Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2518170 C 2011/07/26

(11)(21) **2 518 170**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2004/02/06
(87) Date publication PCT/PCT Publication Date: 2004/09/16
(45) Date de délivrance/Issue Date: 2011/07/26
(85) Entrée phase nationale/National Entry: 2005/09/06
(86) N° demande PCT/PCT Application No.: DE 2004/000198
(87) N° publication PCT/PCT Publication No.: 2004/079033
(30) Priorité/Priority: 2003/03/07 (DE103 09 968.9)

(51) Cl.Int./Int.Cl. *C23C 4/02* (2006.01), *C23C 4/18* (2006.01), *H01M 8/12* (2006.01)

(72) Inventeurs/Inventors:
VASSEN, ROBERT, DE;
HATHIRAMANI, DAG, DE;
BUCHKREMER, HANS PETER, DE;
TIETZ, FRANK, DE;
DOERING, JENS-ERICH, DE;
SIEGERT, ROBERTO, DE;
TRAEGER, FRANZISKA, DE;
STOEVER, DETLEV, DE

(73) Propriétaire/Owner:
FORSCHUNGSZENTRUM JUELICH GMBH, DE

(74) Agent: SMART & BIGGAR

(54) Titre : PROCEDE DE FABRICATION D'UN SYSTEME A COUCHES COMPORTANT UN SUPPORT METALLIQUE ET UNE COUCHE A FONCTION D'ANODE

(54) Title: METHOD OF MAKING A LAYER SYSTEM COMPRISING A METALLIC CARRIER AND AN ANODE FUNCTIONAL LAYER

(57) Abrégé/Abstract:
The aim of the invention is to produce complete high temperature fuel cells by means of thermal injection processes (e.g. atmospheric plasma injection, vacuum plasma injection, high speed flame injection). The production method is especially simplified and is economical by virtue of the fact that the carrier substrate is also produced on a base with the aid of a thermal injection method. The base or an intermediate layer placed thereon can be advantageously dissolved or decomposed such that the carrier substrate provided with layers arranged thereon can be separated in a very simple manner from the base which becomes unnecessary. Said method advantageously enables the production of all layers of a high temperature fuel cell, exclusively with the aid of a thermal injection method.

ABSTRACT

The aim of the invention is to produce complete high temperature fuel cells by means of thermal injection processes (e.g. atmospheric plasma injection, vacuum plasma injection, high speed flame injection). The production method is especially simplified and is economical by virtue of the fact that the carrier substrate is also produced on a base with the aid of a thermal injection method. The base or an intermediate layer placed thereon can be advantageously dissolved or decomposed such that the carrier substrate provided with layers arranged thereon can be separated in a very simple manner from the base which becomes unnecessary. Said method advantageously enables the production of all layers of a high temperature fuel cell, exclusively with the aid of a thermal injection method.

TRANSLATION

DESCRIPTION

METHOD OF MAKING A LAYER SYSTEM COMPRISING A METALLIC CARRIER AND AN ANODE FUNCTIONAL LAYER

The invention relates to a method of making a layer system, especially for producing a layer system comprising at least one metallic carrier and an anode functional layer. Such a layer system is generally used in high temperature fuel cells.

STATE OF THE ART

For producing individual components for a high temperature fuel cell, various methods have been found to be suitable. Among these methods are, among others, atmospheric plasma spraying, vacuum plasma spraying and high speed flame spraying. The plasma spraying is a modern technique for providing surfaces of components with coatings having special characteristics. As carriers for the coatings (substrates) a relatively large number of materials can be used. In the production of the coatings, powder-form [pulverulent] particles are melted in a hot plasma beam, accelerated and sprayed therewith onto the substrate surface. There the molten material solidifies and remains adherent. By the repeated application of particles, also layers of greater thickness can be built up.

A problem with the use of thermal spray processes for the production of individual fuel cell components is that one must use a carrier in the form of a substrate for the coating. For that purpose up to now as a rule, skeletons of metallic fibers or metallic felts or porous powder metallurgically made plates have been used. On these structures (carriers), a first functional layer, for example the anode, is applied.

The disadvantages here to be mentioned are the high cost of the substrate and an expensive fabrication technique.

