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D-14129 Berlin (DE)54 **PROCESS FOR PRODUCING OXIDE CERAMIC COATING.**

57 A process for producing an oxide ceramic coating from a sol comprising a solution of a metallic compound, which aims at solving problems involved in various processes for producing an oxide ceramic coating, such as the vapor-phase methods including the chemical and physical vapor deposition methods which are generally low in productivity and the sol-gel method which, too, is low in productivity because only a thin coating of 0.1-0.3 μm in thickness is formed in one coating run and in which a thick coating, even when formed, is apt to crack because gel shrinkage occurs in evaporating off the alcohol component from the sol. The invention process permits production of a noncracking uniform oxide ce-

ramic coating by electrostatically atomizing a sol comprising a solution of a metallic or silicon compound to form a gel coating scarcely containing solvent molecules on the surface of a substrate, followed by firing.

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TECHNICAL FIELD

The present invention relates to a process for producing oxide ceramics film or membrane using, as a starting material, a solution or a sol of a metal compound. Oxide ceramics films have contributed to the development of various industries by utilizing their characteristics as functional materials such as heat-resistant coatings, abrasion-resistant coatings and reflection-preventive films, ultraconductive materials, ion conductive materials, electron materials such as capacitor and memory materials, and sensors and actuators utilizing a piezoelectrical property and pyroelectrical property.

BACKGROUND ART

Various processes for producing oxide ceramics films have been used with the recent utilization of various functional ceramics. As the methods for producing the ceramics films, mention may be made of a chemical vapor phase deposition method, a physical vapor deposition method, typically sputtering, and a liquid phase method, typically a sol gel method. Among these, the gaseous phase method is the most widely industrialized. Generally, however, this method has a low productivity and has difficulty controlling a complicated composition. To the contrary, according to the liquid phase method, several advantages can be obtained, e.g., a complicated and uniform composition can be readily obtained, and a sintering temperature can be relatively low. In the liquid phase method, however, the productivity is also not necessarily high. For example, by dipping in the sol gel method, only a film having a thickness of 0.1 - 0.3 μm can be obtained with one coating. Thus, depending upon an object for use, several tens to several hundreds of coating times are required. Another reason why a thick film is difficult to obtain according to the sol gel method is that gel shrinks when alcohol in the sol vaporizes, which may readily lead to cracks. This tendency becomes noticeable with an increase in the thickness of a film.

In the case where a solvent is intended to be removed by an air-drying gel formed on the surface of an object to be treated according to the sol gel method, the formed gel may shrink and crack as drying proceeds. This is because the boundary between a gel skeleton (solid), a solvent (liquid) and air (gas) is formed on the surface layer of the object in the course of drying so that capillary action of pulling the gel skeleton into a pore is generated. Against this action, the inside of the gel tries to maintain a constant volume. Thus, when the tension of the surface layer is greater than the strength of the gel skeleton, the surface layer may crack, and when this difference is extremely large,

the gel structure may be destroyed. The capillary action is generally shown by the following formula:

$$\Delta P = 2\gamma \cdot \cos \theta / r \quad (I)$$

wherein r represents capillary radius, θ represents wet angle and γ represents surface tension.

DISCLOSURE OF THE INVENTION

Accordingly, the object of the present invention is to provide a uniform film, without cracking, by electrostatic spraying a solution to form fine particles to thereby be vaporized between a spraying portion and an object to be treated so that a gel film substantially free from solvent molecules is formed on the surface of the object, whereby the generation of the capillary action defined by the formula (I) is prevented.

Further, the object of the present invention is to form a thick film by a one-pass process and to remarkably raise productivity.

In accordance with the present invention, there is provided a process for producing an oxide ceramics film characterized by electrostatic spraying of an alcohol solution, an aqueous solution or a sol of a metal compound or a silicon compound, then coating the resulting sprayed product on the surface of an object to be treated to form a film having a uniform thickness, followed by calcinating so that a ceramics film is formed on the surface of the object.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention can be broadly classified into three processes for achieving the above-described objects.

