

A Review Paper

Recent Trends and Developments in Surface Hardening Technology: A Focus on New Ceramics for Surface Modification in Industry.

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Abstract

It has been predicted that the 21st century will witness unprecedented technological revolution in all fields of engineering. The development of materials which will imitate human intelligence, and have advanced functional properties will dominate the technological arena in the 21st century. This prediction is already being fulfilled and new ceramics are playing a very vital role. This paper looks at recent trends and developments in surface hardening technology with a focus on new ceramics for surface modification industry. The paper has reviewed various ceramic coating processes which mainly produce the film of nitrides, carbides, oxides, and borides. The paper has dealt with new ceramics from the view point of their properties, performance, and coating methods, and the principle that develops the effective technology for surface modification. More research is still going on in order to perfect some coating processes using new ceramics; the areas of application of these new ceramics are limitless

.Keywords: industry, new ceramics, recent trends, surface modification, technology.

1 INTRODUCTION

In recent times various kinds of oxides, nitrides, carbides, and borides are playing an important role as new ceramics for surface modification in industry because of their excellent characteristics and performance [1]. Ceramics occupy the number one

position on the list of industries with the greatest potential for commercial development, according to data that has been compiled by Japan's Ministry of International Trade and Industry [2]. The highly desirable characteristics offered by these new ceramics will impact a broad segment of the industrial sector such as the automotive, electronics, aerospace, medical

and telecommunications segments. New ceramics will no doubt play a vital role in the development of smart and intelligent materials in the 21st century. Coatings and bearings for orthopedic or dental implants are also available. Some of these materials function as resorbable materials to provide temporary support until the human body can gradually replace it, while others are surface active materials which form a bond with the surrounding tissue in order to stimulate growth. The use of ceramic coatings in automobile engines by Japanese companies has led to the development of engines which are 30 to 40% more fuel efficient than the current generation of engines, and furthermore, these engines run at higher temperatures without lubrication or cooling [2].

These ceramics such as nitrides, carbides, oxides, and borides are coated in order to give their effective properties and performance to materials surfaces [3]. The ceramic coating is a process which produces composite material consisting of ceramics as film and other materials e.g metals as substrate. Therefore ceramic coating will be given a great deal of attention not only as a coating technology but also as a manufacturing process for composite materials or preliminary process for joining [3]. As representative process of ceramic coating, chemical vapor deposition (CVD), physical vapor deposition (PVD), chemical densified coating (CDC), molten salt method, spray coating, ion implantation etc, are mentioned in this paper. And in addition diamond coating and sol-gel processes are recently developed and being advanced very actively. They too are mentioned in this paper.

The objective of this paper is to review various ceramic coating processes which mainly produce the film of nitrides, carbides, oxides, and borides. This will

be dealt with from the viewpoint of their properties, performance, and coating methods, and the principle that develops the effective technology for surface modification.

2 CERAMICS, CERAMIC FILMS AND THEIR SIGNIFICANCE

2.1. Ceramics

Ceramics occupy the number one position on the list of industries with the greatest potential for commercial development, according to data that has been compiled by Japan's Ministry of International Trade and Industry [2]. The markets for structural ceramics are projected to total between \$1billion and \$5 billion in the year 2000 and the principal ingredients of these markets are presented in figures 1 and 2. This new generation of fine ceramics bears little resemblance to the sand and clay combinations of terrestrial materials utilized by homo habilis in the Mesolithic and Neolithic periods for the fabrication of earthenware utensils. These new materials feature minerals such as aluminum oxide, silicon nitride and silicon carbide which are manufactured as extremely pure, fine powders prior to consolidation at high temperatures to yield a durable dense structure. The control of these new ceramics provides the design engineer with a class of ceramics which are stronger, lighter, and harder than most metallic competitors. Furthermore, the ceramics can operate at much higher temperatures and they do not degrade significantly due to oxidation as do commercial metals such as the irons and steels [2],[4].

These materials do, however, have an Achilles heel: brittleness. This brittleness is associated with a number of extremely small flaws such as cracks, voids, and impurities

present in the material, and also the amount of energy required in fracturing the material in the presence of these flaws. Thus the manufacturing processes must be extremely and carefully controlled, since flaw as small as 10 to 50 micrometers can reduce the strength of a ceramic part to only a few percent of its ideal strength thereby rendering the part useless. While material toughness is a major limitation of the current generation of advanced structural ceramics, the many significant advantages of these have not deterred further research on these compounds while other research efforts are

focused on this limiting material characteristic. These latter efforts are typically focused on synthesizing tougher materials through the prosecution of research on microstructural design, transformation toughening, and ceramic composites where the incorporation of ceramic particulates, whiskers, or continuous fibres in a ceramic matrix can yield a composite material that absorbs more energy during fracture, than a geometrically identical part fabricated in the matrix material alone [2], [4].

