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54 **Method for ceramic coating on metals.**

57 The invention is a ceramic-coated heat-resistant metal article and process for preparing the article. An aluminum phosphate coating is applied to the metal substrate and a ceramic coating is applied over the aluminum phosphate coated metal substrate. The aluminum phosphate coating can be applied chemically or electrolytically. The ceramic coating can be applied by known methods such as dipping, spraying, chemical vapor deposition, sputtering and flame coating.

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## METHOD FOR CERAMIC COATING ON METALS

BACKGROUND OF THE INVENTION

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1. Field of the Invention

The present invention is a method for ceramic coating of metals.

10 In recent years, interest has arisen in ceramic coatings which do not delaminate under high temperature exposure.

2. Statement of Related Art:

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In recent years metals which require higher heat resistance and oxidation resistance are treated with ceramic coatings.

According to the report entitled "Review of Ceramic Coating Technologies in Terms of Development Attitudes Towards Utilization to New Industrial Fields", published by Japan Industrial Technology Association in March 1985, pages 206-209, ceramic coatings with carbides such as TiC, SiC, nitrides such as TiN, Si<sub>3</sub>N<sub>4</sub>, borides such as TiB<sub>2</sub>, oxides such as Al<sub>2</sub>O<sub>3</sub> or silicides such as MoSi<sub>2</sub> can provide metals with improved heat and oxidation resistance.

The ceramic coatings can be applied to metals by flame spray methods, ion sputtering methods, chemical vapour deposition methods (CVD), dry-in-place (coating-drying) methods, baking-in-place (coating-baking) methods and the like.

25 In the case of baking-in-place processes, one method is to treat a metal coated with frit at a temperature as high as 677-871 °C (Jap.Pat.Publ SHO 55-26714/1980). Generally the method is carried out at a temperature used for inorganic coating materials. In the known processes the ceramic coating is applied directly on the surface of the metal which has been cleaned mechanically or chemically. The "Review on Ceramic Coatings" discloses that, in the case of metal alcoholate type coating material, a satisfactory coating can be applied to the substrate with alkali cleaning alone (page 25); in the case of alkali-metal silicate type coating material, reaction with the substrate metal is required in addition to sand blasting to provide a rough surface for adhesion of the coating. In the case of coating material for high temperature use, chemical combination should take place between the ceramic and the metal.

35 Recently, a new heat-resistance coating material of the silicone type has been placed on the market. This material comprises a denatured silicone varnish binder and alumina-silica short fibers as the ceramic material (Nikkei New Material, p.101, 5-19, 1986). According to this article, one of the advantages of the material is the capability of the film to follow the expansion of the substrate metal.

40 In all of the known methods with perhaps the exception of the CVD process, the adhesion between the coating film and substrate metal is poor and the ceramic coatings delaminate because of the difference between the coefficient of thermal expansion of the substrate metal and the ceramic. Delamination can also be caused by oxidation of the substrate metal when exposed to high temperature.

To overcome these problems, attempts have been made to enhance the reaction between the coating material (ceramic) and the metal. However, since this method relies upon the type of metal and the coating material's composition, there are inherent limits in the method.

45 An object of the present invention is to provide a method for ceramic coating of metals; which coated metals can be used at high temperature without delamination. A further object of the invention is to provide a coating which protects the metal substrate from oxidation.

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BRIEF DESCRIPTION OF THE INVENTION

Applicants have unexpectedly discovered that forming an aluminum phosphate coating over a metal substrate before forming a coating with a ceramic material effectively suppresses substrate metal oxidation as well as improves the resistance to delamination of the ceramic coating at high temperatures.

The metal article comprising the aluminum phosphate coated metal substrate with the ceramic coating overlay also comprises the invention.

DETAILED DESCRIPTION OF THE INVENTION

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

The term "aluminum phosphate coating" as used herein refers to a film obtained by the method described in Jap.Pat.Pub.SHO 53-6945/1978 by the present applicants, wherein a coating is formed by a chemical conversion treatment or electrolytic treatment with an acidic liquid at a pH from 1.5 to 5 containing aluminum ion in a concentration of from about 0.01 to about 10 g/l and phosphate ion in about 1.0 to about 100 g/l, the principal component of such a film being aluminum phosphate ( $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ ). Jap.Pat.Pub. SHO 53-6945/1978 is incorporated herein by reference.

