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(54) **COATING ALUMINIUM OXIDE CERAMICS WITH HYDROXYL APATITE**

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(57) **ABSTRACT**
The invention relates to a method for producing hydroxyapatite coated ceramics components. In a first step of the inventive method the ceramic component is provided with a Ti coating and in a second step a hydroxyapatite is applied to the Ti coating. The invention further relates to hydroxyapatite coated ceramic components produced according to the inventive method.

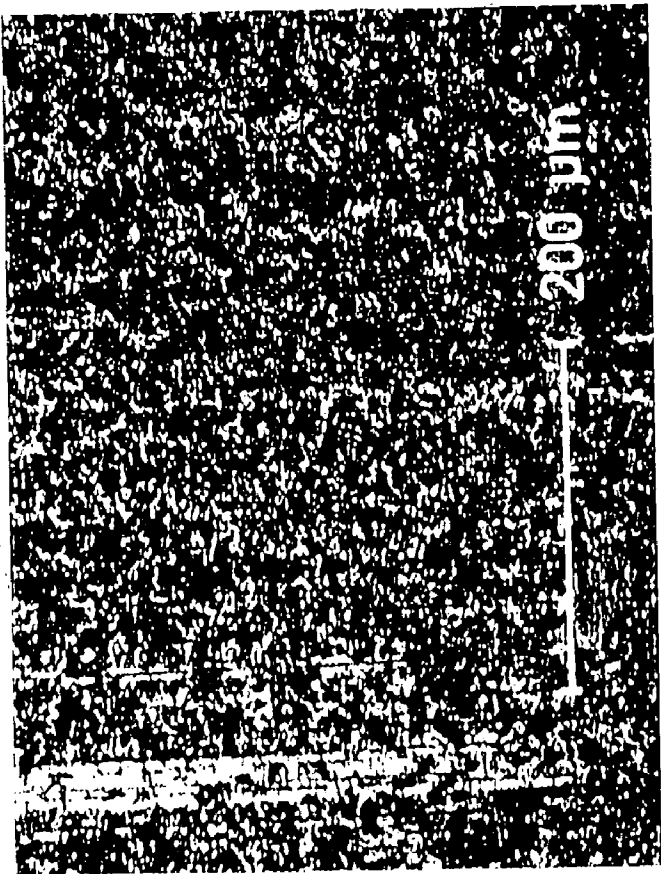


FIG. 2

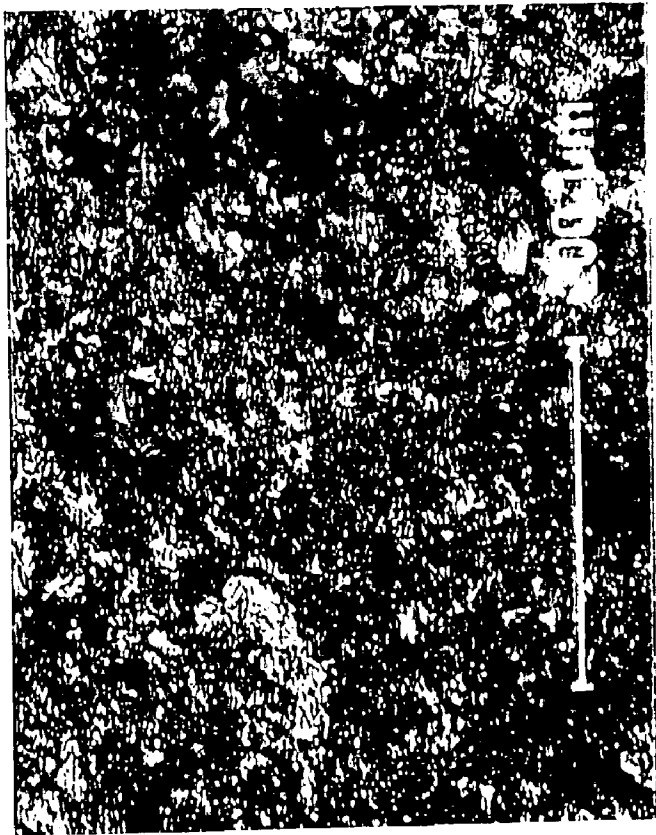


