Carbide Coating Process by Use of Molten Borax Bath in Japan

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Pore-free and smooth surface carbide layers can be formed on metals and carbon immersed in a molten borax bath above 1073 K. The carbide layers, consisting of VC, NbC, TiC, or Cr_7C_3, are formed by the reaction between the carbon atoms in the substrate and the carbide forming element atoms dissolved into the fused borax from additive powders such as iron-vanadium, iron-niobium, iron-titanium, iron-chromium, and chromium. Core hardening of steel substrates can be simultaneous or by reaustenitizing after carbide coating. Carbide coated steels show excellent resistance to wear, seizure, corrosion and oxidation. The carbide layers are adherent to the substrate and do not exfoliate in severe service as in cold forming. The process effectively improves performance of dies, tools, machine parts, and is applied in various fields of Japanese industries.

The titanium carbide coating process (TIC) is a chemical vapor deposition successfully applied to metal forming dies and cutting tools in some countries.[1,2]

In this process, metals are heated in hydrogen gas containing $TiCl_4$ and hydrocarbon. This process requires complicated furnace equipment, is relatively low in productivity, and core hardening during cooling is difficult to produce.

The boriding process, by use of a molten borax bath under ambient atmosphere, has been developed.[3,4] The equipment for this process is simple and the chemicals are low in cost. However, the boride layers may not be tough enough to be widely used for some metal forming dies and tools.

The authors undertook studies to develop a new coating process, to combine the excellent performance of the

TiC coating with the simplicity of the boriding process. They succeeded in the development of a carbide coating process by use of molten borax under ambient atmosphere at temperatures from 1073 to 1473 K.

FORMATION OF CARBIDE LAYERS

To examine the surface layers on metals immersed in various kinds of borax baths, specimens were held in molten borax baths containing powders of alloys and pure metals such as silicon, aluminum, magnesium, titanium, vanadium, niobium, tantalum, chromium, and so forth; quenching was in oil, water, or air. Surfaces and cross sections were examined by microscopy, X-ray diffraction and electron probe microanalysis with the following results.

Table I identifies the layers formed on steel and the additives in the bath.[5] Iron boride layers were formed on steels immersed in the bath containing calcium, silicon, aluminum, magnesium, zirconium, and rare-earth

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metals powders or the alloy powders. Vanadium, niobium, or chromium carbide layers were formed on carbon containing steel, immersed in the bath containing ferrovanadium, ferroniobium, ferrochromium or chromium powders.[5] In Fig. 1, diffraction lines of VC can be clearly observed.[5] Figure 2 identifies vanadium and carbon as principal constituents in the layer.[6] These experimental results revealed that carbide layers consist of VC, NbC, or $Cr_7C_3 + Cr_{23}C_6$, respectively.

The relationship between kinds of formed layers and additives can be further clarified, by taking the free energy of oxide formation and carbide formation into account. The boride layers formed in the bath contain elements which have a smaller free energy of oxide formation than B_2O_3, while the carbide layers formed in the bath contain elements which have a larger free energy for oxide formation.

Baths containing titanium and manganese have a smaller free energy of oxide formation than B_2O_3 and a relatively smaller free energy for carbide formation form carbide or iron-boride layers on high carbon and low carbon steels. These carbides consist of TiC, $Mn_5C_2 + (Mn, Fe)_7C_3 + (Mn, Fe)_3C$. Iron-boride particles or layers were also observed, adjacent to the carbide layer.[5]

Neither carbide nor boride layers are formed in the bath containing elements which have larger free energies both for carbide and oxide formation.

From experimental results with these carbide forming baths,[7] it is concluded that carbide layers are formed in the following steps:

1. Carbide forming elements dissolve into borax from added powders.

2. Carbon in steel combines with the carbide forming element, to produce a carbide layer on the surface.

3. The carbide layer grows at the surface front through reaction between carbide forming elements and carbon atoms successively supplied from the substrate.

