

STUDIES ON THE SURFACE MODIFICATION AND MEASUREMENTS

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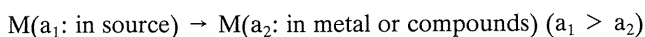
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Abstract

At first, important points and trends of the development of the surface modification engineering were mentioned and discussed in terms of its application according to wear resistance, hardness and corrosion resistance etc..

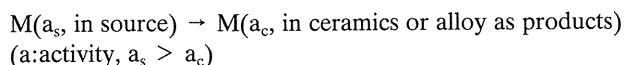
Then by means of disproportionation reaction in molten salts, new surface modification process was studied in details.

1) Surface coating treatment by chemical transport using disproportionation reaction in molten salts was studied comprehensively. The metal such as Si, Cr, Ti, V, Zr, Ta and etc. was deposited to form alloy and compound coating on the surface by application of the disproportionation reaction in molten halide salts, KCl-BaCl₂-NaF-Metal-Metal salts system. The overall reaction can be represented as follows.



Various films were coated on steels by this method: ferrosilicon and ferrosilicon-graphite composite, chromium carbide, titanium carbide, vanadium carbide, tantalum carbide and boride films of these metals. The surface hardness (Hv) of these films ranged from 1000 to 3000 and they had very high wear resistance.

2) The formation of some functional carbide films and alloy ones were performed on some substrates like steels by immersing substrates into such molten salts system as KCl(-NaCl)-BaCl₂-NaF-Metal powder-Metal oxide or halide. These formation reactions of films is a disproportionation reaction which is proceeded through the difference of metal activities between in source and in films. Total reaction is as follows:



This paper represents the mechanisms and characteristics of some ceramic films, such as boride, nitride and silicide film as the progress and application of surface modification by disproportionation reaction. As though substrates for this investigation don't have any component elements of films, they can be

formed on substrate by multifold processes using each disproportionation reaction in molten salts, respectively. These films were submitted to various inspections such as X-ray analysis, microscopic observation, EPMA and corrosion test. They were excellent at tests of surface hardness, wear resistance and corrosion resistance.

I. Fundamentals of Surface Modification

1. Introduction

Surface modification is one of the most important technology which can satisfy the demands for various properties of material surface. Nowadays material science and technology have made remarkable progress, and then materials must be often used under an extreme situation such as high pressure, high vacuum, high temperature, high speed, long hours, high load, and etc.. Therefore surface modification technology is very important in the view point of the economy as well as the development of materials.

In this review, several fundamental points and trends of the development of the surface modification technology will be mentioned and discussed in terms of its application. This technology can be applied to both structural materials and electronic materials (functional materials). Here various surface properties of the former such as wear resistance, heat resistance, oxidation resistance, corrosion resistance, hardness and so on will be discussed.

2. View point of surface modification and its materials components

Surface modification process can be classified into two principal categories.

(1) Method by change of substrate surface itself

Mechanical treatment method, Chemical modification method, Laser surface treatment, Ion nitriding, Ion carburization, Boriding, Metal diffusion treatment, Ion implantation, Plating-heat treatment.

(2) Method by coating the substrate surface with special thin film

Spraying coating process, Electroplating, Composite process, Ion-beam mixing, PVD, CVD, Chemical densified coating method.

Various methods, elements, and compounds are used as material component of surface modification. Here carbides, nitrides and borides are mainly discussed. TiC, VC, TaC, WC, NbC, ZrC, Mo₂C, Cr₇C₃, Cr₃C₂, B₄C and SiC can be mentioned as carbides, TiN, VN, TaN, NbN, ZrN, HfN, CrN, Si₃N₄, BN, AlN as nitrides, TiB₂, VB₂, WB₂, ZrB₂, MoB₂, NbB₂, CrB₂, AlB, SiB₂ as borides, TiO₂, ZrO₂, Nb₂O₅, Ta₂O₅, Al₂O₃, MgO, SiO₂, Cr₂O₃, Fe₃O₄, In₂O₃, SnO₃ as oxides. And moreover TiSi, MoSi, ZrSi, CrSi as silicide, sulfides, BP, C, B, i-carbon, diamond can be mentioned.

All these material components have high melting point, hardness (1000 ~ 2000Hv), oxidation resistance, corrosion resistance, low coefficient of thermal expansion ($5 \sim 10 \times 10^{-6}/^{\circ}\text{C}$). Users can select an appropriate component for the purpose.

2.1 Nitride and carbide

Properties of various nitrides and carbides are shown in Table 1 and Table 2, respectively.

Table 1. Properties of various nitrides

nitride properties	TiN	ZrN	HfN	VN	TaN	NbN	BN	Si ₃ N ₄	AlN	CrN	Cr ₂ N
crystal system	cubic	cubic	cubic	cubic	cubic	cubic	hexagonal cubic	hexagonal (α , β)	hexagonal	cubic	hexagonal
density(g/cm ³)	5.44	7.35	13.94	6.08	14.1	8.26 8.4	2.15 3.48 2.27 3.49	3.18 3.19	3.25 3.30	6.1	6.51
melting point(°C)	2900 3220	2930 2980	3300 3307	2050 2360	2980 3360	2050	decomposition 2720~ 3000	decomposition 1900	decomposition 2200~ 2300	1500	—
specific resistance ($\mu\Omega \cdot \text{cm}$)	22 130	11.5 14.0	32	86	135	200	1.7×10^{11}	$> 10^{11}$	2×10^{11}	600 680	79 89
thermal conductivity (CGS)(RT)	0.07	0.04	0.052	0.027	0.021	0.009	orientation	0.035 0.041	0.004	0.0261 0.0307	0.0514 0.0523
microhardness (kg/mm ²)	1800 2100	1400 1600	1500 1700	1500	1060	1400	—	2670 3260	1225 1230(KH)	1000 1188	1522 1629
elastic modulus (kg/mm ²)	25500	—	—	—	58700 (ϵ -TaN)	49300	1160~ 8370 (α -BN)	5620 21800	28100 35200	—	—
coefficient of thermal expansion ($10^{-6} \cdot \text{deg}^{-1}$)(°C)	9.31~9.39 (25-1100)	7.24 (20-1100)	6.9 (20-1100)	9.2 (20-1100)	3.6 (20-700)	10.1 (20-1000)	0.5~1.7 (α -BN) —	2.75 (20-1000)	4.8 (20-300)	2.3 (20-800)	9.41 (20-1100)

Table 2. Properties of various carbides

carbides properties	TiC	ZrC	HfC	VC	TaC	NbC	WC	B ₄ C	SiC	Cr ₃ C ₂	Cr ₇ C ₃	Cr ₂₃ C ₆
crystal system	cubic	cubic	cubic	cubic	cubic	cubic	hexagonal	rhombohedral	cubic hexagonal	orthorhombic	trigonal	cubic
density(g/cm ³)	4.85 4.93	6.44 6.9	12.20 12.70	5.36 5.77	14.48 14.65	7.82	15.6 15.7	2.50 2.54	3.21 3.22	6.68	6.92	6.97 6.99
melting point(°C)	3180 3250	3175 3540	3885 3890	2810 2865	3740 3880	3500 3800	2627 2900	2350 2470	decomposition 2200~ 2700	1895	1782	1518
specific resistance ($\mu\Omega \cdot \text{cm}$)	70 173	50 64	60	150 160	20 175	74 254	53	0.3×10^4 0.8	10 ¹¹ 10 ¹¹	70 80	105 113	125 129
thermal conductivity (CGS)(RT)	0.041 0.06	0.049	0.053	0.010	0.053	0.034 0.041	0.070	1.065 0.069	0.098 0.100	0.045 0.047	0.035 0.038	0.041 0.053
microhardness (kg/mm ²)	2900 3200	2600	2533 3202	2800	1800	2400	2400	2400 3700	3000 3500	1800	1882	1663
elastic modulus (kg/mm ²)	31600 44800	32300 48900	43300	26000 27400	37100 38900	34400	53600 72100	29500 45800	34450 42200	38000	—	—
coefficient of thermal expansion ($10^{-6} \cdot \text{deg}^{-1}$)(°C)	7.95 (25-1000)	7.01 (25-1000)	6.80 (25-1000)	7.25 (25-1000)	7.09 (25-1000)	7.21 (25-1000)	3.84 —	4.5 25	4.7 (20-2127)	11.7 (20-1100)	9.4 (20-1100)	10.1 —

Most of nitrides have high melting point ($> 2000^{\circ}\text{C}$). Their resistivity ranges from $10 \sim 20 \mu\Omega \cdot \text{cm}$ like ZrN and TiN to $10^{19} \mu\Omega \cdot \text{cm}$ like Si_3N_4 . Their hardness attains more than 1200 kg/mm^2 e.g. Si_3N_4 ($2600 \sim 3200 \text{ kg/mm}^2$) and TiN ($1800 \sim 2100 \text{ kg/mm}^2$). However in general, nitrides have low elasticity and are brittle.

On the other hand, density of carbides ranged widely from $2.5 \sim 15 \text{ g/cm}^3$ as well as that of nitrides and specific resistivity from TaC of $20 \sim 175 \mu\Omega \cdot \text{cm}$ to SiC of $10^9 \sim 10^{11} \mu\Omega \cdot \text{cm}$. In carbides, there are no insulators such as Si_3N_4 in nitrides. Melting point of carbides is generally higher than that of nitrides, and that of most carbides attains more than 2500°C . Thermal conductivity of carbides is generally larger than that of nitrides, which can be supposedly applied to various uses. Microhardness of carbides is much higher than that of nitrides, which can be supposedly applied to various uses. Microhardness of carbides is much higher than that of nitrides i.e. 1800 kg/mm^2 for TaC and $3000 \sim 3500 \text{ kg/mm}^2$ for SiC. Elasticity of carbides is slightly higher than that of nitrides, but they have also low elasticity and are brittle in general.

2.2 Oxides and borides

Various properties of oxides and borides are shown in Table 3 and 4.

