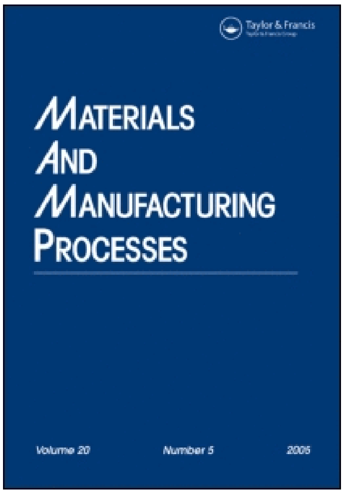


Materials and Manufacturing Processes
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597284

Novelty in Diffusion Coating Technology

Božidar Matijevi [a]; Mladen Stupnišek [a]
[a] Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia

To cite this Article Matijevi, Božidar and Stupnišek, Mladen(2009)'Novelty in Diffusion Coating Technology',Materials and Manufacturing Processes,24:7,887 — 893

To link to this Article: DOI: 10.1080/10426910902917710

URL: http://dx.doi.org/10.1080/10426910902917710

Materials and Manufacturing Processes, 24: 887–893, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6914 print/1532-2475 online
DOI: 10.1080/10426910902917710

Novelty in Diffusion Coating Technology

Božidar Matijević, and Mladen Stupnišek

Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia

Diffusion forming of a hard carbide layer has been used for many years, mostly in Japan (Toyota Diffusion Process, TDR) and in the USA (Thermoreactive Deposition, TRD) but not so much in Europe. Carbide layers on constructive parts and tools formed by a diffusion process, especially a vanadium carbide layer, have excellent tribological properties and some technical and economical advantages in comparison with carbide layers formed by chemical vapour deposition (CVD) and physical vapour deposition (PVD) processes. Diffusion formed layers are thicker with very strong bond to steel substrate and are produced using significantly cheaper equipment than for deposition coating. The process has one disadvantage: partial decarburization of the steel surface beneath the carbide layer reducing hardness and loading capacity of the surface. This disadvantage is eliminated by a developed and patented duplex process introducing previous carburizing to prevent decarburization and to form a hardened case under layer beneath the carbide layer. The new developed process should contribute to widely application of diffusion carbide coating for automotive industry. Mathematical model and program for optimization of process is presented as well as some examples of application: extruders for medium with very abrasive particles, aluminium die casting moulds, etc.

Keywords Abrasive wear; Adhesive wear; Carbide layer; Cold-work tool steels; Diffusion; Duplex process; High-speed steels; Hot-work tool steels; Thermoreactive deposition; Tribochemical wear; Vanadising; Vanadium carbide.

1. Introduction

The quality and lifetime of tools and dies are important factors in production, particularly in large batch and sophisticated production. For many years, considerable efforts have been put into attempts to increase wear resistance and service life by using different technological procedures. Attempts have been made to apply higher quality materials and adequate heat treatment, and to apply different procedures of modification and coating of surfaces in order to increase durability. Surface layers differ from the treated base material with respect to the chemical composition, microstructure, crystal lattice, and other physical and chemical properties which result in different properties in use. Among the surface modification and coating procedures, the treatment of chromium plating and the thermochemical treatment (nitriding) are rarely applied, and lately, it has been the case with the physical vapor deposition—PVD (PACVD) procedures (TiN, TiCN, TiAIN, CrN). In addition to one-layer coating (e.g., TiN) and multilayer coating (TiCN, Al_2O_3, TiN), duplex processes, such as ion nitriding + PVD TiN, are also applied. Using PVD processes, thin and hard layers are formed on high-precision tools since the preceding heat treatment has been carried out at the temperatures which are higher than the temperatures at which the PVD processes are carried out. For some time now, concurrently with the PVD processes, diffusion coating processes have also been applied. These processes have their origin in the Toyota Diffusion Process [1] and in several patents [2, 3], and they have some technical and economic advantages over the PVD processes, but also some limitations in application. The advantages of diffusion coating processes are that they generate layers of greater thickness and higher hardness, as well as having superior tribological properties, higher resistance to abrasion and tribocorrosion. A drawback or a limiting factor of this process is the application on parts with close dimensional tolerances. As the process is performed at high temperatures causing a change in the microstructure of the substrate, the result is that dimensions are changed, and a layer is generated on the machine parts surface. Thus, dimensional changes are greater than with the application of PVD processes. Diffusion formation of carbide layers is typically used in the same applications as the PVD (PACVD) coatings, but there are some applications where diffusion formation of carbide layers has proven to be superior: aluminium and zinc die-casting components (moulds, cores, etc.), hot forging dies, and tools for stamping and forming stainless steels. Table 1 below shows the comparison of three major coating processes.