Table I. Chemical Species of the Surface Layer Formed on 1010 Steel Specimens and Free Energy Change (ΔG) of Borax Reducing Reaction at 1273 K, kJ/mol

| Additives	Layer thickness,* μm	Layer structure*	ΔG
B_4C	400	$FeB + Fe_2B$	—
Ca-Si	300	$FeB + Fe_2B$	− 368
Ca-Al-Mn	270	$FeB + Fe_2B$	− 368
Ca-Al-Mn-Si	300	$FeB + Fe_2B$	− 368
La-Ce	230	$FeB + Fe_2B$	− 335
Mg	140	Fe_2B	− 276
Fe-Zr	170	$FeB + Fe_2B$	− 209
Al	300	$FeB + Fe_2B$	− 205
Fe-Ti	100	Fe_2B	− 151
Fe-Si	270	$FeB + Fe_2B$	0
Fe-V	5	VC	+ 33
Fe-Nb	5	NbC	+ 42
Fe-Mn	160	Fe_2B	+ 59
Fe-Cr	20	Fe-Cr(s,s)	+ 117
Zn	—	—	+ 226
Co	—	—	+ 377
Ni	—	—	+ 377
Cu	—	—	+ 494
SiC	—	—	+1351
TiC	—	—	+2448
TiN	—	—	+ 305
Si_3N_4	—	—	+1117
ZrO_2	—	—	−
Al_2O_3	—	—	−
SiO_2	—	—	−

*1273 K, 14400 s
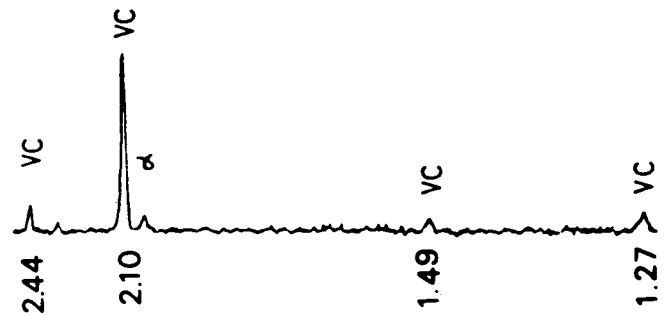
Fig. 1—X-ray diffraction pattern on vanadium carbide layer of low carbon steel (AISI 1010).
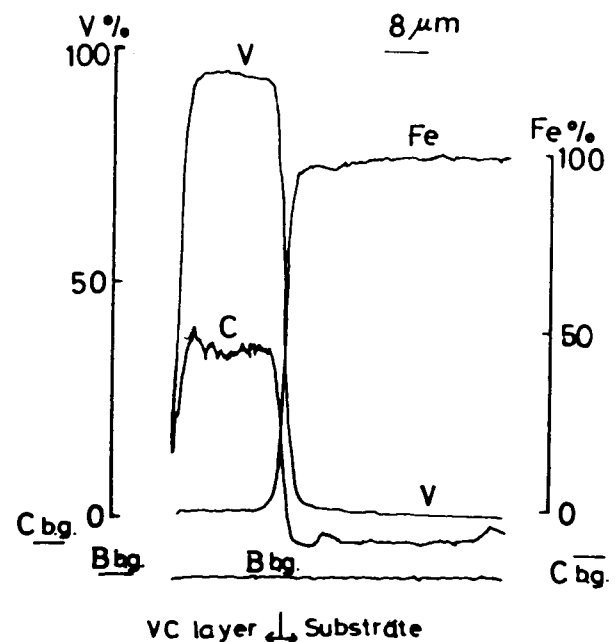

Fig. 2—In depth variation of X-ray intensities of C, V, Fe, and B in the vanadium carbide layer formed on high carbon steel (AISI W1).

Vanadium and chromium diffuse into the steel substrate to form iron-chromium or iron-vanadium solid solution layers beneath the carbide layer. The solid solution layers were formed on low carbon steel at high treating temperature.[5]

There is minor diffusion of iron and other elements from the substrate into the vanadium carbide and niobium carbide layers. Less than 1 pct of iron and other elements were identified, even with highly alloyed steels.[6] In the case of chromium carbide, a fair amount of iron is observed in the carbide layer adjacent to the substrate.[5] Thus, the composition of carbide layers is practically independent of the chemical composition of substrate.

Carbide layers were easily formed on nonferrous metals, and cemented carbide.[8,9]

The depth of carbide layers is *independent of the bath composition* if carbide forming elements are added to the bath in a sufficient amount, *i.e.,* more than 10 pct in powders of ferrovanadium, ferroniobium, ferrochromium, and chromium.

