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Diffusion Carbide Coatings Formed in Molten Borax Systems

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Abstract. Carbide coatings can be formed on carbon containing materials such as steels, nickel and cobalt alloys, cemented carbides, and carbon itself, by immersion in a molten borax based bath, often used as a basis for boriding. Coatings, thus formed, consist of VC, NbC, TaC, TiC, and Cr_7C_3. They are superior to coatings formed by conventional surface hardening techniques in resistance to wear, seizure, oxidation, and corrosion. Selected additives to a borax bath can produce either a carbide layer, a borided layer (the boride of the main element in the substrate), or no layer at all. An understanding of additive behavior as dictated by the free energies of carbide formation and oxide formation of elements added to molten borax will explain such behavior.

Materials carbide coated by the process have excellent tribological, mechanical, and chemical properties, and are very similar to Titanium carbide coatings produced by chemical vapor deposition, in performance in industrial applications. Unlike some conventional surface hardening techniques, the improved surface properties are not achieved at the expense of the mechanical strength; there is no significant reduction in strength between conventionally hardened steel and that coated by this process.

INTRODUCTION

In recent years, three new technologies have been developed to apply thin coatings of very hard material, such as carbides, nitrides, and oxides, to dies and tools. The three techniques are: (a) chemical vapor deposition (CVD); (b) physical vapor deposition (PVD) (ion plating, reactive sputtering); and the salt bath immersion process developed by ourselves [1]. The salt bath process involves immersion of materials to be coated in a molten borax bath (usually 850–1050° C) that contains the relevant carbide forming element (usually vanadium, niobium, or chromium), under ambient atmosphere. The temperature of the molten borax bath is generally adjusted to be around the hardening temperature of the substrate steel; so that coating and substrate hardening are performed in the one operation. Thus, the salt bath process can be said to be of the kind used for the salt bath heat treatment of steels, and slow cooling can be done easily.

Unlike CVD and PVD, which are confined to die and tool application, the salt bath process involves relatively simple equipment (e.g., there are no requirements for vacuum or controlled atmospheres) and is low in coating cost. Thus, the process has been used for small machine parts such as fastners, roller chains and pumps as well as for dies and tooling. The carbide forming element (CFE), which dissolves in the molten borax, reacts with carbon in the material, thus gradually building up a layer of carbide. Typical coating thickness is 2–15 μm. The borax bath features good bath stability and life.

REACTION IN MOLTEN BORAX BATHS

As carbide coatings are formed through the reaction between the CFE in the borax bath and carbon atoms in the substrate, the salt used in the process comprises a mixture mainly of borax plus compounds containing the CFE.

The boriding process by use of the molten borax baths containing selected additives, had been reported before the development of the carbide coating process. To make clear the relationship between the kind of additive and the coating formed, we examined the surface layers on metals immersed in various kinds of

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borax bath with added powders of alloys and pure metals containing the relevant elements [1,2].

As a result, we conclude, the relationship between the kinds of layers formed and the additives can be clarified, by taking the free energy of oxide formation and carbide formation into account. The boride layers are formed in the bath containing elements which have a smaller free energy of oxide formation than B_2O_3, as shown in Figure 1, through the diffusion of boron atoms, thus produced by the reduction of B_2O_3. The carbide layers can easily be formed on carbon containing materials in the bath containing elements that have a relatively small free energy for carbide formation, the CFE, as shown in Figure 2. If the elements with small free energy for carbide formation also have a smaller energy of oxide formation than B_2O_3, there may be an opportunity for both carbide formation and boride formation. Titanium, tantalum, and manganese belong to this category [2,3]. As illustrated in Figure 3, the carbon content in the steel and the amount of such an element added to the borax bath are controlling factors in determining the coating formed.

In the bath containing elements which have large free energies both for carbide and oxide formation, neither carbide nor boride layers can be formed. However, if the said elements should have relatively small atomic size, solid solution layers can be formed. Even in the case of CFE, solid solution layers can be formed on metals unless the metals have the critical amount of carbon sufficient to produce carbide layers, which are dependent on the carbide type and bath temperature [4], as exemplified in Figure 4.