Density of oxides ranges from $4 \sim 10 \text{ g/cm}^3$. Melting point of oxides is lower than that of both nitrides and carbides. Specific resistance of oxides is much higher than that of nitrides and carbides ($10^7 \sim 10^{22} \mu\Omega \cdot \text{cm}$), and many oxides can be used as insulator. Thermal conductivity ranges from 0.001 to 0.01, which can be concluded from the value of specific resist-

Table 3. Properties of various oxides

oxide properties	TiO ₂	ZrO ₂	HfO ₂	V ₂ O ₅	Ta ₂ O ₅	Nb ₂ O ₅	WO ₃	Al ₂ O ₃	Cr ₂ O ₃
crystal system	tetragonal	tetragonal	cubic	orthorhombic	orthorhombic	hexagonal	tetragonal	hexagonal	orthorhombic
density(g/cm ³)	4.24	6.27	9.68	3.36	8.73	4.95	6.47	3.97	5.21
melting point(°C)	1855 } 1885	2900	2780 } 2790	670 } 685	1755 } 1815	1470 } 1510	1473 } 2130	2050	2309 } 2359
specific resistance ($\mu\Omega \cdot \text{cm}$)	3×10^{16}	—	—	3×10^7	1×10^{11}	—	2×10^{11}	1×10^{22}	—
thermal conductivity (CGS)(RT)	0.008 } 0.015	0.0047	0.0011	0.0010	—	—	—	0.095	—
microhardness (kg/mm ²)	1000	1300 } 1500	940 } 1100	—	890 } 1290	726	—	2300 } 2700	2915
elastic modulus (kg/mm ²)	24000 } 29000	25000	—	—	—	—	—	37000	—
coefficient of thermal expansion ($10^{-6} \cdot \text{deg}^{-1}$)(°C)	8.85 (25-1000)	10.8 (25-1200)	6.45 (20-1700)	—	—	—	—	8.1 (20-1000)	9.6 (20-1400)

Table 4. Properties of various borides

boride properties	TiB ₂	ZrB ₂	HfB ₂	VB ₂	TaB ₂	NbB ₂	W ₂ B ₅	CrB ₂	FeB	Fe ₃ B
crystal system	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	orthorhombic	tetragonal
density(g/cm ³)	4.38	6.17	10.5	5.06 5.28	12.38	6.97	11.0	5.22	7.15	7.34
melting point(°C)	2790	3200	3250	2400	3037	3000	2370	2200	1650	1410
specific resistance ($\mu\Omega \cdot \text{cm}$)	6.4 9.1	9.7	10.6	22.7	32.5	25.7	22.0	30	80	38
thermal conductivity (CGS)(RT)	0.154	0.138	0.122	0.101	0.038	0.057	0.125	0.076	0.029	0.072
microhardness (kg/mm ²)	3310 3430	2230 2274	2400 3400	2797 2813	2460 2540	2600	2650 2675	2020 2180	1600 1700	1290 1390
elastic modulus (kg/mm ²)	54000	35000	—	27300	26200	65000	79000	21500	35000	29000
coefficient of thermal expansion ($10^{-6} \cdot \text{deg}^{-1}$)(°C)	4.6 (27-1027)	5.9 (27-1027)	6.3 (27-1027)	7.6 (27-1027)	8.2 (27-1027)	8.0 (27-1027)	7.8 (27-1027)	10.5 (27-1027)	~12 (400-1000)	11.5~ 12.1 (20-800)

ance, and is very low in general. (However thermal conductivity and specific resistance of BeO are exceptionally high. Both microhardness and elasticity of oxides are lower than those of carbides and nitrides. Especially Al₂O₃ and Cr₂O₃ have high hardness which can be utilized in various application.

On the other hand, the density of borides ranges from 4.5 ~ 12 g/cm³ which are similar to those of the other three compounds.

Melting point of borides is much higher than those of the other compounds and is similar to those of several carbides whose melting point is very high. This property will be often utilized for high heat resistance in the future. Specific resistivity of borides ranges from 6 to 30 $\mu\Omega \cdot \text{cm}$ and is lower than that of carbides. This property will be utilized for special purpose like conductor at high temperature, too. Thermal conductivity of borides ranges from 0.04 to 0.15. Hardness of borides is the highest in these four compounds (> 2000kg/mm²). And it is very important that this property will be applied to practical uses. Elasticity is very low and brittle as well as the other compounds.

As already mentioned above, these ceramics have low thermal expansion coefficient, good thermal resistance, corrosion resistance, electric properties, although their thermal-shock resistance and mechanical strength are often not so good. The low elasticity of these ceramics is detrimental rather than beneficial. The new ceramics coating is one of the treatments which can resolve such a disadvantage by combining brittle films with ductile substrates. Therefore it might be called one of composites process. Recently the difference of properties between ceramic films and ceramics themselves have turned out, which is very interesting in the view point of surface functions. Ceramic coatings can give some new functions moreover the properties as composite to the material surface.

Table 5. Hardness of various carbides compared with other substances

form of compound	hardness (Hv)	example	hardness (Hv)
M_3C	1150~1760	Fe_3C	1150~1340
$M_{23}C_6$	1000~1800	$(Cr \cdot Fe)_{23}C_6$	1000~1520
M_7C_3	1800~2800	$(Cr \cdot Fe)_7C_3$	1820
M_2C	1800~3000	Mo_2C_2	1800~2200
		W_2C	3000
		Cr_2C	1900~2500
M_6C	1600~2300	Fe_4Mo_2C	1670
		Fe_4W_2C	1700~1800
MC	2250~3200	MoC	2250
		WC	2400~2740
		VC	2500~2800
		TiC	3200<
		ZrC	
		NbC	2400<
		TaC	1800<
Fe_2B			1400~2000
FeB			1900~2300
nitride layer			1000~1100
hard chromium plated steel			900~1000
quenched and tempered steel			700~800

Main applications of ceramic coatings are described as follows. Components for wear resistance, hot resistance and packing resistance, and mechanical seals are Al_2O_3 , TiN, TiC, SiC and etc.. Electric materials (functional materials) such as transparent conductive films are In_2O_3 , SnO_2 , and etc., for infrared cut filters and strong dielectric substances $BiTi_3O_{12}$ is used, and for piezoelectric films ZnO is used. Moreover Al_2O_3 is applied to coating of lens by utilizing its transparency. AlN is used as insulation film, Si_3N_4 and SiC as semiconductor devices, TiN, TiC, TaN and TaC as emitter materials, and transparent SiO_2 thin film as infrared ray cut filter, resistance devices, dielectric substances and lens coating.

As mentioned above, it is frequently required nowadays that mechanical components can undergo higher loading and that electronic materials have more various functions. And then their uses are inclined to increase. If the properties of those ceramics are studied and turned out further (e.g. the electric, magnetic, thermal and mechanical properties of nonstoichiometrical compounds by reactive ion plating and etc.), the uses of new ceramic coating will increase more and more. In this point, the application of new ceramic coating which

shows new properties, is very significant.

Hardness of several ceramics compared with other hardened surfaces are shown in Table 5.

3. Surface modification by the change of surface structure

3.1 Mechanical treatment method

Various mechanical treatments are applied to surface modification. In shot peening processing, hard particles or metal shots are knocked at the material surface, and then the surface layer deforms plastically and hardens through work hardening, which results in the increase of wear resistance. The similar effects are attained by barrel processing. Embedding of hard particles such as SiC in the material surface increases wear resistance. Injection and deposition of hard micropowder in molten steel results in surface hardened materials whose hardness are about Hv 2300. Surface rolls, rolling working, cBN machining and etc. will be effective moreover as surface treatments.

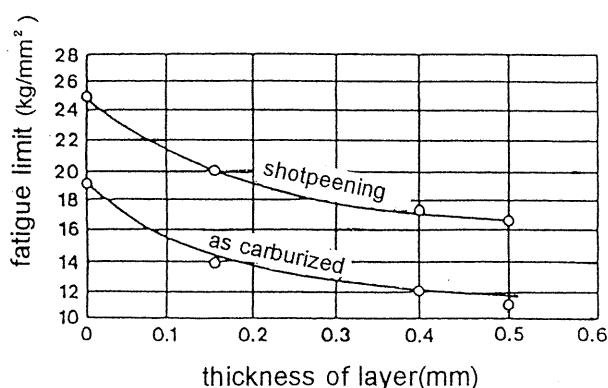


Fig. 1 Effects of shotpeening on carburized layer.
(0.6% normalized steel)

3.2 Chemical modification method (for example: oxidation method)

For steel rolls, for example, the black film (magnetite) formed on the surface by oxidation has high wear resistance. This film reduces wear of surface of a practical roll, although microcracks are formed in the film by heat. At the temperature above the transformation temperature of magnetite (570°C), self oxidation of rolls is occurred mainly. Appropriate temperature of this treatments about 600°C, because wuestite is formed at more than 600°C. Film thickness of magnetite in this treatment ranged from 2 μm to 10 μm and the property is very tight.

3.3 Laser surface treatment

Conventional heat treatments such as high frequency quenching can increase wear resistance, but strain is usually formed through these treatments. This problem is able to be resolved only by surface quenching by laser. Merits of this treatment are described as follows.

- a) Applications to various modifications
- b) an abundance of available materials
- c) Local and selective treatments
- d) Minimum amount of heat which reduces thermal strain
- e) Ability of control of hardened depth and area
- f) Application to products whose shapes are complicated
- g) Non-pollution treatments due to non-oil or non-water

Glazing or Laser Surface Melting (LSM) and Laser Surface Alloying (LSA) can be mentioned as the representative methods. The CO₂ laser has high capacitance and is used usually, but the pulse laser (YAG, ruby) which has long wavelength and high energy is often used, too.

3.4 Ion nitriding

In the conventional gas nitriding, nitrides are formed on the surface of steel by N atom from the decomposition of NH₃ gas. The merits are low treatment temperature (500 ~ 550°C), slight thermal deformation and high hardness. But this gas nitriding method is used only for low grade alloy steel containing Cr, Al and Mo, because the efficiency is low, treatment time is long, and formed nitride is brittle. These defects can be resolved by ion nitriding method. Nitriding in ionic gas increases the efficiency, prevents the embrittlement of nitride layer and reduces the treatment time (about 1/3 ~ 1/5). N₂ + H₂ or NH₃ gas are induced (about 80% N₂), and glow discharge by direct voltage 200 ~ 1000V ionizes gas, which results in better nitriding. It is recently one of the best surface modifications.

3.5 Ion carburization

The merits of ion carburization are described as follows:

- 1) The rate of supplying carbon is high.
- 2) The control of carburized layer is easy.
- 3) Work surface is clean and bright.
- 4) Abnormal carburized layer such as decarburized layer and grain boundaries cannot be formed.
- 5) Soot cannot be formed. (C₃H₈ gas of several Torr)
- 6) Pretreatment is easy.
- 7) Strain occurs seldom.
- 8) The efficiency of carburizing and work environment is good.
- 9) Multiple heat treatment of vacuum brazing and ion carburizing can be utilized.

This method is one of the plasma treatments.

3.6 Boriding

Gas boriding method is classified into boron trichloride method and diborane (hydride) method. The former utilizes the reduction reaction: $\text{BCl}_3 + 3/2\text{H}_2 \rightarrow 3\text{HCl} + \text{B}$, and requires more than 600°C. On the other hand, the latter uses the following reaction: $1/2\text{B}_2\text{H}_6 \rightarrow \text{B} + 3/2\text{H}_2$, and requires more than 700°C. The solubility of boron in α -iron or γ -iron is very low and there are two intermetallic compounds, FeB and Fe₂B. In general, FeB and Fe₂B are formed inwardly from the surface in this order. But the appropriate treatment condition can produce the single layer, FeB or Fe₂B. The morphology of both iron boride layers are needlelike. It is often pointed out that boride layers have residual compress stress.

