

[54] CERAMIC COATED POROUS METAL
STRUCTURE AND PROCESS THEREFOR

[75] Inventors: Raymond J. Elbert, Middleburg
Heights; Ernest G. Farrier, Parma,
both of Ohio

[73] Assignee: Union Carbide Corporation, New
York, N.Y.

3,022,187	2/1962	Eyraud et al.	117/127 X
3,238,056	3/1966	Pall et al.	117/99 X
3,248,266	4/1966	Rampel.	117/131 X
3,353,982	11/1967	Blaha.	117/99 X
2,671,955	3/1954	Grubel et al.	117/129 X
2,672,426	3/1954	Grubel et al.	117/129 X
2,826,512	3/1958	Rex.	117/129 X
2,858,235	10/1958	Rex.	117/129 X
3,536,480	10/1970	Winkler.	117/99 X

[22] Filed: Nov. 30, 1971

Primary Examiner—Edward G. Whitby

[21] Appl. No.: 203,364

Attorney—Harrie M. Humphreys et al.

[52] U.S. Cl. 117/129, 75/20 F, 106/38.27,
117/5.3, 117/99

[57] ABSTRACT

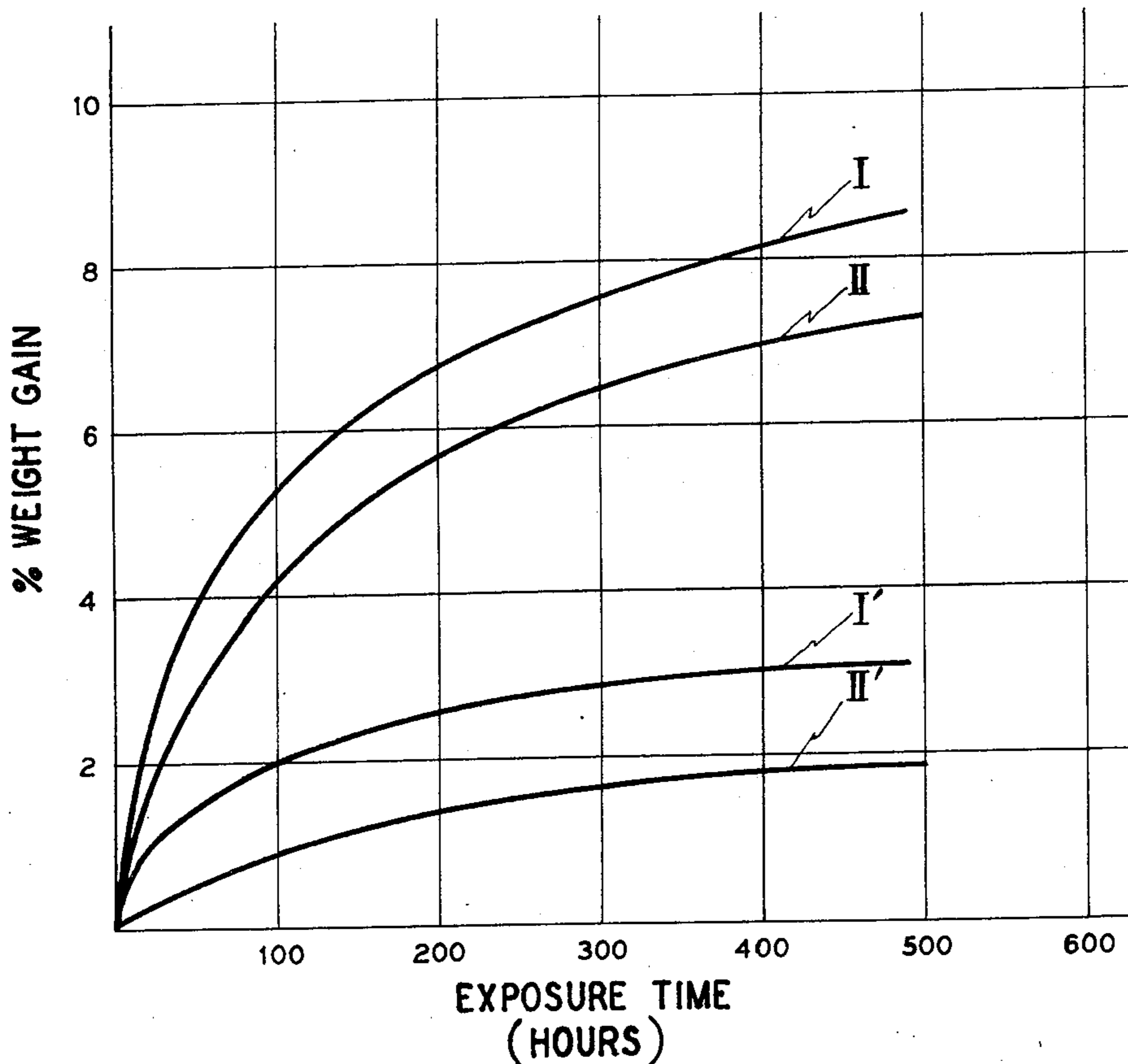
[51] Int. Cl. B44d 1/02

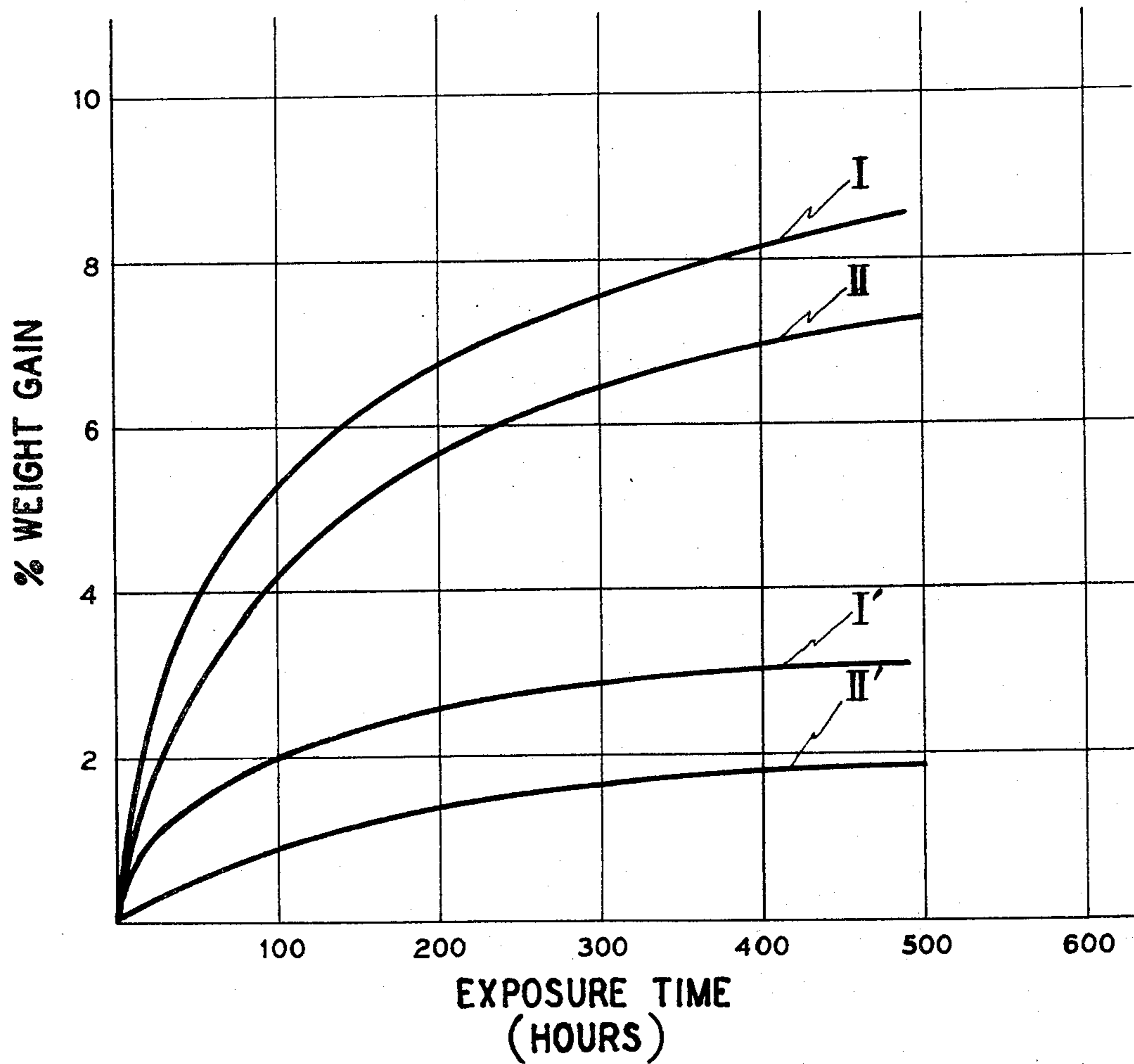
A porous metal structure, and process therefor, having a thin coating of a ceramic material deposited on its surface and on the internal walls of all accessible pores which substantially improves the oxidation resistant characteristics of the structure while effectively maintaining its mechanical properties.