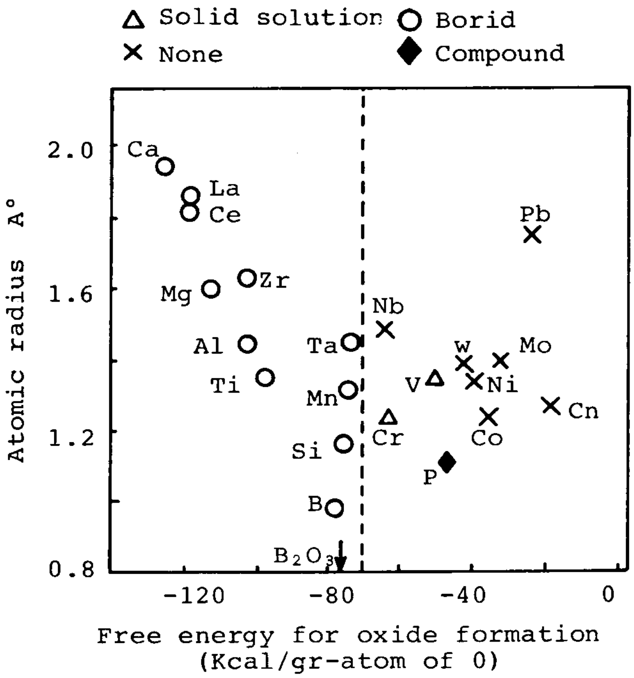

Fig. 1. Relationship between free energy for oxide formation and atomic radius of elements added to a borax bath and layers formed on pure iron at 1273 K.

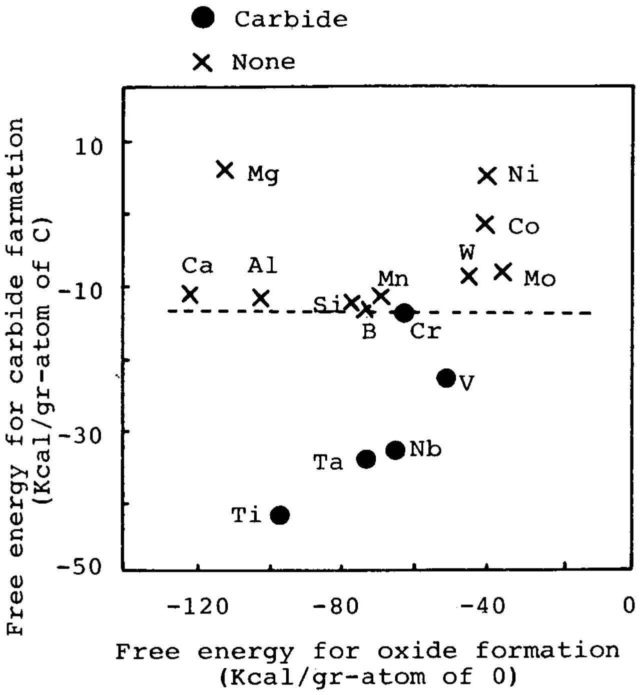

Fig. 2. Relationship between formation free energies of elements added to a borax bath and carbide formation on graphite at 1273 K.

Figure 5 graphically illustrates the relationship between the kinds of layers formed on high carbon steel in the borax bath and the free energies both for carbide formation and oxide formation.

Figures similar to Figure 2 and Figure 5 have been produced with nickel alloys and cobalt alloys containing no carbon and appreciable carbon, respectively.

To dissolve CFE into the borax baths, not only metal powders but also a CFE oxide can be introduced. However, an additive containing the elements which have smaller free energies for oxide formation than the CFE oxide, a reducing agent, must be added together with the CFE oxide, and too much reducing agent results in the formation of a boride layer due to excess boron generated in the bath through the reduction of B_2O_3, as shown in Figure 6 [5].

We found, moreover, the fact that complex carbide layers are formed on metals in the baths with additions of both CFE oxide and metal powders containing other CFE, irrespective of comparative free energy for oxide formation, as exemplified in Figure 7. Complex carbide layers are formed also in the bath with metal powders containing two or three different CFE, to obtain a combination of advantageous properties [6].