FIG. 1

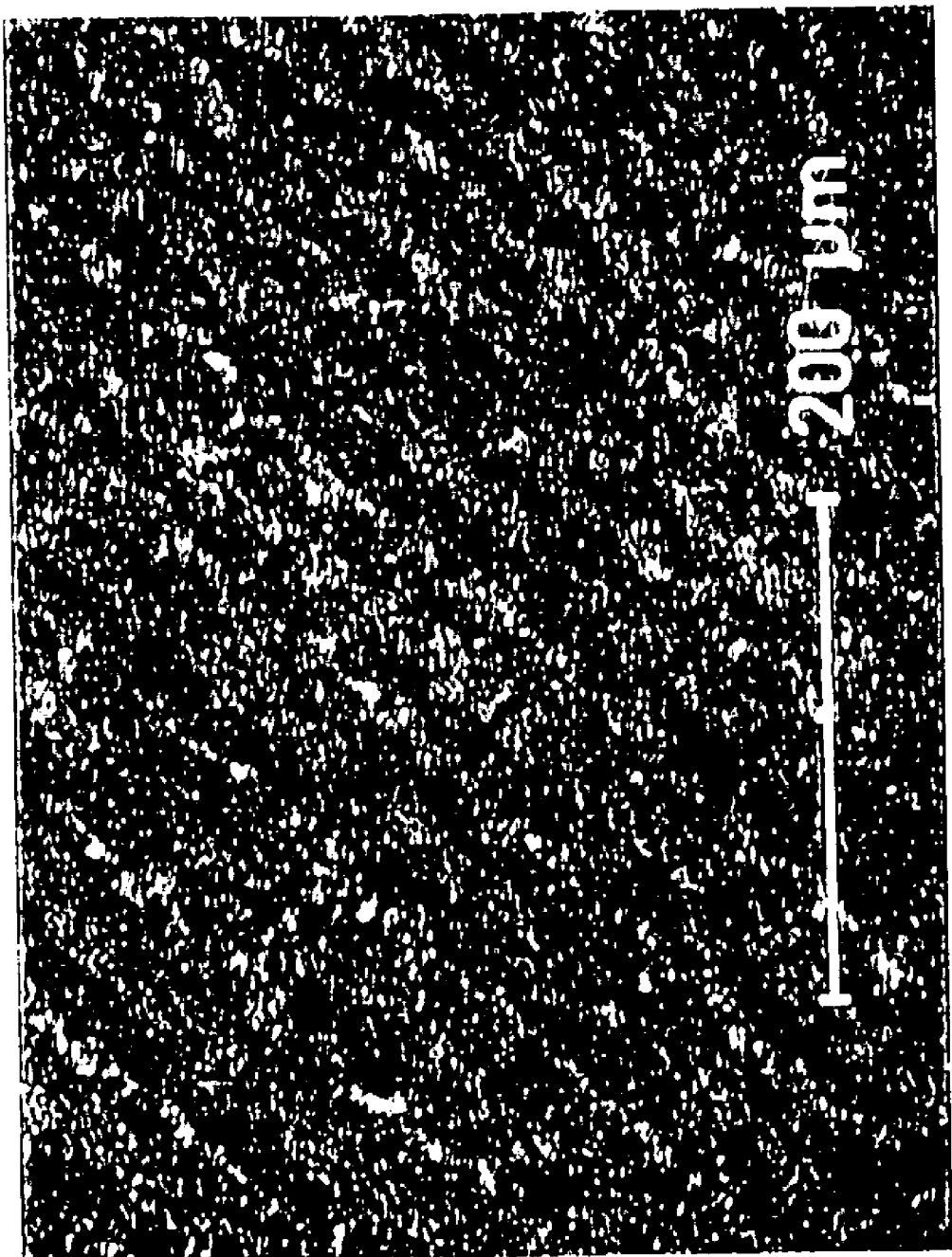


FIG. 3



FIG. 5



FIG. 4

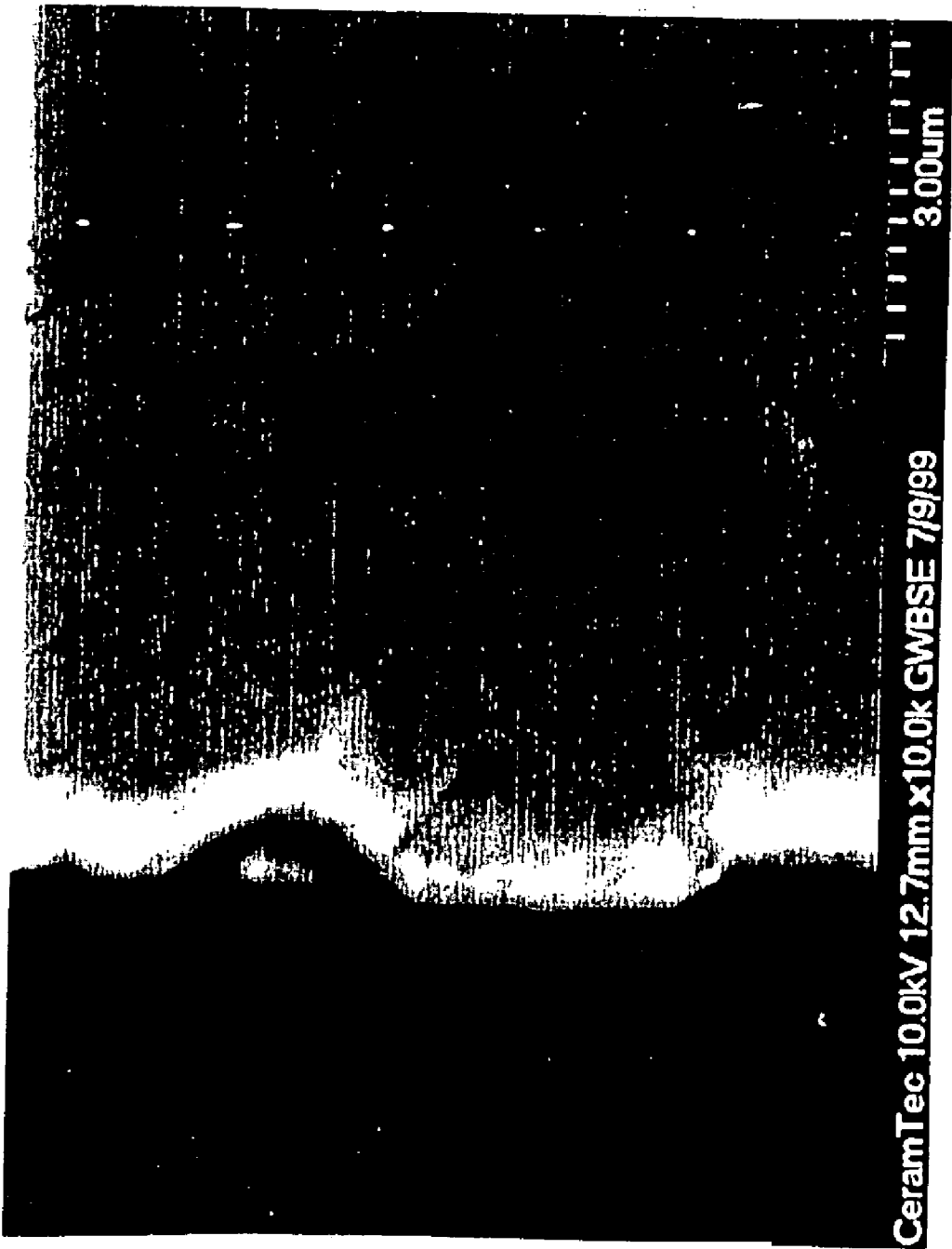


FIG. 6

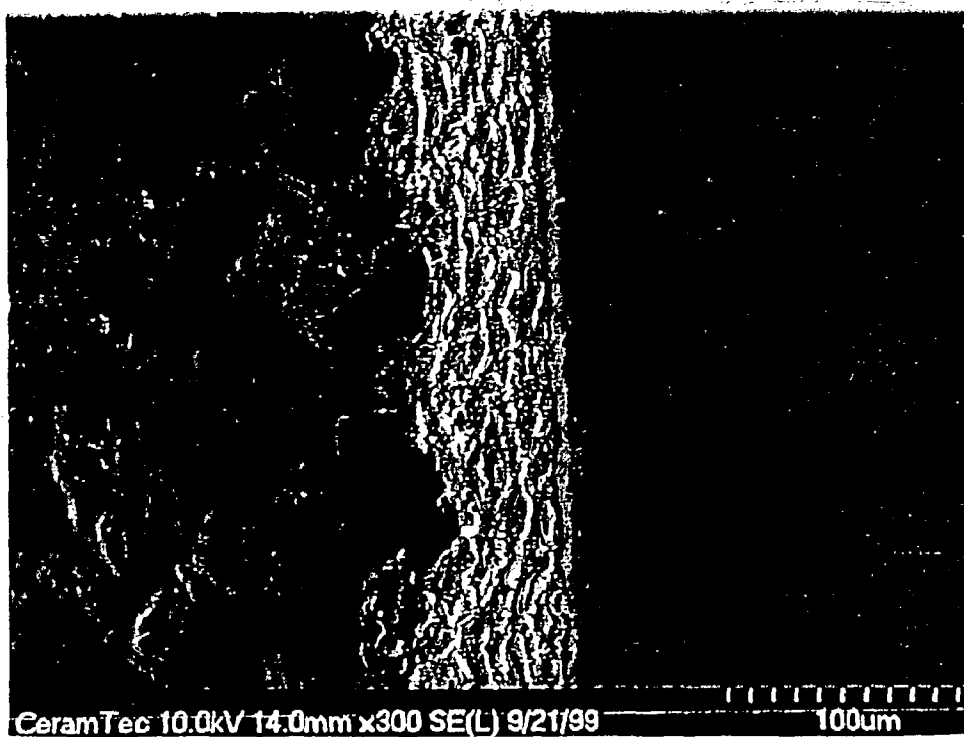


FIG. 7

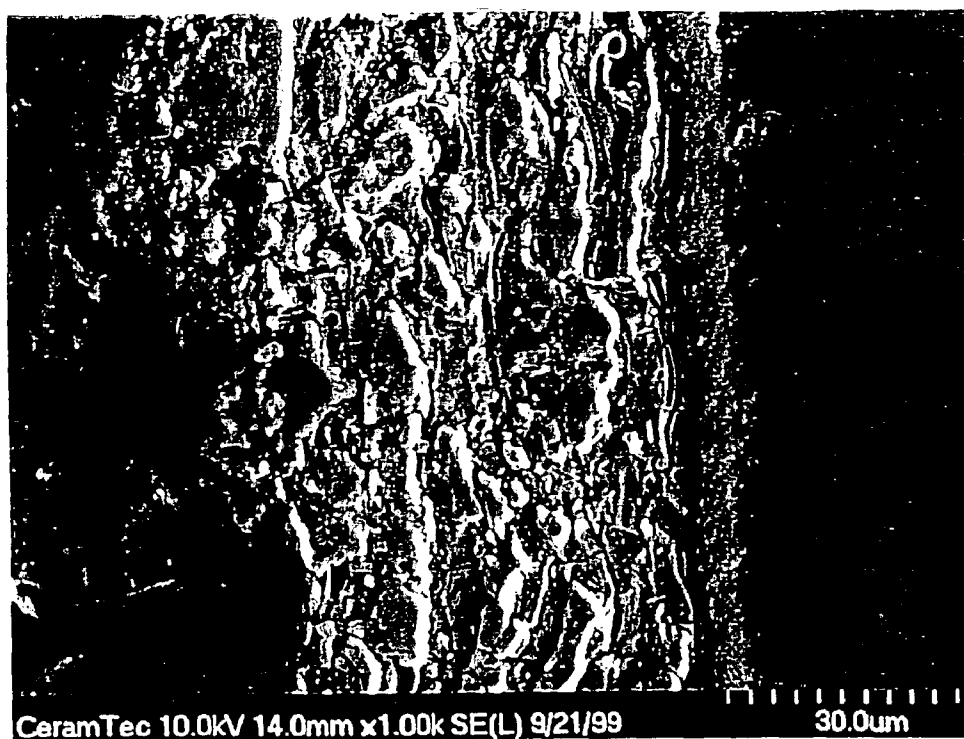


FIG. 8

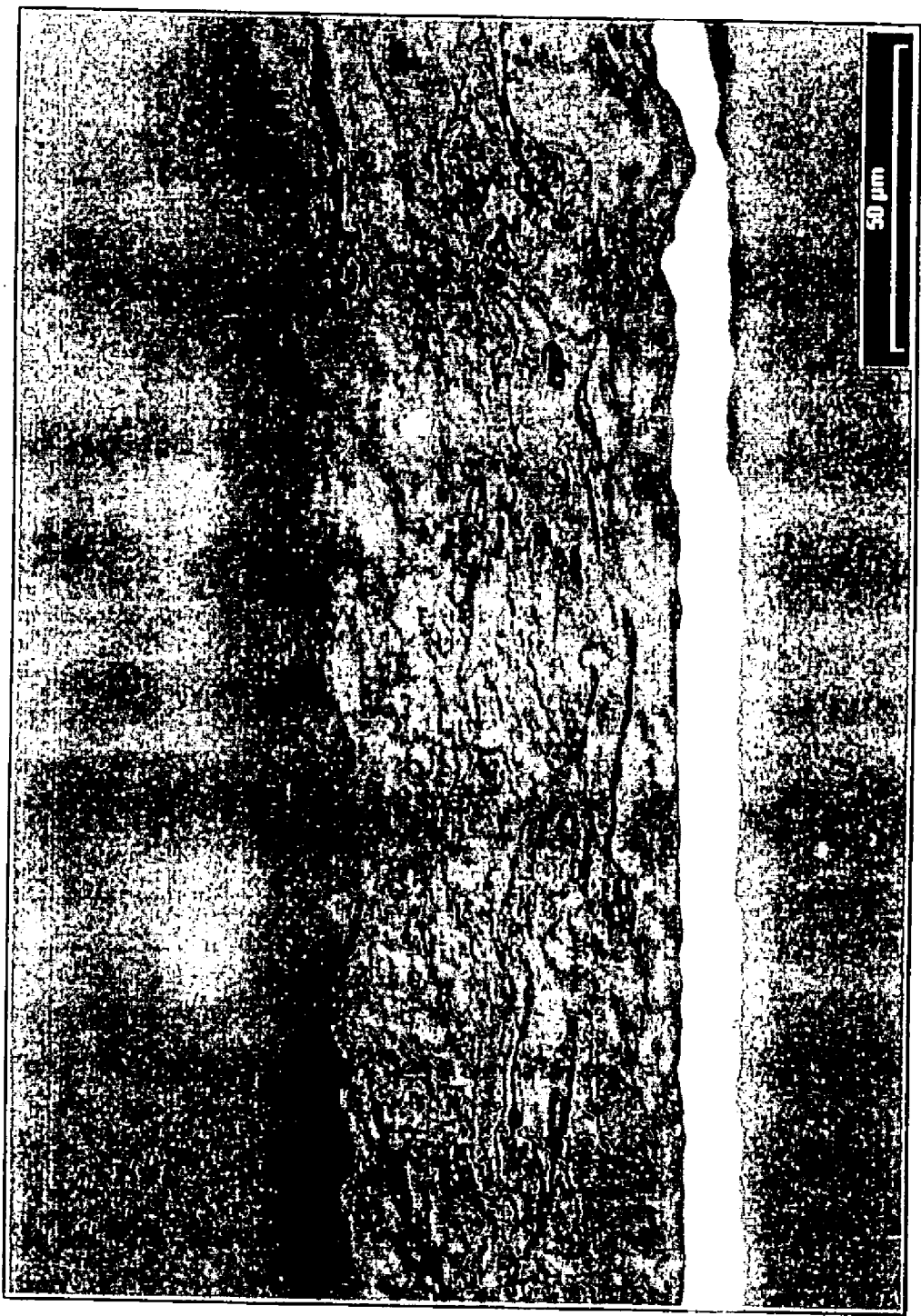


FIG. 9

COATING ALUMINIUM OXIDE CERAMICS WITH
HYDROXYL APATITE

[0001] The subject of the present invention is a method for the manufacture of ceramic components coated with hydroxyapatite, as well as the ceramic components which can be manufactured by this method.

[0002] It is known that prostheses which have a hydroxyapatite coating display an especially good ingrowth activity. Care must be taken, however, to see that the hydroxyapatite coating firmly adheres to the prosthesis. In the coating of titanium shafts with hydroxyapatite an especially great strength of adherence can be achieved when the metal surface is given a roughness of $R_a \approx 40\text{--}50\text{ }\mu\text{m}$.