Boron trichloride method requires 0.05 mol% BCl₃ and 0.95 mol% H₂ generally and utilizes the exchange reaction, $\text{BCl}_3 + 3/2\text{Fe} \rightarrow 3/2\text{FeCl}_2 + \text{B}$ or the reduction method, $\text{BCl}_3 + 3/2\text{H}_2 \rightarrow 3\text{HCl} + \text{B}$, all of which require more than 600°C.

Diborane method requires the mixture of diborane and hydrogen whose mixture ratio ranges from 1:25 to 1:225. It is pointed out that the mixture ratio of 1:100 is the best one generally. When a specimen is treated in 2 hours at 850°C the depth of the boride layer will be about 120 μm .

3.7 Metal diffusion method

The metal diffusion method is one of the surface modifications for wear resistance and corrosion resistance, and utilizes the deposition and diffusion of Cr, Al, Zn, Si and etc. into the material. The merits of this method are described as follows.

- 1) There is a diffusion layer of diffused metal in the surface.
- 2) The layers have high adhesion.
- 3) The dimension changes with the treatment.
- 4) The substrate is affected by heat.
- 5) The combination of the substrate and diffused metal must enable the mutual diffusion.

3.8 Ion implantation method

Ion implantation method utilizes the collision phenomenon. In this treatment, atoms are ionized, accelerated in an electric field and collide with a material surface. As results, atoms are injected in the certain depth of the material. Therefore the arbitrary atom can be added into a certain material in principle. In this method, an artificial surface or a thin layer can be formed at relatively low temperature. Recently this method is applied not only to the field of semi-conductor but also to that of metal, ceramic and polymer materials. The merits of this treatment are described as follows.

- 1) The combination of implanted ion and the substrate is selected arbitrarily.
- 2) The purity of implanted atoms is very high.
- 3) The profile of the concentration of implanted atoms can be controlled.
- 4) The temperature used in this process is relatively low.
- 5) The change of dimension is slight.
- 6) The treatment has high accuracy and is reproducible.

In practical uses, ion implantation coating of nitrogen increases the wear resistance and corrosion resistance of tools. For example, ion implantation of C, N, B for the wear resistance, Ba, Sr, Ca, Yb and Eu for oxidation resistance, (Ti, Fe), Ta, Ti and Cr for corrosion resistance and Ti for the improvement of adhesion between metal and ceramic.

4. Surface film processing

4.1 Spraying coating method

In this treatment, micropowders consisting of molten metal and/or ceramics are sprayed to products, which results in the formation of films. In practical uses, the method is classified into four type: powder spraying, arc spraying, flame spraying and plasma spraying. Cement carbides, alloys and ceramics are used as substrate. The properties of surface films formed by spraying coating are the followings.

- 1) The adhesion between film and substrate is mechanical.
- 2) Films contain a number of pores.
- 3) Hardness and electric resistance is very high, because films contain oxides.
- 4) Tensile strength and bending resistivity are low.
- 5) Surface is coarse.

In general, plasma spraying is often used. Recently low pressure spraying is used frequently, too. In the future, laser spraying will be supposedly developed. Especially low pressure spraying has following merits, i.e. increasing of adhesion, minimum change of phase and increasing of high temperature area.

4.2 *Electroplating method*

A Cr plated film has high corrosion resistance and hardness. The reasons come from its fine grain size, internal stress, hydrogen absorption, abnormal crystal system, the mixture of two types of Cr-crystal system and Cr oxides having high hardness, adhesion and corrosion resistance. In electroless Ni plating, heat treatments increase the hardness of film from 550 ~ 600Hv to 1100Hv which is similar to that of hard chromium film. This film contains phosphorous of 4 to 15% and is amorphous. The film is recrystallized at about 280°C and Ni₃P is deposited at higher temperature, which results in hardening of the film. It is pointed out that the hardness of film is about 1100Hv at 400°C. This alloy film has high corrosion resistance, too. It is very interesting that most of these amorphous films before heat treatment are non-magnetic. Ni-B alloy film has high hardness and wear resistance. Sodium borohydride (high temperature bath at 90°C) and amine borane (low temperature bath at 65°C) are used as the plating bath. The film formed at high temperature bath contains boron of 5 to 7% and is amorphous. The heat treatment at 400°C increases the hardness of films from 700Hv to 1200Hv. The melting point of Ni-B is about 1400°C and is higher than that of Ni-P (about 800Hv). The film formed at low temperature bath contains boron of 0.5 ~ 1.0% and its grain size is fine. The heat treatment increases the hardness slightly higher than 800Hv as deposit.

4.3 *Carbide coating by diffusion method*

Carbide films are formed by dipping the specimen containing carbon with metal component as carbide former into the neutral molten salt or molten borax. This method can produce carbide films of high wear resistance, thermal resistance and corrosion resistance similar to those of hard alloys on the substrate, even if low grade steels are selected as substrate. Composite films such as V-Nb-C and Ti-V-C can be formed by this method.

This carbide film method can be grouped in several categories, but the molten salt method is frequently used. If the specimen is dipped into molten salts containing boron, some borides such as FeB and Fe₂B can be formed. It is pointed out that the mechanism of the reaction is mainly disproportionation reaction. In general, vanadium carbide film is frequently used, but the other carbide film such as NbC, TiC, Cr₇C₃, Cr₂₃C₆ and etc. can be used for several applications. Hardness of carbide films by this method is very high, e.g. hardness of VC and TiC attain more than 3000Hv. These films maintain their hardness at high temperature. (For example, 800Hv at about 800°C) And moreover these films have all kinds of wear resistance such as adhesion wear, grinding wear, corrosion wear and so on. In general, values of these wear resistance are similar to those of cement carbide. And these films have baking resistance, chipping resistance and oxidation resistance.

The steels being coated by such carbide films are used for many applications. For example, there are cutting tools for metal, rubber, plastic and woods, metal mold for press, and powder metallurgy and dies wearied due to adhesion resistance, baking resistance, and chipping resistance. Various ceramic tools, components of civil engineering machine, agricultural machine, and pump with grinding resistance, grinding holder, jigs of grinder, nonferrous cutting tools, fiber-guide and components of pumps with grinding wear resistance, molds for plastic, components of chemical mechanical machine, components of plastic deforming machine with grinding wear resistance and corrosion wear resistance, components of oil-, air-pressure machine with erosion resistance, components of various chemical mechanical

machine with corrosion resistance and oxidation resistance, mold for aluminium, die cast and device for molten zinc dipping plating for oxidation method with corrosion resistance and long life time.

4.4 Composite

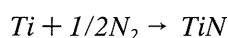
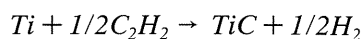
In the electrodeposition, powders are dispersed in the electrodeposited film, which results in the increase of wear resistance and lubricating properties according to the properties of the dispersed particles. Nickel is used mainly as matrix metal. But Co, Cu and Cr are often used, too. SiC, WC, Al₂O₃, TiO₂, ZrB₂ and etc. are used as dispersed powders for the increase of wear resistance. For other purposes, TiC, B₄C, diamond, CrB₂, ZrC, CrC, SiO₂, ZrO₂ and etc. are used. In general, the size of co-deposited powders ranges from 1 to 3 μm, but the larger particles can be used, too. For the deposition of nickel, electroplating and electroless deposition are available.

4.5 Ion beam mixing

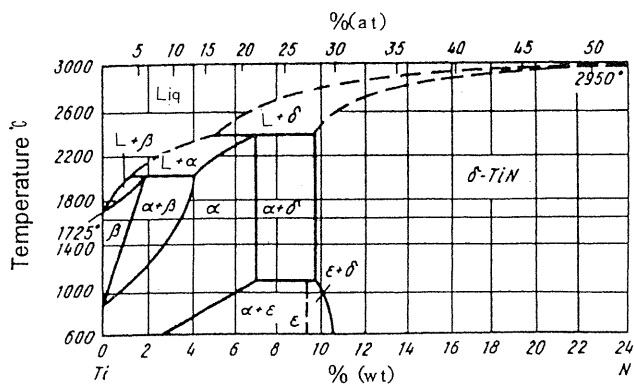
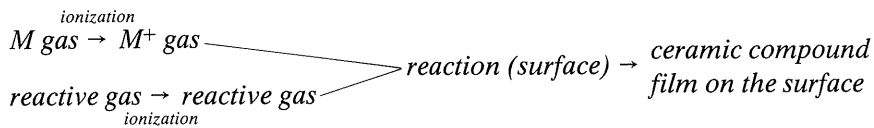
Ion beam injected into the deposited film enables alloying and compounding in films, promotes alloying and compounding of films with substrates and increases the adhesion of films. In compare with ion implantation, gas can be ionized more easily and this method shows the effect by a little amount of injection of rare gas.

4.6 PVD method

Coating components are vaporized and splashed as atom or molecule and deposit on the substrate in a vacuum chamber. Vacuum vapor deposition, sputtering and ion plating are the representative methods. In the vacuum vapor deposition, the system is vacuum pumped off at 10⁻⁴ to 10⁻⁵ Torr and the coating component could be deposited on the substrate. The properties of the film depend on the distances between substrate and vapor sources. In the sputtering, Ar gas is induced into the vacuum chamber at about 10⁻⁵ Torr. Voltage of 1 ~ 5kV is applied between substrate as positive electrode and target as negative electrode. In this electric field, glow discharge occurs, which promotes the ionization of Ar gas. These positive Ar ions collide with target in plasma, and fricked atoms off the substrate, which results in the formation of films on the substrate. Magnetron sputtering making use of magnetic field enables the control of the rate of film formation at the order of 1 μm/min. This method enables high melting point materials to evaporate at relatively low temperature. And the control of film composition is relatively easy. In the ion plating method, the chamber is in generally drawn off at 10⁻⁴ ~ 10⁻⁵ Torr and then Ar gas is induced at 10⁻² Torr. Substrate as negative electrode is cleaned by ion collision. After ion cleaning, coating components are evaporated in the atmosphere of Ar or vacuum. Bias voltage is applied between substrate and metal vapor source, which results in the ionization of evaporated metallic gas and deposition on the substrate. The film formed by this method has the highest adhesion in these three methods. PVD method enables coating of Ti, Al and many refractory materials which cannot be plated in aqueous solutions. On the other hand, reactive method enables the formation of TiN, TiC, Al₂O₃ and AlN which have high wear resistance and thermal resistance. In the application to cement carbide tools, the life increases remarkably. The total reaction can be described as follows for example of TiC and TiN.



This method enables the formation of Al_2O_3 , TaC, ZrC, ZrB_2 , TiB_2 , SiC and etc.. This reaction can proceed at nonequilibrium state, therefore various TiN and TiC films can be produced as shown in Fig.2. This artificial new ceramic coating is very interesting and prospective one. The mechanism can be considered as follows.