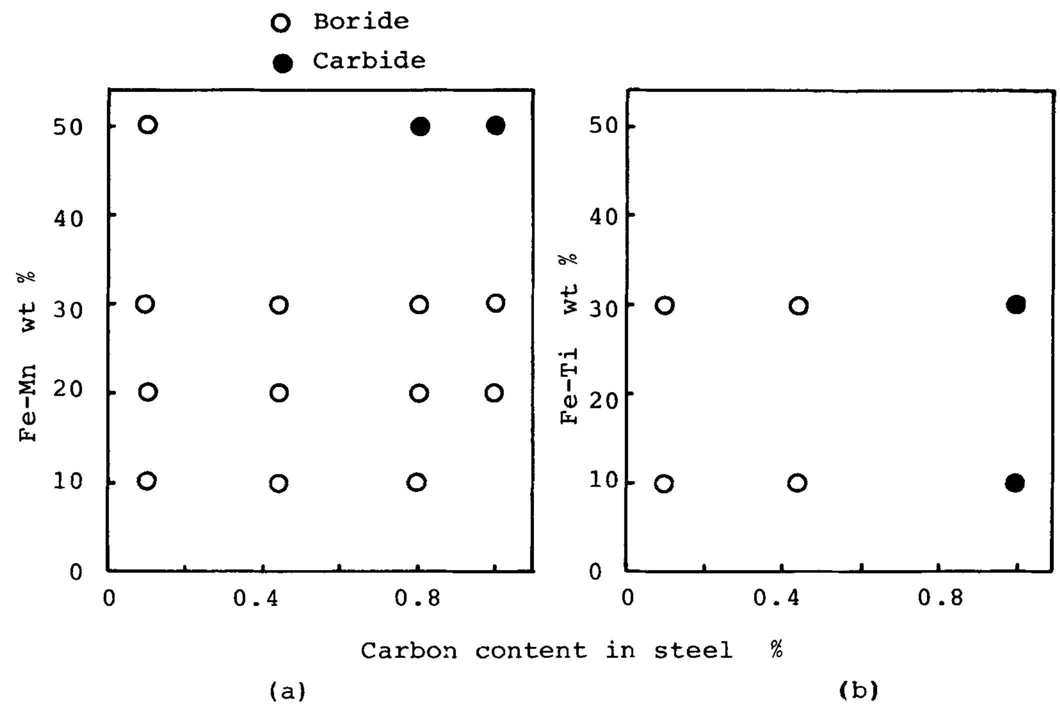

Fig. 3. Relationship between amount of Fe-Mn (a) and Fe-Ti (b) added in borax bath and layers formed on plain carbon steels containing different carbon contents at 1273 K.