Carbide layer depth is affected by the following factors:[6]

1. Bath temperature;
2. Immersion time;
3. Kinds of substrate steel;
4. Kinds of carbide;
5. Section thickness of component processed.

As the bath temperature rises, the diffusion rate of carbon in the layer is increased; in alloyed steels the carbon content in the matrix phase is also increased, resulting in the increased depth of the layer. The bath temperature affects the thickness of the layer as shown by the following equation:

$$d^2/t = K = K_O \exp(-Q/RT) \qquad [1]$$

where d: Thickness of layer (cm);
  t: Immersion time (s);
  K: Layer growth rate constant (cm²/s);
  K_O: Constant term of layer growth rate constant (cm²/s);
  Q: Activated energy (kJ/mol);
  T: Absolute temperature (K).

The amounts of Q for vanadium carbide, niobium carbide, and chromium carbide obtained from experimental data are about 192, about 209 and about 167 kJ/mol, respectively. K_O tends to increase with the increase of carbon content in the matrix phase.

The relation between the immersion time and the thickness of a layer is given by the following equation for the parabolic law:

$$d^2 = K \cdot t \qquad [2]$$

where t shows time (s) and K shows layer growth rate constant (cm²/s).

The relation between the depth and time is shown by a parabola and the relation between the depth and the square root of time is shown by a straight line.

The depth of the layer and the carbon content in the matrix phase are nearly linearly related to each other, as shown in Fig. 3. Therefore, in the case of alloyed steels, the rise of bath temperature increases the carbon content in the matrix phase, as well as the diffusion rate of carbon atoms in the carbide layer, resulting in the considerable increase of layer depth.

Generally, the difference in layer depth among vanadium, niobium and chromium carbides is negligibly small. As the layer formation is metallurgical rather than an electrochemical process, the layer depth is uniform, even in small openings.

PROCESSING TECHNIQUE FOR THE CARBIDE COATING

Materials treated are immersed in a molten salt bath containing borax solvent and alloy powders for several hours. The bath temperature is selected aroung the hardening temperature of the substrate steel ranging from 1073 to 1473 K. Immersion time is determined
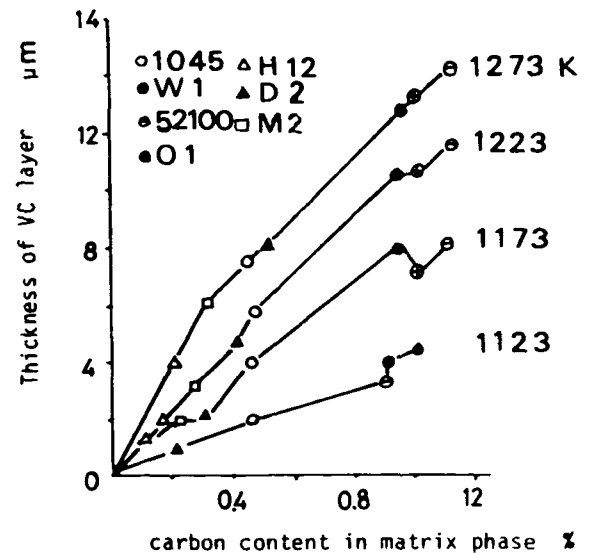
Fig. 3—Effect of carbon content in matrix phase and temperature on the thickness of vanadium carbide layer.

according to the required layer depth, varying from 30 min to 10 h.

The depth of carbide layers can be varied by controlling the bath temperature, immersion time and substrate selection. Carbide layers from 5 to 15 μm are reported satisfactory for most applications. Quenching can be in water, oil, salt, or air, depending on the required core hardness, size of component and hardenability of the material processed.

Simultaneous carbide formation and core heat treatment is practiced with satisfactory results. *Reaustenitizing hardening also can be carried out.* Tempering can be done in air, vacuum, protective gas, or chloride salt. Before or after tempering, treated materials are dipped in hot water for removal of attached salt. Procedures for formation of solid solution layers are similar to those for carbide coating.

Those coating processes are quite similar to those in conventional salt bath hardening. The work environment is clean because of no gas vaporization from the bath. This process gives rise to no pollution problems and *needs no complicated equipment* for treating emission and waste water.