Generally, a layer with a thickness from 1 to 20 μm and hardness from 3200 to 3800 HV is produced. The basic difference between diffusion formation of carbide layers and deposition coating processes is that, in the diffusion formation of carbide layers, the substrate is the most important factor affecting the carbide layer formation, as shown in Fig. 1.

2. Diffusion formation and properties of carbide layers

Diffusion formation of a carbide layer on the surface of steel has a growing application in industry. This is due to the fact that relatively low investment costs for equipment are needed in order to enable the carrying out of the process and to obtain carbide layers of high

---

Received June 10, 2008; Accepted August 10, 2008

Address correspondence to Božidar Matijević, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Ivana Lucica Street 5, Zagreb 10 000, Croatia; E-mail: bozidar.matijevic@fsb.hr

TABLE 1.—The comparasion of the three coating process [4].

PVD	CVD	TRD
Performed in a vacuum chamber (10^{-2} to 10^{-4} Torr)	Can be performed in controlled atmosphere or vacuum	Performed in an elemental salt bath
Relatively low process temperature (200° to 800°F or 100° to 450°C)	High temperature process (1925°F or 1050°C)	High temperature process (1650° to 1900°F, or 900° to 1050°C)
Line of sight process: will coat areas directly exposed to ion source	Reactive gas process coats wherever atmosphere contacts tool surface	Reactive bath process coats wherever molten bath contacts tool surface
Coating exhibits a physical bond to the substrate's surface	Coating exhibits a chemical and metallurgical bond to the substrate	Coating exhibits a diffusion type bond to the substrate
Average thickness: 2–5 μm, or 0.00008–0.0002″	Average thickness: 6–10 μm, or 0.00024–0.0004″	Average thickness: 5–15 μm, or 0.0002–0.0006″
Suitable for a wide range of substrates	More limited range of substrates than for PVD	More limited range of substrates than for PVD, but less limited than CVD
Ideal for closely tolerated components (+/−0.0001″, 0.0025 mm is appropriate)	Requires relatively close tolerances (example: +/−0.0005 per 1.0″ diameter, 0.0012 mm per 25.4 mm)	Requires relatively close tolerances (example: +/−0.0005 per 1.0″ diameter, 0.0012 mm per 25.4 mm). May be more forgiving than CVD
No heat-treating required after coating due to low process temperature	Post-coating heat-treating required on steel parts due to high process temperature	Post-coating heat-treating required on steel parts due to high process temperature
Good for sharp edges: no excessive coating buildup	Requires hone on sharp edges due to heavier coating buildup	Requires hone on sharp edges due to heavier coating buildup
Coating will generally replicate existing surface finish—mirror finishes can be maintained	Difficult to maintain mirror finish (post-coating polishing will improve finish)	Difficult to maintain mirror finishes; however, post-coating polishing can achieve near mirror finishes

hardness (from 3200 to 3800 HV) and of high abrasion and tribocorrosion resistance. The process is most often carried out in a salt bath of an appropriate composition, with the addition a carbide-forming element (V, Cr, Nb, W, Ti). A carbide-forming element (e.g., vanadium, V) reacts on the surface of steel with carbon (C), which is at high temperature (≈1000°C) atomically dissolved in austenite, thus forming a very stable V_8C_7 carbide or some other carbide (NbC, Cr_7C_3, WC, TiC) [5, 6]. The carbide layer grows on the surface in the diffusion process of carbon from the surface layer of steel towards the carbide layer, and through it to a newly forming surface where it reacts with the carbide-forming element. A smaller amount of the carbide-forming element diffuses through the forming carbide layer into the surface layer of steel. In addition to high temperature, the rate of carbide layer formation is greatly affected by the chemical composition of steel. Experimental results obtained at the same time confirmed the developed mathematical modes of the pattern, and a computer program, enabling the determination of technological parameters of the vanadizing process in order to achieve a required thickness of the layer for a chosen steel type, was also developed [7]. Vanadium carbide has high thermal stability, more than 800°C, as is shown in Fig. 2.