[0003] The adhesive strength of hydroxyapatite apatite on ceramic surfaces, especially on Al_2O_3 ceramics, is not sufficient for the desired use. Thus any direct coating of an aluminum oxide ceramic with hydroxyapatite, such as would be very advantageous for the direct fixation of the femur part of a knee prosthesis, is impossible. Even if the surface roughness is made similar to the roughness of the titanium shafts, the strength of the adhesion of hydroxyapatite is not assured. This has been proven in experiments in which ground and sand-blasted samples were used. In comparison with titanium materials the surface roughness of ceramic base materials thus treated is substantially lower. Coating tests with the standard parameters for titanium shafts resulted in no strength of adhesion between hydroxyapatite and aluminum oxide ceramic. Inasmuch as no coating adhered to aluminum oxide bodies under standard conditions, the spray parameters was also modified in the plasma coating apparatus. But even the modified process parameters did not lead to success. The cause of the poor strength of adhesion was determined to be the differences in roughness between the metal and the ceramic. A surface roughness of $R_a \approx 30\text{ }\mu\text{m}$ cannot be achieved by conventional abrasive methods.

[0004] Even methods which lead to increased depth of roughness did not bring the desired success. To produce a greater defined surface roughness, similar specimens were prepared for laser machining under various settings. In this manner it was possible to produce a lasting effect on the surfaces of the Al_2O_3 ceramic. While in the case of normal grinding a raw depth of no more than $1\text{ }\mu\text{m}$ could be achieved, the laser treatment succeeded in producing a raw depth of $R_a \approx 9\text{ }\mu\text{m}$. FIG. 3 shows the typical surface after the laser treatment. The lasered surface of the aluminum oxide ceramic was then subjected to plasma coating with hydroxyapatite. For the first time a few places on this surface were detected, on which the hydroxyapatite coating could be detected. Of course, it was not possible even by this preliminary treatment to apply a continuous coating. FIGS. 4 and 5 show the surfaces of the lasered and hydroxyapatite (HA) coated specimens.

[0005] Even though it was possible for the first time to prove the deposition of hydroxyapatite on the roughened surfaces of the aluminum oxide ceramic, the strength of adhesion of the coating was very poor. Quantification of the strength of adhesion was impossible, as was the preparation of a transverse section; the coating fell off immediately. Again, when the raw depth was analyzed it was compared with that of metal materials. With an R_a of $9\text{ }\mu\text{m}$ the raw depth of the TiAl6V4-1 alloy ($R_a \approx 40\text{ }\mu\text{m}$) could not be

achieved. It was necessary to refrain from any further roughening of the surface in the ceramic substrate, since the aluminum oxide ceramic, unless metallic materials, has an absolute cleavage fracture tendency. If a “predamage” of $40\text{ }\mu\text{m}$ is induced, this “flaw” can trigger breakage. Thus, any further increase of the roughness is impossible from the viewpoint of fracture mechanics.

[0006] The present invention is addressed to the problem of making available a method by which ceramic components can reliably be provided with a hydroxyapatite coating.

[0007] The problem to which the invention is addressed has been solved by a method with the features of the principal claim. Preferred embodiments are described in the subclaims.

[0008] Surprisingly it was possible according to the invention to coat a ceramic component, preferably a component made of aluminum oxide ceramic, with hydroxyapatite if the surface of the ceramic component is coated with a titanium layer. By the method of the invention it is surprisingly possible for the first time to deposit hydroxyapatite on the surface of a ceramic component, with sufficient strength of adhesion.

[0009] According to the invention, first ceramic components are provided with a thin titanium coating, for example by PVD (physical vapor deposition). According to the invention, the surface of the ceramic component can be previously roughened,—ground or lasered, for example. The thickness of the titanium layer was about $1\text{ }\mu\text{m}$; a coating $5\text{ }\mu\text{m}$ thick also led to success. FIG. 6 shows the transverse section of a specimen coated in this manner.

[0010] The hydroxyapatite layer was sprayed onto this intermediate layer. The transverse section of this built-up coating is represented in FIGS. 7 and 8 at different enlargements.

