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The development of the Ceramics Nano-Film Coating having both high corrosion resistance and excellent heat resistance

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ABSTRACT

The exhaust pipes of the motorcycle were always exposed to high temperature exhaust gas. There was a problem of the tarnish or the rust during use, and it might be sometimes complained from a user.

Therefore we developed new surface treatment and could prevent these problems.
New surface treatment is "Nano-film Coating" by the DC reactivity magnetron sputtering method (PVD method). We developed SiOxNy ceramic Nano-film of the thickness of 20-150 nm on the metal substrates.

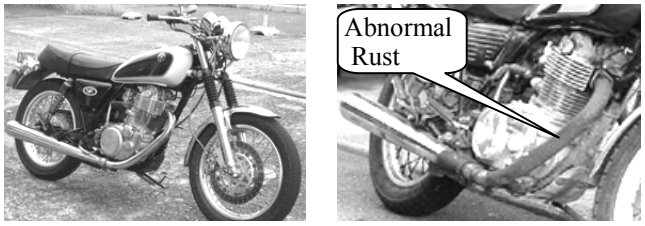
This Nano-film was evaluated heat resistance, corrosion resistance, wear resistance and optical characteristics. It is able to get these performance satisfied enough. And the metal coloration is possible by controlling a refractive index and a film thickness of the Nano-film. The film was deposited in a three-dimensional shape by controlling the reactive gas composition, the gas ratio and sputtering power.

The exhaust parts are colored by three patterns that is "transparent and colorless", "gold " and "blue". The Nano-film Coating continues being mass-produced in 4 models since it was adopted in YAMAHA FZ1 in 2008.

INTRODUCTION

A used exhaust pipe has a problem of the tarnish and the rust for a long time. If surface temperature abnormally becomes higher, these are burnt, and rust is easy to become occur.

Figure 1 is an appearance photograph of a motorcycle used in a market. It is the photograph after the 15,000km run and before a run. Even if the whole is good-looking as for the vehicle after the long run, only the exhaust pipe is abnormally rusted. When most metal products are exposed to high temperatures as well as an exhaust pipe, tarnish and rust advance. (e.g. heat reflector of oil stove and a boiler pipe)



Before use After run 15,000km
Fig.1 Photograph of a motorcycle used

High temperature oxidation of metals

The exhaust pipe might be made with double or triple pipe structure to lower the surface temperature because high temperature gas flow in. When it maintains 573K or more for a long time, a metal surface is oxidized, And a change of color and rust are generated. Most of exhaust pipes with the metallic luster are made with a pipe of austenitic stainless steel or the chrome plated pipes. At first the

result of a high temperature oxidation test of these metals is shown in figure 2.

Both metals change color from golden to purple, to blue by the heating more than 623K.

Sample 1 : Chrome plated mild steel sheet
Sample 2 : austenitic stainless SUS304 (AISI 304)
Size : 100L×60W×1.2t
Surface : mirror finish
Heating condition : 573K~873K×24hr in Air
at Electric Furnace

Oxidation Resistance Coatings

Conventionally, there are various methods to make a gas barrier film on the surface to prevent the high temperature metal oxidation. It is heat resisting paint , ceramics thermal spray, Sol-Gel method and PVD/CVD. These coating film thicknesses are wide with 0.03μm to several mm and the color of the appearance varies. However, there were very little the transparent and colorless coating films that could maintain metallic luster. For example, TiN coating by ion plating was difficult to be applied to high temperature of above 773K uses due to their poor oxidation resistance. (1, 2) Several researchers have reported that the amorphous SiO2 oxidized from SiN played a major role as the oxidation barrier. (3,4) A characteristic of many heat resistance coating is shown in table 1. We evaluated the oxidation resistance by the heating test in atmospheric furnace and corrosion resistance by CASS test.

There was not a good film by the commercial coating to satisfy all for an exhaust pipe.