Publication SHO 53-6945/1978 is directed to preventing ferrous materials from corrosion by providing an alternative coating as a substitute for coatings of zinc, manganese, and calcium phosphate or the like and chromate coating for painting, and particularly for painting with acrylic-based paint.

We discovered that an aluminum phosphate coating is an excellent base coat for a ceramic coating. The characteristics of an aluminum phosphate coating have been investigated in more detail.

Figure 1 shows thermal weight change and differential thermal analysis up to 500 °C of an aluminum phosphate coating obtained according to the method described in the above-cited patent publication. The coating of aluminum phosphate is amorphous  $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ , undergoes loss of  $x\text{H}_2\text{O}$  at about 150 °C to 200 °C (weight loss of about 12%), then up to about 500 °C it is the stable form of  $\text{AlPO}_4$ . The thermal analysis shows that the loss of adsorbed water and crystal water takes place respectively at 50-100 °C and at about 150 °C but at over 200 °C no weight change occurs. This is an indication of the thermal stability of  $\text{AlPO}_4$ .

In the present invention, the drying of the aluminum phosphate coating is not critical. With air-drying of the film, residual moisture and water of crystallization are removed during baking without affecting the adhesion of the ceramic coating.

During baking of the ceramic coating or chemical vapor deposition, the temperature of the substrate rises and the moisture is removed. The  $\text{AlPO}_4$  provides a base for high adhesion with the ceramic coating. The  $\text{AlPO}_4$  undergoes no further decomposition than the above-mentioned dehydration.

If a ceramic coating is deposited on cleaned metal surfaces according to known methods, the metal surface is oxidized when subjected to the heat resistance test and is accompanied by delamination of the ceramic coating.

In the case of a ceramic coating deposited over an aluminum phosphate coating, when subjected to the heat resistance test, such a ceramic coating is free of delamination and oxidation of the metal substrate is suppressed. By the present process, the function of a ceramic coating primarily aimed at improved heat resistance can be enhanced further.

The composition containing aluminum ion for use in forming the  $\text{AlPO}_4$  coating is a liquid prepared by adding an aluminum compound such as nitrate, hydroxide or sulphate in the form of a solid or liquid to an acidic phosphate solution. The pH is adjusted so that the mixture is acidic. The content of aluminum ion in the mixture is from about 0.01 to 10 g/l, preferably 0.2 to 3 g/l. When less than about 0.01 g/l of Al ion is present, the deposit of aluminum phosphate is not sufficient. When the aluminum ion content exceeds about 3 g/l, economical disadvantages result.

The acidic phosphate liquid mixture is prepared by diluting phosphoric acid, sodium dihydrogen phosphate or disodium hydrogen phosphate and the like with water so as to contain 1 to 100 g/l, preferably 5 to 50 g/l, of the phosphate ion. As an example, a liquid mixture prepared by addition of an aluminum compound to phosphoric acid is adjusted to pH = 1.5-5.0 by means of caustic soda, caustic potassium, ammonia or the like. When the pH is less than about 1.5, the metal being treated receives a large amount

of etching. When the pH is above about 5.0, precipitation of aluminum phosphate and aluminum hydroxide take place in the treating bath.

It is also useful to add as an oxidizer or a coating formation accelerator a nitrate ion in an amount of from 0 to about 20 g/l preferably 1 to 5 g/l, chlorate ion in an amount of from 0 to about 20 g/l preferably 1 to 5 g/l, or nickel ion in an amount of from 0 to about 5 g/l preferably 0.01 to 2 g/l. It is also useful, for the purpose of increasing coating weight, to add sulphate ion in an amount of from 0 to about 10 g/l.

The metals to which the method of the present invention is applicable are those metallic materials which require improved heat resistance and which can be etched by phosphoric acid. Metals such as iron, steel, stainless steel, heat-resistant steel, aluminum, aluminum alloy, etc., can be treated by the method of the present invention.

The metal substrate can be coated with the  $\text{AlPO}_4$  coating by:

1) an immersion in or spraying with an acidic phosphate liquid mixture at a temperature 30 to 90 °C for 1 to 5 minutes. The process is similar to the conventional conversion coating treatment.

2) an alternating current electrolytic conversion treatment where both electrodes are a work piece or the opposite electrode is a material such as graphite, aluminum or stainless steel. The electrodes are generally spaced a distance of from 20 to 500 mm. Current density is in the range of from 0.1 to 20 A/dm<sup>2</sup> preferably 3 to 5 A/dm<sup>2</sup>. The electrolysis time can be from 5 sec. to 5 min.