Substrates which are made by powder technology shaping methods of composite materials like Ni/YSZ (Yttrium oxide stabilized zirconium oxide) or NiO/YSZ, have the drawback that they are not very stable mechanically. In the production of such a layer system for a high temperature fuel cell by thermal spray methods, generally excessive temperature fluctuations arise which can produce enormous thermal stresses, in the substrate leading to the rupture thereof.

Additional problems which arise with carrier substrates which have been used for some time up to now have been associated with the relatively large porosity resulting usually from plasma spraying. This can lead to a disadvantageously insufficient electrochemical efficiency of the fuel cell.

OBJECTS AND SOLUTION

An object of the invention is to provide a suitable carrier substrate, especially for the production of fuel cell components. A further object of the invention is to provide an economical and simple method for making available such carrier substrates.

According to one aspect of the present invention, there is provided a method of making a layer system comprising at least one metallic carrier and an anode functional layer as a component for a carrier-based high-temperature fuel cell, the method comprising the steps of sequentially: spraying a metal powder upon a substrate with the aid of a thermal spray process to form a porous, metallic carrier; applying a further component as an anode functional layer upon the porous, metallic carrier with the aid of a thermal spray process to form the layer system; and removing the layer system from the substrate.

According to another aspect of the present invention, there is provided the method as described herein in which the substrate is a plastic which thermally decomposes at a temperature above 300°C to release the layer system.

According to still another aspect of the present invention, there is provided the method as described herein in which the substrate prior to the application of the porous metallic carrier is coated with an intermediate layer and wherein the release of the layer system from the substrate is effected by the removal or dissolution of the intermediate layer.

According to yet another aspect of the present invention, there is provided the method as described herein in which the intermediate layer is a plastic layer which thermally decomposes at a temperature above 300°C to release the layer system.

According to a further aspect of the present invention, there is provided the method as described herein in which the substrate is a salt from which the layer system can be released by dissolution of the salt with a solvent.

According to yet a further aspect of the present invention, there is provided the method as described herein in which the intermediate layer is a salt layer from which the layer system can be released by dissolution of the salt layer with a solvent.

According to still a further aspect of the present invention, there is provided the method as described herein in which the removal of the layer system from the substrate is effected by a mechanical machining.

According to another aspect of the present invention, there is provided the method as described herein in which the mechanical machining is by sawing or peeling.

According to yet another aspect of the present invention, there is provided the method as described herein in which the metal powder has a thermal expansion coefficient between 10 x 10^{-6}/K and 13 x 10^{-6}/K.

According to another aspect of the present invention, there is provided the method as described herein in which the metal powder comprises a ferritic steel or a chromium based alloy.

According to still another aspect of the present invention, there is provided the method as described herein in which the porous, metallic carrier has a porosity in excess of 15%.

According to yet another aspect of the present invention, there is provided the method as described herein in which the porous, metallic carrier has a porosity in excess of 20%.

According to a further aspect of the present invention, there is provided the method as described herein, wherein the porous, metallic carrier is formed by spraying the metal powder and at least one organic powder.

According to yet a further aspect of the present invention, there is provided the method as described herein, wherein the at least one organic powder comprises one or both of polyester and carbon.

According to still a further aspect of the present invention, there is provided the method as described herein, in which the one or more organic powder is thermally removed from the carrier layer following formation of the carrier layer.

According to another aspect of the present invention, there is provided the method as described herein in which the further component for the formation of the anode functional layer is fully stabilized zirconium oxide and nickel or nickel oxide.

According to yet another aspect of the present invention, there is provided the method as described herein in which the fully stabilized zirconium oxide and nickel or nickel oxide has a grain size less than 5 μm.

According to another aspect of the present invention, there is provided the method as described herein in which the fully stabilized zirconium oxide and nickel or nickel oxide has a grain size less than 1 μm.

According to still another aspect of the present invention, there is provided the method as described herein in which the anode functional layer is applied with the aid of a thermal suspension spray process.

According to yet another aspect of the present invention, there is provided the method as described herein in which an electrolyte layer is applied on the anode functional layer by thermal spray process.

According to a further aspect of the present invention, there is provided the method as described herein in which the electrolyte layer is fully stabilized zirconium oxide.