The type of carbide can be easily changed—vanadium carbide to chromium carbide or its reverse—by changing the bath mixture *together with the pot retaining them.*

A salt bath furnace is simple in structure. No protective atmosphere is needed and agitation is *seldom necessary.* A heat resisting steel pot, eqivalent to ASTM HH, with a wall thickness of 14 mm, is commonly used with

1 to 1.5 years life when used at bath temperature of 1273 K.

Selective coating is accomplished easily by the use of copper or stainless steel masks, and so forth, plating, thermal spraying or wrapping with foils.

The process is applicable to most kinds of carbon, tool, structural, and stainless steels, cast iron, stellite and cemented carbides. High carbon-high chromium die steels equivalent to AISI D2 are widely used for metal working dies. D2 steel is frequently replaced by leaner alloy steels with improved machinability, toughness and reduced costs.

Constructional steels can be used for machine parts and dies. Low carbon steels are frequently carburized prior to the process. The process competes with cemented carbides which are used for cold forging, sheet metal forming, and wire drawing tooling.

The process temperatures used are compatible to the hardening temperatures of the substrate material. The basic method to minimize the problem of distortion of the process is preliminary hardening. This minimizes or eliminates size change caused by change of crystal structure, from pearlite to martensite.

The dimensional control by decomposition of retained austenite and tempering of martensite is also used, as well as straightening techniques and finish grinding.

In Japan, this process is applied on articles which needed dimensional accuracy of better than ± 10 μm.

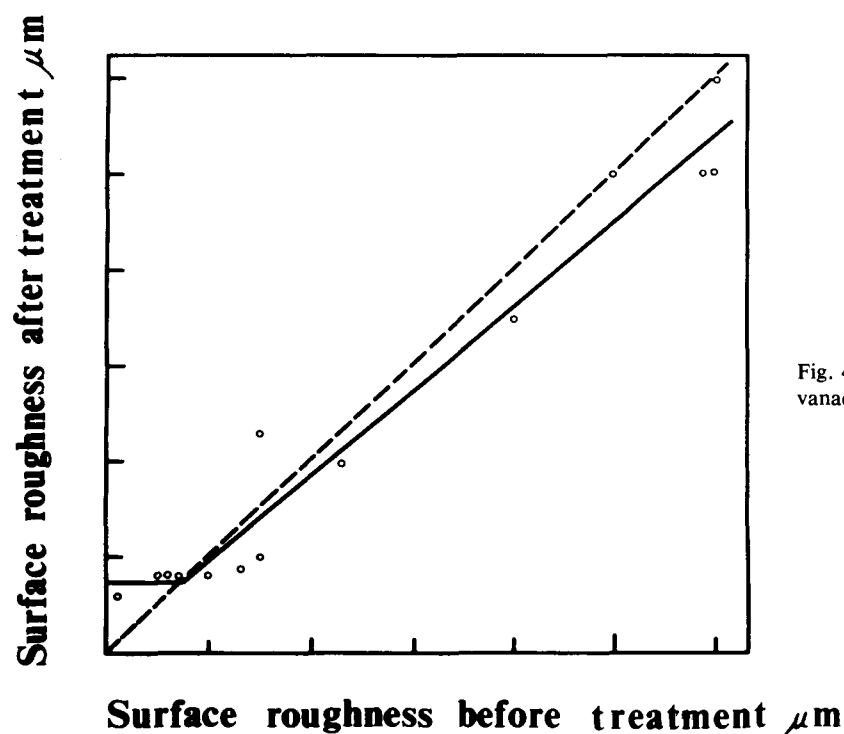Figure 4 indicates that surface roughness is generally unchanged except below 0.5 μm, thus eliminating the

Fig. 4—Change in surface roughness through application of vanadium carbide coating.

Surface roughness before treatment μm

need for further finishing. If a greater degree of smoothness (such as mirror finish) is needed, lapping with diamond powder is employed.

Results obtained from functional parts confirm absence of cracks, spalls or exfoliation.

Features of TD process are summarized as follows:
1. Simple equipment required;
2. Ease of operations;
3. Easy change of coating elements;
4. Selective carbide coating;
5. Uniform coating, even in narrow recessed areas;
6. No air pollution and easy water treatment;
7. Good bath stability and life;
8. Low cost.

PROPERTIES OF CARBIDE COATED STEELS

As seen in Fig. 5, which shows vanadium carbide layer formed on D3 steel, the carbide layer is pore-free and has a smooth surface.