3) a cathodic electrolytic conversion treatment where the work piece to be treated is the cathode and the opposite electrode is a conductive material such as graphite, aluminum, stainless steel and the like. A combination of an electrolytic conversion treatment and an immersion or spray conversion treatment can be used.

The coating formed is dried and preferably baked at a temperature above about 150 °C.

With respect to ceramic applied over the  $\text{AlPO}_4$  coating, there is no specific restriction placed on the ceramic coating compositions as long as their heat resistance can withstand the baking temperature and high temperature use contemplated.

Ceramics such as carbides, nitrides, borides, oxides, silicides, mixtures or compositions containing these and the like are useful. Alkali metal silicate type coating compositions, metal alcoholate type coating compositions, silica sol type compositions and silicone compositions and the like can be used in the process.

The baking-in-place (coating/baking) process of the present invention for ceramic coating can provide a coating film with adhesion to the substrate comparable to that provided by conventional CVD processes.

In the CVD process the substrate becomes hot so that the heat resistance of aluminum phosphate can be utilized in the ceramic coating. Heating the substrate, during the ceramic coating, up to about 200 to about 400 °C is also useful. A similar effect occurs in the ion sputtering process or flame spray process.

The present invention is described in more detail by way of the following Examples which are provided for illustration only and are not limiting.

#### EXAMPLE 1

##### Conversion treatment

Test piece: SPCC steel sheet (70 x 150 x 0.8 mm) was used.

The composition of the treating liquid was as follows:

$\text{PO}_4^{3-}$  22.8 g/l

$\text{Al}^{3+}$  0.9 g/l

$\text{NO}_3$  3.1 g/l

This liquid was neutralized with sodium hydroxide to adjust the pH to about 2.5. The metal test piece was surface cleaned and immersed in the treating liquid for 3 minutes. The treating liquid was maintained at a temperature of 60 °C. The test piece was removed from the treating liquid, rinsed with water and dried. A coating weighing 1 g/m<sup>2</sup> was formed on the test piece.

The test piece was dip-coated with GLASCA 90 (a product of Nichiban R&D Ltd., metal alcoholate type: colorless transparent, ceramic component: alkoxysilane 19-23%), then baked at 150 °C for 30 minutes to form a colorless, transparent ceramic coating. The film thickness was 5 μm.

EXAMPLE 25 Electrolytic treatment

An SPCC steel sheet (70 x 150 x 0.8 mm) test piece which was previously surface cleaned was subject to an electrolytic treatment in a liquid of the composition

$\text{PO}_4^{3-}$  25.0 g/l

10  $\text{Al}^{3+}$  1.2 g/l

$\text{NO}_3$  9.0 g/l

The liquid was neutralized with sodium hydroxide to adjust the pH to 2.5. The test piece was immersed in the liquid and was electrolytically treated with direct current at a temperature of 65 °C, a current density of 5A/dm<sup>2</sup> for 30 seconds. The opposite electrode was a graphite plate at an electrode distance of 40 mm and  
15 electrode ratio of 1:1. After the electrolytic coating, the test piece was rinsed with water and dried.

A ceramic coating as in Example 1 was applied to the coated test piece.

For comparison, a ceramic coating as in Example 1 was applied to a test piece without precoating (the steel sheet was surface-cleaned with a cleaner).

The test pieces: without precoating, and Example 1 and Example 2, were heated in an oven at 250 °C, 400 °C or 500 °C for 2 hours, then cooled in air. The result of an appearance inspection is shown in Table  
20 1. The discoloring of the metal surface by oxidation was visually observed either through the transparent ceramic coating or, in the case the ceramic coating was delaminated, directly on such portions of the metal.

As can be seen from the test results, forming an aluminum phosphate coating prior to applying a ceramic coating provides for improved adhesion of the coating at high temperature and the discoloring of  
25 the substrate which is associated with oxidation of the metal is also suppressed. The effect is due to the heat resistance provided by the aluminum phosphate coating.

