

# PACK AND SALT BATH DIFFUSION TREATMENTS ON STEELS

*Traditional, mature pack and immersion diffusion treatments provide the ability to produce high-performance wear and corrosion resistant coatings using relatively simple, low-cost processes.*

**L.C. Casteletti,  
F.A.P. Fernandes,  
and S.C. Heck**

São Carlos School of Engineering,  
EESC-USP, São Carlos, SP, Brazil

**C.K.N. de Oliveira**

Universidade Regional do Cariri, Crato,  
CE, Brazil

**A. Lombardi-Neto**

AEROALCOOL, Franca, SP, Brazil

and

**G.E. Totten\*, FASM**

Portland State University, Portland, Oreg.

\*Member of ASM International and member,  
ASM Heat Treating Society

**D**iffusion coatings obtained using a pack diffusion process or by immersion in molten salt baths are relatively simple and low cost processes that produce high performance wear and/or corrosion resistant layers. The coatings are formed by diffusion of metals or nonmetals into a substrate at elevated temperatures. Coating processes using molten salt baths are used to produce carbides or boride coatings, depending on bath composition. The diffusion elements modify the surface chemical composition and produce new phase transformations. Although they are relatively old techniques, they remain under-used given their potential benefits<sup>[1]</sup>.

## TRD Treatment

Thermo-reactive deposition and diffusion (TRD) treatment is a process by which a carbide-former element is deposited onto the surface of a substrate containing carbon to produce carbide layers of that element<sup>[1,2]</sup>. The characteristics of these layers are high hardness and wear resistance, low coefficient of friction, good oxidation and corrosion resistance, and a metallurgical bond with the metal substrate, making the process very effective for obtaining a product with excellent tribological properties<sup>[1,3]</sup>.

The layers produced by TRD treatment are used for the same industrial applications as TiC, TiN, and TiCN coatings obtained using CVD (chemical vapor deposition) and PVD (physical vapor deposition) methods, with the advantage of being a simpler, less costly processes. TRD coatings can be produced in heat treatment furnaces, using crucibles or metal boxes, and in air, without requiring special atmospheres<sup>[4,5]</sup>.

The most frequent applications for carbide coatings are in matrix for metal stamping, for hot and cold forging operations, in wire and tube drawing, for aluminum pressure casting, in cutting tools for metals and nonmetals, and

for precision parts for the textile industry<sup>[3]</sup>.

The VC and NbC coatings provide the best wear performance of the TRD coatings tested in this work. Wang showed that a VC layer exhibited wear resistance between 9 and 30 times greater than that of a hardened steel<sup>[6]</sup>. Another great advantage of this coating is that TRD processed tools can be reprocessed to reconstruct the layer at a later time. Arai and Harper reported that some tools were re-treated up to eight times<sup>[1]</sup>.

TRD treatments performed in borax baths with the addition of carbide-former elements (CFEs) are referred to as the TD (Toyota Diffusion) process. In this process, a carbon-containing substrate is immersed into a borax bath containing V, Nb, or Cr to obtain layers of VC, NBC, Cr<sub>7</sub>C<sub>3</sub> and Cr<sub>23</sub>C<sub>6</sub><sup>[1]</sup>. Steels subjected to such treatment must possess a carbon content exceeding 0.3% (by weight). The layer is formed by the chemical reaction of the carbon in the substrate with the CFE dissolved in the bath<sup>[7]</sup>.

If any of the dissolved elements have relatively low carbide and oxide free energies of formation, the B<sub>2</sub>O<sub>3</sub> reduction reaction can occur with a subsequent release of the boron atoms, thus enabling the formation of borides and carbides<sup>[4]</sup>. CFEs are introduced into the bath as ferroalloy or oxide, together with the required addition of a reducing agent such as aluminum or B<sub>4</sub>C<sup>[1,8]</sup>.