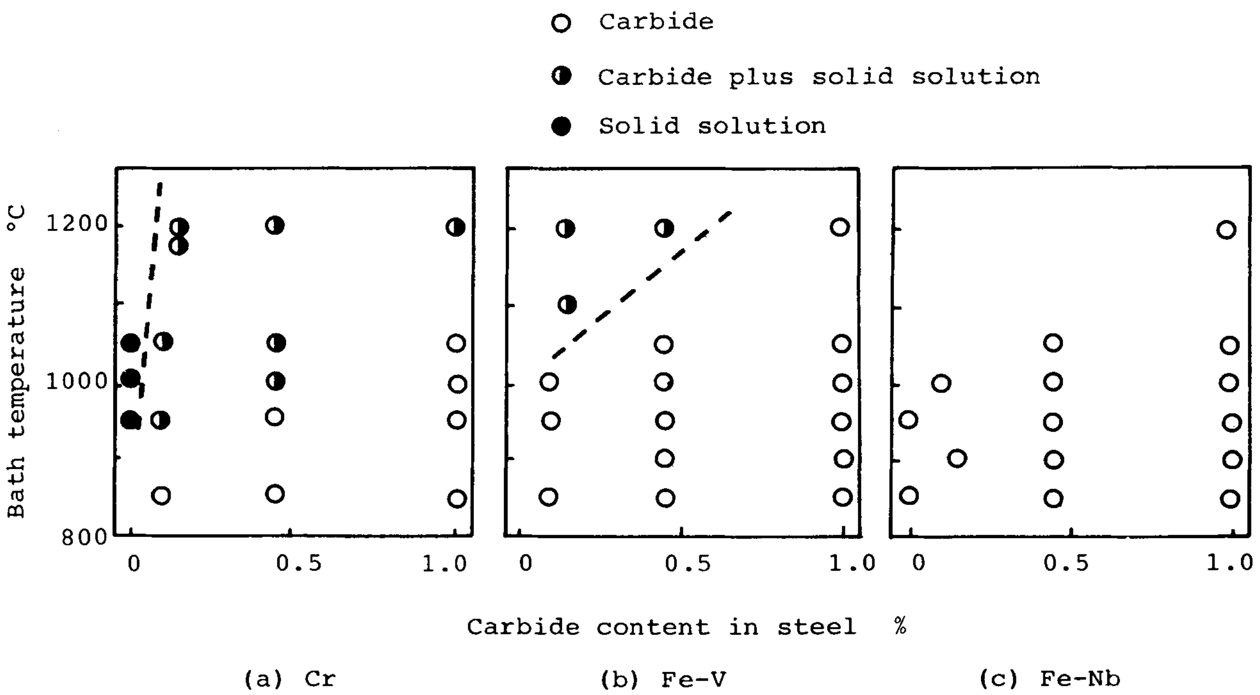

Fig. 4. Relationship between temperature of borax baths, with appreciable amount of Cr, Fe-V, and Fe-Nb powders added and layers formed at varying carbon contents, at 1273 K.

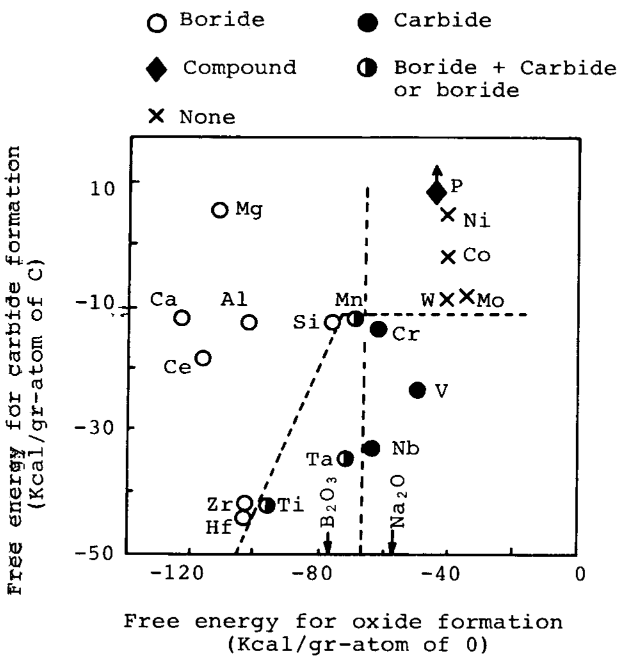

Fig. 5. Relationship between formation free energies of elements added to a borax bath and kinds of layers formed on high carbon steel at 1273 K.

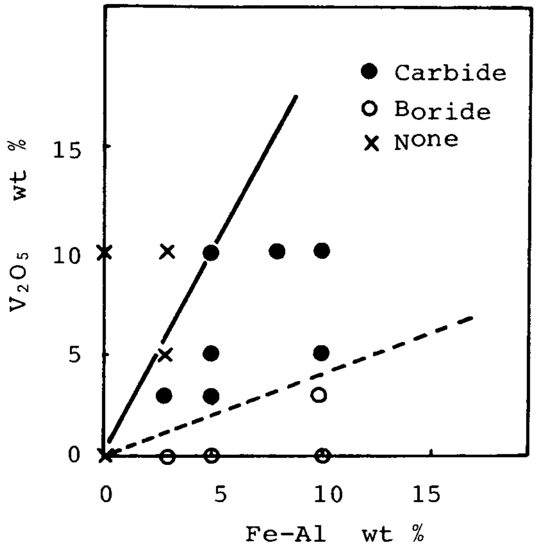

Fig. 6. Relationship between amount of vanadium oxide and ferro-aluminum added to a borax bath and layers formed on high carbon steel (W1) at 1223 K.