According to yet a further aspect of the present invention, there is provided the method as described herein in which the electrolyte layer is applied at a temperature above 180°C.

According to still a further aspect of the present invention, there is provided the method as described herein in which the electrolyte layer is applied at a temperature above 200°C.

According to another aspect of the present invention, there is provided the method as described herein in which the electrolyte layer is applied with a layer thickness of at least 5 μm.

According to yet another aspect of the present invention, there is provided the method as described herein in which the electrolyte layer is applied with a layer thickness of at least 20 μm.

According to another aspect of the present invention, there is provided the method as described herein in which the electrolyte layer is applied by way of a thermal suspension spray method.

According to another aspect of the present invention, there is provided the method as described herein in which a cathode function layer is applied to the electrolyte layer by way of a thermal spray method.

According to still another aspect of the present invention, there is provided the method as described herein in which the cathode function layer comprises a mixture of a perovskite and fully stabilized zirconium oxide.

According to yet another aspect of the present invention, there is provided the method as described herein in which the cathode function layer is applied with a layer thickness of at least 5 μm.

According to a further aspect of the present invention, there is provided the method as described herein in which the cathode function layer is applied with a layer thickness of at least 20 μm.

According to yet a further aspect of the present invention, there is provided the method as described herein in which the cathode function layer is applied with the aid of a thermal suspension spray method.

According to still a further aspect of the present invention, there is provided the method as described herein in which a further layer is applied to the cathode functional layer with the aid of a thermal spray method.

According to another aspect of the present invention, there is provided the method as described herein in which the further layer comprises at least one perovskite.

According to yet another aspect of the present invention, there is provided the method as described herein in which the further layer further comprises at least one further organic component.

According to still another aspect of the present invention, there is provided the method as described herein in which the further layer is made from a material in powder form having a grain size greater than 50 μm.

SUBJECT OF THE INVENTION

The concept upon which this invention is based is that not only can the individual functional layers of a high temperature fuel cell be made advantageously with the aid of plasma spraying but that also the carrier substrate required can be made in this manner as well.

With the method according to the invention described here, advantageously the suitable substrate, referred to in the following as a carrier structure, is made directly by means of a thermal spray process. For producing this carrier structure, a suitable metal powder is sprayed onto a surface by a thermal spray process. Preferably this surface is provided with an easily removable coating (separating layer or parting layer). This removable parting layer enables in a simple manner the release of the carrier substrate after the coating process from the surface. It can for example be formed by a plastic coating which can be applied by an immersion or dipping process or by a spray process. The removal or separation of the substrate or carrier from the surface can then be effected thermally in that case. A parting layer or coating can however also be formed by a salt layer upon for example the drying of a solution or also deposited by a thermal spray method. In such case the parting layer can be removed by a suitable solution (for example water). Alternatively, the carrier structure can be removed from its substrate by mechanical machining (sawing or peeling or levering it off).

The carrier structure itself is produced by spraying a metal powder which can have the following characteristics especially for producing fuel cell components. It should advantageously have a thermal coefficient of expansion which is matched to that of the usual fuel cell components, which is about 10×10^{-6} /K to 13×10^{-6} /K. In addition, it should at elevated temperatures and under oxidizing conditions be capable of forming an oxide skin on its surface which is electrically conductive. Preferably for this purpose ferritic steels which form chromium oxide cover layers or manganese oxide cover layers are used. Alternatively, chromium based alloys, for example of a CrFeY-basis can find application for this purpose. The carrier structure should have a high open porosity (especially greater than 15%) so as not to create an excessive resistance to the gas transport.

Corresponding porosities can be easily produced by the thermal coating. Preferably relatively coarse powder (particle size > 50μm) can be used as previously has been employed with cold spray techniques, that is with only partial melting of the metal particles. An additional increase in porosity can be achieved by including organic components for example (polyesters) or carbon or other suitable place holders during the thermal spraying. These organic components or place holders can be easily subsequently removed by a thermal treatment. Effective layer thicknesses for the carrier structure are especially between 0.3 mm and 3 mm.

