materials science and engineering
Lodz, Poland

- Aug 1993–Aug 1993* **Poznan University of Technology**
Ph.D., Construction and use of machines
Poznań, Poland
- Oct 1980–Jun 1985* **Poznan University of Technology**
M.Sc.Eng., Mechanics
Poznań, Poland

Research Experience

- Oct 2012–present* **Professor (Associate), Head of Division of Metal Science and Surface Engineering**
Poznan University of Technology, Institute of Materials Science and Engineering, Poznan, Poland
- Jan 2008–Sep 2012* **Assistant Professor**
Poznan University of Technology, Institute of Materials Science and Engineering, Poznan, Poland
- Oct 1997–Dec 2007* **Assistant Professor**
Poznan University of Technology, Institute of Materials Science and Engineering, Poznan, Poland
- Feb 1994–Sep 1997* **Assistant Professor**
Poznan University of Technology, Institute of Mechanical Engineering and Technology, Poznan, Poland
- Dec 1984–Feb 1994* **Research Assistant**
Poznan University of Technology, Institute of Mechanical Engineering and Technology, Poznan, Poland
- Jul 1984–Dec 1984* **Technical worker**
Poznan University of Technology, Institute of Mechanical Engineering and Technology, Poznan, Poland

Awards & Grants

- Mar 2018* Award: Certificate of Outstanding Contribution in Reviewing (Thin Solid Films)
- Dec 2017* Award: Certificate of Outstanding Contribution in Reviewing (Surface and Coatings Technology)
- Nov 2017* Award: Certificate of Outstanding Contribution in Reviewing (Materials Science and Engineering A)
- Nov 2017* Award: Certificate of Outstanding Contribution in Reviewing (Optics and Lasers in Engineering)
- Aug 2017* Grant: Nanomechanical properties of laser-modified iron nitrides produced on medium-carbon steel by gas nitriding
- May 2017* Award: Certificate of Outstanding Contribution in Reviewing (Optics and Laser Technology)
- Mar 2017* Grant: Mechanism of wear and tribofilm formation on the nickel-based sintered materials with self-lubricating addition

- Feb 2017* Award: Certificate of Outstanding Contribution in Reviewing (Tribology International)
- Dec 2016* Award: Certificate of Outstanding Contribution in Reviewing (Applied Surface Science)
- Oct 2016* Award: Certificate of Outstanding Contribution in Reviewing (Vacuum)
- Nov 2015* Award: Certificate of Outstanding Contribution in Reviewing (Surface and Coatings Technology)
- Jul 2015* Award: Certificate of Outstanding Contribution in Reviewing (Optics and Lasers in Engineering)
- May 2015* Award: Certificate of Outstanding Contribution in Reviewing (Optics and Laser Technology)
- Jun 2014* Award: Certificate of Excellence in Reviewing (Optics and Laser Technology 2013)
- Jul 2013* Grant: Microstructure and properties of boride layer formed on Nimonic 80A alloy
- Oct 2009* Grant: Application characteristics of gradient iron borides layers formed by borocarburing and laser surface modification
- Oct 2001* Grant: The effect of phase and chemical composition on the performance of complex borocarbured and borocarbonitrided layers produced on chromium-nickel steels
- Oct 1997* Grant: The structure and the properties of the borided layers produced on the substrate of different carbon content
- Oct 1996* Grant: Research of stress state and performance of carburized and carbonitrided layers produced in low- and high-carbon structural steels
- Oct 1992* Grant: Study of equilibrium systems Fe-X-N

Scientific Memberships

- member of Polish Materials Science Society
- member of the Metal Science Section of the Committee of Metallurgy of Polish Academy of Sciences
- member of the Committee on Materials Science of Polish Academy of Sciences, Office in Poznan

Most important publications

Books

M. Kulka: The gradient boride layers formed by borocarburing and laser surface modification. In: Kulka M (ed), 03/2009, Publishing House of Poznan University of Technology. ISBN: ISSN-0551-6528

Book Chapters

Frackowiak M, Makuch N, Dziarski P, Kulka M, Taktak S (2018) Fracture toughness of plasma paste-borided layers produced on nickel-based alloys. In: *Advances in Manufacturing, Part of the Lecture Notes in Mechanical Engineering book series*, 01/2018, pp 923–932, ISBN: 978-3-319-68618-9. https://doi.org/10.1007/978-3-319-68619-6_89

Journal Publications

Keddam M, Kulka M, Makuch N (2018) Modelling of the growth kinetics of boride layers during the diffusion annealing process. *Phys Met Metallogr* 119(10):927–935, 10/2018. <https://doi.org/10.1134/S0031918X1810006X>

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Paczkowska M, Makuch N, Kulka M (2018) The influence of various cooling rates during laser alloying on nodular iron surface layer. *Opt Laser Technol* 102:60–67, 06/2018. <https://doi.org/10.1016/j.optlastec.2017.12.027>

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Mikołajczak D, Kulka M, Makuch N, Dziarski P (2017) Laser alloying of 316L steel with boron and nickel. *J Achievements Mater Manuf Eng* 1(84):32–40, 09/2017. <https://doi.org/10.5604/01.3001.0010.7567>

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according to Scopus

Index

A

- Aluminothermic technique of boriding, 19
- Anode plasma electrolytic boriding, 116–118, 122, 126, 261, 267
- Anode plasma electrolytic borocarburing, 119, 122, 126, 261
- Anode plasma electrolytic saturation, 127
- Anode plasma electrolytic saturation with boron, carbon, nitrogen and sulfur, 119–121, 123, 126, 261
- Atmospheric plasma spraying with boron, 212–216, 255, 268

B

- Beam line boron ion implantation, 134, 138–141, 257, 268
- Boriding in chloride, fluoride or carbonate molten salt baths using reducers with boron, 36–39, 258, 267
- Boriding in chloride, fluoride or carbonate salt baths using reducers with boron, 258
- Boriding in fluidized bed, 58–63, 258–260, 267
- Boriding in gaseous media, 17, 64
- Boriding in hydrous electrolytes, 63, 267
- Boriding in liquid media, 17, 35, 48
- Boriding in molten borate baths using reducers with boron, 40–43, 258, 267
- Boriding in molten borate baths using reducers without boron, 44–48, 258, 267
- Boriding in solid media, 17, 33
- Boriding under glow discharge conditions, 2, 99

C

- Cathode plasma electrolytic boriding, 116, 118, 121, 126, 127, 258, 259, 265, 266
- Cathode plasma electrolytic borocarbonitriding, 119–122, 126, 127, 260
- Cathode plasma electrolytic borocarburing, 119–122, 125–127, 260
- Cathode plasma electrolytic boronitriding, 119–122, 260
- Cathode plasma electrolytic saturation, 127
- Cathode plasma electrolytic boriding, 117

D

- Detonation gun spraying spraying with boron, 219
- Detonation gun spraying with boron, 222–226, 255, 268, 269
- Double glow plasma boriding, 132, 133
- Double glow plasma surface alloying with boron, 131–133, 258, 259, 265, 266

E

- Electrochemical boriding, 2, 44, 48–57, 258, 260, 264, 266
- Electrochemical boriding in molten salt baths, 48, 51, 53, 54, 258
- Electron beam boriding, 178, 180, 261
- Electron beam surface alloying with boron, 173, 178–187, 192, 261, 262, 268

F

- Flame spraying with boron, 197, 198, 218, 255, 270

G

- Gas boriding, 2, 64–67, 69–76, 78–81, 109, 257, 259, 260
- Gas boriding under reduced pressure, 64, 79, 81, 259, 267
- Gas boriding using boron coating, 81, 259, 267
- Gas boriding using boron trichloride, 64–70, 72, 73, 81, 259, 264, 266
- Gas boriding using boron trifluoride, 71, 75–78, 259
- Gas boriding using diborane, 78, 79
- Gas boriding with the use of boranes, 17, 64, 78, 258, 264, 266
- Gas boriding with the use of boron coating, 64
- Gas boriding with the use of boron halides, 17, 64, 258

H

- HVOF flame spraying with boron, 199–207, 218, 255, 268, 269

L

- Laser boriding, 151, 167, 169, 170, 261
- Laser cladding with boron, 232, 234, 235, 237, 238, 255, 268, 269
- Laser surface alloying with boron, 2, 99, 149, 151, 161–169, 171, 188, 192, 261–263, 265, 266

P

- Paste boriding, 17, 30, 32–35, 258, 260, 267
- Plasma cladding with boron, 228–232, 255, 268, 269
- Plasma electrolytic boriding, 116–118, 121, 125, 126, 258, 259, 261, 265
- Plasma electrolytic borocarbonitriding, 119–122, 126, 260

- Plasma electrolytic borocarburing, 119, 120, 122, 125, 126, 260, 261
- Plasma electrolytic boronitriding, 119, 120, 260
- Plasma electrolytic saturation, 116, 119, 120, 122–124, 126, 127
- Plasma electrolytic saturation with boron, carbon, nitrogen and sulfur, 119–121, 261
- Plasma gas boriding, 99–101, 103–110, 114, 258–260, 264, 266
- Plasma immersion boron ion implantation, 143–147, 257, 268
- Plasma paste boriding, 99, 110–114, 257–260, 265, 266
- Plasma spraying with boron, 212, 218, 255, 268, 269
- Plasma surface alloying with boron, 99, 187, 188, 190–193, 231, 261, 262, 265, 266
- Powder-pack boriding, 2, 17, 19–21, 23–31, 33, 258, 260, 264, 266, 267
- Powder-pack boriding in electrically conductive boriding agent, 23
- Pulsed bipolar nanocrystalline plasma electrolytic borocarburing, 119, 121

S

- Spark plasma sintering boriding, 127–131, 258, 259, 268

V

- Vacuum plasma spraying with boron, 212, 213, 216, 255, 268

W

- Wire arc spraying with boron, 208–211, 218, 255, 270