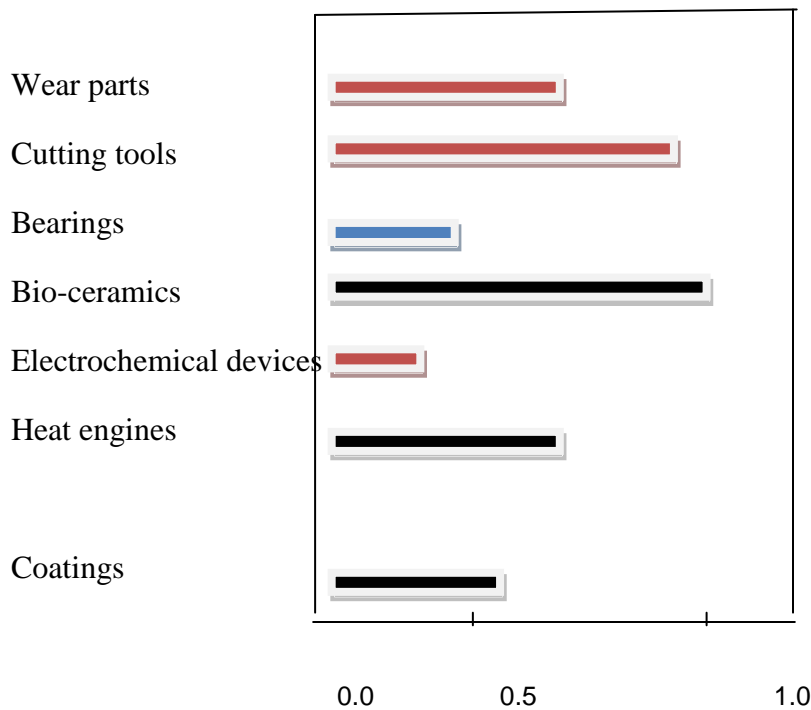


Fig. 1. Projected US Markets for Structural Ceramics in the Year 2000. Source: Gandhi and Thompson[2]

Applications	Performance advantages	Examples
Wear parts - Seals - Bearings - Valves - Nozzles	High hardness, low friction	Silicon carbide, alumina.
Cutting Tools - Lathe tools - Milling cutter	Hot hardness, high strength	Silicon nitride
Heat Engines - Diesel components - Gas turbines	Thermal insulation, high temperature strength, fuel economy.	Silicon carbide, silicon nitride, zirconia.
Medical Implants - Teeth - Joints	Surface bonds to tissue, corrosion resistance, biocompatibility	Bioglass, alumina, zirconia, hydroxylapatite.
Construction - High ways - Bridges - Buildings	Improved durability, lower overall cost	Advanced cements and concrete.

Fig. 2. Future Applications of Structural Ceramics.

2.2 Ceramic Films and their Significance

Ceramics are classified into carbides, nitrides, borides, oxides, silicides etc. in the carbide group we have, TiC, VC, TaC, WC, NbC, ZrC, MoC, Cr₇C₃, Cr₃C₂, B₄C, SiC, etc. TiN, VN, TaN, NbN, ZrN, HfN, CrN, Si₃N₄, BN, AlN etc are listed in the nitride group. TiB₂, VB₂, TaB₂, WB₂, ZrB₂, MoB₂, NbB₂, CrB₂, AlB, SiB₂ etc, are in the boride group. TiO₂, ZrO₂, Nb₂O₅, TaO₅, Al₂O₃, MgO, SiO₂, Cr₂O₃, Fe₃O₄, In₂O₃, SnO₂ etc are in the oxide group. And in addition various silicides such as TiSi, MoSi, ZrSi, and CrSi are in the silicide group. Various sulphides, BP, C, B, i-carbon, diamond, etc are also listed as ceramics. It must be noted that some of these ceramics are not yet in general usage but still undergoing research and development.

Generally speaking ceramics mentioned above have high melting point, surface hardness (1000-2000 HV) good oxidation resistance, acid and alkaline resistance but they are brittle. Their coefficients of thermal expansion are about $5-10 \times 10^{-5} / ^\circ\text{C}$. Therefore one can select a certain ceramic and utilize it as coating according to the purpose. On the other hand ceramic coating films are classified into two large groups from the viewpoint of applications, i.e those use as construction materials, and electronic (functional) materials. The former needs corrosion resistance, surface hardness, heat resistance, wears resistance, acid resistance and so on. And the later requires the properties of semiconductor (insulation, passivation), magnetism, dielectric properties (thin film condenser, surface wave device, pressure sensitive element),

photoelectric properties (thin film laser, transparent electrode, optical coating). But the discovery of new properties will lead us to more useful applications in future [1],[2], [6].