Ti-N system

Ti-C system

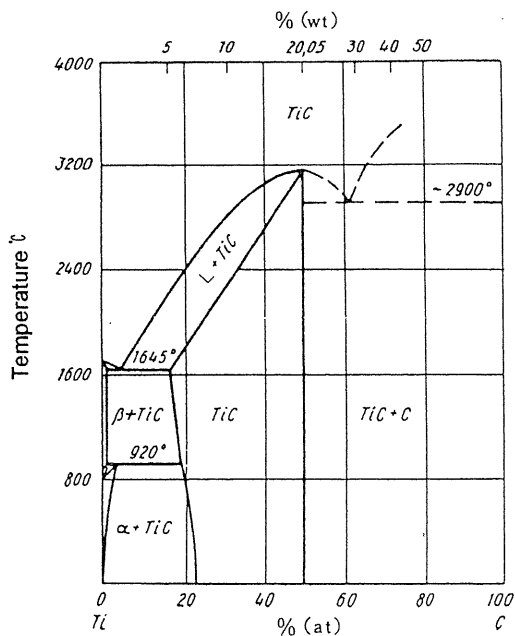
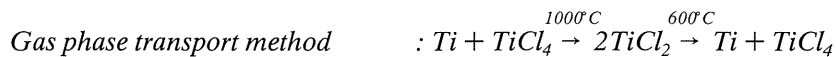
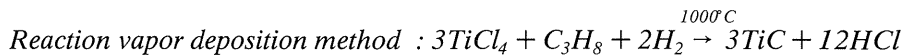
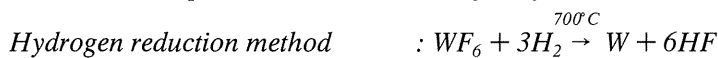
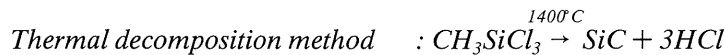
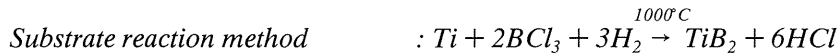


Fig. 2 Phase diagram (Ti system)

N_2 , NH_3 gas and etc. are used for nitrides, CH_4 , C_2H_2 , C_2H_4 , C_3H_8 and etc. for carbides, O_2 gas for oxides and BH_3 , BCl_3 and etc. for borides.

4.7 CVD method

Chemical reaction at the interface between substrate and gas phase, i.e. catalytic contact reaction, produces the film formation of metal and compounds. This method can be classified into substrate reaction method, thermal decomposition method, hydrogen reaction method, reactive vapor deposition method, gas phase transport method and etc., and requires the reaction temperature from 700 to 1000°C in general. Now low temperature plasma CVD method is developing, because thermal strain occurs at the relatively high temperature. In this treatment, plasma increases the reactivity at the low temperature. Low pressure reaction method, which promotes gas flow, is developing, too. Recently such various CVD method is developing. Laser CVD method, CVD coating of carbon fiber are mentioned as such an example. The material treated by CVD is applied to friction parts of components and cutting tool as well as PVD treated materials. In recent years, this method has been applied to diamond coating or BN coating.



· *i*-carbon and diamond film method

Diamond has the highest hardness of all substances. Its electric conductivity is very low but thermal conductivity is very high. The coating technology which can control the morphology is required to utilize the properties adequately.

· CVD and plasma CVD method

The synthesis at high pressure using metal solvent is not suited for the formation of diamond films, but for large grains of diamond. On the other hand, the synthesis at low pressure can be applied to diamond coating. Such a diamond film can be used as high wear resistant material or semi-conductors which have high thermal resistance. This method is classified into chemical transportation method, thermal filament CVD, radio wave CVD and microwave plasma CVD. In the CVD method using thermal decomposition of compounds such as hydrocarbon, graphite deposits with diamond on the substrate, which disturbs the growth of diamond films. On the other hand, plasma CVD method deposits a diamond film from carbon or hydrocarbon ionized in plasma state by thermo-electron and etc.. It is important that methylradical ($\cdot CH_3$) which has the mixed orbital, SP^3 (as well as diamond) must be formed. Radical hydrocarbon having π bonding e.g. double bonding or triple bonding are inclined to deposit graphite. The appropriate treatment conditions of CVD method have not been defined in details yet. But supposedly they depend on the temperature of filament and substrate, the mixture ratio of hydrocarbon and hydrogen, the rate of gas flow and pressure. Especially the mixture ratio, the rate of gas flow and the temperature of filament effect strongly on the formation of a diamond film. For example, the temperature of filament of 2000°C, the temperature of substrate of 980°C, the concentration of methane gas of 1vol%, the rate of

gas flow of 10ml/min, the pressure of several dozens of Torr. The method and properties of the film in this treatment are shown in Table 6. The lattice of deposited diamond is cubic. The atomic hydrogen participates in the synthesis of diamond by thermal filament CVD and plasma CVD. This atomic hydrogen reacts with graphite, eliminates it or reacts with methane gas, which results in the formation and decomposition of methylradical ($\cdot\text{CH}_3$). That is, the hydrocarbon and atomic hydrogen are requisite for the formation of a diamond film. At low pressure, amorphous-like diamond can be formed, which is called i-carbon or diamond-like carbon.

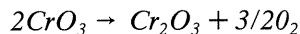
Table 6. Diamond and i-carbon films

process	induced gas	pressure (Torr)	temperature (°C)	deposit
low pressure CVD	CH_4	$< 10^{-1}$	< 1100	graphite diamond
thermal filament CVD	CH_4+H_2	< 50	< 1000	diamond
plasma CVD high frequency	CH_4+H_2	< 50	700~1000	diamond
ion beam deposition				
DC	C_2H_2 $\text{C}_6\text{H}_6+\text{Ar}$	0.05~0.07 10^{-2}	150~300 r. t.	i-carbon i-carbon
high frequency	CH_4 or C_2H_6	10^{-2}	r. t.	i-carbon
ion beam deposition				
non magnetic separation	C^+ , (40[eV])	10^{-6}	r. t.	diamond like carbon
m.f. separation	C^+ , (30-100[eV])	10^{-6}	25~50	diamond, calvin
m.f. separation	C^+ , (900[eV])	10^{-6}	700	diamond

4. 8 Chemical densified coating method

This method utilizes the decomposition reaction of compounds on the surface layer of substrate. The coating of chromium oxide is utilized in practical uses. This example is explained as follows.

Anhydrous chromic oxide is dissociated by heat. The reaction can be described as follows.



Cr_2O_3 is deposited by this reaction. In practical uses, the substrate is coated by $\text{SiO}_2\text{-Al}_2\text{O}_3$ compound called 'base coat' at the thickness of about 30 ~ 100 μm , chromium acid solution as binder is added into the film and heated. As a result, the ceramic film of more than 1200 ~ 1300Hv can be obtained. Even if the base coat is not used, a thin Cr_2O_3 film can be coated.

This is one of the best and prospective surface modifications in the point of making use of good properties of Cr_2O_3 . Such a ceramic coating by chemical thermal decomposition will advance the surface modification technology further.

5. Prospects for the future

Needs for surface modification technologies are increasing more and more. New technique such as heat sources evaporation method and the method of ionization are developed one after another. The development of laser will make the film formation by laser deposition easy and enable the formation of BN coating. CO_2 laser is available, because it can be absorbed by ceramics. The structure of films by these methods are generally amorphous. The hardness of cBN is similar to that of diamond, its thermal conductivity is similar to that of metals and its chemical stability is higher than that of diamond. For example, it is pointed out that cBN does not suffer wear in air at 1100°C . Surface modification technology is interesting in the view point of new functional properties and composite formation of surfaces. It will be one of the interesting and prospective ways which industries should make for the future.

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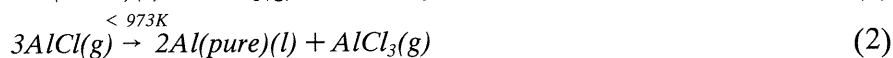
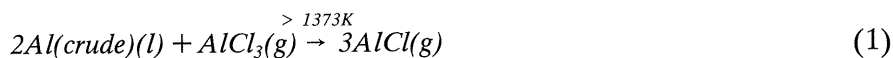
II. Disproportionation Reaction in Molten Salts and Their Application to Surface Coating Treatment

1. Introduction

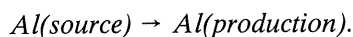
Many surface treatments have been done in an attempt to improve the performance characteristics of material surface (1). The diffusion treatment is well known as a representa-

tive one. The disproportionation in molten salts can precipitate an active metal on the surface, which is able to alloy and compound by reaction with the component of substrate. In this investigation, activity change of metal at the same temperature was used for the surface coating of alloy and compounds. This method by means of disproportionation reaction is one of the chemical transport process in molten salts.

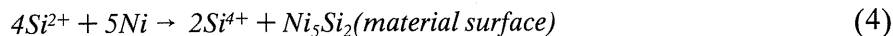
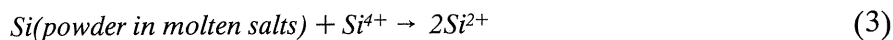
The disproportionation reaction is defined as the redox reaction of metal ions with the same metal, like the following disproportionation reaction of Al (2) (formula (1) and (2)). Disproportionation reaction can be performed by two kinds of driving force: one is the difference in temperature between reaction system and production system, and the other is that in activity. The former has been utilized for refining aluminium (2). The reactions can be described as follows.



Temperature difference should be requisite to proceed this reaction,



On the other hand, the latter can be applied to coating of substrate by precipitation in molten salts. For example, Gay and his coworkers (2) found that nickel can be siliconized by dipping into molten KCl-NaCl-NaF-Na₂SiF₆ salts containing silicon powder. The reaction was described as follows.



The difference in activity of silicon between powder and intermetallic compound should be requisite to perform these disproportionation reactions (3) and (4) at the same temperature. Here in this paper, the latter disproportionation will be applied to produce the coated films on substrate.

2. Results and discussion

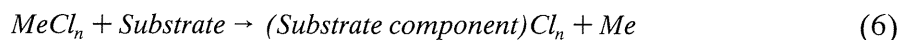
2.1 Pre-consideration about the mechanism of precipitation in molten salts

The mechanism of precipitation in molten salts was suggested as the following processes.

(1) Collision mechanism



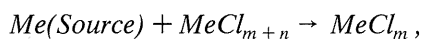
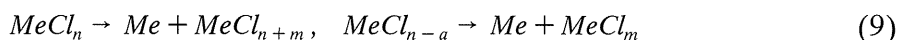
(2) Exchange mechanism



(3) Disproportionation mechanism



or



There were many discussions about these mechanisms (3)–(11), where there are many results for which the collision mechanism cannot give an explanation. This experiment was performed in order to evaluate the disproportionation mechanism and apply it to preparation of surface coating on substrate.