3. DIFFUSION COATING OF TOOL STEELS

3.1. Cold-Work Tool Steels

This is of particular importance for high-carbon high-alloyed steels, which have one part of the carbon combined in the carbides at the processing temperature. These carbides in steel are mostly stable carbides of chromium, tungsten, or other carbide forming elements. Therefore, as a first step it is necessary to determine the amount of carbon dissolved in the solid solution of austenite. Carbon is effective in the process only in this form, i.e., substitution dissolved in the austenite. A quantitative presentation and a possibility of determining carbon distribution (and the distribution of other elements) are provided by the isothermic phase diagrams. By an example of isothermic cross-section of the phase diagram in the system Fe–C–Cr in Fig. 3, it is demonstrated how the concentration of carbon and chromium dissolved in the austenite can be determined

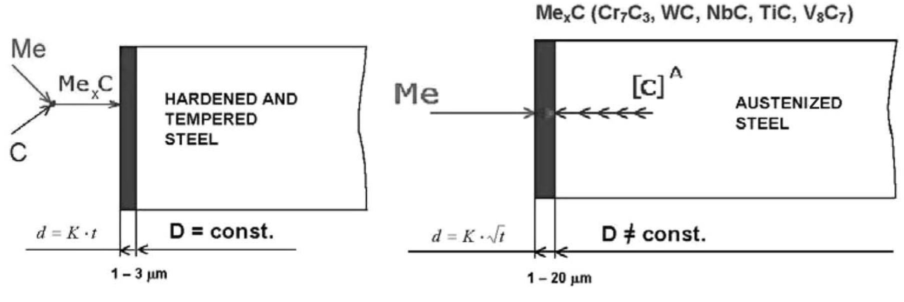


FIGURE 1.—Schematic presentation of the basic difference between the processes of deposition coating (left) and diffusion carbide layer formation (right).

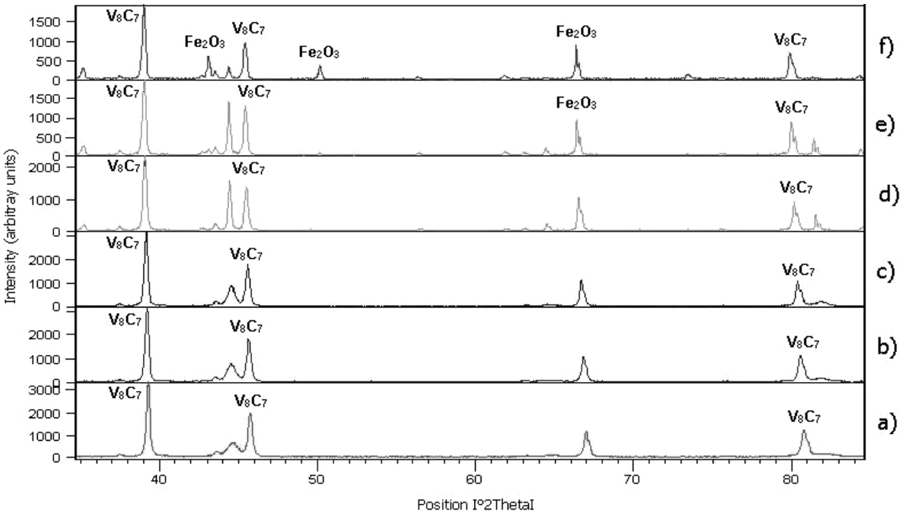
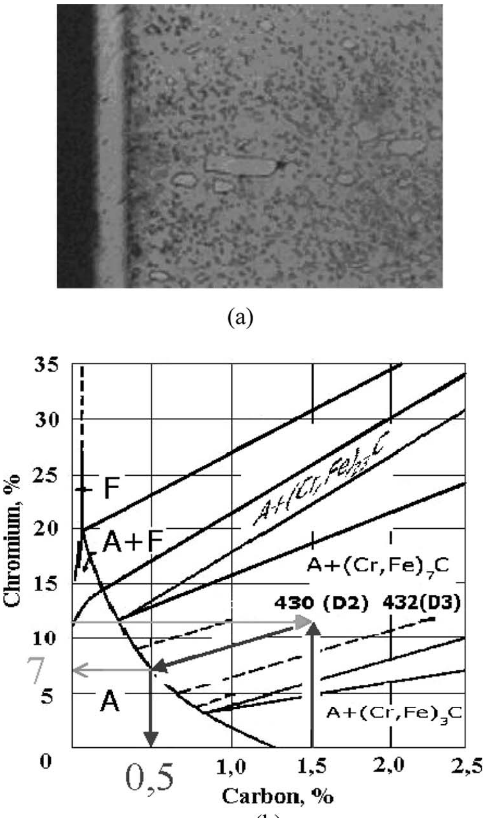