3 Nitrides and Carbides

Properties of various nitrides and carbides are shown in Tables 1-2. Most nitrides have high melting point ($<2000^{\circ}\text{C}$). Their resistivity ranges from $10 - 20 \mu\Omega\cdot\text{cm}$; these include ZrN and TiN. Si_3N_4 has a resistivity of greater than $10\mu\Omega\cdot\text{cm}$. Their hardness is more than $1200\text{kg}/\text{mm}^2$ e.g Si_3N_4 ($2600-3200\text{kg}/\text{mm}^2$) and TiN ($1800-2100\text{kg}/\text{mm}^2$), but generally their elasticity is low and they are brittle.

On the other hand, density of carbides ranges widely from $2.5-15\text{g}/\text{cm}^3$ the same goes for nitrides. The specific resistivity for TaC ranges from $20 - 175\mu\Omega\cdot\text{cm}$ and SiC from $10^9 - 10^{11} \mu\Omega\cdot\text{cm}$. in carbides there are no insulators such as Si_3N_4 and melting points of carbides are generally higher than that of nitrides. They have melting point which is more than 2500°C . Thermal conductivity of carbides is generally larger than that of nitrides, and they can be applied to various uses. Microhardness of carbides is much higher than that of nitrides, for example $1800\text{kg}/\text{mm}^2$ for TaC and $3000 - 3500\text{kg}/\text{mm}^2$ for SiC. Elasticity of carbides is slightly higher than that of nitrides but they have also low elasticity and are brittle in general. Although these ceramics as thin film they deviate slight from their intrinsic properties, however the tendency of their property remains constant [1],[6].

4 Oxides and Borides

Various properties of oxides and borides are shown in Table 3 and 4. Density of oxides ranges from $4 - 10\text{g}/\text{cm}^3$. 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 ($10^7 - 10^{22} \mu\Omega\cdot\text{cm}$), and many oxides can be use as insulators. Thermal conductivity ranges from $.001$ to $.01$ (CGS), which can be deduced from the value of specific resistance, and is very low in general (however, thermal conductivity and specific resistance of BeO is exceptionally high). Both microhardness and elasticity of oxides are lower than those of carbides and nitrides. Al_2O_3 and Cr_2O_3 however have high hardness which can be utilize in various applications [1], [6]. On the other hand the densities of borides range from $4.5-12\text{g}/\text{cm}^3$ which are similar to those of the other three compounds.

Melting point of borides is much higher than that of the other compounds (and is similar to that of several carbides whose melting point is very high). This property will be 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 conductors at high temperature. Thermal conductivity of borides ranges from 0.04 to 0.15 (CGS). Hardness of boride is the highest in the four compounds, generally greater than $2000\text{kg}/\text{mm}^2$, and it is very important that this hardness property be applied to practical uses. But elasticity is also very low and brittle as well as the other compounds. These ceramics have low thermal expansion

TABLE 1
PROPERTIES OF VARIOUS NITRIDES

Nitrides	TiN	ZrN	HfN	VN	TaN	NbN	BN	Si ₃ N ₄	AlN	CrN	Cr ₂ N
Crystal system	cubic	Cubi c	Cubi c	Cubi c	cubic	cubic	Hexagonal cubic	Hexagonal (α, β)	Hexagonal	cubic	Hexagonal
Density (g/cm ³)	5.44	7.35	13.9 4	6.08	14.1	8.26- 8.4	2.15-2.27 3.48-3.49	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	Decompositi on 2720- 3000	Decompositi on 1900	Decompositi on 2200- 2300	1500	-
Specific resistance (μΩ.cm)	22- 130	11.5 - 14.0	32	86	135	200	1.7x1019	>1019	2x1017	600- 680	79-89
Thermal Conductivity (CGS)(RT)	0.07	0.04	0.05 2	.027	.021	.009	Orientation	.035-.041	.004	.026 1- .030 7	.0514- .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)	2550 0	-	-	-	5870 0 (ε- TaN)	4930 0	1160-8370 (α-BN)	5620-21800	28100- 35200	-	-
Coefficient of thermal expansion (10 ⁶ 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 (21- 1100)

SOURCE: Oki, T (2008)1

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
Crystal system	Cubic	Cubic	Cubic	cubic	cubic	cubic	hexagonal	Rhombohedral	Cubic hexagonal	orthorhombic	trigonal
Density (g/cm ³)	4.85- 4.93	6.44- 6.9	12.2- 12.7	5.36- 5.77	14.48- 14.65	7.82	15.6-15.7	2.5-2.54	3.21-3.22	6.68	6.92
Melting point °c	3180- 3250	3175- 3540	3885- 3890	2810- 2865	3740- 3880	3500- 3800	2627- 2900	2350-2470	Decomposition 2200-2700	1895	1782
Specific resistance (μΩ.cm)	70-170	50-64	60	150- 160	20-175	74- 254	53	.3x10 ⁴ -.8x10 ⁴	10 ⁹ -10 ¹¹	70-80	105- 113
Thermal conductivity (CGS)(RT)	.041- .06	.049	.053	.010	.053	.034- .041	0.070	1.065-1.069	.098-.100	.045-.047	.035- .038
Microhardness (kg/mm ²)	2900- 3200	2600	2533- 3202	2800	1800	2400	2400	2400-3700	3000-3500	1800	1882
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 .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)