## Boriding

Boriding is a surface treatment that produces layers consisting of borides of the elements in the substrate. During treatment, the boron atoms diffuse into the substrate and react with the metal base, forming the boride layer. This process can be used in a variety of materials (both ferrous and nonferrous), and are used to produce surface layers with high hardness, high wear resistance and low coefficient of friction. The combination of high hardness with

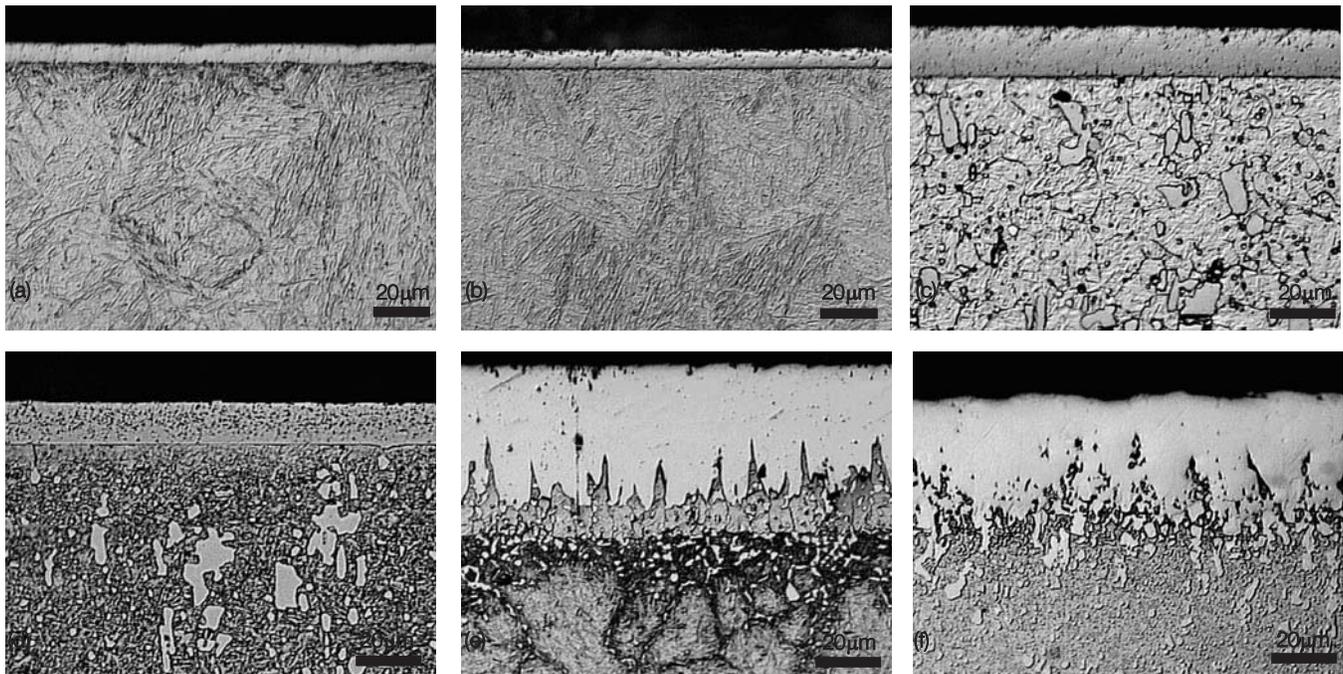


Fig. 1 — Optical micrograph of cross sections of TRD treated samples: (a) NbC layer on H13 steel, (b) VC layer on H13 steel, (c) NbC layer on D2 steel, (d) VC layer on D2 steel, (e) boride layer on H13 steel, and (f) boride layer on D2 steel.

Table 1 — Conditions for salt bath immersion treatment

Steel	Coating	Bath composition	Temperature, °C	Time, h
H13 and D2	NbC	16% Fe-Nb, 3% Al, Borax (bal.)	1000	4
H13 and D2	VC	10% Fe-V, 3% Al, Borax (bal.)	1000	4
H13 and D2	Borides	10% Al + Borax (bal.)	1000	4

Table 2 — Conditions for pack diffusion treatments

Steel	Coating	Powder composition	Temperature, °C	Time, h
1060	Chromium	25% Cr, 69% Al <sub>2</sub> O <sub>3</sub> , 6% NH <sub>4</sub> Cl	1000	9
1060	Borides	82% B <sub>4</sub> C, 15% Borax, 3% NH <sub>4</sub> Cl	1000	4

low friction coefficient prevents the main wear mechanisms<sup>[9]</sup>.