[58] Field of Search. 117/129, 99, 5.3;
75/20 R, 20 F; 106/38.27

[56] References Cited
UNITED STATES PATENTS
3,300,331 1/1967 Collins, Jr. 117/99

15 Claims, 1 Drawing Figure





INVENTORS
RAYMOND J. ELBERT
ERNEST G. FARRIER
BY *Conelium F. Quinn*
ATTORNEY

CERAMIC COATED POROUS METAL STRUCTURE AND PROCESS THEREFOR

FIELD OF THE INVENTION

This invention relates to ceramic coated porous metal structures admirably suited for use in oxidation environments as abrasible seals, bearings or bearing retainers, and filters.

DESCRIPTION OF PRIOR ART

There are many methods presently being utilized for forming porous bodies using powdered metallurgical techniques. Generally, powder metallurgical processes involve the steps of shaping metal powder into green compacts by such techniques as loose packing, compaction, extrusion, rolling or the like, and then consolidating the green composite so formed by the mechanism of sintering. Many of these processes are described in "Treatise on Powder Metallurgy" by C. G. Goetzl, Interscience Publishers, Inc., New York, N.Y. (1949), and "Fundamental Principles of Powder Metallurgy" by W. D. Jones, Edward Arnold Publishers, London, England (1960). Further methods for fabricating porous metal sheets and the like are disclosed in U.S. Pat. No. 3,433,532, in copending U.S. application Ser. No. 798,142 by R. J. Elbert filed Feb. 10, 1969 now U.S. Pat. No. 3,577,226, in copending U.S. application Ser. No. 164,516 by R. J. Elbert filed July 21, 1971, and in copending U.S. application Ser. No. 128,182 by R. J. Elbert, et al., filed Mar. 25, 1971.

Porous metal structures, such as porous sheets, are admirably suited for use in such applications as filters, abrasible seals, sound suppression structures, bearings and bearing retainers, energy absorbing material and the like. One disadvantage of porous structures, however, is that the metal component of the structure, while being relatively oxidation resistant when present in the bulk state in the temperature range of up to 1000°C, is subject to oxidation when fabricated into a porous state because of its fine structure and extensive surface area. Thus, porous metal structures are somewhat limited in their applications to uses wherein they will not be exposed to high temperature oxidizing environments. Abrasible seals and bearing materials which are designed for aerospace applications or the like are intended to be subjected to oxidation environments thus curtailing their useful and functional life. This limited life usage for porous metal structures intended for use in oxidation environments necessitates the additional expenditure of time and money for replacing such structures after a relatively short period of operational time and consequently weakens the reception accorded these structures in the aerospace or like industry. To compensate for this limited life usage, it has been recommended that oxidation coatings, such as metal oxides, be applied to the porous structures. However, if the commercially available oxidation coatings deposited by known techniques are employed on these porous metal structures, the abrasibility of such structures will be seriously affected when they are intended for use in abrasible seal applications, and likewise, the lubricant filling characteristics of bearings, and bearing retainers will also be affected.

