METHOD FOR PRODUCING THICK CERAMIC FILMS BY A SOL GEL COATING PROCESS

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

FIELD OF THE INVENTION

This invention relates to the production of thick ceramic films, including composite films, on selected substrates, using a sol-gel coating technique. More particularly this invention relates to a technique for depositing polycrystalline ceramic films such as lead zirconate titanate and partially stabilized zirconia, in thicknesses greater than 10 μm.

BACKGROUND OF THE INVENTION

Ceramic coatings can be prepared by thermal or plasma spraying and physical vapour deposition (PVD) techniques. In plasma spray, a bulk powder is passed through a plasma and directed towards a substrate where it cools on contact. Films up to 10 mm thick can be produced in this way but usually need post-deposition heating as the deposited film tends to be porous (10% porosity is considered good). Another drawback of the plasma spray technique is that only line of sight geometries can be successfully coated. In PVD, expensive vacuum systems are required to coat high quality ceramic films of less than 10 μm. In addition this technique is also limited to line of sight geometries.

An alternative method, which has gained considerable ground and credibility in recent years, is sol-gel processing. Organo-metallic precursor compounds of the desired ceramic oxides are mixed and dissolved in a suitable solvent. The resultant solution is then hydrolysed to form a structured solution or gel containing organo-metallic polymers or macroclusters. Additives can be added to control the viscosity and surface tension of the sol gel solution. Films are prepared by either spin, dip or spray coating or painting onto an appropriate substrate. The coated substrate is then fired to remove the organic material and a post-fire heating step is usually performed to fully develop the final ceramic structure. The sol gel process has several advantages over other fabrication methods. It is simple, more economically feasible and permits coating of complex geometries, not necessarily line of sight. Usually ceramic films up to about 0.5 μm can be deposited in a single layer but films up to about 3.0 μm have been produced using a complex vacuum controlled firing treatment. Thicker films, up to about 10 μm in thickness have been produced by successive coatings in 0.1 μm layers. Clearly a 10 μm film made 0.1 μm at a time is a very time consuming and laborious process. In order to exploit the desired properties of the ceramic, it is essential that the ceramic film should be crack-free. Sol Gel films are, however, very susceptible to substrate interaction, defects and stresses within the film. Generally the thinner the film the lower the internal stresses and the number of defects. Solvents and organics can escape from 0.1 μm layers relatively easily but for thicker layers this is not so resulting in defects which can act as nucleation centres for crack propagation. Sol gel films are also substrate dependent and most films are limited to metallized silicon or other highly polished substrates. Conventional sol gel technology cannot, therefore, be used to produce thick, large area sol gel films.

OBJECT OF THE INVENTION

An object of the present invention is to provide an improved method for applying adherent ceramic films to metallic substrates in thicknesses greater than 5 μm and at least up to 200 μm without cracking.

Another object is to provide an improved sol-gel process for producing polycrystalline ceramic coatings on a wide range of substrates.

BRIEF STATEMENT OF THE INVENTION

By one aspect of this invention there is provided a process for producing a crack-free polycrystalline ceramic film on a substrate comprising:

(a) mixing a selected organo-metallic sol-gel solution with up to about 90% by weight of said solution of a selected finely divided ceramic powder so as to produce a uniform stable dispersion;

(b) applying said stable dispersion to a selected said substrate so as to provide a coating thereon up to about 6 μm thick; and

(c) firing said coated substrate at a temperature to between 400° and 1000° C. so as to remove organic constituents and produce a stable crack-free polycrystalline metallic oxide film on said substrate.

By another aspect of this invention there is provided a process for producing a crack-free crystalline film selected from stabilized zirconia [or] *and* titania on a substrate selected from aluminum foil and stainless steel, comprising:

(a) mixing sol gel mixture selected from titania and zirconia and a solution of a metal salt with up to 90% by weight of yttria or ceria stabilized zirconia powder or pure titania powder in a size range between .1 and 10 microns so as to produce a stable dispersion.

(b) applying said stable dispersion to a selected said substrate so as to provide a coating up to 6μm thick; and

(c) firing said coating substrate at a temperature up to about 500° C. so as to produce a stable crack-free polycrystalline film on said substrate.

By yet another aspect of this invention there is provided a process for producing crack-free polycrystalline composite ceramic films on a substrate comprising:

a) mixing a first selected organo-metallic sol gel solution with up to about 90% by weight divided ceramic powder so as to produce a first uniform stable dispersion;

b) mixing a second selected organo-metallic sol gel solution with up to about 90% by weight of said solution of a second selected finely divided ceramic powder so as to produce a second uniform stable dispersion;

c) applying a first coating of one of said first and second stable dispersions to a selected said substrate;

d) firing said first coating at a temperature up to about 1000° C. so as to remove organic constituents and produce a stable crack-free polycrystalline first metal oxide film on said substrate;

e) applying a second coating of the other of said first and second stable dispersions to said oxide film on said substrate;

(f) firing said second coating at a temperature up to about 1000° C. so as to remove organic constituents and produce a stable crack-free polycrystalline second metal oxide film on said first metal oxide film.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

As noted above, sol-gel processing techniques first require the preparation of an organo-metallic solution of the