FIGURE 2.—XRD patterns of carbide layer taken from a different examination temperature: a) 20°C, b) 250°C, c) 400°C, d) 620°C, e) 780°C, f) 870°C.

in the phase diagram for a given composition of steel at the temperature of 1000°C. This case demonstrates that in the case of the ledeburitic tool steel of D2 grade (1.5% C, 12% Cr), only 0.5% of carbon is dissolved in the austenite during vanadizing at 1000°C, while the balance of carbon is combined into the carbide M_7C_3. Moreover, it should be noted that 7% of chromium is dissolved in the austenite, which, according to principles of physical chemistry, affects the thermodynamic activity of carbon in austenite.



(a)

(b)

FIGURE 3.—Metallographic cross-sections of vanadized cold work steel, 200:1, (top) and isothermic cross-section in Fe–C–Cr system on 1000°C (bottom) [8].

The temperature of diffusion formation of the carbide layer is determined in dependence on the hardening temperature, which enables direct hardening. It is also possible to perform subsequent hardening by using adequate inert gas atmospheres or vacuum.

3.2. Hot-Work Tool Steels

This class of tool steels is characterized by a medium carbon content, as well as a medium content of alloying elements. These elements (Cr, W, . . .) generally reduce the thermodynamic activity of carbon in austenite, while Si and Ni increase the thermodynamic activity of carbon in austenite. The occurrence of partial decarburization just beneath the carbide layer is a characteristic side effect

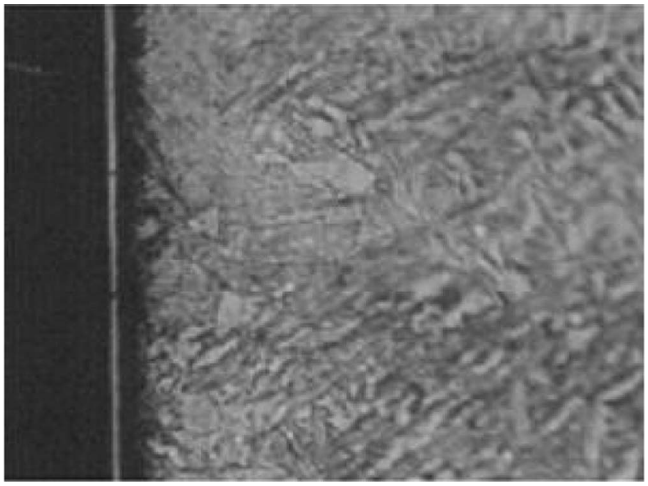


FIGURE 4.—Microstructure of the vanadium carbide coating on the hot work steel which is partially decarburized; 200:1.

in the carbide diffusion coating process. In the formation of a V_8C_7 carbide layer containing approx. 16 wt% C, the concentration of carbon in the underlying zone of steel is reduced resulting in reduced hardness in the same zone after quenching, Fig. 4, [9].

In the case of more severe decarburization, the layer of reduced hardness may adversely affect the loading capacity of a thin, extremely hard carbide layer. This fact required improvement of the process, consisting in introducing the process of carburizing prior to diffusion coating. Technological parameters of the carburizing process which would introduce the required amount of carbon into austenite to produce a specified carbide layer in the subsequent diffusion coating are calculated using the developed computer program, Fig. 5 [10]. By applying the duplex process, the occurrence of partial decarburization and softening beneath the carbide layer is eliminated. Another advantage of this process is that the increased offer of carbon contributes to the increased carbide layer growth rate, resulting in reduced process time, Fig. 6.