One of the primary objectives of this invention is to provide an oxidation resistant coating for porous metal structures composed of a ceramic-containing material which will not adversely affect the abrasibility of po-

rous metal structures when intended for abrasible seal applications and will extend the maximum oxidation protection temperature of porous structures intended for bearing applications.

SUMMARY OF THE INVENTION

Broadly stated, the invention relates to an oxidation resistant ceramic-containing coating for porous metal structures that will not substantially affect the abrasibility of such structures when intended for abrasible seal application usage, nor substantially affect the characteristics required of porous structures intended for bearing application or filter usage.

Basically, the process for applying an oxidation resistant ceramic coating on a porous metal structure would initially entail preparing a colloidal-like suspension of a finely ground ceramic-containing material in a liquid suspending vehicle. The colloidal-like suspension can then be deposited on a porous metal structure to be coated, after which the coated structure is dried to substantially remove the liquid suspending vehicle thereby leaving a dispersed deposition of the ceramic-containing material on the walls of the accessible pores throughout the structure. Thereafter, the ceramic-containing material dispersed on the porous metal structure is heated to a temperature below the melting point of the metal components of the porous metal structure, but sufficient to cause the ceramic-containing material to fuse and wet the wall surfaces of the pores in the structure. Thus, the porous metal structure will have a ceramic coating which will act as a barrier so as to minimize attack of foreign gases, such as oxygen, on the metal.

The above process of depositing and drying the colloidal-like suspension on the porous metal structure can be repeated so as to obtain a desired degree of coating or to increase the coating thickness. A ceramic-containing coating on porous structures usually between about 0.01 micron and about 10 microns thick and preferably between about 0.01 micron and about 5 microns thick would be admirably suited for abrasible seal applications. For bearings and bearing retainer applications, a ceramic-containing coating on porous structures between about 1 micron and about 30 microns would be suitable. The exact coating thickness on a porous metal structure for a particular application can be determined by any artisan, familiar with porous materials, using the process of this invention.

Colloidal-like suspension is intended to mean a suspension of finely ground particles wherein said particles are substantially uniformly dispersed throughout the suspending liquid and are sized to less than 10 micron particle size.

A porous metal structure having a nominal pore size of 100 microns or less can be fabricated by known techniques using any metal or metal alloy that is available in powdered, flaked, or fibrous form and that can be sintered with substantially uniformly controlled pore sizes ranging anywhere from submicronic to 100 microns and higher. Examples of alloy compositions suitable for porous metal abrasible seals include such alloys as Hastelloy X, Haynes 25, Haynes 188, DH 242, Type 347 Stainless Steel, Type 430 Stainless Steel, Waspalloy, NiCrBi alloys, FeCrAl Y alloys, and the like.

A ceramic-containing material is intended to include such materials as ceramics, ceramals, cermets, metam-

ics, glass and glass ceramics, in any and all proportions and combinations. Ceramics are basically a class of inorganic, nonmetallic substances as opposed to organic or metallic substances. All ceramic materials will not be suitable as coatings for porous metal structures but only those which have a melting point below that of the particular metal or metal alloy used in the fabrication of the porous metal structures and which adhere to the surface during thermal cycling. Thus, once the metal or metal alloy component of a porous metal structure is determined, a suitable ceramic-containing material can be selected as the coating material. For example, when at least one base component of a porous metal structure is selected from the group consisting of nickel, chromium, cobalt, and iron, a suitable ceramic-containing material could be selected from at least one material selected from the group consisting of silicon dioxide, chromium oxide, titanium oxide, aluminum oxide, boron oxide, sodium oxide, and potassium nitrate. Depending on the particular component selected for the porous metal structure, various other ceramic groups can be used such as the oxides, carbides, borides, nitrides, and silicides of such materials as aluminum, magnesium, sodium, lithium, beryllium, cesium, titanium, zirconium, hafnium, tungsten, molybdenum, iron, cobalt, and the like.