After the deposition of the carrier structure on a substrate, the carrier structure is coated with an anode functional layer, for example, of a fully stabilized zirconium oxide (YSZ) with a nickel or nickel oxide addition, with the aid of a thermal spray coating process. The weight ratio of YSZ and nickel or nickel oxide should advantageously lie at about 50% /50%. An especially fine porosity can be obtained by the use of a suspension as a starting material for the thermal spraying (thermal suspension spraying). In this manner, the material which is applied (for example 8YSZ/NiO) can be deposited as a powder with a relatively small particle size (< 1 μm) by the spray process. A preferred coating thickness lies between 5 and 50 μm.

Thereafter, the anode functional layer can be optionally provided by a thermal spray process with a dense electrolyte. Preferred materials for a suitable electrolyte are also here fully stabilized zirconium oxides (for example YSZ). The density of the electrolyte is established by the use of suitable spray parameters. What is important in this case is also the use of a high substrate temperature (T > 200°C), and generally the hottest possible spray parameter, that is a spray parameter which will result in the greatest degree possible of melting of the particles, and the highest possible coating thickness per pass (greater than 5 μm), since these parameters are effective to avoid micro cracks and thus enable a dense coating deposition. In any case, the parameters should be so selected that segmenting cracks as arise a rule with high coating thicknesses, will be precluded. The metallic carrier substrate offers the advantage, by comparison with conventional anode substrates on an NiO/YSZ basis and also generally by comparison with ceramic materials, that it can be thermally loaded to a greater extent and thus the requisite hot spray conditions can be used therewith. In case the porosity of the electrolyte layer should be reduced still further an after treatment of the coating is possible. Alternatively, here as well the thermal suspension spray can be used since the fine particles employed with suitable processing enables a dense layer deposition. The layer thicknesses lie in the range between 5 μm and 100 μm.

As further, optional layers, layers can be deposited by thermal spraying which can include a cathode functional layer, for example a mixture of a perovskite (for example $La_{0.65}Sr_{0.3}MnO_3$ or an La/Sr/Fe/Co based perovskite with YSZ). As typical layer thicknesses here, thicknesses between 5 and 50 µm can be mentioned. Here as well, fine porous structures can be produced by thermal suspension spraying.

As a final layer for a high temperature fuel cell, optionally the cathode of perovskite (for example $La_{0.65}Sr_{0.3}MnO_3$) can be applied by a thermal spray process.

In this case, like with the formation of the carrier substrate, primarily coarse powder (greater than 50 µm) is used with cold spray parameters.
Here as well the use of organic components to increase the porosity is possible.

Special Description Part

In the following, the subject matter of the invention is described based upon three figures and an exemplary embodiment in greater detail without thereby limiting the scope of the invention thereto.

They show:

FIG. 1: an image of the carrier layer formed by plasma spraying from a ferritic steel with or porosity of about 22%.

FIG. 2: an image of a carrier layer formed by atmospheric plasma spraying with the addition of polyester and wherein the carrier layer is formed from zirconium oxide with a porosity of about 33%.

FIG. 3: an image of a fine porous layer of fully stabilized zirconium oxide (YSZ) produced by suspension plasma spraying.

Embodiment Example:

By atmospheric plasma spraying with an F4 burner, a Cr5FeY alloy is deposited on a polymer coated ST37 steel substrate. As an organic additive component to the spray, polyester is used. The use of cold process parameters (power about 40 kW, 120 mm spray spacing) in combination with the polyester additive, enables a setting of a porosity of significantly above 30% following the burn off of the polyester. The layer thickness amounted to about 1 mm.

Upon this layer, using atmospheric suspension plasma spraying a fine-porous coating (Porosity >25%) of 55% NiO/45% YSZ was deposited. The solids content of the suspension was about 25 weight %. The spray distance amounted to 70 mm with a power of the F4 burner of 47 kW.

The electrolyte coating was deposited subsequently with the aid of atmospheric plasma spraying with the use of fine grain molten broken YSZ powder. The substrate temperature amounted at that point to about 350°C. The burner power was 50 kW, the spray distance 80 mm the layer thickness which was established was 50 µm.

Thereafter, using atmospheric suspension plasma spray, a cathode functional layer was deposited as a finely porous layer (Porosity > 25%). The suspension used was comprised of

$La_{0.65}Sr_{0.3}MnO_3$/YSZ with a solids content of about 25 weight percent. The layer thickness was 30 μm. The spray distance amounted to 70 mm with a power of the F4 burner of 47 kW.