In the second version of the duplex process, during carburizing the process introduced carbon in an amount greater than needed for carbide formation. Only one part of introduced carbon participate in carbide layer forming and larger part of carbon in hardened underlayer causes a higher hardness in the case hardened underlayer, Fig. 7. This underlayer supports a very hard carbide layer increasing loading capacity of the tool surface and increased compressive stresses which contribute to higher resistance to surface fatigue including thermal fatigue.

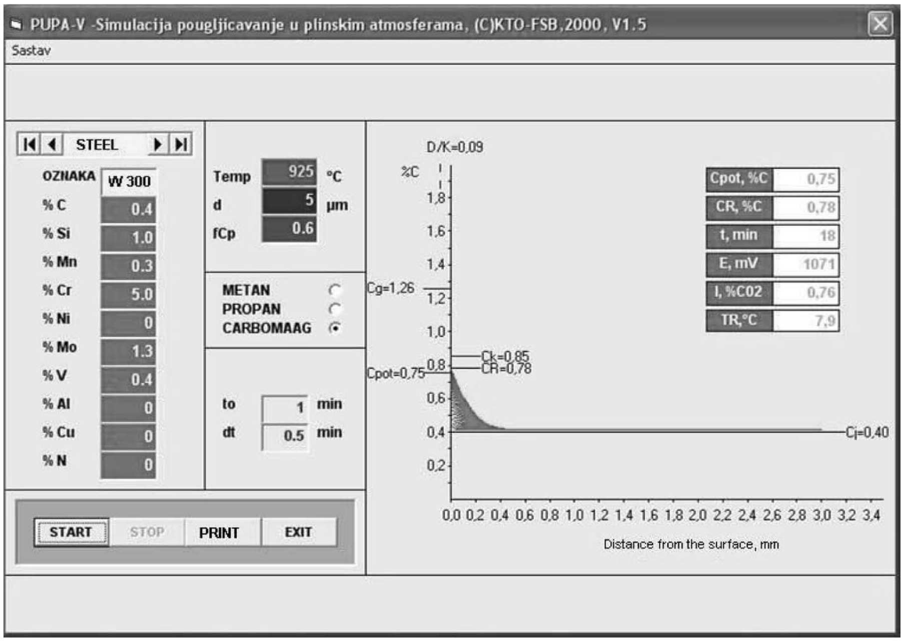
By the introduction of pre-carburization, three advantages over standard procedures of diffusion formation of carbide layers are achieved: a harmful phenomenon of partial decarburization which occurs with standard processes of diffusion formation of carbide layers is eliminated; due to higher accumulation of carbon, the rate of carbide layer formation is increased; and, an additional hard under layer is obtained. These advantages over the existing processes of diffusion formation of carbide layers are of major importance, and the original contribution of the idea was confirmed by the European Patent Office which accepted the patent [11, 12]. Technological parameters of the carburizing process which would introduce more carbon into austenite to produce a specified carbide layer in the subsequent diffusion coating are calculated using the developed computer program. Vanadium carbide has high resistance to reactive soldering, it prevents contact of molten aluminium and steel substrate, and it is stabile at high temperature, Fig. 2.

3.3. *High-Speed Steels*

This steel class has a medium carbon content and high content of alloying elements, especially of strong carbide forming elements such as Cr, W, and Mo which reduce the thermodynamic activity of carbon. Due to this fact, the rate of carbide layer forming is lower but can be significantly increased by increasing the temperature of the process since the temperature of austenitization of these steels is higher. In this case, PVD or PA CVD coating have advantages in comparison to thermoreactive deposition (TRD).