A preferred method of coating porous metal structures is to first pulverize the ceramic-containing material and then suspend it in a liquid suspending vehicle to form a colloidal-like suspension. The liquid suspending vehicle with the substantially dispersed ceramic-containing material can then be deposited on the surface of a porous structure by any conventional technique such as painting, spraying, rolling, or dipping the structure into the colloidal-like suspension. The technique for depositing the colloidal-like suspension on and in the porous structure should be adequate so that a layer of the solution is applied to the surface of the porous structure including the internal walls of accessible pores. The coated porous metal structure can be slightly heated, or dried at room temperature, so as to substantially remove the liquid suspending vehicle from the ceramic-containing material so that the latter will be left adhering to the surface of the porous structure. Thereafter, the structure is subjected to a heated environment at a temperature sufficient to cause the ceramic-containing material to assume a molten state whereupon it will fuse and wet the surface of the porous structure providing the substantially uniform layer thereon. Thus, in the operational mode of the coated porous metal structure, the walls of the internal pores will be substantially protected against the penetration of foreign gases, such as oxygen.

In order to achieve a ceramic-containing coating which can be deposited as a thin layer on a porous metal structure, it is necessary to initially pulverize the ceramic-containing material to a size smaller than about 10 microns and preferably less than about 1 micron. It is to be understood that the exact size of the pulverized ceramic-containing material is somewhat dependent on the pore size of the porous metal structure to be coated. Thus, when coating a porous metal structure having a nominal pore size of about 100 microns, it will be desirable to pulverize the ceramic-containing material to less than about 10 microns, while coating a porous metal structure with a nominal pore size of 10 microns will preferably require the

ceramic-containing material to be pulverized to less than about 1 micron. The purpose for pulverizing the ceramic-containing material to a fine fraction is to enable the material to be deposited within the walls of accessible pores in the porous metal structure without substantially plugging the pores.

The liquid suspending vehicle can be any liquid capable of suspending the selected pulverized ceramic-containing material in a substantially uniformly dispersed manner and which is capable of wetting the metal or metal alloy of the porous structure. The liquid suspending vehicle is added in a sufficient amount to form a slurry with the pulverized ceramic-containing material so that when the colloidal-like suspension is deposited on and in the porous metal structures, it will be substantially removed from the porous metal structure thereby leaving the pulverized ceramic-containing material dispersed on the wall surfaces of the accessible pores in the porous metal structure. It is recommended that the viscosity of the colloidal-like suspension be about 100 centipoises or less and preferably about 10 centipoises. Suitable liquid suspending vehicles are alcohol, alcohol containing liquids, methanol, acetone, heptane, and kerosene.

A preferred embodiment of this invention would be to select a ceramic-containing material which has a softening range rather than a melting temperature, such softening temperature range being the preferred operating temperature of the coated porous metal structure. Thus, glass type ceramics are admirably suited for use in this invention and preferably those materials having a soft or molten state at temperatures between about 1600°F and 2300°F. Once the ceramic-containing material having good oxidation resistant properties is selected, it is finely pulverized and suspended in a slurry or colloidal-like suspension which will wet and fill the pores of the porous structure. For example, ceramic-containing materials can be pulverized to a submicron particle size in a liquid suspending vehicle using nickel base alloy balls in a nickel based alloy container so as to minimize contamination. The mixture can be ball milled for a time sufficient to cause the resulting mixture to approach a colloidal suspension, that being evidenced by no visible separation of the ceramic-containing material in the liquid. The colloidal-like suspension can then be diluted with a liquid suspending vehicle, preferably the same used in the mill operation, to obtain a viscosity of between about 100 centipoises and about 1 centipoise and preferably about 10 centipoises. The viscosity of the colloidal-like suspension can be varied depending on the porous metal structure to be coated.