The last layer was again applied by atmospheric plasma spraying with an addition of polyester powder. Cold spray parameters were used in combination with polyester which could be burned out to a porosity of greater than 30%. The polyester powder was injected through a separate injector into a relatively cold region of the plasma flame to avoid burnoff in the plasma. The latter thickness amounted to 50 μm.

As a final method step, the layer system is maintained at 600°C in air to release the layer system from the substrate and to remove the polyester. Alternatively, the burnoff of the polyester can be carried out at start up of the fuel cell.

70577-140

CLAIMS:

1. A method of making a layer system comprising at least one metallic carrier and an anode functional layer as a component for a carrier-based high-temperature fuel cell, the method comprising the steps of sequentially:

spraying a metal powder upon a substrate with the aid of a thermal spray process to form a porous, metallic carrier;

applying a further component as an anode functional layer upon the porous, metallic carrier with the aid of a thermal spray process to form the layer system; and

removing the layer system from the substrate.

2. The method according to claim 1 in which the substrate is a plastic which thermally decomposes at a temperature above 300°C to release the layer system.

3. The method according to claim 1 in which the substrate prior to the application of the porous metallic carrier is coated with an intermediate layer and wherein the release of the layer system from the substrate is effected by the removal or dissolution of the intermediate layer.

4. The method according to claim 3 in which the intermediate layer is a plastic layer which thermally decomposes at a temperature above 300°C to release the layer system.

5. The method according to claim 1 in which the substrate is a salt from which the layer system can be released by dissolution of the salt with a solvent.

6. The method according to claim 3 in which the intermediate layer is a salt layer from which the layer system can be released by dissolution of the salt layer with a solvent.

7. The method according to claim 1 in which the removal of the layer system from the substrate is effected by a mechanical machining.

8. The method according to claim 7 in which the mechanical machining is by sawing or peeling.

9. The method according to any one of claims 1 to 8 in which the metal powder has a thermal expansion coefficient between 10 x 10^{-6}/K and 13 x 10^{-6}/K.

10. The method according to any one of claims 1 to 9 in which the metal powder comprises a ferritic steel or a chromium based alloy.

11. The method according to any one of claims 1 to 10 in which the porous, metallic carrier has a porosity in excess of 15%.

12. The method according to any one of claims 1 to 10 in which the porous, metallic carrier has a porosity in excess of 20%.

13. The method according to any one of claims 1 to 12, wherein the porous, metallic carrier is formed by spraying the metal powder and at least one organic powder.

14. The method according to claim 13, wherein the at least one organic powder comprises one or both of polyester and carbon.

15. The method according to claim 13 or 14, in which the one or more organic powder is thermally removed from the carrier layer following formation of the carrier layer.

16. The method according to any one of claims 1 to 15 in which the further component for the formation of the anode functional layer is fully stabilized zirconium oxide and nickel or nickel oxide.

17. The method according to claim 16 in which the fully stabilized zirconium oxide and nickel or nickel oxide has a grain size less than 5 μm.

18. The method according to claim 16 in which the fully stabilized zirconium oxide and nickel or nickel oxide has a grain size less than 1 μm.

19. The method according to any one of claims 1 to 18 in which the anode functional layer is applied with the aid of a thermal suspension spray process.

20. The method according to any one of claims 1 to 19 in which an electrolyte layer is applied on the anode functional layer by thermal spray process.

21. The method according to claim 20 in which the electrolyte layer is fully stabilized zirconium oxide.

22. The method according to claim 20 or 21 in which the electrolyte layer is applied at a temperature above 180°C.

23. The method according to claim 20 or 21 in which the electrolyte layer is applied at a temperature above 200°C.

24. The method according to any one of claims 20 to 22 in which the electrolyte layer is applied with a layer thickness of at least 5 µm.

25. The method according to any one of claims 20 to 22 in which the electrolyte layer is applied with a layer thickness of at least 20 µm.

26. The method according to any one of claims 20 to 25 in which the electrolyte layer is applied by way of a thermal suspension spray method.