TABLE 3

PROPERTIES OF VARIOUS OXIDES

Oxides Properties	TiO₂	ZrO₂	HfO₂	V₂O₅	Ta₂O₅	Nb₂O₅	WO₃	Al₂O₃	Cr₂O₃
Crystal system	Tetragonal al	Tetragonal al	Cubic c	Orthorhombic bic	orthorhombic bic	hexagonal al	tetragonal al	hexagonal al	orthorhombic bic
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 (μΩ.cm)	3x10 ¹⁰	-	-	3x10 ⁷	1x10 ¹¹	-	2x10 ¹¹	1x10 ²²	-
Thermal conductivity (CGS)(RT)	.008-.015	.0047	.001-1	.0010	-	-	-	.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 .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

Borides properties	TiB₂	ZrB₂	HfB₂	VB₂	TaB₂	NbB₂	W₂B₅	CrB₂	FeB	Fe₂B
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 (μΩ.cm)	6.4-9.1	9.7	10.6	22.7	32.5	25.7	22.0	30	80	38
Thermal conductivity (CGS)(RT)	.154	.138	.122	.101	.038	.057	.125	.076	.029	.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 .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)

Source: Oki, T. (2008) [1]

coefficient, good heat resistance, corrosion resistance, electric properties,

although their thermal – shock resistance and mechanical strengths are not good

yet. The low elasticity of these ceramics is detrimental rather than beneficial. The new ceramics coating is one treatment which can resolve such a disadvantage by combining these brittle new ceramic films with ductile substrates. Therefore it might be regarded as a composite manufacturing process. Recently the differences in properties between ceramic films and ceramics themselves have become clear, which is very interesting in the view point of surface functions of these ceramics [1], [6].

5 Significance of Fine or New Ceramic Coating

Ceramic coatings can give some new functions, particularly the properties which are composite to the material substrate surface. Main applications of the ceramic coatings are described as follows: components for wear resistance, hot resistance and packing parts, and mechanical seals; these are coated with Al_2O_3 , TiN, TiC, SiC etc. Electrical materials (functional materials) such as transparent conductive films are In_2O_3 , SnO_2 , etc, for infrared cut filters and strong dielectric substances $\text{BiTi}_3\text{O}_{12}$ is used, and for piezoelectric films ZnO is used. In addition Al_2O_3 is applied in the coating of lens by utilizing its transparency. AlN is used as insulative 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, resistant devices, dielectric substances and lens coating [1],[2],[6]. It is normally required nowadays that mechanical components should undergo higher loading, and that electronic materials have more diversified functions. Materials usages are inclined to increase more and more in this twenty first century, if the properties of

ceramics are studied and revealed further (e.g. the electric, magnetic, thermal and mechanical properties of non-stoichiometrical compounds by reactive ion plating, etc), the uses of new ceramic coating will definitely increase more and more. Recent trends in the application of new [1], [3], [6] ceramic coatings with new properties is very significant.

Ceramic coating processes can be classified as follows:

i). Chemical Vapour Deposition (CVD)

CVD utilizes chemical reactions in gas phases in order to coat the new ceramic on a substrate. Low pressure CVD for controlling the surface state and plasma CVD which promotes reactions at relatively low temperatures are recently being developed.

ii) Physical Vapour Deposition (PVD)

All PVD processes are considered as vacuum vapor deposition as well its application process. For new ceramic coatings there are many processes utilizing chemical reactions, e.g vacuum vapor deposition, sputtering, ion plating and so on with and without reactive gases. Low temperature plasma is utilized effectively to improve reactivity and characteristics of produced films. Ion implantation being new in the lime light is one of PVD processes and very interesting [1],[7].

iii) Chemical Densified Coating Process (CDC)

This process utilizes the decomposition reaction of compounds crated on the substrate. The coating of chromium oxide is utilized in practical uses to improve the wear resistance of components and materials [1], [8] some

rocket parts and jet engine components are coated using this process.

vi) Other Processes

Besides the above mentioned processes, carbide coating, and boride coating using molten salts, ion nitriding, ion carburizing, spray coating, composite plating, diamond coating and i-carbon coating are being developed. These processes have the characteristic that film formation takes place through catalytic contact reactions of the

interface between substrate and gas phases or liquid phases, [1],[8]. This various properties will be explained.