The first process comprises the preparation of a starting solution. Metal compounds or silicon compounds which are the supply source of constituent elements are required to be dissolved in a solvent and desirably have a low vapor pressure (for example, 60 mmHg or less). As these compounds, mention may be made of alkoxides such as $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Al}(\text{OC}_3\text{H}_7)_3$, metal acetyl acetates such as $\text{In}(\text{COCH}_2\text{COCH}_3)_3$, metal carboxylates such as $\text{Pb}(\text{CH}_3\text{COO})_2$ and $\text{Y}(\text{C}_{17}\text{H}_{35}\text{COO})_3$, and nitrates such as $\text{Ni}(\text{NO}_3)_2$ and $\text{Y}(\text{NO}_3)_3$. Even if the starting materials per se have a high vapor pressure, they can be used in the present invention, provided that they can be converted to compounds having a low vapor pressure as the result of a reaction in a solution. Especially, alkoxide compounds are suitable, because if they are used with a small amount of water, they are converted to a high molecular weight substance through hy-

drolysis and polycondensation reaction in a solution.

Solvents used in the present invention are required to dissolve the above-described metal compounds and silicon compounds, and desirably have a low specific heat and a high vapor pressure. Examples of such solvents include ethyl alcohol, methyl alcohol, isopropyl alcohol and dimethoxyethane. Especially, compounds having a hydroxyl group having a high infrared absorption are more desirable because the vaporization thereof can be accelerated by irradiation with infrared radiation.

Although the mixing of the above-described metal compound or silicon compound with a solvent can be effected by using an optional process, if it is desired to prevent a reaction with water in the air, the mixing is desirably effected in an atmosphere of dried nitrogen or dried argon. When the mixing is effected in the air, a stabilizer (chelating agent) can be added to prevent a reaction with water. Examples of the stabilizer include diethanolamine and acetylacetone. Further, to a solution can be added a viscosity regulator, an acid or an alkali depending upon the purpose of use thereof.

The second process of the present method comprises a coating process by electrostatic spraying. In this process, an earthed or grounded object to be treated is used as an anode and a solution spraying unit is used as a cathode. A high negative electric voltage is applied to the cathode to form an electrostatic field between these two electrodes, and fine negatively charged particles are sprayed to effectively coat the opposite electrode, i.e., the object to be treated. The high voltage is preferably within a range of -30 to -120 kV, more preferably within a range of -30 to -70 kV. The distance between the two electrodes is preferably 5 to 40 cm, more preferably 10 to 30 cm. When this distance is greater than 40 cm, the electrostatic field becomes weak so that the coating efficiency possibly lowers, which is undesirable. Contrary to this, when the distance is narrower than 10 cm, there is a possibility that fine solvent particles become hard to vaporize, which is also undesirable. When a solution has an electrical conductivity of 10^{-8} Scm⁻¹ or more, an electrostatic voltage and the solution should be kept insulated until immediately before spraying.

In order to ground an object to be treated, the surface to be treated is required to at least have some electrical conductivity. The shape of the object, however, is not severely restricted. Even if the object has a curved surface, a uniform film can be formed. The surface to be treated is desirably highly wettable with a sol. If it is not so wettable, a surface treatment may be applied to the surface. As desirable examples of objects to be treated,

mention may be made of various metals such as iron and copper, conductive glass and quartz glass having platinum deposited thereon.

The vaporization of solvent particles can be accelerated by irradiating infrared radiation or microwaves between electrodes. Infrared irradiation generation units are not particularly limited. For example, a type wherein irradiation from an infrared radiation lamp is made parallel by a gold mirror can be used. The output of the microwave is not particularly limited. However, it is preferably 500 to 3000W, more preferably, 1000 to 2000W.

The third process of the present process comprises calcinating an object to be treated. Depending upon an object for use, the calcinating can be effected in the air, nitrogen atmosphere or in vacuo. The calcinating temperature differs depending upon the kind of ceramics. The desired ceramics, however, can be obtained preferably around 400 to 1200 °C. A temperature elevation and lowering process is desirably controlled, for example, by a temperature controller.

EXAMPLE

The present invention will be further illustrated by, but by no means limited to, the following Examples.

Example 1

The formation of titanate lead zirconate ceramics film on a stainless steel surface.

To about 20 ml of 2-propanol (produced by Wako Junyaku Industry K.K., SC grade) was added 21.2g of diethanolamine (produced by Wako Junyaku Industry K.K., guaranteed reagent), followed by thoroughly stirring. To the resulting solution, further, 27.0g of titanium isopropoxide (produced by Kanto Kagaku K.K.) and 45.2g of zirconium-n-propoxide (produced by Soekawa Rikagaku K.K.) were successively added, followed by stirring for about one hour.