4. APPLICATIONS OF VANADISING

Vanadium carbide, V_8C_7 has a cubic lattice of high hardness (from 3200 to 3800 HV) with very good tribological properties. Abrasion resistance is very high because the vanadium carbide layer is harder that most hard mineral materials. Tribocorrosive adhesion resistance is very high because the layer is very stable and



OZNAKA W 300
% C 0.4
% Si 1.0
% Mn 0.3
% Cr 5.0
% Ni 0
% Mo 1.3
% V 0.4
% Al 0
% Cu 0
% N 0

Temp 925 °C
d 5 µm
fCp 0.6

METAN ○
PROPAN ○
CARBOMAAG ●

to 1 min
dt 0.5 min

Cpot, %C 0,75
CR, %C 0,78
t, min 18
E, mV 1071
I, %C02 0,76
TR,°C 7,9

FIGURE 5.—Program interface for the calculation of pre-carburization parameters for the introducing of carbon required for the formation of a carbide layer of required thickness (5 µm).

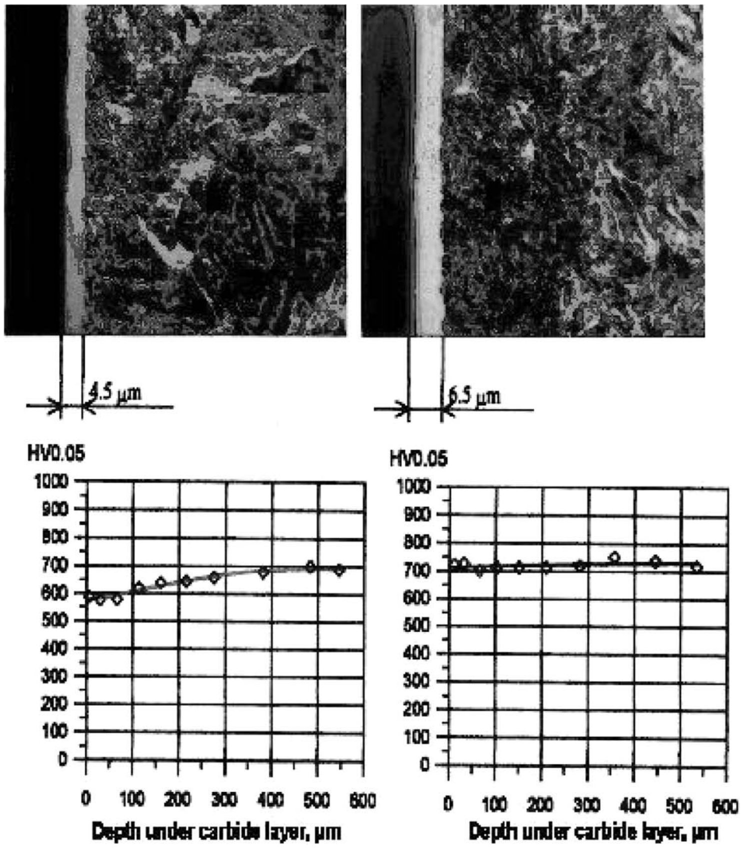


FIGURE 6.—Comparison of the thickness of the vanadium carbide layer and the hardness beneath this layer, achieved by applying the classic (left) and new duplex process (right) [10].

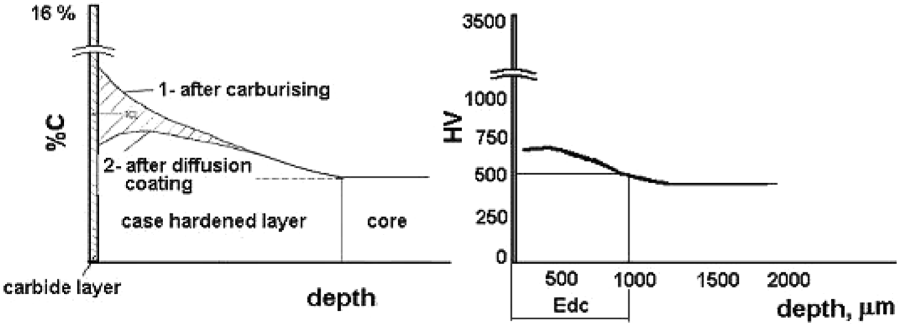


FIGURE 7.—Changes of carbon concentration in the process of duplex layer formation (carburizing + diffusion carbide layer formation) and microhardness distribution [10].