6 CHEMICAL VAPOR DEPOSITION (CVD)

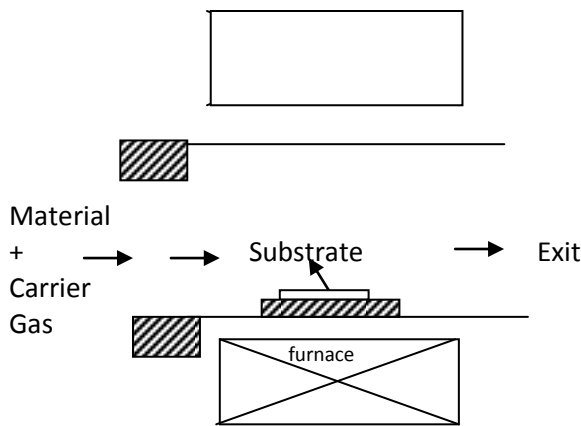
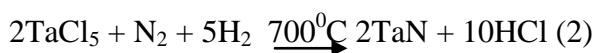


Fig. 3. Schematic Illustration of CVD Process

Basic apparatus is shown schematically in figure 3. CVD is the process in which metal nitrides, carbides, borides and other compounds are deposited on material substrate surfaces through catalytic contact reactions at the

$$3\text{TiCl}_3 + \text{C}_3\text{H}_8 + 2\text{H}_2 \xrightarrow{1000^\circ\text{C}} 3\text{TiC} + 12\text{HCl} \quad (1)$$


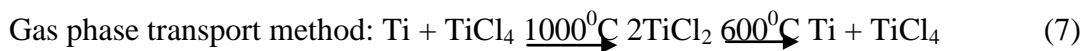
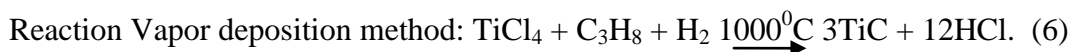
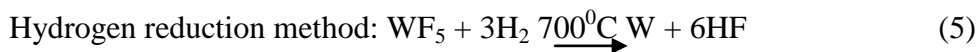
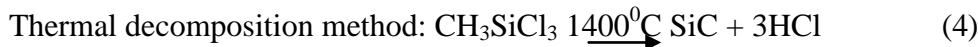
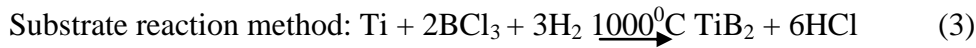
In many CVD processes, excessive heat affects film formation, elevated

interface between substrate and vapor phases. For example the following reactions take place on the surface of steels to produce titanium carbide and tantalum nitride.

temperatures in the range of 700°C to 1000°C normally create adhesion

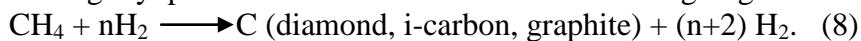
problem. In order to avoid this disadvantage intermediate undercoating is sometimes required. Recently plasma CVD in which low temperature plasma makes the film formation at relatively

low temperature possible is being investigated to overcome such disadvantage. Representative CVD processes are listed below:



On the other hand diamond and i-carbon coating by plasma CVD are of recent

research interest and many studies are going on in this area [7].



The diamond has high hardness and good thermal conductivity, in spite of its high insulation. Therefore diamond coatings are very interesting and it is expected that the technology will develop more in the future [7].

7 PHYSICAL VAPOR DEPOSITION (PVD)

Generally speaking, PVD is the process in which vaporized materials deposit as compounds on the substrate through reactions with reactive gases, ceramic coating can be achieved by evaporation or sputtering ceramics e.g several oxide films are produced only by evaporation. PVD processes are mainly classified into the vacuum vapor deposition, the reactive sputtering and the reactive ion plating. See figure 4 for the schematic illustration of the processes.