The thermochemical boriding process in a salt bath uses a boriding medium containing a source of boron (e.g., Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, KBF<sub>4</sub> or K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) and a reducing agent (mainly B<sub>4</sub>C, SiC, Fe-Al, or Al). The thermochemical reduction reaction that occurs in the boriding mixture releases elemental boron, which diffuses into the substrate. The boron atoms react with the metal base, forming the boride layer<sup>[9-12]</sup>.

Due to their relatively small size and high mobility, the boron atoms can diffuse easily in ferrous alloys to form the FeB and Fe<sub>2</sub>B compounds<sup>[11, 13]</sup>. The formation process of the boride layer is controlled by the diffusion of boron through the lattice of the substrate. The growth rate and chemical composition of the layer are determined by the concentration of elemental boron in the

bath (boriding potential), the treatment temperature, and chemical composition of the substrate<sup>[10, 12]</sup>.

The phases that are formed are dependent on the chemical composition of the substrate. In steel, the layers are composed predominantly of Fe<sub>2</sub>B and FeB, as well as borides of the substrate alloys such as Cr, V, Mo and Ni<sup>[9, 14]</sup>. Borided layers may be constituted by a single Fe<sub>2</sub>B phase or a double FeB + Fe<sub>2</sub>B phase<sup>[15, 16]</sup>. In tribological applications, a boride layer consisting of the single stage Fe<sub>2</sub>B is usually more desirable, since the FeB phase, rich in boron, is more fragile<sup>[14]</sup>. The fracture toughness of the Fe<sub>2</sub>B phase is approximately four times greater than the FeB phase<sup>[12]</sup>.

#### Pack Cementation Process

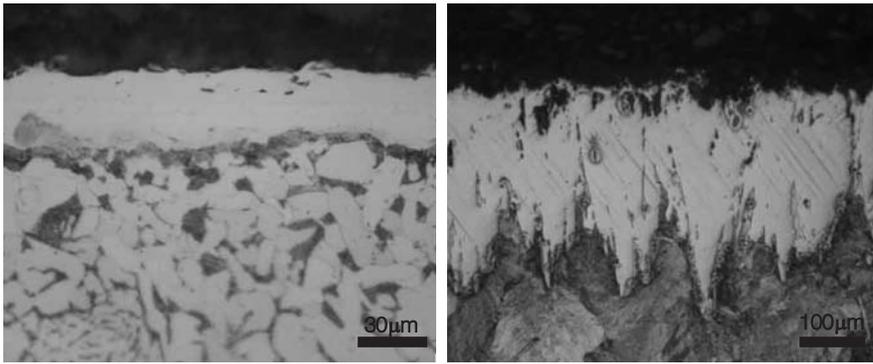
The pack-cementation process originally involved pack carburizing,

which is the process of diffusing carbon into the surface of iron or low-carbon steel by heating in a closed container filled with activated charcoal. This process has given rise to other pack-diffusion processes including aluminizing, siliconizing, chromizing, and boronizing<sup>[17]</sup>. In the process, parts to be pack coated are placed in a retort with a mixture of metal powder of the coating material, a ceramic powder filler (usually aluminum oxide) to prevent sintering of the mix during high temperature processing, and a volatile-halide activator (usually an ammonium halide) to serve as a chemical transfer medium for the metal, and brought up to the coating temperature. The salt vaporizes and combines with the coating material to generate the transporting vapor species. When the temperature is sufficiently high, the coating material reacts with the salt forming a metallic halide vapor, which contacts the surface of the parts to form the coating<sup>[18, 19]</sup>. Both pack diffusion and salt bath processes create strong metallurgical bonds between the substrate and the diffusion layer.

#### Materials and Methods

Following are examples of the production of wear and corrosion resistant coatings on different steels by various diffusion processes obtained in this work.