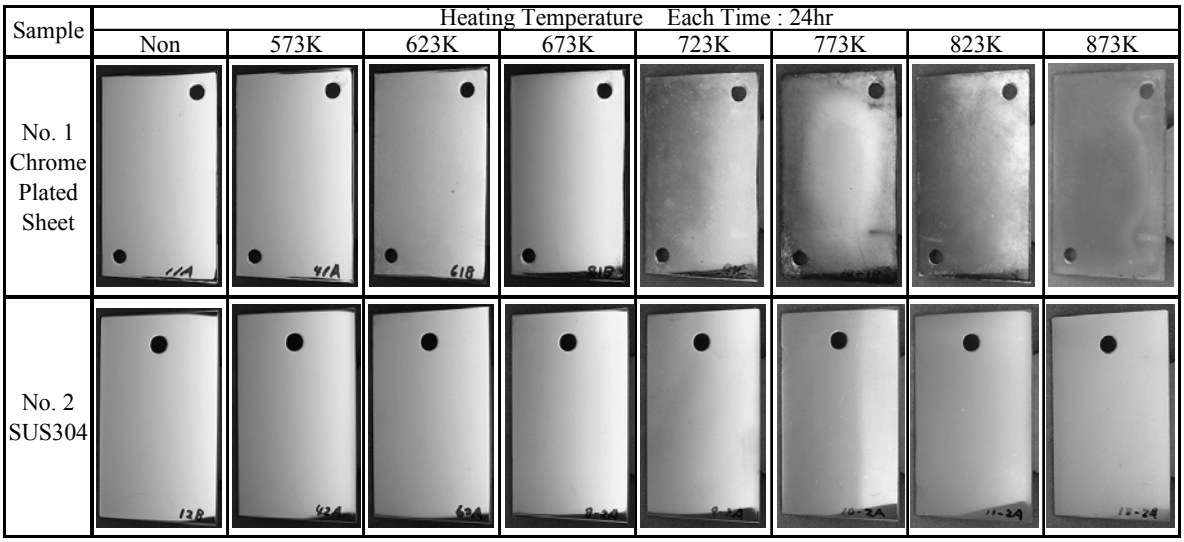


Fig.2 Appearance after heating test

Table 1 Comparison of various heat resistance coating

	Method	Compotion of Film	Thickness μm	U.T.L. [1] K	Appearance Luster	Appearance Trans-parent	Appearance colorless	Heat Resistance [2] Change of color	Heat Resistance [2] Adhesion	Corrosion [3] Resistance after Heating
1	Thermal Spray	Ceramics	200-2000	2273	×	×	×	○	○	○
2	Painting	Glass,Ceramics	100-500	1473	×	×	×	○	△	○
3	Sol-Gel	SiO2	0.1-0.5	673	○	×	×	×	○	×
4	Sol-Gel	ZrO2	0.1-0.5	773	○	×	×	×	○	×
5	Ion Plating	SiO2	0.05-1	673	○	○	○	×	○	—
6	Ion Plating	TiN, TiAlN	0.5-2.0	673	○	×	×	×	○	—
7	Ion Plating	CrN, CrAlN	0.5-2.0	973	×	×	×	×	○	—
8	Sputtering	TiO2	0.05-0.1	673	○	×	○	×	○	—
9	Sputtering	Al2O3, AlN	0.05-0.1	873	○	○	○	×	○	—
10	Sputtering	SiO2, SiN	0.03-0.1	673	○	○	○	×	○	×

1) Upper Temperature Limit , Cataloge data
2) Oxidation Test : 773K-24hr keepin in air
3) CASS Test : 16hr -5 cycles

○ : best △ : good × : no good

Development of the New Coating Method

It was started development of new surface treatment to solve these problems. The characteristic of the film set five next targets.

1) Heat-resistant：without the tarnish after 773K-24hr heating
2) Corrosion resistance：more than RN 9 in SST 6cycles
3) Hardness：more than 1.2 times of the hardness of the substrate
4) Color： transparent and colorless, many coloration
5) Appropriate productivity and cost

In the choice of the film composition, we referred to a gas barrier film. As steam barrier film and oxygen gas barrier film, the transparent SiO2 film and the Si3N4 films are deposited on polymer substrates by the sputtering method is known. (6,7) The Si3N4 films have attracted much interest for over two decades for their important applications in microelectronic and optoelectronic industry. (8-10)

Therefore we examined it whether these films on metal substrate were usable.