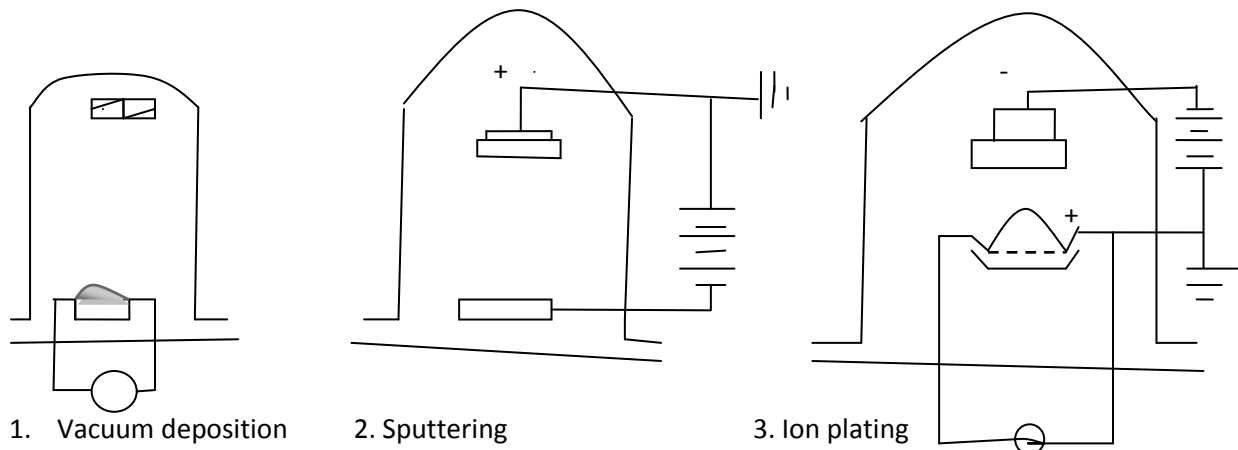


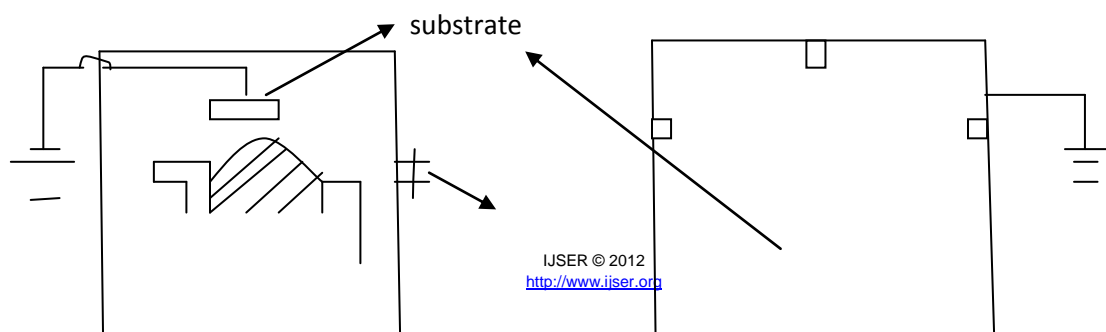
Fig. 4. Schematic Illustration of PVD Process.

In the vacuum vapor deposition process, the system is evacuated at 10^{-4} - 10^{-7} mmHg to have various compound films deposited on the substrate.

In the sputtering processes, Ar gas is induced into the vacuum chamber at 10^{-3} - 10^{-2} mmHg. Voltage of 1 - 5kv is applied to the intended ceramics as negative electrode. And glow discharge takes place in the vacuum chamber, where positive argon ion collides with the negative ceramic target and sputters part of it to deposit on the substrate. Prominent features of this process are to produce films of high melting point materials at relatively low temperatures, to keep the composition constant from target to

film and to be able to form various kinds of ceramic film by reacting with induced gases. It's very interesting to consider sputtering as one method of vaporizing at low temperatures.

Reactive ion plating is the process in which vaporized metal is ionized or activated to produce compound film on material surfaces through reaction with environmental gases. In this process plasma promotes the chemical reactions and adhesion of produced films at relatively low temperatures. Ion plating is classified into various types from the view point of the way of ionization or activation, see figure 5



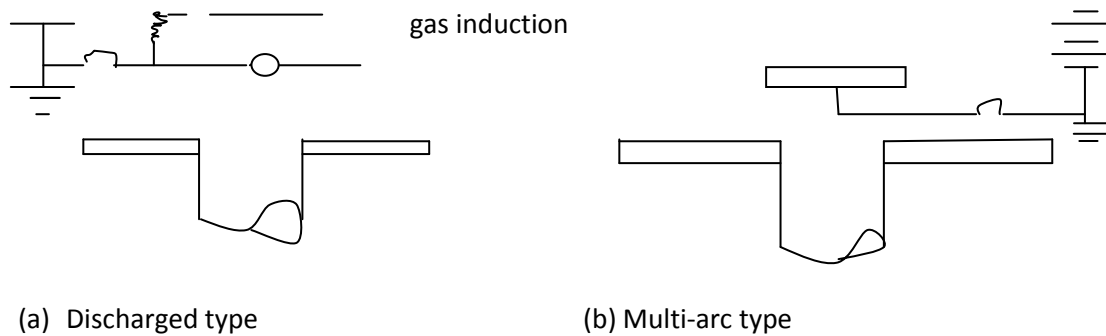
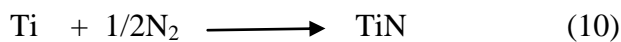
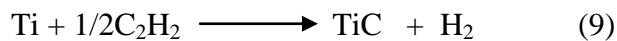


Fig. 5. Schematic Diagram of some ion Plating Devices

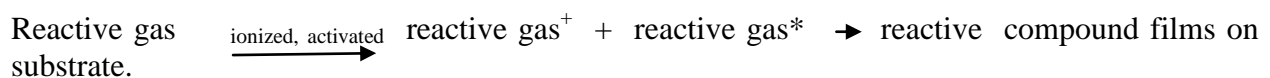
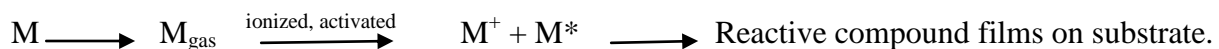
For example total reactions for the formation of titanium carbide and titanium nitride is described as follows:



Reactive ion plating makes it possible to produce Al_2O_3 , TaC, ZrC, ZrB_2 , SiC, films, etc as the reaction in this process proceeds in the non-equilibrium state, various phases of titanium nitrides and carbides are produced on the surface of the substrate. The principle leads to the development of the coating

process of new ceramics which is term the artificial new ceramics.