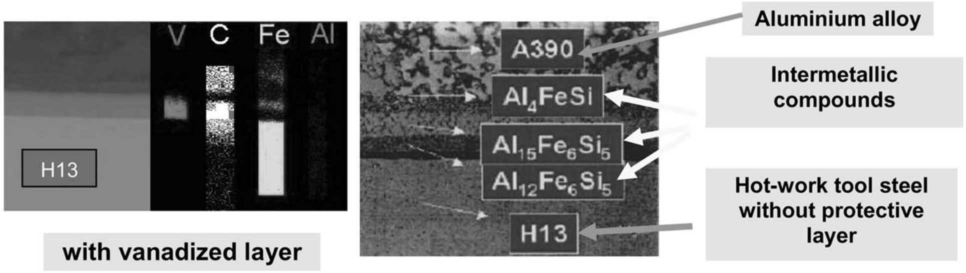


FIGURE 8.—Cross-section of aluminium die-casing with and without vanadium carbide layer [12].

TABLE 2.—Applications of TRD process [14].

Application	Tool
Sheet metal working	Draw die, bending die, pierce punch, form roll, embossing punch, coining punch, shave punch, seam roll, shear blade, stripper guide pin and bushing, pilot pin, etc.
Pipe and tube manufacturing	Draw die, squeeze roll, breakdown roll, idler roll, guide roll, etc.
Pipe and tube working	Bending die, pressure die, mandrel, expand punch, swaging die, shear blade, feed guide, etc.
Wire manufacturing	Draw die, straightening roll, descaling roll, feed roll, guide roll, cutting blade
Wire working	Bending die, guide plate, guide roll, feed roll, shear blade
Cold forging and warm forging	Extrusion punch and die, draw die, upsetting punch and die, coining punch and die, rolling die, quill cutter, etc.
Hot forging	Press-forging die, rolling die, upsetting die, rotary swaging die, closed-forging die, etc.
Casting (aluminum, zinc)	Gravity-casting core pin, die-casting core pin, core, sleeve, etc.
Rubber forming	Form die, extrusion die, extrusion screw, torpedo, cylinder sleeve, piston, nozzle, etc.
Plastic forming	Form die, injection screw, sleeve, plunger, cylinder, nozzle, gate, etc.
Glass forming	Form die, plunger, blast nozzle, machine parts, etc.
Powder compacting	Form die, core rod, extrusion die, screw, etc.
Cutting and grinding	Cutting tool, cutting knife, drill, tap, gage pin, tool holder, guide plate, etc.

chemically resistant to aggressive agents (NaOH, HCl, etc.). High hardness of the carbide layer indicates that the layer is brittle, and therefore, the resistance to surface fatigue is reduced. A strong metallurgical bond between the carbide layer and the base material (steel substrate) gives good adhesion of the surface layer to the substrate. Even considerably greater thickness of hard surface layers of 5–20 μm, in comparison with the thickness of PVD layers of 1–3 μm, can be achieved. The industrial application of diffusion vanadizing on a larger scale started in Japan (Toyota Diffusion Process) and then has spread to other industrially developed countries due to excellent tribological properties of vanadium carbide surface layers. The application of vanadizing on structural elements and tools in different branches of engineering contributes to a significant increase in their durability (Table 2). The application of vanadizing to the manufacture of tools has produced excellent results with numerous tool types which are subjected to adhesive and tribochemical wear in their use. For abrasive wear, vanadizing is the right choice for treating tools that are exposed to wear by hard abrasive particles. Surface layers of vanadium carbide extend the tool life by several times. Typical examples are tool parts for powder compacting and extruder worms. Regarding adhesive wear, vanadizing is applied to the tools for metal forming processes such as extrusion, forging, and drawing. As far as tribocorrosive wear is concerned, the vanadium carbide surface layer efficiently protects the tools used in very aggressive media, even in HCl and HNO_3. The carbide layer is particularly useful in reactive soldering for aluminium die casting tools [13]. The process has a broad range of applications, from feeding attachments to the forming of punches and dies, and provides a considerable performance improvement. The largest industrial application is punches for piercing and extrusion. The application on various die steels is also evident. However, vanadium carbide on cemented carbide dies is also utilized with a notable improvement of die life. The ability to change from cemented carbide to cold work die steel or high speed steel, and from high speed steel to cold work die steel, has been realized in various punches and dies. The process is also successfully utilized in the forging of stainless steel, ball bearing steel, and nonferrous metals. Dies used in the hot forging of stainless steel are also treated by this process. The vanadium carbide coating is continuously applied even for hot forging dies. The lifetime increases several times due to the elimination of galling problems. As a result, a great saving on die consumption has been achieved. Additional advantages, other than savings on die consumption, were in some cases far greater.