EXPERIMENTAL

Materials and Apparatus

At first we used the ion plating and CVD method for the film deposition method, but the good quality film was not provided. In addition, the CVD method decided not to use because a work becoming high temperature and using the dangerous silane gas.

Then the thin films of SiOx or SiNy were deposited on metal substrates by DC magnetron sputtering method. In reactive sputtering, the deposited film is formed by chemical reaction between the Silicon target material and Ar gas, N2 gas and O2 gas which are introduced into the vacuum chamber. Varying the relative pressures of Ar and reactive gases can control the composition of the film. (10)

The film stoichiometry is an important parameter for optimizing functional properties like the color variation and the index of refraction and gas barrier property.

The metal substrates used a SUS304 sheet of the mirror surface finish and a decorative chrome plated mild steel sheet. These samples were set in a vacuum chamber after alkali washing and air-drying. And the surface of the sample is cleaned more due to bombardment with Ar gas plasma before the film deposition. The SiOx and SiNy layer thicknesses were varied between 10–150 nm, respectively. The film deposition condition is shown in table 2.

Table 2 Sputtering Condition

Attained Vaccum	3×10-3 Pa
Sputtering Pressure	3×10-1 Pa
Flow Gas	N2 , O2 , Ar
Flow Rate	less than 400 sccm
Sputtering Power	less than D.C. 10kw
Heating of Sample	non
Working Distance	200 - 600mm
Thickness	10 - 150nm

The coated sample was evaluated oxidation resistance, corrosion resistance, and wear resistance. And the film properties examined surface observation, the color measurement and hardness test. A Si wafer was coated a film at the same time and measured thickness and the optics fixed number by an ellipsometer.

High Temperature Oxidation Test

The sample after the coating heats in an atmospheric furnace at 773K – 24hrs keeping. Then we examined appearance viewing and the change of the color was measured CIE1976 - L*a*b* values and then calculated ΔE* using a colorimeter. The results are shown in Figure 3. Both sample 1 and 2 which coated SiO2 film or SiNy film change color after heating and a color difference △E* is large, these film are inferior to gas barrier characteristics. However, the sample coated SiOxNy film superior in gas barrier characteristics does not have the change of the appearance after heating, and △E* is less than 1.

In addition, as for each film, the quantitative analysis of the depth profile is used by GDS, and the film composition is confirmed.

Film	SiO2		SiNy		SiOxNy	
Thickness	22 nm		25 nm		23 nm	
Heating	before	after	before	after	before	after
No. 1 Chrome Plated Sheet						
△E*		28.2		33.2		0.5
judgment		×		×		◎
No. 2 SUS304						
△E*		9.3		18.5		0.2
judgment		×		×		◎

Fig. 3 Result of high temperature oxidation test

Corrosion Test

The Cr plating can be superior to corrosion resistance, but it suddenly worse after oxidized. The samples of coating SiOxNy film or not, there were compared the corrosion resistance by CASS test after heating in the atmosphere furnace. The Result is showed in Figure 4.

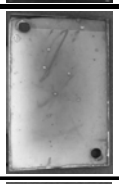
Film	Not Coating	SiOxNy 22 nm
Before heating		
After Haeting		
After CASS 6 cycle		
R.N.	5.0	10.0
Judge	NG	◎

Fig. 4 Result of CASS by coating or not

In addition, the SUS304 specimen performs etching by a marble reagent (3% copper sulfate water solution) to check a microstructure. Therefore we performed a marble-dropping test. The reagent was dropped 1cc to the surface of SUS304 coating or not coating specimen and it was observed a change after 180sec. This result is shown in Figure 5.