27. The method according to any one of claims 20 to 23 in which a cathode function layer is applied to the electrolyte layer by way of a thermal spray method.

28. The method according to claim 27 in which the cathode function layer comprises a mixture of a perovskite and fully stabilized zirconium oxide.

29. The method according to claim 27 or 28 in which the cathode function layer is applied with a layer thickness of at least 5 µm.

30. The method according to claim 27 or 28 in which the cathode function layer is applied with a layer thickness of at least 20 µm.

31. The method according to any one of claims 27 to 30 in which the cathode function layer is applied with the aid of a thermal suspension spray method.

32. The method according to any one of claims 27 to 31 in which a further layer is applied to the cathode functional layer with the aid of a thermal spray method.

33. The method according to claim 32 in which the further layer comprises at least one perovskite.

34. The method according to claim 33 in which the further layer further comprises at least one further organic component.

35. The method according to any one of claims 32 to 34 in which the further layer is made from a material in powder form having a grain size greater than 50 μm.

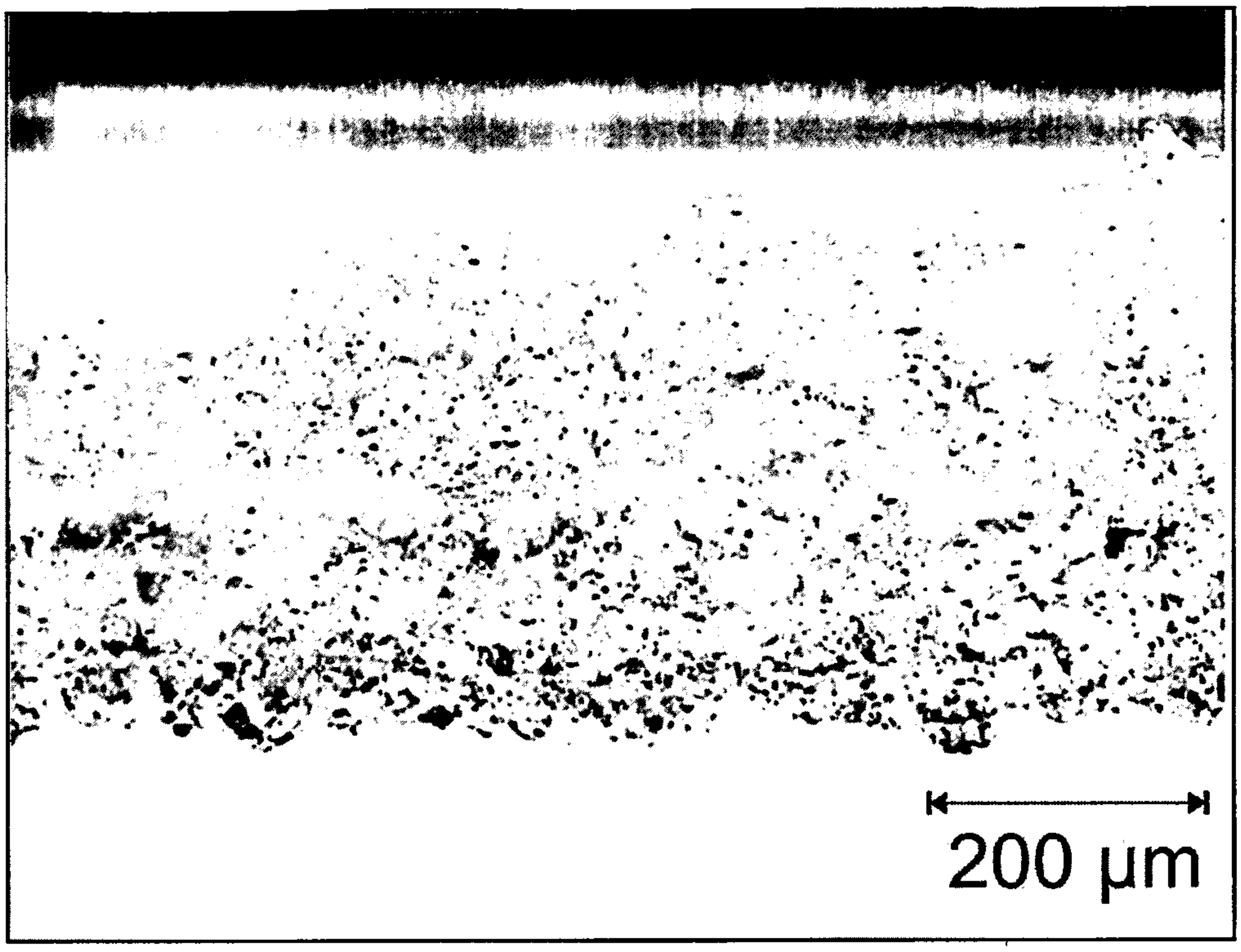

Figure 1

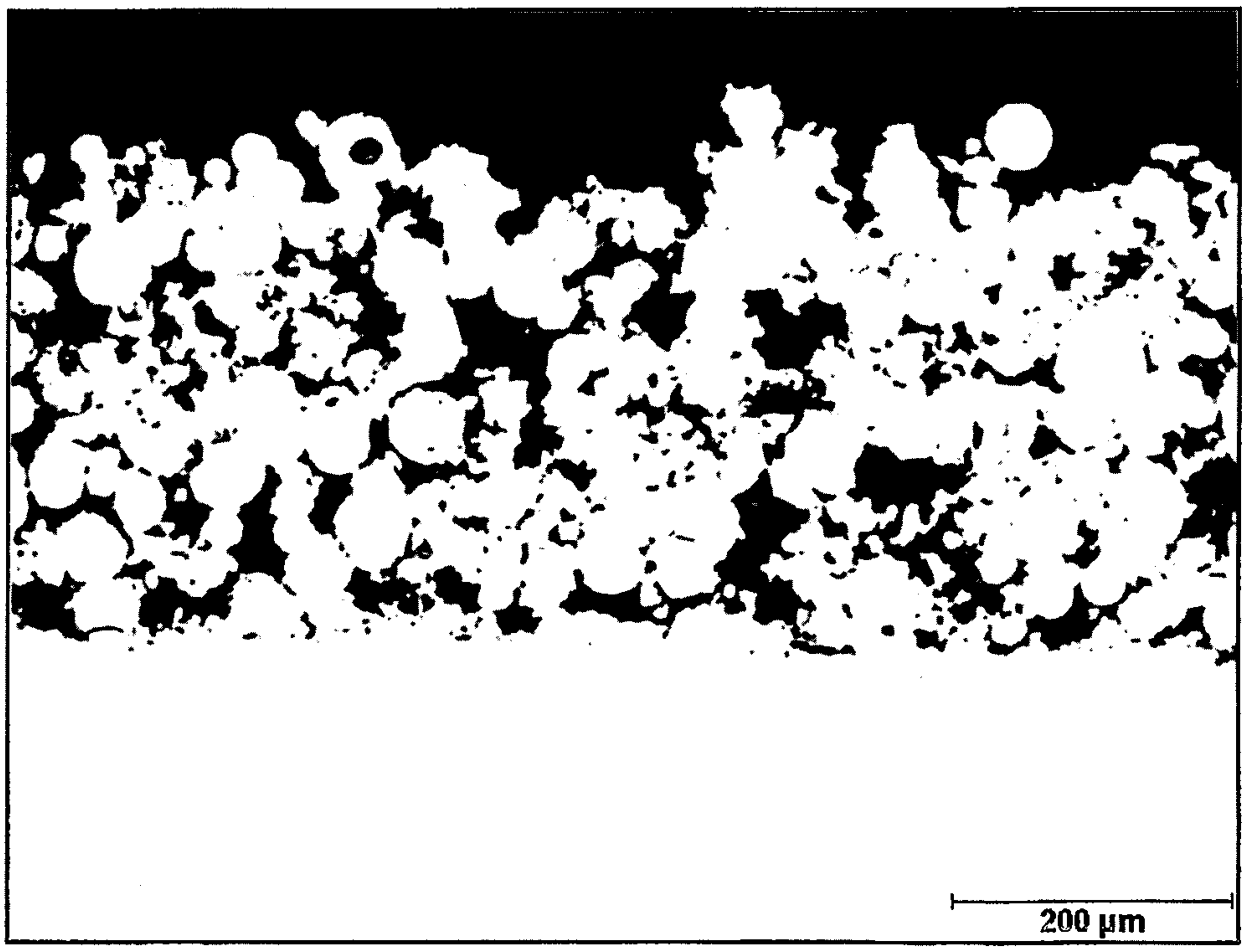

Figure 2

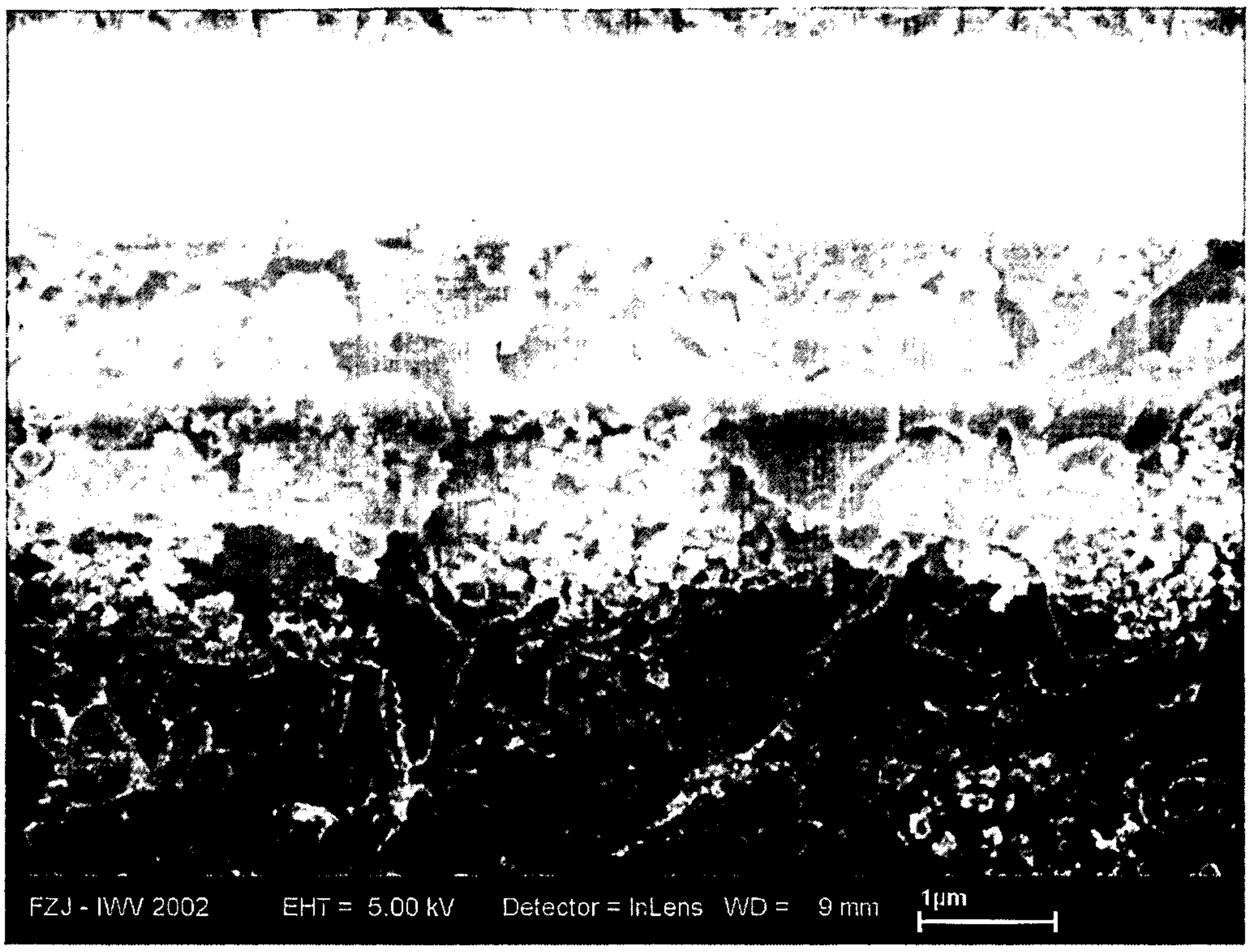

Figure 3