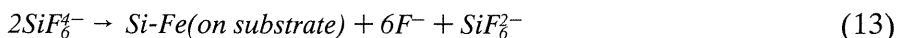
2.2 The formation of ferrosilicon and ferrosilicon-graphite composite film on steel as alloy film formation (12), (13)

Table 1 shows the chemical composition and the original hardness of the specimens. It was immersed into the molten salts and hardness (Hv) of the specimens NaCl-KCl-NaF at 973 ~ 1173K, which contained Na₂SiF₆ and silicon powder as additives. After dipping of 3.6 ~ 10.8ks, the specimen was taken out of the crucible, washed with water, dried and used in several tests.

Table 1. Chemical composition (mass%) and hardness (Hv) of the specimens

	C	Mn	P	S	Si	Hv
A	0.1	0.29	0.013	0.019	—	149
B	0.8	<0.50	<0.030	<0.030	<0.35	210
C	3.5	0.30	0.01	0.02	0.5	162

In this treatment, the following disproportionation reaction was speculated.



Silicon which deposits on the material surface diffuses into the material and forms intermetallic compounds. Therefore the activity of deposited silicon is lower than that of silicon powder. Then the reactions (12), (13) occurred steadily.

Fig. 1 shows the relationship between the amount of coating and the molar ratio of silicon powder to Na_2SiF_6 . The amount of coating increased with added silicon powder.

Fig. 2 shows the relationship between the amount of coating and NaF or Na_2SiF_6 quantity, while the amount of silicon powder was constant. The amount of coating increased with increasing these components. Also the lack of either Si or silicon salts resulted in non-coating. All these results suggest that Si precipitation occurs through the disproportionation reaction.

And X-ray analysis confirmed that the ferrosilicon films were formed inwardly from surface to reduce silicon ratio in this order: FeSi_2 , FeSi , Fe_3Si . The hardness at the vicinity of the surface was about 700Hv. (Fig. 3)

2.3 Chromium carbide and other (TiC, VC, ZrC and TaC) films on steel as metal carbide film formation (14)–(23)

In this experiment, CrF_3 and chromium powder were added into fused NaCl-KCl-NaF . The specimen was dipped into the molten mixture salt at 1173K for 10.8ks.

Fig. 4 shows the profile of Vickers hardness in the surface area of the specimen. It was about 1200 ~ 2000. Cr_7C_3 and Cr_2C were confirmed in surface films by X-ray analysis. The amount of coating was influenced by the concentration of NaF, CrF_3 and chromium powder. (Fig. 5) It increased with increasing concentration of each element under constant concentration of the others. These results suggest also the following disproportionation reaction.

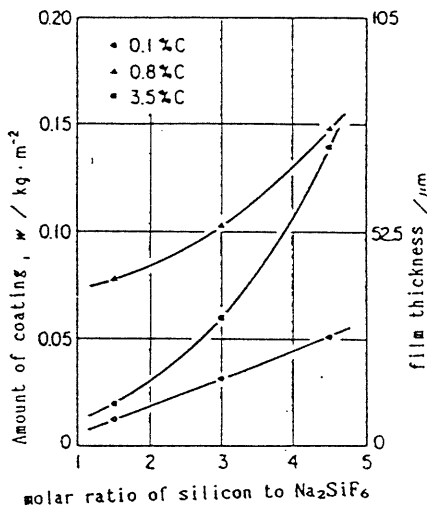
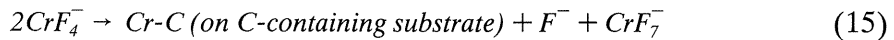


Fig. 1 The relationship between the amount of coating and molar ratio of silicon.

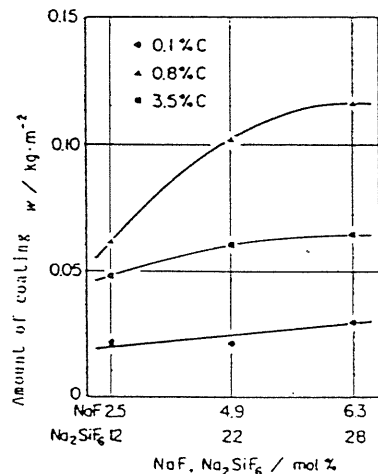


Fig. 2 The relationship between the amount of coating and NaF, Na_2SiF_6 concentration.

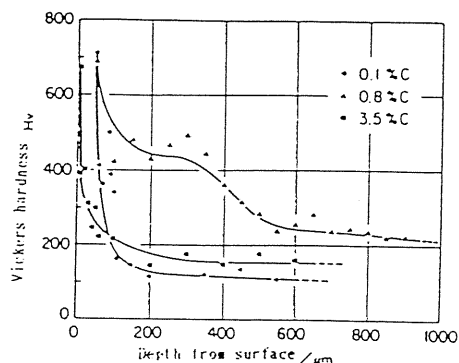


Fig. 3 The profiles of Vickers hardness (Hv) in ferrosilicon graphite composite film.

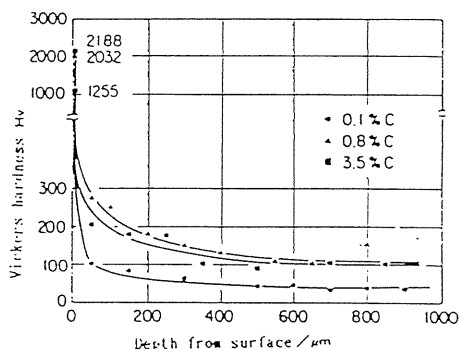


Fig. 4 The profiles of Vickers hardness (Hv) in chromium carbide film.

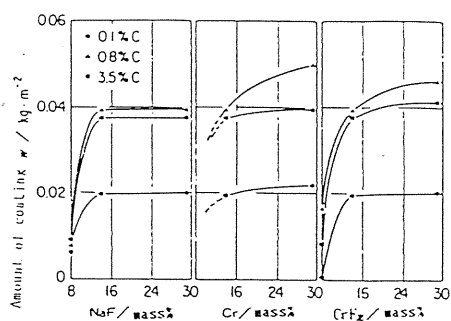


Fig. 5 The effect of NaF, Cr and CrF_3 concentration on chromium carbide coating.

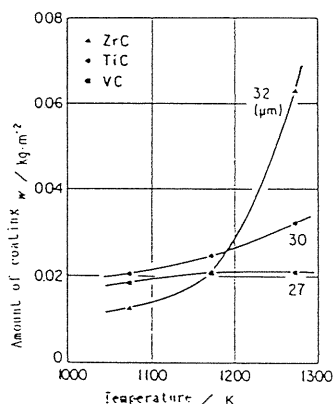


Fig. 6 The effect of treatment temperature on ZrC, TiC and VC coating.

In addition, it was proved that the proportion of chromium ions before the treatment ($44\% \text{Cr}^{3+} + 56\% \text{Cr}^{6+}$) changed with reaction, and that the relative concentration of Cr^{3+} increased. (After the treatment, $96.1\% \text{Cr}^{3+}$, $3.9\% \text{Cr}^{6+}$). This change suggests that the reaction (14) proceeds faster than the reaction (15) at last stage. In other words, the formation of chromium carbide may be controlled by consumption of precipitated chromium.

The other carbide films could be formed on steel by the same method. The molten $\text{KCl-BaCl}_2\text{-NaF}$ salts were used as main supporting salts in all cases. K_2TiF_6 and sponge titanium for titanium carbide, VCl_3 and Fe-V alloy for vanadium carbide, K_2ZrF_6 and Fe-Zr alloy for zirconium carbide, K_2TaF_6 and tantalum for tantalum carbide were used as additives, respectively. SKD11 (JIS) (1.5% C) was used as C-containing substrate for all cases and moreover S55C (JIS) (0.5% C) and SKD3 (JIS) (1.0% C) especially for TaC film.

Fig. 6 shows the effect of the treatment temperature on the amount of coating for TiC, VC and ZrC (treatment time: 3.6ks). In either case, the amount of coating increased with increasing temperature. The each film thickness at 1273K are indicated in Fig. 6.

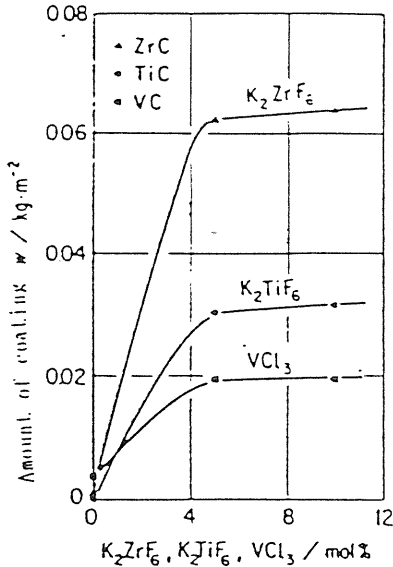


Fig. 7 The effect of K_2ZrF_6 , K_2TiF_6 and VCl_3 concentration on ZrC, TiC and VC coating, respectively.

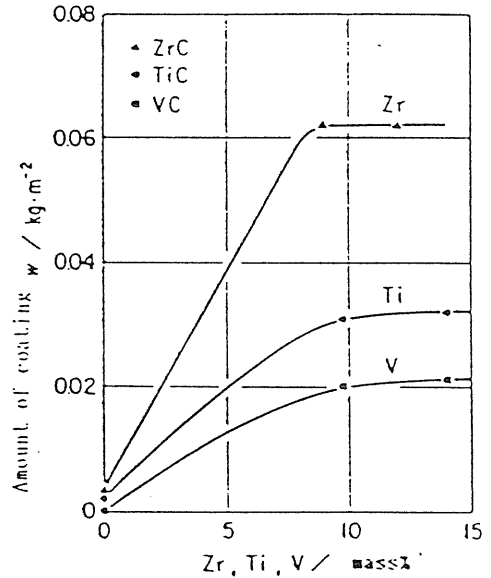


Fig. 8 The effect of added Zr, Ti and V quantity on ZrC, TiC and VC coating respectively.

The effects of additives on the amount of coating for ZrC, TiC and VC are shown by Fig. 7 and Fig. 8. And the lack of either metallic salt or metal made it difficult to form carbide films. These results suggest the following disproportionation reaction for each carbide film.