Lead (II) acetate trihydrate (produced by Wako Junyaku Industry K.K., guaranteed reagent) was thermally dried at 120 °C in vacuo for 3 hours to obtain anhydrous lead acetate. 64.9g of the product obtained was added to the solution prepared above taking care not to cause solidification. At this point, lead acetate was still undissolved. Further, 40g of distilled water diluted with isopropyl alcohol was added dropwise thereto with stirring, whereby lead acetate was completely dissolved to form a uniform sol. The sol obtained was used as a sol for coating.

A plate made of stainless 304 (10 cm × 10 cm × 1.5 mm thickness) was thermally treated at 1050 °C in vacuo for one hour, and the treated product was then subjected to mirror surface

polishing. The resulting product was used as an object to be treated.

The electrostatic spraying was conducted by an electrostatic coating device ESG-110 model manufactured by Iwata Toso K.K. The coating compound spouting rate was controlled to 1 ml/sec and air pressure for spraying was controlled to 3 kgf/cm². A voltage of -60 kV was applied to a needle electrode in an electrostatic ionizing portion.

The distance between the stainless plate, the object to be treated and the coating device was kept at 22 cm and the coating device was scanned from right to left at the speed of 20 cm/sec to effect electrostatic spray coating. In order to thicken a film thickness, this scanning can be repeated several times. The film thickness after calcinating by one coating was about 0.35 μm.

The stainless plate coated by three scans was allowed to stand for about 2 minutes to dry. Thereafter, the dried plate was placed into an electric furnace (muffle furnace AMF-20-2P, manufactured by Asahi Rika Seisakusho). The temperature of the furnace was elevated to 600 °C at the rate of 15 °C/min, the furnace was kept at that temperature for 1 hour, and thereafter, was allowed to stand for cooling. By this method, a uniform fine titanate lead zirconate film free from cracks was obtained. A perovskite structure inherent to this compound was confirmed by X-ray diffraction.

The film thickness after calcinating was determined by two methods: a method utilizing an interference band generated by infrared radiation and a method utilizing a weight difference of the stainless plate before and after coating. The results were both 1.05 μm.

INDUSTRIAL APPLICABILITY

According to the process for producing oxide ceramics of the present invention, an oxide ceramics film can be readily produced on the surface of an object to be treated without causing cracking. Further, the process has a high coating efficiency, can be applied to a curved surface and employs a relatively low sintering temperature. Thus, the present process can greatly contribute to improvements of processes for producing an oxide ceramics film.

Claims

1. A process for producing an oxide ceramics film characterized by electrostatically spraying an alcohol solution, an aqueous solution or a sol of a metal compound or a silicon compound, then coating the resulting sprayed product on the surface of an object to be treated to form a film having a uniform thick-

ness, followed by sintering so that a ceramics film is formed on the surface of the object.

2. A process for producing an oxide ceramics film as claimed in claim 1, wherein a space is formed between a spraying portion and the surface of an object to be treated, then sprayed products transferred within the space by the electrostatic spraying are irradiated with infrared radiation or microwaves whereby an alcohol and water are vaporized.
3. A process for producing an oxide ceramics film as claimed in claim 1, wherein at least one compound of metal compounds or silicon compounds is an alkoxide compound.
4. A process for producing an oxide ceramics film as claimed in claim 2, wherein at least one compound of metal compounds or silicon compounds is an alkoxide compound.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/01718

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl ⁶ C23C18/12		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl ⁵ C23C18/12, C01B13/34, B05D1/04		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926 - 1994		
Kokai Jitsuyo Shinan Koho 1971 - 1994		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 63-277770 (Nippon Soda Co., Ltd.), November 15, 1988 (15. 11. 88), (Family: none)	1-4
Y	JP, A, 49-98732 (Deki Kosan K.K. & Kazuo Honjo), September 18, 1974 (18. 09. 74), (Family: none)	1-4
Y	JP, A, 63-291665 (Nisshin Steel Co., Ltd.), November 29, 1988 (29. 11. 88), (Family: none)	1-4
Y	JP, A, 51-91949 (Dai Nippon Toryo Co., Ltd.), August 12, 1976 (12. 08. 76), (Family: none)	2
Y	JP, A, 61-107974 (Pitor Ribuniz), May 26, 1986 (26. 05. 86), (Family: none)	2
Y	JP, A, 5-246701 (Sekisui Chemical Co., Ltd.), September 24, 1993 (24. 09. 93), (Family: none)	2
P	JP, A, 6-137805 (Matsushita Electric Co., Ltd.), May 20, 1994 (20. 05. 94), (Family: none)	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
December 14, 1994 (14. 12. 94)		January 10, 1995 (10. 01. 95)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.