The mechanism can be generally described as follows:



For the formation of nitride films, N_2 and NH_3 gas are used as reactive gas, CH_4 , C_2H_2 , C_2H_4 , C_3H_3 , etc for carbide films, O_2 gas for oxide films and BH_3 and BCl_3 for borides [7,9,10]

8 CHEMICAL DENSIFIED COATING AND OTHER PROCESS

8.1. Chemical Densified Coating (CDC)

This process utilizes the chemical- thermal decomposition to coat porous structural

ceramic films and to densify them. The example of the coating is chromium oxide as explained below:

A hydrous 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 1200-1300 HV can be coated on the substrate. 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 aspect of making use of the good properties of Cr_2O_3 [1], [6]. Ceramic coating by chemical thermal decomposition will advance surface modification technology further as research to perfect the process continues [8].

8.2. Carbides Coating and Borides Coating.

Process by Molten Salt

When materials containing carbon are immersed into molten neutral or borax salts into which carbide forming elements are added as powder, carbide films form on material substrate surfaces. And the treatment in boron containing molten salts leads to the formation of FeB or Fe_2B ; the hardness range is 1800 - 2100 kg/mm^2 . This process enables low grade steels to have high wear resistance, heat resistance and corrosion resistance. Composite films such as V-Nb-C and Ti-V-C can be produced by this process. The disproportionate reaction is considered as the main mechanism [1],[6].

8.3. Spray Coating

These processes; such as high temperature plasma spray coating, explosion spray coating and so on

requires high temperature or energy. They are not suitable for ceramics decomposing at elevated temperatures. Ceramic films are inclined to be porous, as the melting points are generally high. If this tendency is taken into consideration, the process has no problem with ceramic coatings. Low pressure spray coating inhibits the change of components by oxidation. A bit of binder is applied to improve the adhesion, when the mixture does not hinder the properties of the ceramics. Even with this treatment the problem of pores, do remain unsolved sometimes [8].

8.4. Composite Plating

Ceramics such as SiC, WC, TiC, Cr_7C_3 , Al_2O_3 are dispersed in plating metal e.g. Nickel, which results in the improvement of wear resistance. Nickel plating dispersed SiC has been put to practical use [11].

8.5. Sol-Gel Process

Metal alkoxides sol such as $\text{Al}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_4\text{H}_9)_3$, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and so on, painted on materials becomes thin films through thermal decomposition and hydrolysis. The calcination temperatures depend on the properties of the produced films and is about 100-1100 $^\circ\text{C}$ [1].

9 POINTS AND CHARACTERISTICS FOR APPLICATION

These processes mentioned above are generally applicable to various material substrates. But one has to pay attention to softening temperatures of substrate, their elasticity and the difference in thermal expansion between substrate and coated ceramics, this is

important for ceramic coatings at elevated temperatures. For this purpose undercoating is often required (particularly for the coating on metal surfaces). As the thickness of the film grows, the larger the effect of thermal expansion becomes. Thermal expansions of various ceramics are summarized in Table 5. For steels multilayer coatings are sometimes needed. For aluminum;

one must pay attention to the oxide surface film and softening, but anode oxide films are often applicable. For copper alloys, low temperature treatments are required to get a good adhesion. If all these points are addressed, ceramic coating can be widely used. It is expected that the processes will be developed by the study on the properties of produced films [1].

TABLE5
COEFFICIENT OF THERMAL EXPANSION A [$10^{-5}/^{\circ}\text{C}$]

Element	Nitride	Carbide	Oxide
Ti(0-100°C) 8.9	TiN(180-27°C) 3.02-4.78	TiC (25-1000°C) 7.95-8.58	TiO ₂ (20°C) Ti ₂ O ₃ (20°C) 7.5 9.0
Zr (0-100°C) 4.4	ZrN (-180-27°C) 4.09-4.62	ZrC (25-1000°C) 7.01-7.42	ZrO ₂ (20°C) 3.8
Hf (0-100°C) 6.0	HfN (20-1000°C) 6.9	HfC (20-1000°C) 6.8-7.13	HfO ₂ (20°C) 3.8
V (0-100°C) 8.3	VN (-180-27°C) 9.2	VC (25-1000°C) 7.25-7.45	-
Ta(0-100°C) 6.5	TaN(20-700°C) 3.6	TaC (25-1000°C) 6.5-7.12	-
Nb (0-100°C) 7.2	NbN (20-1000°C) 10.1	NbC (25-1000°C) 6.88-7.25	-
W(0-100°C) 4.5	-	WC(25-1000°C)	WC ₂ (20°C) WO ₃ (20°C) 2.6 16.4
Al(0-100°C) 23.5	AlN(20-300°C) 4.8	-	Al ₂ O ₃ (20°C) 5.4
Cr(0-100°C) 6.5	CrN(20-800°C) 2.3	Cr ₇ C ₃ (20-1000°C) 9.4	Cr ₂ O ₃ (20°C) 8.8
B (20°C) 4.7	α-BN(20°C) 1.8	B ₄ C (20°C) 4.5	-
Si(0-100°C) 9.6	Si ₃ N ₄ (20-1000°C) 2.75	β-SiC(25-1000°C) 4.7	SiO ₂ (20°C) 10.3