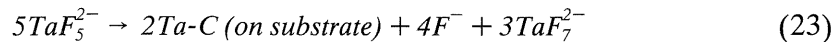
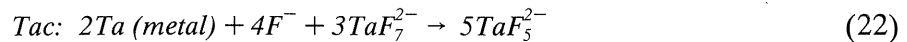
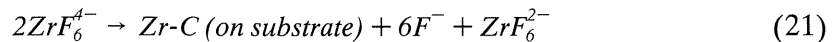
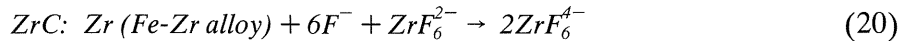
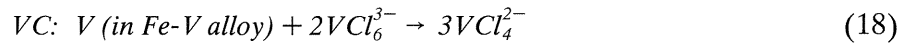
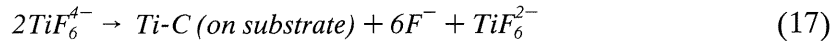
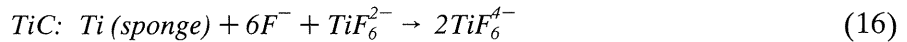


Fig. 9 shows the profiles of vickers hardness in surface area for ZrC, TiC and VC coating. The hardness at the immediate vicinity of surface for each film is 1490, 1750 and

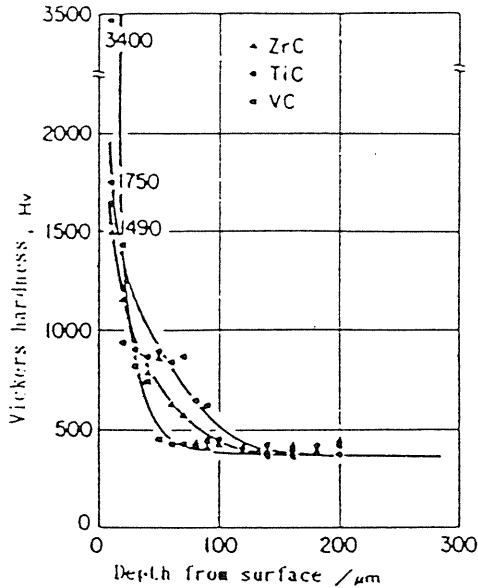


Fig. 9 The profiles of Vickers hardness in ZrC, TiC and VC films.

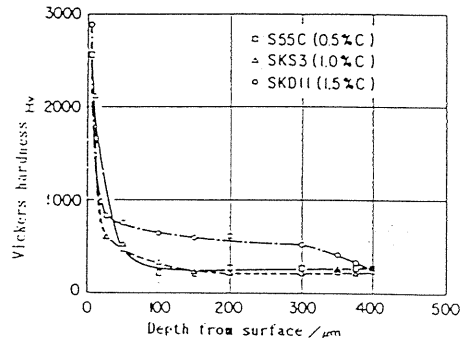


Fig. 10 The profiles of Vickers hardness in TaC film.

3400Hv, respectively. Fig. 10 represents the profiles of hardness for TaC film coating. It reached about 2800 ~ 3000 (Hv) at the immediate vicinity of the surface.

2. 4 The formation of boride film on steel (15) as boride film formation

The boriding of metal substrate in molten salts was investigated by means of disproportionation reaction, too. B₂O₃ and ferroboron were added as additives into the molten KCl-BaCl₃-NaF salts. The reaction temperature ranged from 973 to 1173K. 10.8ks was adopted as treatment time.

The dipping of SKD11 in these molten salt resulted in the formation of Fe₂B film, which was confirmed by X-ray analysis. It is indicated in Fig. 11 ~ 13 that the amount of coating depends on the concentration of NaF, B₂O₃ and ferroboron. This suggests the following disproportionation reaction for film formation.

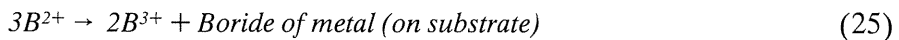


Fig. 14 shows the profiles of vickers hardness in surface area. When austenitic stainless steel (AISI304, 316) were dipped, CrB film were formed on its surface.

On the other hand, dipping Cr plated steel resulted in the formation of CrB₂ film, which showed high corrosion resistance.

Besides, other various boride films on steel were formed by combination of carbide formation and boriding. The specimen with TiC, VC and ZrC film were immersed in boride forming molten salts, and TiB₂, VB₂ and ZrB₂ films were made. This indicates that the

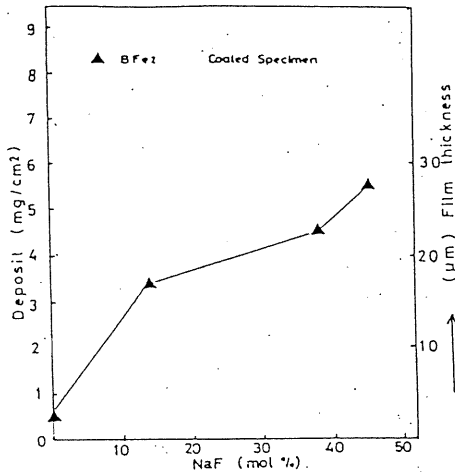


Fig. 11 Relation between deposit and NaF.

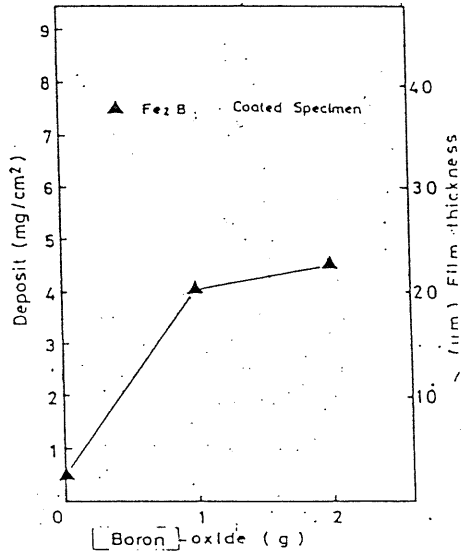


Fig. 12 Relation between deposit and metal oxide.

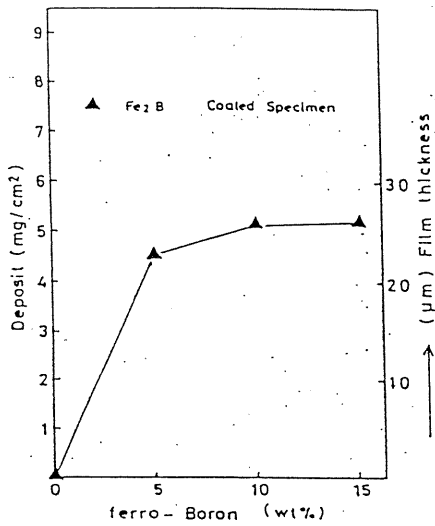


Fig. 13 Relation between deposit and ferro-alloy.

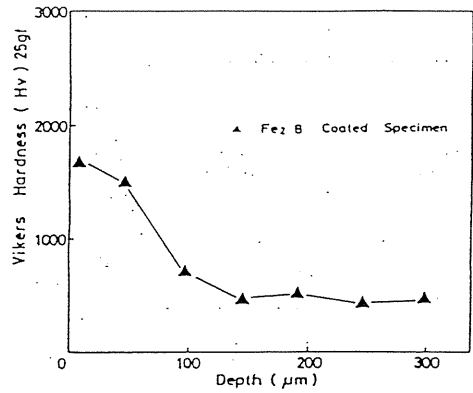


Fig. 14 Vickers hardness profiles from surface.

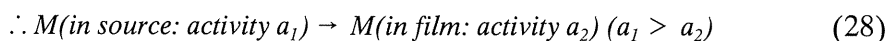
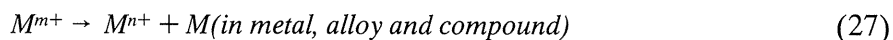
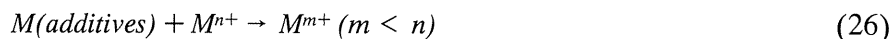
affinity of metal-boron is much greater than that of metal-carbon. The Vickers hardness of all these boride films ranged from 1200 ~ 3000Hv.

2.5 Crystal orientation of the produced films

The crystal orientation of various carbide films were investigated by X-ray analysis. The special orientation could not be found for TiC, WC and ZrC films. On the contrary, (002) plane was preferentially oriented for VC film and (421) plane for Cr₇C₃ film. The orientation of Cr₇C₃ film could not be found under the lack of NaF. The orientation of film is intimately and complicatedly connected with its formation process, and it is supposedly of great value to examine it furthermore.

2.6 Conclusion

It was turned out that ferrosilicon and ferrosilicon-graphite composite film, various carbide films and boride films could be formed by utilizing the useful disproportionation reaction in molten salts. The specimen was immersed into molten salts at high temperature, which contained the metal for coating (M) and its salt. In general, the following reaction occurred.



The precipitated M onto the specimen diffused immediately inward to form various type films. These forward and backward disproportionation reactions proceeded at the same temperature. This method can be called one of the chemical transportation method in molten salts.

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III. Progress in Application of Disproportionation Process in Molten Salts

1. Introduction

There are many techniques (1) for surface modification such as PVD, CVD, ion-implantation, diffusion-cementation, electro- or electroless plating, spray coating, sol-gel method and so on. This process is a kind of chemical transport method using disproportionation reaction (2–7) and has the following advantages in comparison with usual other chemical transport processes such as gas process, solid process and electrolytic process in molten salts: (1) Relatively low temperature process (973K ~ 1173K). (2) The molten salts can avoid the reaction between substrate and air easily. (3) The presence of NaF makes it possible to add metal oxide powder and to be active metal.

In this paper, the author investigated the formation mechanism and characteristics of films whose elements don't exist in substrates, which are metal boride films (6) such as titanium boride, vanadium boride and chromium boride, nitride one (7) such as chromium nitride, titanium nitride, zirconium nitride and vanadium nitride, and silicide one like chromium silicide using this process.

2. Experimental procedure

2.1 Specimens and molten salts

The steels whose chemical composition were shown in Table 1, were used as specimen. They were cut into test pieces like a square shape with sides of 0.01 m long, and with 0.005 m thickness. Their surfaces were polished with emery papers, buffed with Al_2O_3 powder and degreased with acetone.

Table 1. Chemical composition of steel specimens

element	C	Si	Mn	P	S	Cr	Mo	V
Steel A (SKD11)	1.4-1.6	<0.45	<0.60	<0.030	<0.030	11-13	0.8-1.2	0.2-0.5
Steel B (SK5)	0.8-0.9	<0.35	<0.50	<0.030	<0.030	-	-	-
Steel C (SPCC)	<0.12	-	<0.50	<0.040	<0.045	-	-	-

Boride film: Steel A, Nitride film: Steel B and C, Silicide film: Steel B

Table 2. Standard composition of molten salts for various film formation

Salts(wt%)	KCl	BaCl ₂	NaF	Others
Metal Boride	30.9	41.2	15.5	2.0wt%B ₂ O ₃ , 10.4wt%ferroboron
Cr Nitride	31.7	31.7	15.9	4.8wt%CrF ₃ , 15.9wt%ferrochromium
Ti Nitride	31.7	31.7	15.9	4.8wt%K ₂ TiF ₆ , 15.9wt%ferrotitanium
V Nitride	31.7	31.7	15.9	4.8wt%V ₂ O ₅ , 15.9wt%ferrovanadium
Zr Nitride	31.7	31.7	15.9	4.8wt%ZrCl ₄ , 15.9wt%ferrozirconium
Cr Silicide	32.7	32.7	12.7	12.7wt%Na ₂ SiF ₆ , 9.1wt%Si powder

The molten salts used in this study were chiefly composed of KCl (–NaCl), BaCl₂, NaF, MF_n and M. M represents an objective metal and metal oxide, and metal chloride were often used in stead of metal fluoride. The standard composition of molten salts was shown in Table 2 classified by each film formation.