[0011] Preferably, before the hydroxyapatite is applied by plasma coating, for example, the titanium intermediate layer is subjected also to a sand blasting process to improve adhesion. An especially high strength of adhesion is achieved if the titanium coating is given a roughness of $R_a \approx 40\text{--}50\text{ }\mu\text{m}$.

[0012] A scratch test on the hydroxyapatite coating confirmed the outstanding strength of adhesion of the coating. Preparation of a transverse section was possible without problems. The measurement of the strength of adhesion was made on five different specimens. The individual values are summarized in Table 1.

TABLE 1

Strength of adhesion of hydroxyapatite on Al_2O_3 with titanium primer		
Specimen	Force [N]	Tension [MPa]
1	718	2.3
2	1203	3.8
3	932	3
4	1490	4.7
5	390	1.2

[0013] From the values obtained by the strength-of-adhesion measurements it can be seen that tensions are surpris-

ingly achieved which are in the range of that of hydroxyapatite coatings on TiAl6V4 alloys.

[0014] According to the invention, it is also possible, instead of the conventional titanium intermediate coating, an intermediate coating of the TiAl6V4 alloy can be deposited, for example by the PVD method.

[0015] FIG. 9 shows the typical building of layers in the preparation of transverse sections. The corresponding strengths of adhesion are listed in Table 2.

Specimen	Force [N]	Tension [MPa]
1	582	1.9
2	700	2.2
3	400	1.3
4	498	1.6

[0016] A ceramic component in the form of a cylindrical test specimen was used in the tests. The cylinders, with a diameter of 20 mm and a thickness of 2 mm, were made he conventional press-turn manufacture as greenbodies, subjected to hot isostatic pressure and annealed. The sintered bodies were then machined with diamond tools to achieve final shape. Other methods for the manufacture of ceramic components can, of course, also be used. Used as the material was a known aluminum oxide material, such as the one known as Biolox® material, for example.

[0017] With the present invention it is thus for the first time possible by providing a titanium intermediate coating to deposit hydroxyapatite directly onto ceramic components. The ceramic components that can be made by the method of the invention are also subject matter of the present invention.

[0018] Thus, according to the invention, ceramic components can for the first time be made, which can be used for medical purposes, for example as prostheses. Such prostheses display an improved ingrowth characteristic.

1. Method for the manufacture of hydroxyapatite coated ceramic components, characterized in that in a first step the

ceramic component is first provided with a Ti coating and in a second step the hydroxyapatite is applied to the Ti coating.

2. Method according to claim 1, characterized in that the surface of the ceramic component is roughened before the first step.

3. method according to claim 1 or 2, characterized in that the Ti coating applied in the first step is rough.

4. Method according to one or more of claims 1 to 3, characterized in that the Ti coating applied in the first step is adjusted to a roughness of $R_a \approx 40$ to $50 \mu\text{m}$.

5. Method according to one or more of claims 1 to 4, characterized in that in the first step the titanium is deposited onto the surface of the ceramic component by means of the PVD process.

6. Method according to one or more of claims 1 to 5 characterized in that, instead of the Ti coating, by means of the PVD process a coating of the TiAl6V4 alloy is deposited.

7. Method according to one or more of claims 1 to 6, characterized in that the Ti or TiAl6V4 coating applied in the first step is $5 \mu\text{m}$ thick.

8. Method according to one or more of claims 1 to 7, characterized in that the Ti or TiAl6V4 layer applied in the first step is between 1 and $5 \mu\text{m}$ thick.

9. Method according to one or more of claims 1 to 8, characterized in that the hydroxyapatite is sprayed onto the Ti or TiAl6V4 coating applied in the first step.

10. Method according to one or more of claims 1 to 9, characterized in that the hydroxyapatite is applied to the Ti or TiAl6V4 coating by plasma coating.

11. Method according to one or more of claims 1 to 10, characterized in that the ceramic component is an aluminum oxide ceramic.

12. Method according to one or more of claims 1 to 11, characterized in that the ceramic component is a medical component.

13. Method according to one or more of claims 1 to 11, characterized in that the ceramic component is a prosthesis.

14. Hydroxyapatite coated ceramic component manufacturable according to one or more of the foregoing claims.

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