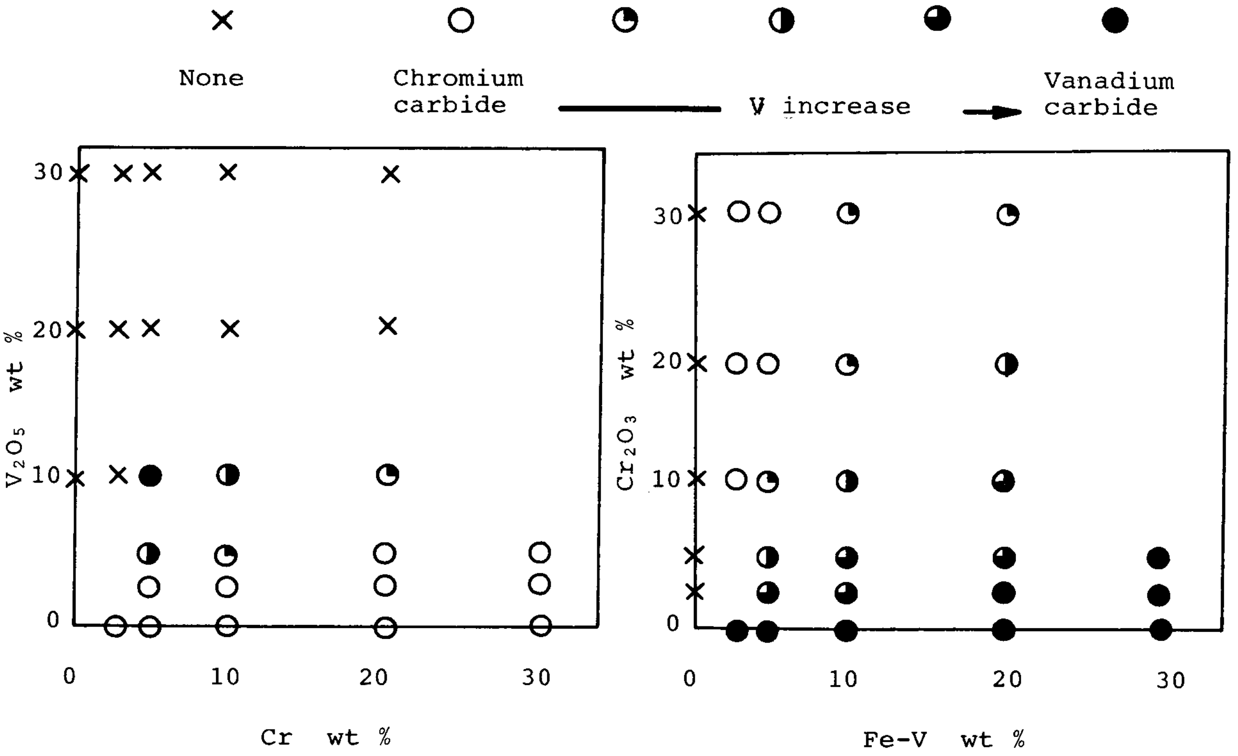

Fig. 7. Relationship between amount of oxides and metal powders added to a borax bath and layers formed on high carbon steel (W1) at 1223 K.

CARBIDE LAYER FORMATION

While immersed in the bath, carbide layers are formed on the surface of materials through a reaction between CFE dissolved in the fused borax and carbon in the materials. The carbide layers grow as the carbide forming reaction is maintained by the continuous supply of carbon atoms to the surface of the coating from the base metal.

The thickness of the carbide layer can be precisely controlled by the length of immersion time, bath temperature and base metal composition. Immersion time ranges from 30 minutes to 10 hours to obtain the optimum thickness of 5–15 μm for most applications.

Carbides, thus formed, are VC, NbC, TaC, TiC, Mn_5C_2, Cr_7C_3, and $Cr_{23}C_6$. Detailed explanation on this items have been already reported by us [1] and the results of further researches will be introduced at other opportunities.

PROPERTIES OF CARBIDE COATED MATERIALS

Materials coated with vanadium carbide and niobium carbide are far superior to cemented carbides and materials surface hardened with conventional processes such as plating, nitriding, and thermal spraying, in surface hardness, resistance to wear, seizure, and corrosion, etc. They are also not inferior to materials with TiC coating produced by CVD method. Coatings applied by this process are also superior to TiN coatings by PVD and CVD in adhesion to substrate (Refer to Figures 8–13 and Table I.).

Chromium carbide coatings are inferior to vanadium carbide and niobium carbide coatings in surface

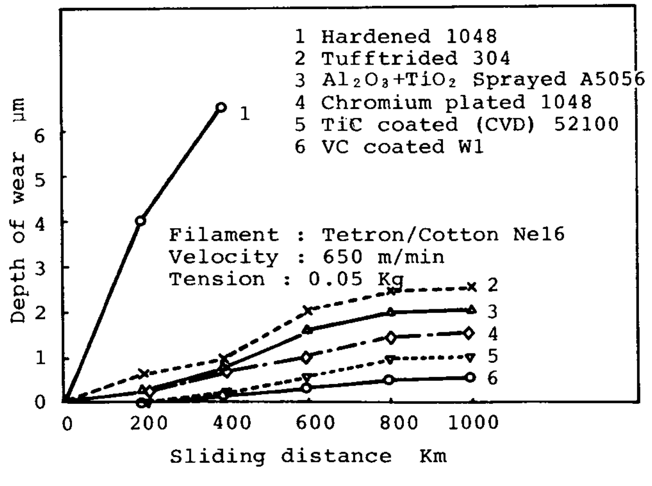

Fig. 8. Comparative depth of wear scar on cylindrical specimens on which a textile fibre is running continuously (N. Miyamoto et al.).