The distinct boundary line is attributable to the difference in physical and chemical properties between the carbide and the steel. As the layers are metallurgically bonded to the substrate, carbide coated steels maintain the excellent properties inherent in the carbides: high hardness, excellent wear, seizure, corrosion, and oxidation resistance. Thus the process has a wide range of practical application.

Hardness

The hardness of the layers mainly depends on the carbide species formed on the surfaces. The Vickers hardness measured is about 3500 for vanadium carbide layer, 2800 for niobium carbide layer, and 1700 for chromium carbide layer.

Wear Resistance

Figure 6 illustrates graphically the results of the test with a disc and flat plane type wear test machine (Ohgoshi type) in which the periphery of the rotating counter disc (30 mm diam × 3 mm thick annealed Cr-Mo structural steel) is made to contact the flat plane made of tested material specimen (carbide coated steel) without any lubricant. Vanadium or niobium carbide coated steels were comparable to titanium carbide coated steels made by CVD, in wear rate within the whole range of sliding speed tested.

Figure 7 shows wear results with carbide coated steels and other materials, subjected to the same test. The wear rate of carbide coated steels is far less than other wear resistant surface hardened materials.

The excellent wear resistance was confirmed against various materials, including nonferrous metals, sand, glass, wood, carbon, rubber, plastic, textile, and paper.

Seizure Resistance

The carbide coated steels demonstrate excellent seizure resistance. In the Falex test, serious scuffing was observed on the surface of hardened D2 steel pins, while no visible change occurred in carbide coated pins.

Table II shows the load at which seizure occurred, when the coated block was contacted under successively increased loading without lubricant. Seizure was estimated to have occurred from the torque curves; the vanadium carbide coated block started to seize under
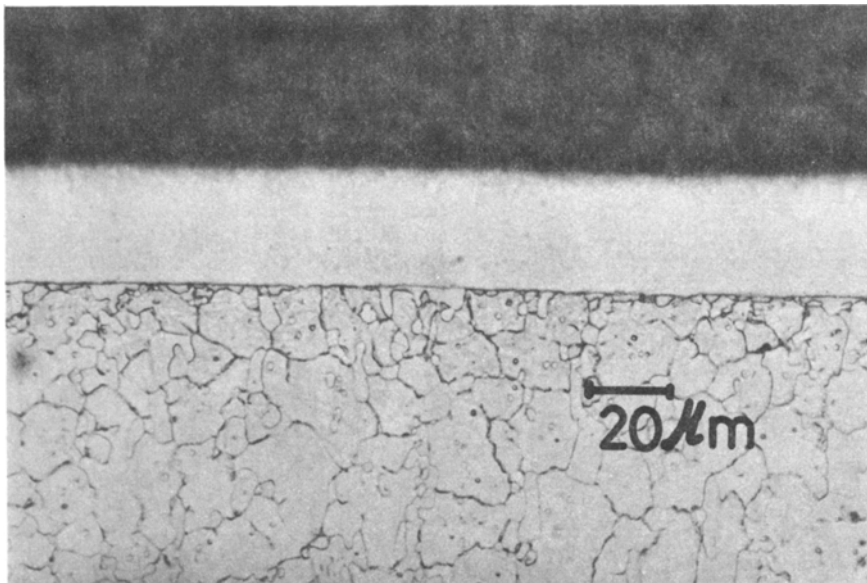

Fig. 5—Microstructure of the vanadium carbide layer formed on high carbon-high chromium steel AISI D3.

much heavier loads than hardened tool, nitrided or chromium plated steels. Niobium, titanium, and chromium carbide coated blocks approximated the same results.

Toughness

As shown in Figs. 8 and 9, the carbide coating does not reduce rupture strength and energy absorption in
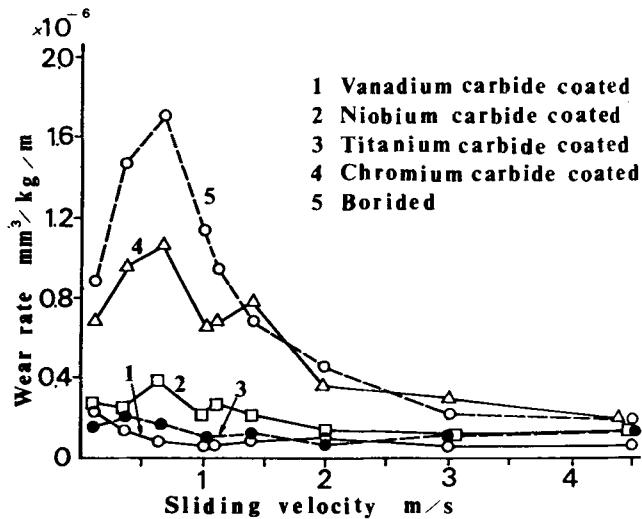
Fig. 6—Comparison of wear rate in the dry wear test (Load: 0.3 → 3.3 kg, Sliding distance: 600 m).