5. CONCLUSION

Diffusion formation of hard carbide layers offers a new possibility in tool processing, which increases wear resistance considerably, thus enabling a longer life in use and, consequently, a more economic application. Different thermochemical processes produce different surface layers with adequate properties for specific applications. On the basis of the knowledge of the basic physical process pattern, an adequate thermochemical treatment process has to be chosen for adequate exploitation conditions. With diffusion formation of hard carbide layers, the choice of substrate, i.e., steel, is of major importance. In addition, due to high process temperatures, dimensions are changed because of subsequent hardening and formation of a carbide layer. In the cases of close dimensional tolerances, a trial treatment needs to be performed in order to correct dimensions to compensate for the changes of dimensions during the forming of hard carbide layers. Processes of diffusion formation of carbide layers cannot replace the PVD process when it comes to cutting tools, milling cutters and reamers, which require close dimensional tolerances. The results obtained in the previous research and technological improvements of the duplex process, together with the developed computer programs, have contributed to the improvement of the original process of carbide layer formation.

REFERENCES

1. Fujita, H.; Arai, T. Carbide Coatings in Molten Borax Bath-Growth Mechanism of Layer, Properties and Application. Proceedings of the 4th Int. Congress of IFHT. Berlin, 1985; 1109–1124.
2. Komatsu, N.; Arai, T.; Toyoake, A. Verfahren und Material zur Erzeugung einer Carbidschicht auf Gegenstaenden aus kohlenstoffhaltiger Eisenlegierung, Patentschrift DE 2819856 C2, 1978.
3. Baudis, U.; Biberbach, P.; Weber, W. Verfahren zur Herstellng von Vanadincarbidschichten auf Eisen, Patentschrift DE 3025033 A1, 1980.
4. Badger Metal Tech, Inc. www.badgermetal.com (last accessed May 4, 2009).
5. Stupnišek, M.; Štefotič, B. Development of the diffusion process for carbide coatings on steels. Proceedings of YUSTOM 1986, Plitvička jezera 1986, 323–330.
6. Fazluddin, S.B.; Koursaris, A.; Ringas, C.; Cowie, K. Formation of VC coating on steel substrates in molten borax, surface modification technologies VI. Minerals Metals and Materials Society **1993**, 45–60.
7. Matijević, B. Kinetics of diffusion formation of carbide layers. Ph.D. thesis, University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture, Zagreb, Croatia, 1997.
8. Roberts, G.A.; Hamaker, J.C.; Johnson, A.R. *Tool Steels*; ASM: Metals Park Ohio, 1961.
9. Stupnišek, M.; Matijević, B. New duplex diffusion coating process, Proceedings of the 8th Seminar of IFHTSE 2001, Dubrovnik-Cavtat, 2001; 209–215.
10. Matijević, B.; Stupnišek, M. Improvement in thermoreactive deposition of carbide layers. Berg-und Hüttenmännische Monatshefte **2006**, *3*, 113–117.
11. Stupnišek, M.; Matijević, B. European Patent Number WO02053793, Duplex Process of Diffusion forming of Hard Carbide Layers on Metalic Materials, 2002.
12. Stupnišek, M.; Matijević, B. Croatian Patent Number P20000916, Duplex Process of Diffusion forming of Hard Carbide Layers on Metalic Materials, 2005.
13. Matijević, B.; Stupnišek, M.; Jukić, I. Selection of Tool Steels for Diffusion Carbide Coating, Proceedings of 7th International Tooling Conference, Torino, Italy, Politecnico di Torino, Italy, 2006; 255–262.
14. Arai, T.; Harper, S. *Thermoreactive Deposition/Diffusion Process*; ASM International, Metals Handbook, Volume 4: Heat Treating. ASM: Metals Park Ohio, 1999.