Samples of AISI H13, D2, and 1060 steels were cut and ground using 600 mesh sandpaper prior to diffusion treatment. The molten borax immer-



**Fig. 2 — Optical micrograph of cross sections of pack diffusion treated samples: (a) chromium compound layer on 1060 steel, (b) boride layer on 1060 steel.**

sion treatments were conducted using samples of the H13 and D2 steels to obtain carbide and boride layers. Pack diffusion treatments were performed on AISI 1060 steel to obtain boride and chromium carbide-nitride compound layers<sup>[17]</sup>. Compositions and treatment conditions of each of the diffusion media used are listed in Tables 1 and 2. To produce the TRD coatings, borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) was melted, and the carbide former element and/or metallic aluminum was added.

Analysis by optical microscopy was performed using a Zeiss microscope with the interference contrast technique after etching the AISI 1060 samples with 1% nital and H13 and D2 samples with 10% nital.

Wear tests were performed using a micro-wear machine with fixed ball configuration without the use of an abrasive. The diameter of the ball was 25.4 mm, with rotation of 148 rpm and load of 18.7 N. Consecutive test times of 5, 10, 15, and 20 min were used to obtain wear scars and the volume loss curve.

### Results and Discussion

Figure 1a-d shows the optical cross sections of the TRD coatings obtained after immersion in a molten borax bath with addition of carbide formers, and the boride layers are shown in Fig. 1e-f. The substrates included AISI H13 and D2 tool steels.

In the case of the carbide coatings, the layers exhibited good uniformity. The AISI H13 substrate exhibited a martensitic microstructure, the AISI D2 steel microstructure was composed of martensite and carbides of the alloying elements of the steel.

In the case of the boride layers, a boride external layer and a sublayer of ferrite was formed on AISI H13 steel. In the AISI D2 steel, only the formation of the boride layer was observed. The morphology of the boride layers in both cases was of the saw-tooth type.

Figure 2 presents the optical micrograph of the cross section of the coatings obtained using the pack-cementation process. Figure 2a shows the chromium compound layer and Fig. 2b, the boride layer. The pack boriding photomicrograph reveals the saw-tooth morphology of the boride layer. For pack chromizing, a homogeneous and continuous chromium compound layer is observed.

Microindentation hardness values of the near-surface region for the layers produced by TRD and pack diffusion treatments are shown below

Material / layer	Hardness, HV
H13 / NbC	2338 ±100
D2 / NbC	2353 ±92
H13 / VC	2471 ±109
D2 / VC	2461 ±93
H13 / boride	1706 ±66
D2 / boride	1717 ±55
1060 / Cr	1780 ±100
1060 / boride	1947 ±90

In all cases, the carbide layers exhibited high hardness comparable to that obtainable using PVD<sup>[20, 21]</sup>. PVD layers are expensive to produce, and adhesion to the substrate is lower than that of the layer produced by diffusion coatings, which is due to the metallurgical bond formation at the interface layer/substrate.

Figure 3 shows the wear curves of the layers obtained by salt bath immersion and pack diffusion processes for the materials tested. Figure 3a shows the wear curves obtained for the coated samples and for the substrates to demonstrate the effectiveness of all the diffusion treatments to increase wear resistances, which verifies the great increase in the wear resistance for all the diffusion coated samples. In the case of the AISI 1060 steel substrate, wear values were not

**IF YOU'RE NOT  
ONLINE,  
WHERE ARE YOU?**

Gain exclusive, valuable access to this industry through these online media channels. Space is extremely limited. Lead generation that's immediate and trackable.

- TSS Community Website
- TSS/Spray Tips e-Newsletter
- PR Marketing Solutions
- Event e-Mail Sponsorship

Cover your marketing completely with TSS Online products. Get the Power of Access. Get Online today. Go to [www.asminternational.org/access](http://www.asminternational.org/access) and bring your marketing full circle.

Be where they're looking,  
when they're looking.

THE POWER OF  
**ACCESS**  
IN PRINT, ONLINE,  
AT THE SHOW.