1 Vanadium carbide coated
2 Niobium carbide coated
3 Titanium carbide coated
4 Chromium carbide coated
5 Borided

1 VC coated
2 TiC Coated
3 NbC coated
4 Cemented WC+Co
5 Thermal sprayed WC+Co
6 Cr plated
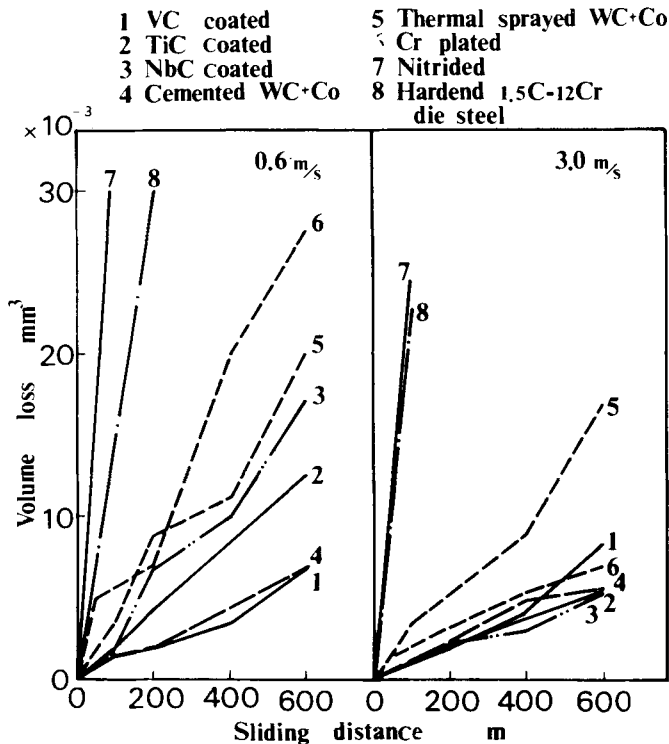7 Nitrided
8 Hardend 1.5C-12Cr die steel

Fig. 7—Comparison of volume loss in dry wear test (Load: 0.3 → 3.3 kg, Sliding velocity: 0.6 or 3.0 m/s).

static and dynamic bending tests. Therefore, when steels with high toughness are used as substrates, tough carbide coated steels can be obtained.

Resistance to Cracking and Flaking

Microcracks in carbide layer were observed on deformed coated steels. The measured critical strain to induce microcracks, invisible to the naked eye, but observable with a microscope, was roughly 0.8 to 1.4 pct under tensile stress, and 0.6 to 1.0 pct under compressive stress, depending on the kind of carbides. No flakes were observed on carbide layer on an 8 mm steel rod bent at an angle of 80 deg.

Hammer tests were carried out to investigate resistance to flaking by use of a ball-pointed hammer, 0.4 kg in weight. A chromium plated layer of 10 μm thickness flaked completely at 50,000 blows; a vanadium carbide layer of the same thickness neither cracked nor flaked at 200,000 blows.

Table II. Comparative Loads at Which Seizure was Observed When Successively Increased Load was Applied, kg

Block Counter ring	VC coated W1	Nitrided H12	Cr plated 1045	Hardened D2
Austenitic Stainless Steel	7.3	4.2	3.6	2.7
Gray Cast Iron	11.8	—	—	4.1
Al-Si Alloy	3.0	1.7	1.8	2.5
VC Coated Steel	>14*	—	—	—