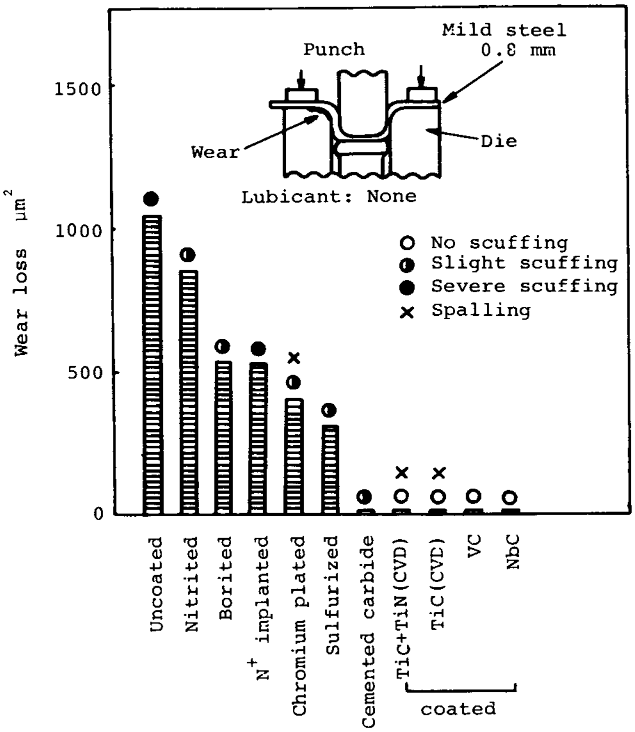

Fig. 9. Comparative cross-sectioned area worn, scuffing and spalling on die radius in a sheet steel bending test.

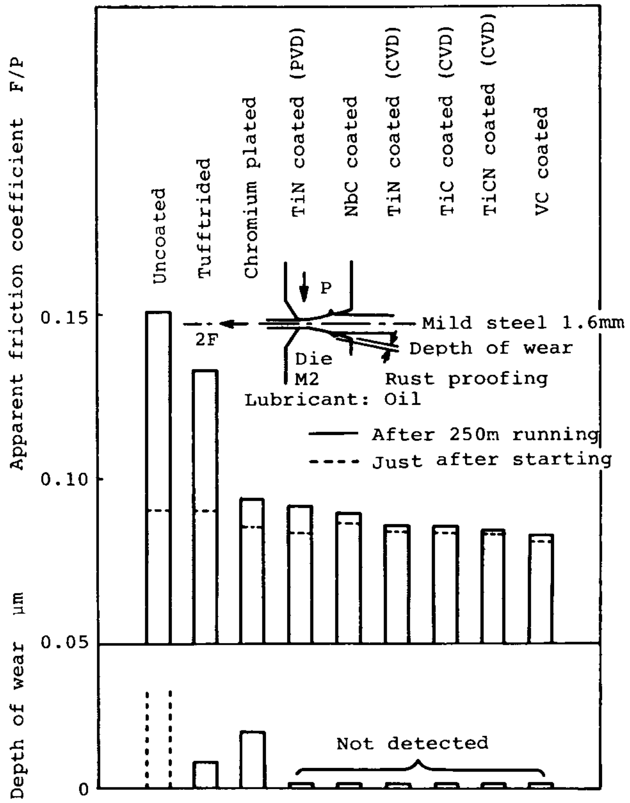

Fig. 10. Comparative friction coefficient and depth of wear on dies in a sheet steel ironing test.

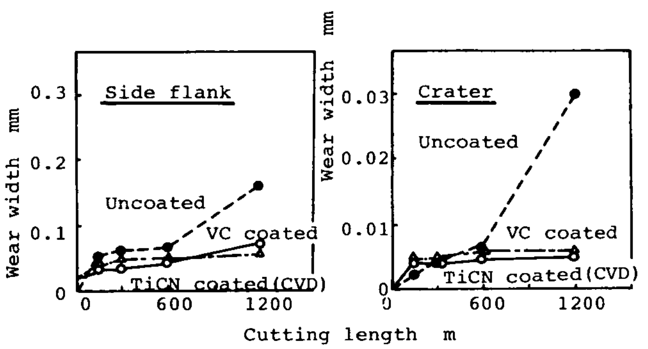

Fig. 11. Comparative width of wear on throw-away tips in a turning test.