TABLE 1

APPEARANCE AFTER HEAT RESISTANCE TEST			
	250 °C / 2 hrs	400 °C / 2 hrs	500 °C / 2 hrs
without precoating	not delaminated	70% delaminated	entirely delaminated
	slight blueing	blueing	blueing
Example 1	not delaminated	not delaminated	not delaminated
	no blueing	no blueing	slight blueing
Example 2	not delaminated	not delaminated	not delaminated
	no blueing	no blueing	no blueing

45 EXAMPLE 3

Test pieces were coated by the conversion treatment of Example 1 or 2. The coated test pieces were then coated with various kinds of ceramic coating compositions and subjected to the following tests which  
50 results are shown in Table 3.

## Test method

## 1. Corrosion resistance

a. Method:

salt fog spray test

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b. Evaluation:

according to ASTM-D714-56 except that evaluation was made by substituting rust development in place of  
10 blistering in the evaluation standard

Rating of rust size:

15

(excellent) 10 no change > 0 large rust (poor)

20 Rust area:

(excellent) F min.density > M > MD > D over entire surface (poor)

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2. Evaluation of heat resistance

30 1. Method:

After receiving the base coat and ceramic coating, test pieces were heated to various temperatures and cooled to room temperature.

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b. Evaluation:

visual inspection of the ceramic coating for adhesion and change of color of the underlying substrate  
40 material

Rating on coating adhesion:

45

(excellent) 5 no delamination > 0 delamination on entire surface (poor)

50 Change of substrate material:

(excellent) 5 no change > 0 blueing (poor)

The ceramic coatings described in Table 2 were applied by dipping; baking was done under respective conditions shown in Table 2. Table 3 shows the results of the tests.

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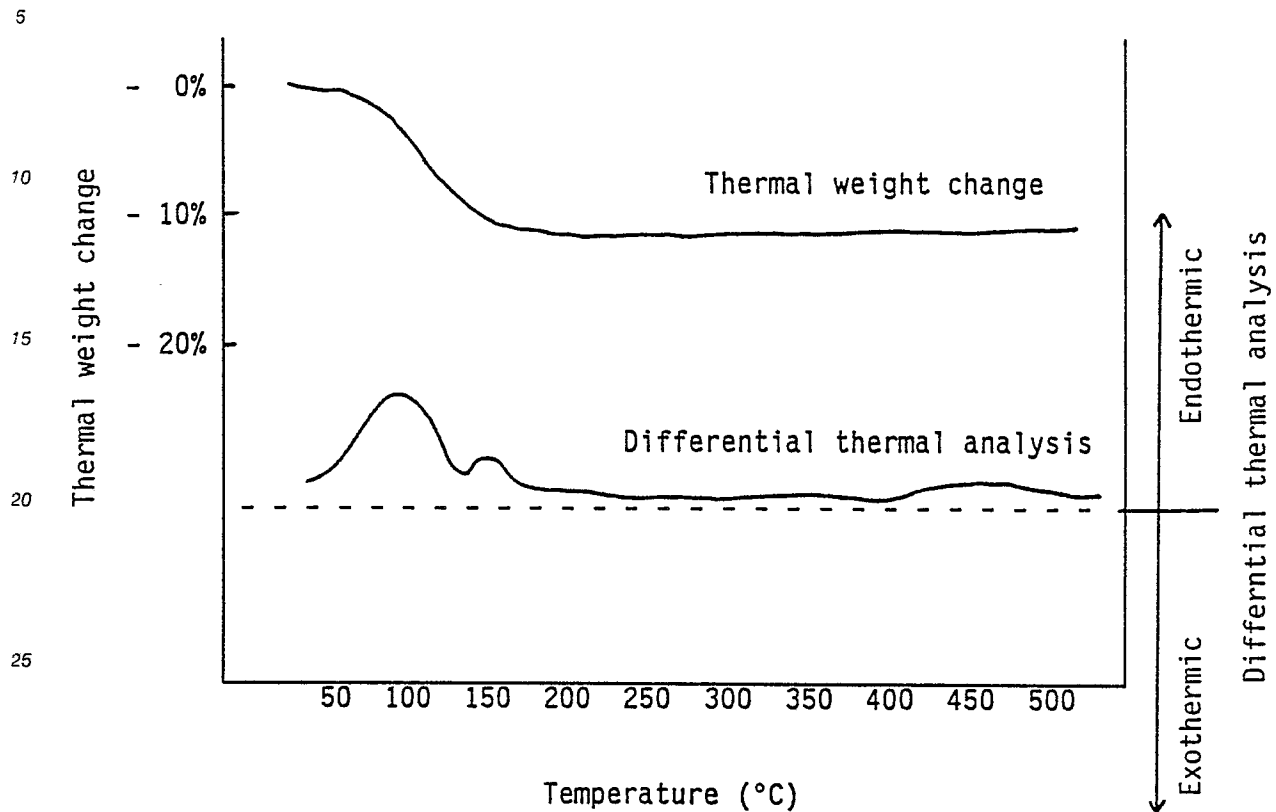
TABLE 2