After depositing the coating material, the colloid coated porous structure is then exposed to ambient so as to evaporate substantially all of the liquid suspending vehicle thereby leaving the ceramic-containing material substantially uniformly disposed on the wall surface of the pores in the structure. The ceramic-containing coated porous structure is then heated to the molten state temperature of the ceramic-containing material whereupon the ceramic-containing material substantially fuses and wets the wall surfaces of the accessible pores in the porous structure thus forming a thin protective coating on and within the structure. Ceramic-containing materials having a softening range between about 1600°F and 2300°F should be heated to between about 1800°F and 2400°F. As stated above, this tem-

perature should be below the melting temperature of the metal components in the porous metal structure. The coated porous structure is thereafter cooled and ready for its intended application.

When the porous metal structures are intended for
5 abrasible seal applications, a ceramic-containing material having good oxidation resistant properties at between about 1200°F and about 2000°F and being soft or molten at temperatures between 1600°F and 2000°F is ideally suited. It is to be understood that the ceramic-containing material selected has to be compatible with
10 the metal components of the porous metal structure so that detrimental reactions do not occur. Ceramic mixtures containing SiO₂, Cr₂O₃, Al₂O₃, and TiO₂ are admirably suited for this purpose.

For applying a thick oxidation preventive coating to a porous metal structure, the above process can be repeated so in effect we have a multiple layer build-up which upon being heated in the final stage will form a
20 substantially homogeneous coating.

The following examples will serve to illustrate the concept of this invention and are not intended to restrict the invention in any way.

EXAMPLE 1

A porous metal abrasible seal, commercially available as Type AB-1, measuring 2 inches by 6 inches and being 0.06 inch thick on an Inconel 600 backing sheet (0.06 inch thick) was obtained from Union Carbide Corporation. This commercial abrasible seal, fabricated by a diffusion-sintered bonding of Ni alloy (nominal 80% Ni-20% Cr) as disclosed in U. S. copending application Ser. No. 128,182, had a void fraction of 0.65 nominal, a bulk density of 3 grams per cubic centimeter, a tensile strength of 500 pounds per square inch nominal, and a hardness of 91 nominal based on a Rockwell B scale of 3/4 inch diameter ball at a 15 kilogram load.

The abrasible seal material was coated with a ceramic mix (cermet) of the following composition:

100 grams of frit (commercially available as No. 6210 from the Ferro Composition, Cleveland, Ohio).
40 grams of technical grade titanium dioxide
6 grams of green label clay
5 grams of chromium oxide
1/2 gram of potassium nitrate

Prior to coating the porous metal abrasible seal, the dry powders of the ceramic mix were loaded into a one quart Inconel 600 ball mill jar containing 8 pounds (1/2 full) of nickel base alloy balls (Type RA 103) along with sufficient liquid methanol to cover the balls. This mixture was ball milled for three weeks to produce a near colloidal suspension of the ground and blended powder with the methanol. The colloidal-like suspension was thereafter separated from the nickel alloy based balls, and then adjusted to 700 grams (21.5 percent solids) to provide a stock solution. The viscosity of this solution was 9 centipoises. The solution was then diluted with additional methanol to 8 percent solids.

The abrasible seal material was then impregnated with the solution which was applied by a roller technique. The coated abrasible seal material was allowed to dry at room temperature for about 8 hours after which it was furnace in a continuous belt furnace at 1150°C for a period of 30 minutes in a hydrogen atmosphere. The coating material which was applied to the

abrasible seal material amounted to 0.8 percent of the weight of the coated material.