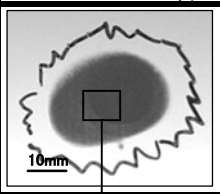
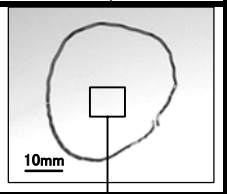
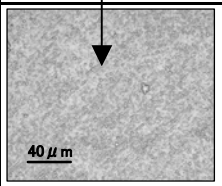
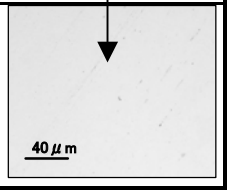
Film	Not Coating	SiOxNy 20 nm
After Dropping 180 sec		
Photo by Metallographic Microscope		
Judge	NG	◎

Fig. 5 Result of Marble Reagent Dropping Test

In the case of a high quality film SiOxNy, the corrosion is not observed at all.

Wear Resistance Test

At first Vickers surface hardness was measured by changing measurement load to examine wear resistance for a coating sample. The hardness of the thin film is not able to measure directly because it was a very thin film.

Figure 6 shows the surface hardness. The coating sample is become harder than substrate in low load.

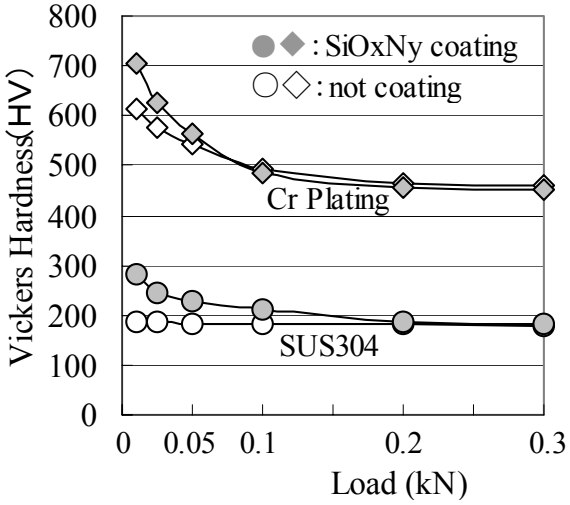


Fig.6 Surface hardness of the thin film

And the wear properties of thin films were investigated using a pin-on-disc type reciprocating sliding tester. As a result, as for this SiOxNy film, it was confirmed that wear resistance improved in comparison with substrate without the coating.

Optical Characteristic

Depending on the model of the motorcycle, colorless metal or the coloration is required in design of the exhaust pipe. Therefore transparence and colorless or colorful is required to a film. The thin film of ceramics produces interference colors by a refractive index and a film thickness. Therefore it is necessary for the Nano-film to control these.

A natural oxidation layer of substrates was removed by Ar bombard before coating. The refractive index of the film changed by controlling N2 and the O2 gas ratio of the reactive gas. The silicon wafer was coated with a sample and it was measured a refractive index and a film thickness using an ellipsometer. Fig.7 presents a refractive index of coating film on Si wafer.

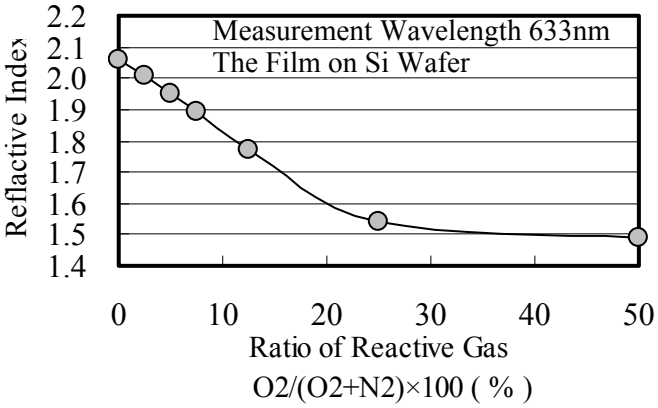


Fig.7 Influence of the reactive gas ratio on refractive index

The film refractive index is directly dependent on the sputtering conditions indicating a correlation with film stoichiometry and microstructure, and could be looked as an indication of film stoichiometry. (11)

SiO2=1.5, Si3N4=2.0 at wavelength 633 nm And the refractive index of formed SiOxNy film changes by the ratio of x and y. It becomes smaller so that the ratio of oxygen is higher, and the composition of this film become near to SiO2. The reverse becomes Si3N4. However, if the film becomes near to SiO2 and Si3N4, heat resistance worsens more. As for the film superior in gas barrier characteristics, a refractive index was around 1.8.

When a film thickness was less than 15nm, a heat change of color might occur partially. The film was able to get colorless film at thickness 15-20nm.In addition, interference colors occur when the refractive index fixed and raises a film thickness. The film produces gold at 25nm and blue at 60nm, so it is used for the coloration of the exhaust pipe.

Chemical Composition

A SUS304 substrate sample coated the good film of SiOxNy 25nm was determined the chemical composition by GDS analysis. The example was shown in figure 8

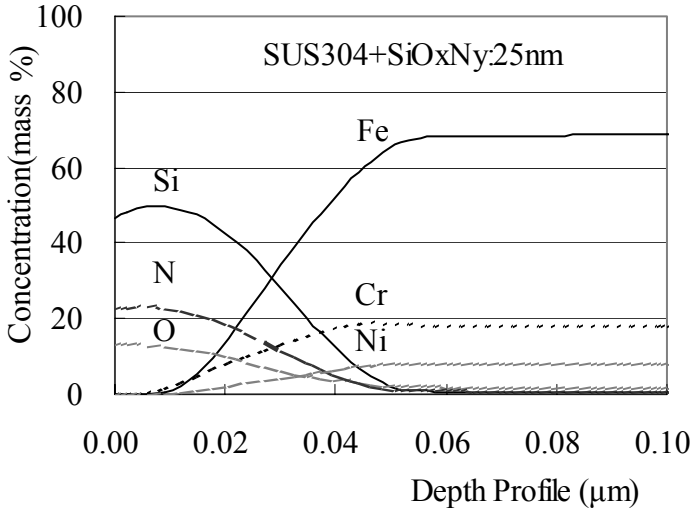


Fig. 8 Chemical composition by GDS depth profile

The refractive index of this film is 1.83.

Productivity

As for the sputtering method, a film deposition rate is slower than ion plating or vacuum deposition, but is superior in adhesion and uniformity.

The adhesion of the film improves furthermore by heating a product, but the productivity deteriorates by

taking heating and cooling time for a long time. There was no heating with the production equipment.

When a product is colored, it is necessary to raise a film thickness, but film deposition time gets longer. Therefore Ar gas was added to reactive gas, it was checked whether a deposition rate improved. The result is shown in figure 9.

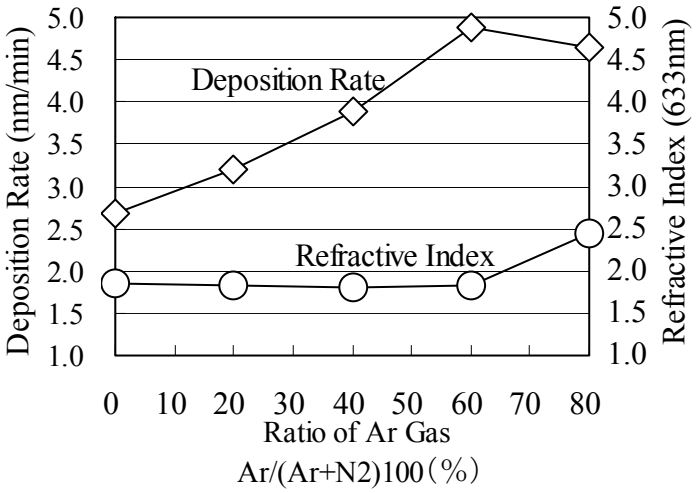


Fig.9 Effect of the Ar gas ratio on film growth

The resultant deposition rate is about two times (reduction of the deposition time) at 60% Ar higher than the rate of the deposition using N2 gas only. The refractive index did not have a change either, and a high quality film was provided. But there was not the effect more than 60 % of Ar gas. Because Si target is more strongly sputtered than N2 plasma by Ar plasma.

Coating to a Three-Dimensional Shape

The PVD method is used commonly by coating the product of a flat shape such as tool, die, FPD and a protection film. (6,7,9) The wrap around characteristics of the film by the sputtering method is worse than electroplating. In addition, a film deposition rate and coherency fall so that working-distance (distance with a target and the product) is long.

When a film is coated for a product bent to the three-dimensional shape such as the exhaust pipe, it is necessary to perform the stable film deposition from a target to the long-distance part. Figure 10 shows the relationship between working distance and the film thickness in the sputtering power.

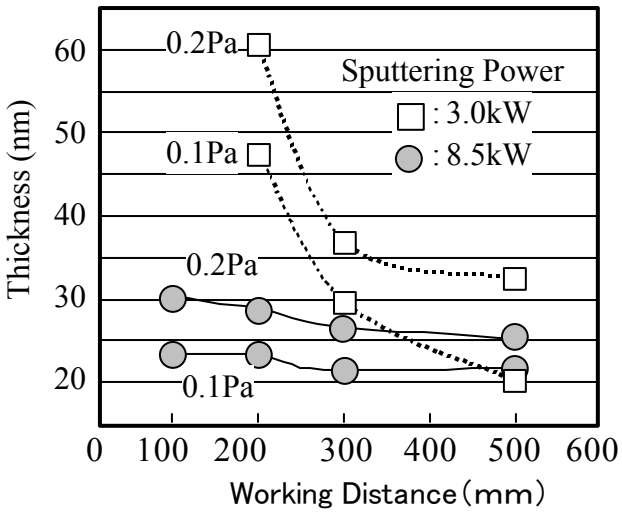


Fig.10 Relationship between working distance and thickness in two step

Even if the product apart from the target, a uniform film thickness is provided by increasing sputtering power. Because the sputtered Si particle being carried far and wide. In addition, the product is coated uniformly to the whole by revolving in front of the target.

CONCLUSIONS

1) The SiOxNy film with good heat-resistant corrosion resistance was provided using the DC reactive magnetron sputtering method.

2) The film was harder than substrate and the wear resistant improved.

3) A transparent and colorless film was able to get by controlled that the refractive index is around 1.8 and the film thickness is 15 – 20nm. And the coloration of gold and the blue was enabled.

4) The film deposition rate was raised to about 1.5 times by adding Ar gas into reaction N2 gas. And a high quality film was provided stably to WD 500mm.

Therefore the thin film coating was enable to the exhaust pipe of three-dimensional bending shape.

The exhaust pipe is made with three colors of patterns now that is "clear and colorless", "gold " and "blue". This method is called “Nano-film Coating “ continues being mass-produced in 4 models since it was adopted in Road Sports Model in 2008 is shown in Fig.11. The exhaust pipes was coated SiOxNy gold color by Nano-film coating method.

Fig.11 Road Sports Model in 2008
(4 Cylinder engine 998cm^3)

ABBREVIATIONS

PVD : Physical Vapor deposition
CVD : Chemical vapor deposition
sccm : standard cc/min
D.C. : Direct Current
N2 : Nitrogen O2 : Oxygen Ar : Argon
Si : Silicon
SiOx, SiO2 : silicon oxide
SiNy, Si3N4 : silicon nitride
SiOxNy : silicon oxynitride
CIE : Commission internationale de l'éclairage
L*a*b* : L: Luminosity, a*,b*: chromatic coordinate
△E* : color difference
SST : Salt Spray Test JIS Z 2371
CASS : Copper-Accelerated Acetic Acid Salt Spray Test (ASTM B368, B117)
RN : Rating number standard drawing
GDS : Glow Discharge Spectrometry
FPD : Flat Panel Display
WD : Working Distance

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