Source: Oki,T. (2008)¹

10 PROSPECTS FOR THE FUTURE

Various properties and new performance of new ceramics or

artificial ceramics has been found, which made this technology more applicable as high performance surface, modified surface, composite surface, and functional surface. For example the practical applications of nitride and

carbide films are shown in Table 6 and 7. Some coating processes such as ion plating can produce non-equilibrium phases on the surface, application field will expand more and more, particularly in this 21st century of advanced technology [13].

It is expected in future that new functional materials by ceramic coating such as semi-conductor, metallic materials, ceramics and plastics will be investigated and developed, and that new

thin films such as ultra fine particle films, amorphous films, super conducting films and diamond films will be developed, and that structural materials on which corrosion resistance, heat resistance, wear resistance films, are formed will be developed. These areas are currently receiving serious studies and investigations, and great deal of progress is been made [1],[2],[12],[14].

TABLE 6
PROPERTIES AND APPLICATION OF VARIOUS NITRIDES

Nitrides	Properties					Application
	Density(g/cm ³)	Melting point (°c)	Specific resistance (μΩ.cm)	Microhardness (kg/mm ²)	Coefficient of thermal expansion [10 ⁻⁶ °C]	
TiN	5.44	2900-3200	22-130	1800-2100	9.35	Wear resistance, cutting tool, die, ornaments, cases for watches.
TaN	14.1	2980-3360	135	1060	3.6	Wear resistance, cutting tools, and ornaments.
AlN	3.25-3.30	Decomposition 2200-2300	2x10 ¹⁷	1225-1230 (KH)	5.0	Heat resistant insulator, ultra-hard heat resistant structural materials
BN	2.15-2.27 3.48-3.49	Decomposition 2200-3000	1.7x10 ¹³	4700	4.8	Heat resistance, corrosion resistance, die cast,

						insulation, electronic materials, and thermal conductivity
Si ₃ N ₄	3.18-3.19	Decomposition 1900	>10 ¹³	2570-3260	2.75	Heat resistance
HfN	13.94	3300-3307	32	1500-1700	6.9	Corrosion resistance
NbN	8.26-8.4	2050	200	1400	10.1	Electric conductance, electric tube for sending images.

TABLE 7

PROPERTIES AND APPLICATION OF VARIOUS CARBIDES

Carbides	Properties					Application
	Density (g/cm ³)	Melting point (°C)	Specific resistance (μΩcm)	Microhardness (kg/mm ²)	Coefficient of thermal expansion [10 ⁻⁴ /°C]	
TiC	4.85-4.93	3180-3250	70-173	2900-3200	6.4	Wear resistance, heat resistance, cutting tool, ceramic tools.
WC	15.6-15.7	2627-2900	53	2400	3.7	Wear resistance, heat resistance, hard metal tools (WC- Co)

TaC	14.48-14.65	3740-3880	20-175	1800	5.6	Wear resistance, ceramic tools, heat resistance
B ₄ C	2.50-2.54	2350-2470	0.3-0.8	2400-3700	4.5	Wear resistance, electron absorber.
SiC	3.21-3.22	Decomposition 2200-2700	10 ⁹ -10 ¹¹	3000-3500	3.3	Wear resistance, heat resistance, corrosion resistance, high grade materials for furnaces
HfC	12.20-12.70	3885-3890	60	2533-3202	4.9	Heat resistance
ZrC	6.44-6.9	3175-3540	50-64	2600	4.0	Heat resistance, heat resistant alloys.
VC	5.36-5.77	2810-2865	150-160	2800	6.2	Wear resistance.

Source: Oki, T.¹

11 CONCLUSION

New ceramic coating processes will be developed as outstanding technical innovations and this will be dreams and hopes come true for the engineers and

material scientists. This breakthrough will introduce diversified and complex technology to our industrial world. The current ceramic coatings have no doubt contributed in raising performance, functionality, durability and efficiency in

most machineries and systems it is believed that new ceramics will play a major role in the development of advanced materials and smart materials which are expected to characterize the 21st century.

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