The coated abrasible seal material was then subjected to an oxidation environment within a furnace at a temperature of 1600°F. The percent weight gained after various exposure times is indicated as Curve 1' on the graph of the drawing. A similar abrasible seal material, except lacking the coating of this invention, was also subjected to the same oxidation environment and showed a substantial weight increase over that of the coated abrasible seal for similar time periods. Curve 1 on the graph represents the uncoated abrasible seal material. A comparison of Curves 1 and 1' demonstratively reveals the increase in the oxidation resistant characteristics of a porous metal structure coated in accordance with this invention.

The coated and uncoated abrasible seal materials specified above were subjected to an abrasibility test utilizing a tester composed of a 7 1/8 inch diameter rotating knife edge having a peripheral speed of 100 revolutions per second and designed to plunge at a depth of 0.001 inch per second until a scar of a 0.030 inch depth was imparted in the material being tested. The horsepower required to produce this 0.030 inch scar in both the coated and uncoated materials was compared and found to be essentially the same, that being about 0.1 of a horsepower. This abrasibility test was conducted on the materials both before and after the materials were subjected to the oxidation environment. Thus, the ceramic oxidation coating on the abrasible seal material produced no detrimental effects to the abrasibility characteristics of the material.

EXAMPLE 2

Abrasible seal material similar to that as in Example 1 except that it had a hardness of 85 nominal as measured by a Rockwell B scale with a 3/4 inch diameter ball under a 15 kilogram load. This material was also fabricated as disclosed in U. S. copending application Serial No. 128,182 and was commercially obtained from Union Carbide Corporation as Type AB-2 abrasible seal material. The abrasible seal material measured 2 inches by 6 inches and was 0.06 inch thick on an Inconel 600 backing sheet (0.06 inch thick).

A ceramic mix identical to that specified in Example 1 was applied to the abrasible seal material as also disclosed in Example 1. The coated abrasible seal material was then allowed to dry at room temperature for about 8 hours after which it was subjected to a hydrogen atmosphere in a heated environment of a continuous belt furnace at a temperature of 1170°C for a period of 30 minutes. The coating material which was added to the abrasible seal material amounted to 0.8 percent of the weight of the coated material.

The coated abrasible seal material was then subjected to an oxidation environment within a furnace at a temperature of 1600°F. The percent weight gained after various exposure times is indicated as Curve 11' on the graph of the drawing. A similar abrasible seal material, except lacking the coating of this invention, was also subjected to the same oxidation environment and showed a substantial weight increase over that of the coated abrasible seal for similar time periods. Curve 11 on the graph of the drawing represents the uncoated abrasible seal material. A comparison of Curves 11 and 11' demonstratively reveals the increase in the oxidation resistant characteristics of a porous

metal structure coated in accordance with this invention.

The coated and uncoated abrasible seal materials specified above were subjected to an abrasibility test utilizing a tester composed of a $7\frac{1}{8}$ inch diameter rotating knife edge having a peripheral speed of 100 revolutions per second and designed to plunge at a depth of 0.001 inch per second until a scar of a 0.030 inch depth was imparted in the material being tested. The horsepower required to produce this 0.030 inch scar in both the coated and uncoated materials was compared and found to be essentially the same, that being below 0.1 of a horsepower. This abrasibility test was conducted on the materials both before and after the materials were subjected to the oxidation environment. Thus, the ceramic oxidation coating on the abrasible seal material produced no detrimental effects to the abrasibility characteristics of the material.

The oxidation resistant coating of this invention is also admirably suited for use on porous metal structures having a bimodal pore distribution, that is, a porous structure having two nominal pore sizes. The colloidal-like suspension of ceramic-containing material could be deposited on the structure in a state that would permit the smaller pores to be filled with the coating by capillary action. After drying, the bimodal porous structure would be heated so that the ceramic-containing material would substantially fuse and wet the walls of the larger pores while substantially filling the cavities of the smaller pores. This would provide the porous structure with a good oxidation resistant coating while not substantially affecting the mechanical properties of the structure.