**ASM Thermal Spray Society**  
An Affiliate Society of ASM International<sup>®</sup>

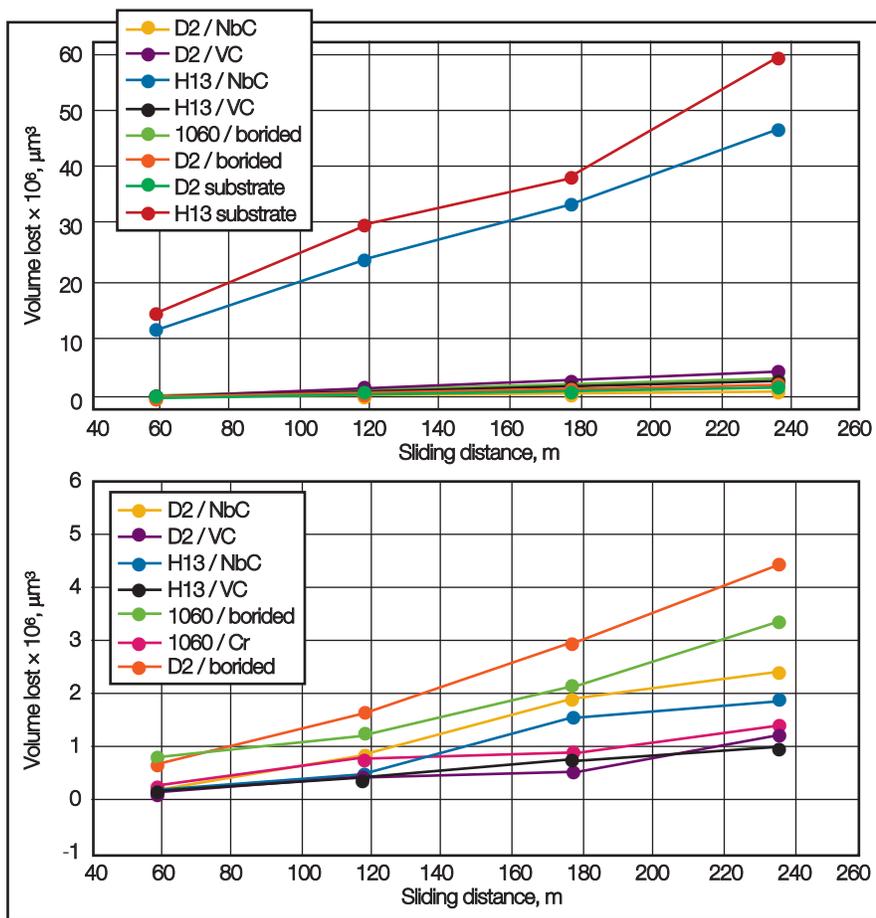


Fig. 3 — Wear curves of the TRD and pack diffusion layers derived from tests using a micro-wear machine with fixed ball configuration without the use of an abrasive.

plotted due to the high levels reached.

The layer obtained after the chromizing treatment had a wear performance close to that of the VC layers. The wear performance of the NbC layers was lower than that of chromized layer, although they had higher hardness. This is probably due to a greater fragility.

For better comparison, wear curves only of the coated samples are shown in Fig. 3b. The VC layers on AISI H13 and D2 resulted in the best wear performance. The chromium nitride-carbide compound layer presented a wear volume close to that of the VC layers, although the hardness of the chromium layer was substantially lower (1780HV) than that of the VC layers (2461HV). The boride layers, obtained by immersion or pack processes, showed the lowest resistance to wear among the coated samples.

### Conclusions

All the diffusion treatments produced layers with good uniformity and high hardness levels, from 1700 to 2470HV, which are much higher than those obtained with carbon cementation and nitriding treatments (900 to 1200HV). The layers produced showed

a large increase in wear resistances in all the cases compared with the substrates. The VC layers produced on AISI H13 and D2 showed the highest hardness values and the best wear performance among the performed treatments. The chromized layers and NbC layers showed intermediate wear behaviors, and the boride layers presented the highest wear among the evaluated layers. The good results obtained in this study indicate the great potential of all diffusion treatments studied in this work to produce high-performance coatings.

HTP

### References

1. Arai, T., Harper, S. Thermoreactive deposition/diffusion process, ASM Handbook, ASM Intl., Materials Park, Ohio, Vol 4, p 448-453, 1991.
2. Chicco, B. Borbidge, W.E.; Summerville, E. Experimental study of vanadium carbide and carbonitride coatings, *Mater. Sci. Eng. A*, Vol 266, p 62-72, 1999.
3. Plumb, S. Toyota diffusion process shows advantages, *Metallurgia*, Vol 52, p 59-61, 1985.
4. Arai, T., et.al., Diffusion carbide coatings formed in molten borax systems, *J. Mater. Eng.*, Vol 9, No.2, p 183-189, 1987.
5. Arai, T. Tool materials and surface treat-

ments, *J. Mater. Proc. Technol.*, Vol 35, p 515-528, 1992.

6. Wang, G.B. Wear mechanisms in vanadium carbide coated steels, *Wear*, Vol 212, p 25-32, 1997.

7. Arai, T. Carbide coatings process by use of molten borax bath in Japan. *J. Heat Treat.*, Vol 1, No. 5, p 15-22, 1979.

Arai, T.; Moriyama, S. Growth behavior of 8. vanadium carbide coatings on steel substrates by a salt bath immersion coating process, *Thin Solid Films*, Vol 249, p 54-61, 1994.

9. Sinha, A.K. Boriding (Boronizing). ASM Handbook, ASM Intl., Vol 4, p 437-447, 1991.

10. Matiašovský, K., et.al., Electrochemical and thermochemical boriding in molten salts, *Surf. Coat. Technol.*, Vol 35, p 133-149, 1988.

11. Genel, K., Ozbek, I., Bindal, C. Kinetics of boriding of AISI W1 steel, *Mater. Sci. Eng. A*, Vol 347, p 311-314, 2003.

12. Ozbek, I., Bindal, C. Mechanical properties of boronized AISI W4 steel, *Surf. Coat. Technol.*, Vol 154, p 14-20, 2002.

13. Sen, S., et.al., Mechanical behavior of borides formed on borided cold work tool steel, *Surf. Coat. Technol.*, Vol 135, p 173-177, 2001.

14. Sen, U., Sen, S. The fracture toughness of borides formed on boronized cold work tool steels, *Mater. Character.*, Vol 50, p 261-267, 2003.

15. Martini, C., Palombarini, G., Carbuicchio, M. Mechanism of thermochemical growth of iron borides on iron, *J. of Matl. Sci.*, Vol 39, p 933-937, 2004.

16. De Oliveira, C.K.N., et.al., Micro-abrasive wear of boride layers on AISI D2 tool steel produced by the thermoreactive process, *Intl. J. of Microstruct. & Matl. Prop.*, Vol 3, p 241-253, 2008.

17. Lee, J.W., Duh, J.G. Evaluation of microstructures and mechanical properties of chromized steels with different carbon contents, *Surf. Coat. Technol.*, Vol 177-178, p 525-531, 2004.

18. Kasprzycka, E., et.al., Diffusion layers produced on carbon steel surface by means of vacuum chromizing process. *J. Matl. Engr. and Perf.*, Vol 12, p 693-695, 2003.

19. Yue-Bo, Z., et.al., Oxidation of Al<sub>2</sub>O<sub>3</sub>-dispersion chromizing coating by pack-cementation at 800°C. *Trans. of Nonferrous Metals Soc. of China*, Vol 18, p 598-602, 2008.

20. Dobrzanski, L.A., Polok, M., Adamiak, M. Structure and properties of wear resistance PVD coatings deposited onto X37CrMoV5-1 type hot work steel, *J. Matl. Proc. Technol.*, Vol 164-165, p 843-849, 2005.

21. Karamis, M.B., Sert, H. The role of PVD TiN in wear behaviour of aluminium extrusion die, *Wear*, Vol 217, p 46-55, 1998.

**For more information:** F.A.P. Fernandes, Department of Materials, Aeronautical and Automotive Engineering, São Carlos School of Engineering, University of São Paulo, Av. Trabalhador São-carlense, n. 400, 13566-590, São Carlos, SP, Brazil; e-mail: codico@gmail.com.