CERAMIC COATING AND BAKING CONDITIONS			
No.	Trade name (maker)	Outline of composition	Baking condition
1	GLASCA 90 (Nichiban R&D)	metal alcoholate (ceramic component - alkoxysilane)	150 ° C x 20 min.
2	CRM-100 (Okuno Chemical Industries Co.Ltd)	alkali silicate type (ceramic component - SiO <sub>2</sub> )	200 ° C x 5 min.
3	MOF Ti-Film (Tokyo Ohka Ind.)	alkali metal salt type (ceramic component - TiO <sub>2</sub> )	500 ° C x 30 min.
4	Sil-B Coat (Central Glass)	alkali silicate type (ceramic component - SiO <sub>2</sub> )	180 ° C x 5 min.
5	CM2000 (Matsushita Electric)	denatured silica type	250 ° C x 20 min.

TABLE 3

CORROSION RESISTANCE AND HEAT RESISTANCE								
pretreatment	ceramic coating	corrosion resistance			heat resistance			
		72 hr	144 hr	240 hr	250 ° C x 2 hr		500 ° C x 2 h	
					A	B	A	B
without pretreatment	GLASCA 90	4F	0	-	5	5	0	0
	CRM 100	1F	0	-	5	5	2	2
	MOF Ti-Film	10	0	-	5	5	4	4
method according to Example 1	GLASCA 90	10	8MD	4MD	5	5	5	5
	CRM 100	10	8D	2D	5	5	5	5
	MOF Ti-Film	10	5F	0	5	5	5	5
method according to Example 2	GLASCA 90	10	9F	3MD	5	5	5	5
	CRM 100	10	6D	0	5	5	4	4
	MOF Ti-Film	10	8MD	2D	5	5	5	5
Remark: A - evaluation of adhesion								
B - evaluation of substrate change								

FIGURE 1



As can be seen from the results of the tests shown in the examples, ceramic coating without precoating permits oxidation of the metal surface, often resulting in delamination. When the metal substrate is precoated with an aluminum phosphate coating, delamination does not take place below about 500°C and oxidation of the metal surface is suppressed.

The heat resistance attained by means of the baking-in-place process of the invention is comparable to that obtained by a conventional CVD process.

The method of the present invention is free of the disadvantages of the CVD process such as long treatment time (as much as 2 to 8 hrs), poor productivity and high apparatus cost. The process of the invention when used with a baking-in-place process provides a simple treatment process with high productivity.

The method of the present invention is also applicable to a CVD process and the like, and provides for excellent adhesion and oxidation resistance.

#### Claims

1. A method for ceramic coating of metals which comprises:
  - a) coating a metal substrate by a chemical conversion treatment or an electrolytic treatment with an aluminum phosphate coating; and
  - b) applying a ceramic coating to the aluminum phosphate coated metal substrate.
2. A process of claim 1 wherein the chemical conversion treatment or electrolytic treatment is conducted in an aqueous phosphoric acid mixture containing from about 0.01 to about 10 grams/liter aluminum ion and from about 1.0 to about 100 grams/liter phosphate ion at a pH of from about 1.5 to 5.0.
3. A method of claim 2 wherein the phosphoric acid mixture contains from about 0.2 to about 3 grams/liter aluminum ion and from about 5 to about 50 grams/liter phosphate ion.
4. A method of claim 3 wherein the phosphoric acid mixture additionally contains from about 0 to about 20 grams/liter nitrate ion.



5. A method of claim 3 wherein the phosphoric acid mixture additionally contains from about 0 to about 20 grams/liter chlorate ion or from about 0 to about 5 grams/liter nickel ion.

6. A temperature and oxidations resistant article comprising a metal substrate, an aluminum phosphate coating on said substrate and a ceramic coating overlying the aluminum phosphate coating.

5 7. A product of the process of claim 1.

8. A product of the process of claim 2.

9. An article of claim 6 wherein the ceramic coating is formed from at least one composition selected from the group consisting of alkoxysilanes, alkali metal silicates, alkali metal type  $\text{TiO}_2$  and denatured silica.

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