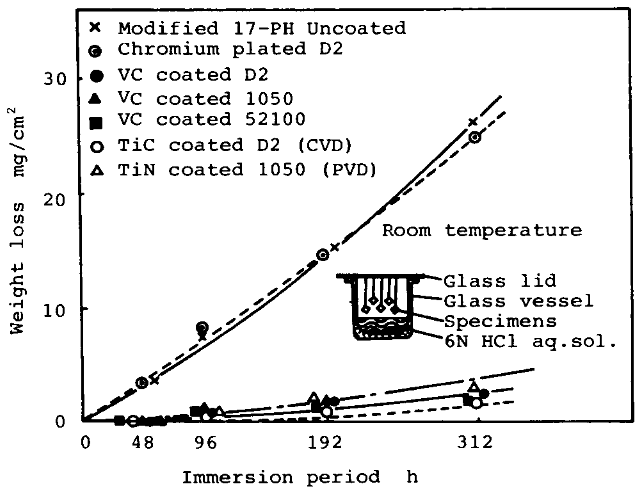

Fig. 12. Comparative loss of weight by corrosion in hydrochloric acid vapour.

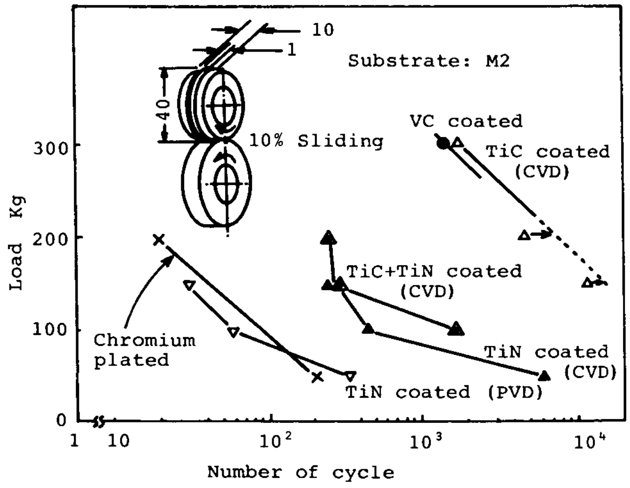

Fig. 13. Comparative number of cycle at which spalling occurred in a rolling test with sliding.

hardness and resistance to wear, while they have excellent resistance to high temperature oxidation as shown in Figure 14.

It should be emphasized that excellent properties, as mentioned above, are produced without being detrimental to the bulk properties such as toughness, fatigue strength [7], etc. as shown in Figures 15–17. Thus, carbide coated materials are characterized by a proper combination of excellent surface properties inherent in the carbides and high strength inherent in the substrate materials. The excellent properties of carbide coated materials have led to the widespread application of the process to a wide variety of industrial articles requiring good resistance to wear, seizure, oxidation, and corrosion.

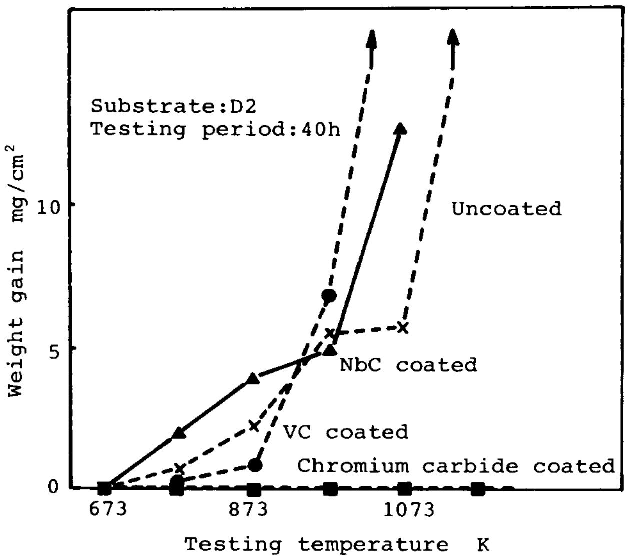

Fig. 14. Comparative weight gain in a high temperature oxidation test.