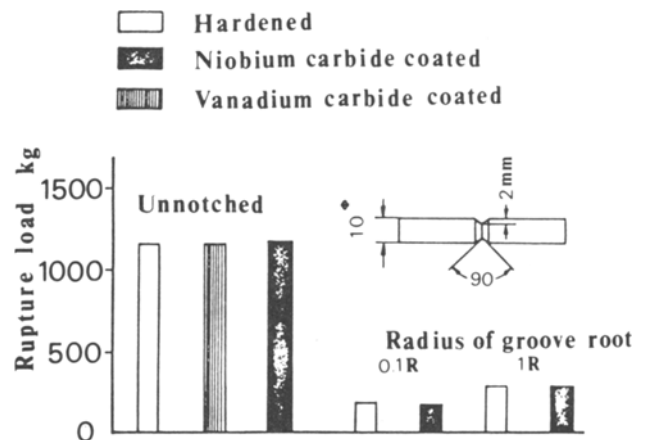*Over the limit value measurable by the test machine.

Fig. 8—Comparison of rupture load in the static bending test with grooved and unnotched cold working die steel (AISI D2) specimens.
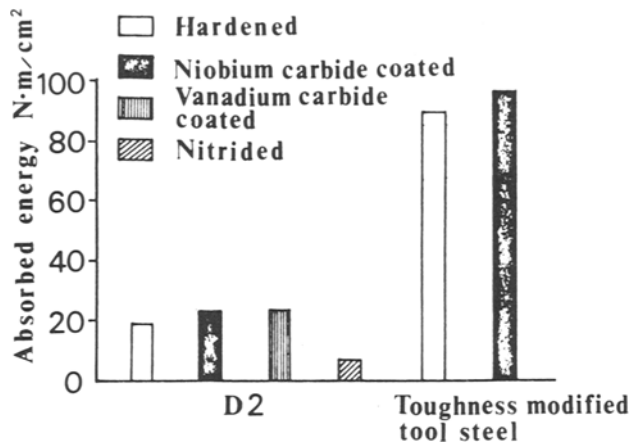
Fig. 9—Comparison of absorbed energy in the Izod type dynamic bending test with grooved tool steel specimens (Specimen size: 14 mmφ × 103 mm, Radius of groove root: 5 mm).

Corrosion Resistance

The carbide coated steels and cemented carbides have good corrosion resistance to various aqueous solutions, such as hydrochloric, sulphuric and nitric acids.

Chromium carbide coated steel exhibited good corrosion resistance outdoors, in a chlorine atmosphere and in the salt spray test. Carbide coated steels provide resistance to the attack of molten metal such as aluminum.

Oxidation Resistance

When exposed to air for a long time at a temperature above 500 °C, vanadium and niobium carbide coated steels were significantly oxidized. However, chromium carbide coated steel was minimally oxidized at temperature to 1073 K.

Resistance to Heat Checking

Resistance to heat checking was investigated in a test of 360 cycles of localized heating to 973 K using high frequency current and water quenching (cycle time: 10 s). Carbide coated H12 hot work die steel exhibited fewer heat checks than the conventionally hardened die steel.

No crack was formed on a carbide coated steel specimen following 830 cycles of immersion in molten aluminum alloy and cooling in air.

Identical results were obtained after 72 cycles of heating to 973 K in electric furnace and water cooling.

Cutting Tool Tests

In turning tests for steel and nonferrous metals, the coated cemented carbides and tool steels showed good

results. Tool wear and chip adhesion was significantly reduced.

Coated steels and cemented carbides produced good performance cutting all metals and nonmetallic materials.

APPLICATION OF THE PROCESS

The Toyota Central Research and Development Laboratories, developer of the process, have named the process TD (Toyota Diffusion Coating Process). The TD process has found substantial acceptance in various metal working areas in Japan since 1971. The most frequent application of the carbide coating process has been for dies used in sheet metal forming and machine parts subject to sliding wear. Other applications include dies for cold forging, aluminum die-casting, cutting tools for both metals and nonmetallic materials and precision parts for textile machinery.

Some specific applications include:

1. Niobium carbide coating to coat pins to prevent soldering in aluminum die casting. Fig. 10 shows the increase in life of niobium carbide coated pins compared to nitrided pins.