2.2 Experimental procedure

The procedure of this method that applies disproportionation reaction in molten salts, is as follows: KCl-BaCl₂-NaF mixed powder was put into mullite crucible (the outside diameter: 0.044 m, the height: 0.053 m) and heated to 1073K in the kanthal wire type electric furnace. Being melted completely, metal sources were added at 973K and the melt were stirred enough. It was heated to 1073K again, and the temperature was kept for 2 hours. And then the temperature of the melts being changed to specified one, substrates were immersed into the molten salts for constant time. Thereafter specimens were cooled slowly in the furnace to room temperature, and taken out of the solidified salts by crushing. They were washed with water to remove salts and dried.

As in this paper, however, substrates don't have any chemical elements of the films, it is necessary to repeat this method, which condition were changed as for metal sources, and so on according to the films. As for boride film formation, at first, steel substrate were immersed into the molten salt for carbide film formation to form titanium carbide, vanadium carbide and chromium carbide, respectively, and then specimens having carbide films were immersed into molten salts for boriding at 973K ~ 1273K for 1 hour ~ 5 hours. This double process resulted in the boriding of titanium boride, vanadium boride and chromium boride respectively. In case of nitride film formation, the steel was immersed firstly into molten salts for nitriding in order to get the nitrided substrate, and then secondly the formation process of nitride ceramics such as chromium nitride, titanium nitride, zirconium nitride and vanadium nitride were done on nitrided substrates at 973K ~ 1273K for 1 hour ~ 10 hours. As for chromium silicide, substrate specimens had chromizing treatment in molten salts and then siliconizing treatment were done on the chromized specimens at 923K ~ 1173K for 1 hour ~ 3 hours.

These surface films were examined by various analyses and tests such as X-ray analysis, microscopic observation, EPMA analysis, corrosion test and so on.

3. Results and discussion

3.1 Metal boride film formation from carbide

At first, steel A (SKD11) substrates were immersed into molten KCl-BaCl₂-NaF- metal salts (K₂TiF₆, CrF₃ and VCl₃ respectively)-ferroalloy (Fe-Ti, Fe-Cr and Fe-V respectively) to form carbide films such as TiC, VC and Cr₇C₃. And then they were immersed into molten salts for boriding. X-ray analysis showed that TiB₂, VB₂ and CrB₂ were formed in the case of these specimens. The amount of deposit (the weight gain per unit area) increased with increasing of reaction temperature and time.

Fig. 1 shows the profiles of vickers hardness in the case. The vickers hardness in the vicinity of surfaces of TiB₂, VB₂ and CrB₂ layers were 4200HV, 3700HV and 3200HV respectively. The thickness of these boride films which are estimated from Fig. 1 are about 20 μm, 40 μm and 20 μm respectively. These values correspond with those estimated from measurements of EPMA and microscopic observation.

Fig. 2 shows that wear resistance of these borided specimens were much higher than that

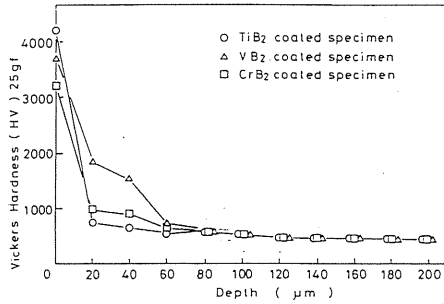


Fig. 1 Profiles of vickers hardness in the surface layer region of metal boride formed at 1000°C.

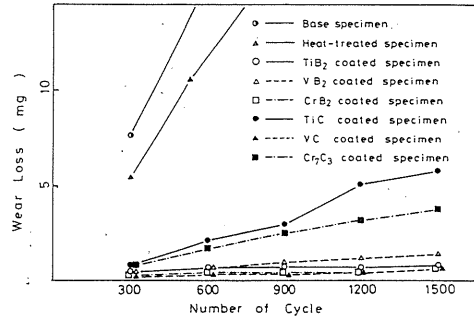


Fig. 2 Wear resistance of some specimens measured with load of 1.2 kgf on SiC paper No.120 (Wear area; 2.4 cm²)

of the steel. When comparing boride layers with carbide layers, wear resistance of TiB₂, CrB₂ were higher than that of the carbides. The wear resistance of VC was slightly higher than that of VB₂.

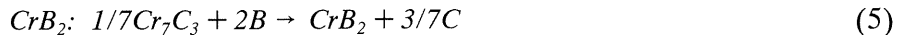
As long as steels are immersed into the molten salts for boride film formation, other boride film except iron boride cannot be expected to form on the material surface. The process of boride formation from carbide became feasible, since the affinities of titanium, vanadium and chromium to boron are higher than those to carbon. The change of free energy of each boride formation is described respectively as follows.



$$\Delta G^0 = -122445 + 80.49T, \quad \Delta G^0 = -19981\text{J/mole at } 1273\text{K} \quad (2)$$



$$\Delta G^0 = -182601 + 98.56T, \quad \Delta G^0 = -57134\text{J/mole at } 1273\text{K} \quad (4)$$

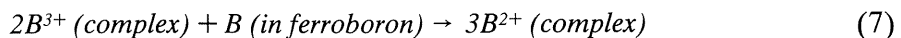


$$\Delta G^0 = -168345 + 4.512T, \quad \Delta G^0 = -162601\text{J/mole at } 1273\text{K} \quad (6)$$

When the order of boronizing treatment is changed with carbide treatment, i.e. boronizing has been done before carbide treatment, boride such as TiB₂, VB₂ and CrB₂ cannot be formed except Fe₂B.

3.2 Boriding mechanism in molten salts

The amount of deposit increased with an increasing the amount of NaF, B₂O₃ and ferroboron for all specimens, as were shown in Figs. 3, 4 and 5, and all of these components were indispensable for boronizing in molten salts. It suggests that the following two step disproportionation reaction played an important roll for the boride film formation.



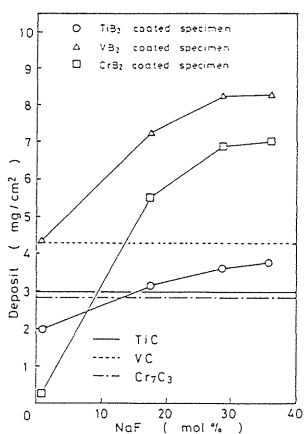


Fig. 3 Relation between amount of deposits and NaF concentration.

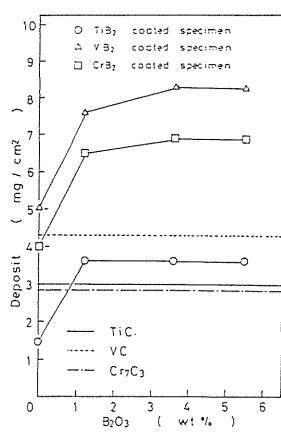


Fig. 4 Relation between amount of deposits and B_2O_3 concentration.

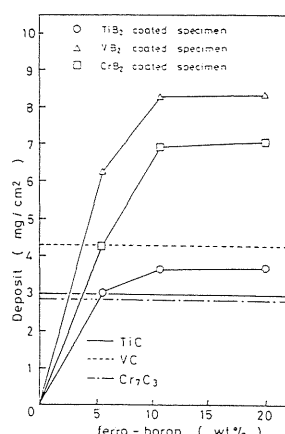
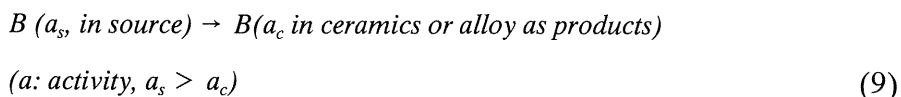


Fig. 5 Relation between amount of deposits and ferroboron concentration.



The reaction (7) can proceed everywhere in molten salts, but the reaction (8) proceeds only on the surface of specimens. These formation reactions of films is a disproportionation reaction which is proceeded through the difference of metal activities between in source and in films. Total reaction is as follows:



3. 3 Metal nitride film formation from nitrided steels

The carbon steels (SK5: high carbon steel and SPCC: low carbon steel) shown in Table 1 were immersed for 3 hours into the standard molten salts containing chromium after pre-nitriding treatment for 5 hours. The results of the X-ray diffraction analysis were shown in Fig. 6. CrN and Fe-Cr solid solution were detected on the surface layer treated at 973K. The surface layer was the composite film with CrN and Fe-Cr solid solution from the X-ray analysis and the EPMA. In the treatment at 1073K, Cr_2N was detected except CrN and Fe-Cr solid solution. Carbide (Cr_7C_3) also formed in the treatment at the temperature above 1173K. In the case of the dipping treatment for low carbon steel (SPCC), the product on the surface were similar to the products shown on high carbon steel (SK5), although the carbide cannot be detected.

On the other hands, the pre-nitriding pure irons were treated in the molten salts with ferrotitanium, ferrovandium or ferrozirconium respectively. The surface layer was Fe-Ti solid solution and TiN, and Fe-Zr solid solution and ZrN in the case of ferrotitanium bath and ferro-zirconium bath respectively. The Fe-V solid solution and two vanadium nitride,

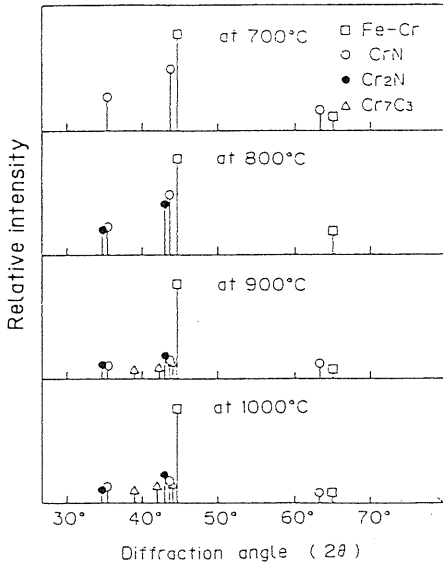


Fig. 6 X-ray diffraction analysis (Cu target) of Cr coating on 5hrs pre-nitriding SK5 for 3hrs.

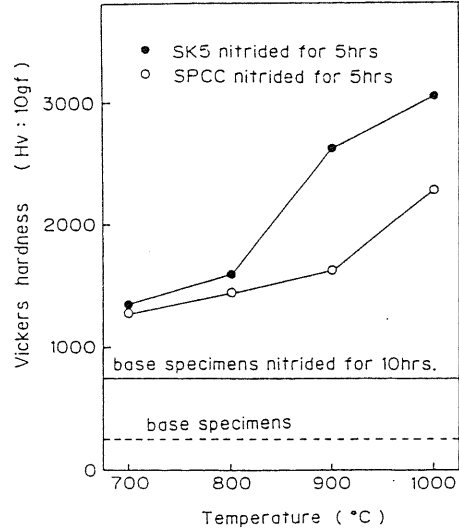


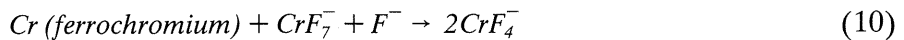
Fig. 7 Relation between surface hardness and treatment temperature.