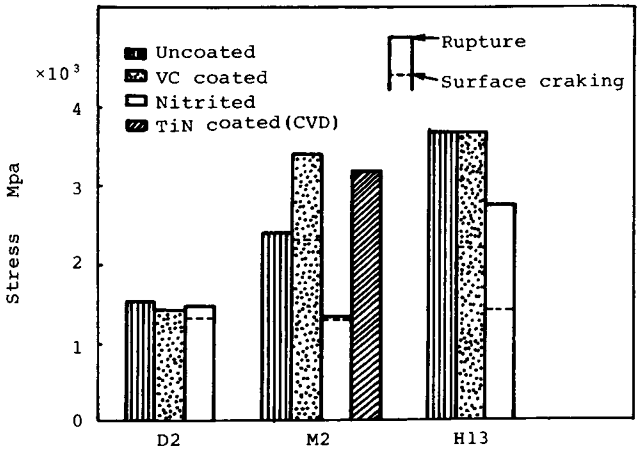

Fig. 15. Comparative rupture and surface craking stress in a static bending test (H.C. Child et al.).

Table I. Comparative loads (kg) at which scoring was observed when a successively increased load was applied without lubricant (sliding velocity: 2.6 m/s)

	Block (10 × 10 × 10 mm)								
Countering 50 mm dia × 10	D2 Hardened	Cemented Carbide	1045 Chromium Plated	1045 Nitrided	W1 Borided	D2 TiC Coated (CVD)	W1 VC Coated	W1 NbC Coated	W1 Chromium Carbide Coated
SUS304	2.7	7.7	3.6	4.2	10.6	7.5	7.3	7.7	4.2
Gray cast iron	4.1	4.0	—	—	3.4	—	11.8	11.2	—
Gray cast iron									
VC coated	—	—	—		>14	—	>14	>1.4	—
NbC coated	—	—	—	—	>14	—	—	>14	10.3
Chromium carbide coated	—	—	—	—	—	—	11.1	13.0	>10.5
A1–20% Si	2.5	2.1	1.8	1.7	3.1	—	3.0	2.4	3.1

> : over the maximum load that can be supplied by the test machine.

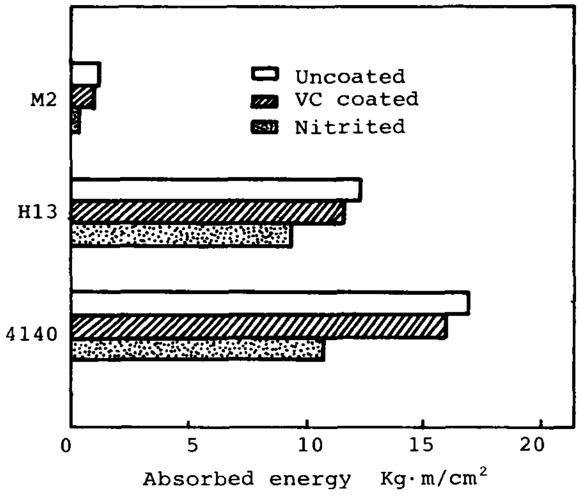

Fig. 16. Comparative absorbed energy in the dynamic bending test.

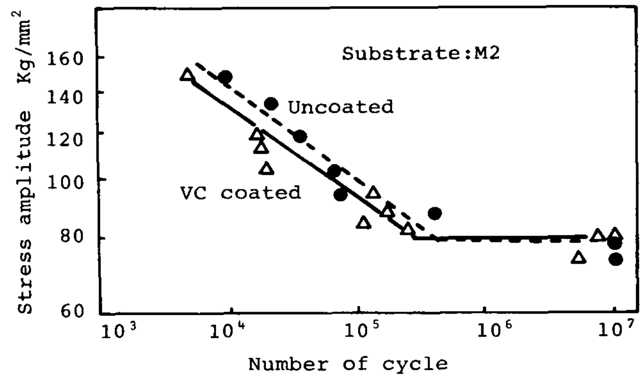

Fig. 17. Comparison of fatigue strength in a rotating bending test.

SUMMARY

The molten borax added with some additives can produce carbide coatings and borided layers on materials immersed therein. The relationship between kind of layer formed and the additives can be clarified by taking the free energy of oxide formation and carbide formation into account. Thin layers of VC, NbC, Cr_7C_3, or other carbides are formed through the combination of carbide forming elements in the bath and carbon in the substrate.

The carbide coating technique based on this phenomenon is highly competitive with CVD and PVD techniques in properties of coated materials and practical applications.

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