2. Vanadium carbide coating for progressive dies involved with piercing, chamfering and embossing on automotive parts, such as shown in Fig. 11. Vanadium
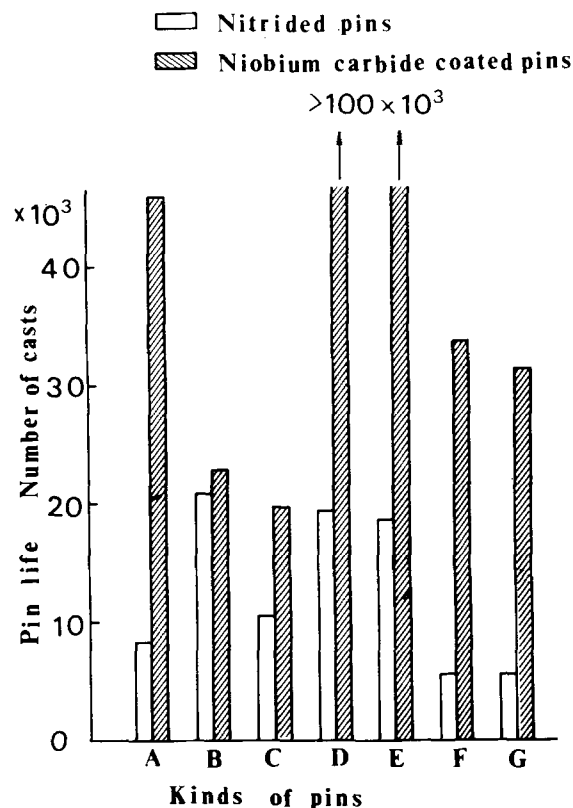

Fig. 10—Life increase of core pins for aluminum die casting through application of the niobium carbide coating.
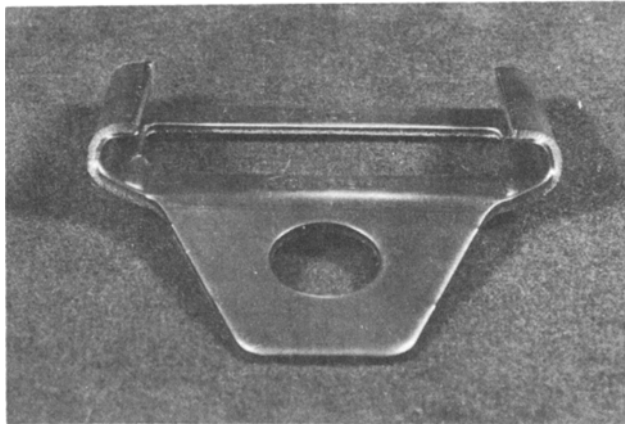
Fig. 11—A product formed with the progressive die set up.

Table III. Improvement in Product Quality Observed by Application of the Vanadium Carbide Coating to the Drawing Die

	Hardened D2 die	Vanadium carbide coated D2 die
Max thickness of t Portion	1.9 mm	2.3 mm
Surface Roughness of w Face	12-18 μm	Less than 3 μm
Ratio of rejected Produce	7 pct	Less than 0.3 pct

carbide has reduced wear and falling caused by excessive hardness of the sheet material.

3. Vanadium carbide coated D2 die steels for drawing dies has reduced die repolishing substantially. Conventional D2 die steel required die repolishing at intervals of 500 to 18,000 parts. The vanadium carbide coated die produced approximately 2,000,000 parts without exhibiting galling, and with optimum surface finish. Table III shows specific improvements due to vanadium carbide coating.

4. Vanadium carbide coatings have been found very effective in reducing wear of extrusion dies used in rubber forming. The life of the dies used to produce window

Table IV. Comparison of Lives Between Punches Made of Hardened Steels and the Vanadium Carbide Coated Punches

Punch Material and Treatment		Life of Punches, Shots
M2	Hardened	Less than 10,000
Cemented carbide	—	25,000 60,000
D2	Vanadium carbide steel	33,500 77,500

seals has increased from 30 h for conventionally hardened die steels, to 900 h for the coated dies.

5. Vanadium carbide coated high speed steel and cemented carbide were successfully used to replace cold work die steels with the results shown in Table IV.

CONCLUSIONS

Compact carbide layers can be formed on steels and other materials by immersing in a bath with borax solvent and carbide forming elements. The process utilizes conventional salt furnace equipment and operates with extensive bath life, and without air or water pollution. The carbide coated steels and cemented carbides have excellent resistance to wear, seizure and flaking, as well as high hardness and adequate toughness. There is substantial service performance documentation as applied to die steels for sheet metal forming, cold forging, die casting, cutting tools and other precision machine parts.

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