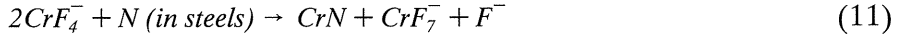
VN and V₂N appeared in the surface layer after the treatment in the molten salts with ferrovanadium.

The effect of treatment temperature on the surface hardness of specimens was shown in Fig. 7 for the nitrided high carbon steel and low carbon steel immersed in the molten salts with ferrochromium. The surface hardness, which was measured by micro-vickers hardness tester on the part of the surface films at the cross section, increased by treatment in the temperature region of 973K ~ 1273K in comparison with the specimen without treatment. The hardness tends to increase with elevating the temperature. This is caused by the carbide formation at higher temperature. The hardness of high carbon steel is larger than that of low carbon steel. This tendency becomes remarkable at higher temperature, because of the difference of the carbide formation between these specimens. The wear resistance increased in the composite film comparing to the steels as nitrided.

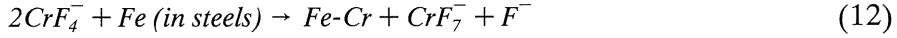
3. 4 Mechanism of nitride composite film formation

From the relation between the component in the molten salts and the weight gains, the weight gains depended on the amounts of NaF, metal salts and ferroalloy in the molten salts. These component is very important for making a composite films, because the films can be no longer formed without the anyone of these three elements. Then, the metal nitride formation mechanism will be shown in the case of chromium as follows. When the product on the surface of nitriding steels is CrN, following reactions are considered for the CrN formation process in the molten salts.





also



These reaction is called the disproportionation reaction and the driving force is due to the difference of Cr activity in source metal and the one in films in total reaction.

The nitrogen atoms near the surface exist as iron nitride before the treatment. It is considered that the iron nitride is easy to decompose during the treatment in the molten salts and the chromium nitride CrN was formed through the bonding of nitrogen atoms in the specimens and chromium atoms diffused from the surface. The decomposed iron reacted with chromium and then the iron-chromium solid solution were also formed in the film phase. In the case of the other metals such as titanium, vanadium and zirconium, by the same reaction mechanism, the composite nitride film formation occurred, as shown in Fig. 8.

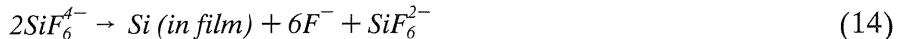
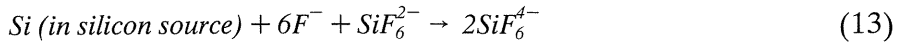
This surface modification process is very easy to give a high hardness (1000HV ~ 3000HV) and also anti-corrosive surface on the pre-nitriding steels.

3.5 Chromium silicide film formation

Fig. 9 shows the results of X-ray diffraction analysis for specimens (steel B, SK5) which suffered only chromizing treatment, chromizing and siliconizing for 2 hours and that for 5 hours at 1073K. Chromized specimens have two types of carbide such as Cr₂₃C₆ and Cr₇C₃. After then siliconizing has been done in the same specimens, peak of CrSi₂ was observed and peak of SiC was also detected weakly in X-ray analysis. It is confirmed from this analysis and EPMA that the products on the surface is mainly chromium-silicide and a slight of silicon carbide existed partially. Moreover peak of ferrosilicon were detected in the specimen siliconized for 5 hours.

The weight gains in unit surface area after siliconizing in molten salts at various temperature for various reaction time, were shown in Fig. 10. The amount of deposits increased with increasing of treatment temperature and time.

Moreover the weight gains depended on the amounts of NaF, Na₂SiF₆ and Si powder in the molten salts. These component is very important for making a film, because the films can be no longer formed without the anyone of these three elements. Then, chromium silicide formation mechanism is a disproportionation reaction and will be shown as follows:



The reacted Si with Cr resulted in Cr-Si, Cr was decomposed from chromium carbide, and a free radical carbon reacted with Si resulted in SiC, the free radical carbon was also decomposed from carbide.

The surface hardness on treated specimens, that were tested by micro vickers tester, were about 2200HV ~ 2500HV, and this specimen shows high wear resistance at the wear resistance test.

Fig. 11 shows the polarization curves of specimens without treatment, with only chromizing treatment and with chromizing and siliconizing treatment in 3% NaCl solution. It is confirmed from this result that the specimen modified with chromium silicide film by this

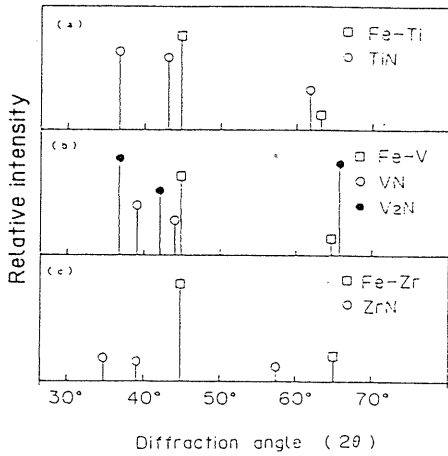


Fig. 8 X-ray diffraction analysis (Cu target) of Ti, V and Zr coating on pre-nitriding iron.

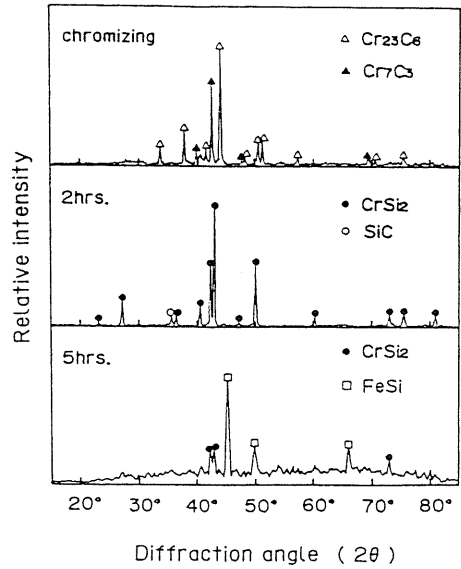


Fig. 9 X-ray diffraction analysis (Cu target) of siliconizing at 800°C.

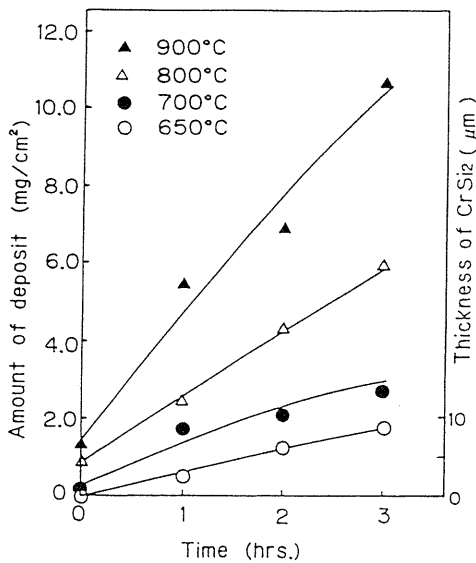


Fig. 10 Relation of amount of deposits and treatment temperature.

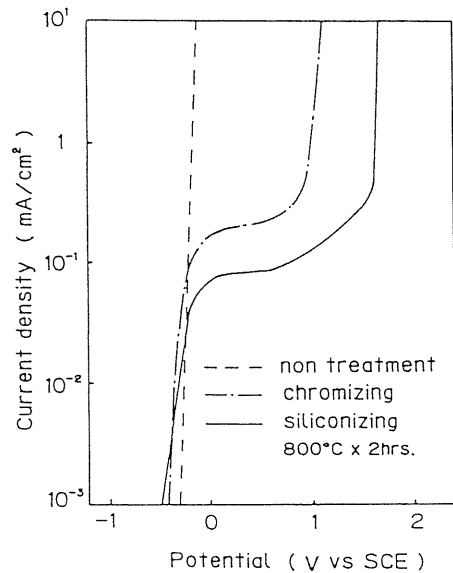


Fig. 11 Polarization curves of some specimens in 3% NaCl

process is better at corrosion resistance, because passive current is smaller, the area of passivation potential is wider and pitting potential is higher than those of chromized specimen which has a good corrosion resistance in comparison with non treated specimen.

4. Conclusions

Some functional ceramics films such as boride films and nitride ones and silicide film have been formed on steels by this surface modification techniques using disproportionation reaction. Even though substrate doesn't have any component elements of films, they can be formed on substrate by diffusing each of components into substrate through multifold processes using this method.

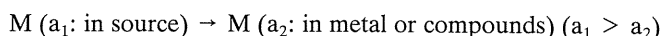
These ceramics films introduced in this paper will be a part of ones that can be formed by this method using disproportionation reaction. It is thought that this functional film formation process will be applied to various materials and to produce some ceramics and alloy films, and then it is useful for various fields.

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Summary

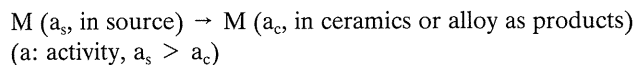
1. Global view of surface modification in fundamentals and trends was discussed in important points in some each process in part I.
2. In part II, surface coating treatment by chemical transport using disproportionation reaction in molten salts was studied comprehensively. The metal such as Si, Cr, Ti, V, Zr, Ta and etc. was deposited to form alloy and compound coating on the surface by application of the disproportionation reaction in molten halide salts KCl-BaCl₂-NaF-Metal-Metal salts system. The overall reaction can be represented as follows.



Various films were coated on steels by this method: ferrosilicon and ferrosilicon-graphite composite, chromium carbide, titanium carbide, vanadium carbide, tantalum carbide and boride films of these metals. The surface hardness (Hv) of these films ranged from 1000 to 3000 and they had very high wear resistance.

3. In part III, the formation of some functional carbide films and alloy ones were performed on some substrates like steels by immersing substrates into such molten salts system as KCl

(-NaCl)-BaCl₂-NaF-metal powder-metal oxide or halide. These formation reactions of films is a disproportionation reaction which is proceeded through the difference of metal activities between in source and in films. Total reaction is as follows:



This paper represents the mechanisms and characteristics of some ceramic films, such as boride, nitride and silicide film as the progress and application of surface modification by disproportionation reaction. As though substrates for this investigation don't have any component elements of films, they can be formed on substrate by multifold processes using each disproportionation reaction in molten salts, respectively. These films were submitted to various inspections such as X-ray analysis, microscopic observation, EPMA and corrosion test. They were excellent at tests of surface hardness, wear resistance and corrosion resistance.

Finally author would like to thank the belonging heartfully of the surf-interface laboratory, school of Eng., Nagoya University.