What is claimed is:

1. A process for coating porous metal structures having a nominal pore size no greater than 100 microns with an oxidation resistant ceramic-containing material comprising the steps:

- a. preparing a colloidal-like suspension of a finely ground ceramic-containing material in a liquid suspending vehicle;
- b. depositing a layer of the colloidal-like suspension of step (a) on the surface of the porous metal structure;
- c. removing substantially all of the liquid suspending vehicle, thereby leaving the ceramic-containing material substantially dispersed on the wall surfaces of the porous structure; and
- d. heating the ceramic-containing deposited porous metal structure to a temperature below the melting point of the metal components of the porous metal structure but sufficient to cause said ceramic-containing material to fuse and wet the wall surfaces of said porous metal structure.

2. The process as in claim 1 wherein the steps (a) through (d) are repeated at least once.

3. The process as in claim 1 wherein the steps (a) through (c) are repeated at least once before step (d) is performed.

4. The process as in claim 1 wherein in step (c) said liquid suspending vehicle is substantially removed at room temperature.

5. The process as in claim 1 wherein in step (a) said ceramic-containing material is selected from at least one of the groups consisting of oxides, carbides, borides, nitrides, and silicides of aluminum, magnesium, sodium, lithium, beryllium, cesium, titanium, zirconium, hafnium, tungsten, molybdenum, iron and cobalt.

6. The process as in claim 1 wherein in step (a) said ceramic-containing material is selected from at least one of the groups consisting of silicon dioxide, chromium oxide, titanium oxide, aluminum oxide, boron oxide, sodium oxide, and potassium nitrate.

7. The process as in claim 5 wherein in step (a) said ceramic-containing material has a softening range at a temperature between about 1600°F and about 2300°F; and wherein in step (d) said porous metal material is heated to a temperature between about 1800°F and about 2400°F.

8. The process as in claim 5 wherein in step (a) said finely ground ceramic-containing material is sized between about 0.01 micron and about 10 microns.

9. The process as in claim 5 wherein in step (a) said liquid suspending vehicle is selected from at least one of the groups consisting of alcohol, an alcohol-containing liquid, methanol, acetone, heptane, and kerosene.

10. The process as in claim 5 wherein the colloidal suspension of step (a) has a viscosity of between about 100 centipoises and about 1 centipoise.

11. The process of claim 5 wherein said coated porous metal structure is intended for abrasible seal applications and wherein in step (d) said layer of ceramic coating material is between about 0.01 micron and about 10 microns.

12. The process in claim 5 wherein said coated porous metal structure is intended for bearing applications and wherein in step (d) said ceramic-containing material is between about 1 micron and about 30 microns thick.

13. A porous metal structure having a nominal pore size no greater than 100 microns and having an oxidation resistant coating of a ceramic-containing material, said coating being deposited substantially on the wall surfaces of the pores in said porous metal structure thereby providing a barrier which substantially minimizes the attack of gases on the metal.

14. The porous metal structure of claim 13 intended for abrasible seal applications wherein said oxidation resistant coating is between about 0.01 micron and about 10 microns thick.

15. The porous metal structure of claim 13 intended for bearing application wherein said oxidation resistant coating is between about 1 micron and about 30 microns thick.

* * * * *

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,773,549 Issue Date November 20, 1973

Inventor(s) Raymond J. Elbert and Ernest G. Farrier

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2 line 63 is changed to read as follows:

"loys as Hastelloy X*, Haynes 25*, Haynes 188*, DH 242**,"

and the following footnote is added at the bottom of column 2:

* Trademark of Cabot Corporation

** Trademark of the Driver-Harris Corporation".

Column 2, line 64, NiCrB1 is changed to "NiCrA1".

Signed and sealed this 16th day of April 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents