



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
29.04.2015 Bulletin 2015/18

(51) Int Cl.:
B22F 3/11 (2006.01) **B22F 3/22** (2006.01)
B22F 7/04 (2006.01) **C23C 24/00** (2006.01)

(21) Application number: **13005046.1**

(22) Date of filing: **22.10.2013**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(71) Applicant: **Linde Aktiengesellschaft**
80331 München (DE)

(72) Inventors:
• **Malas, Akin**
85757 Karlsfeld (DE)
• **Foret, Pierre**
80796 München (DE)

(74) Representative: **Gellner, Bernd et al**
Linde AG
Patente und Marken
Dr.-Carl-von-Linde-Strasse 6-14
82049 Pullach (DE)

(54) **Method for modifying the surface structure of a metal body**

(57) Method for modifying the surface structure of a metal body (100), comprising the following steps:
- application of a paste (110), comprising a binder (112) and a metal powder (114) to a surface of the metal body (100),

- subjecting the metal body to a first heat treatment to remove the binder from the paste and to sinter the metal powder onto the surface of the metal body to provide a modified metal body surface.

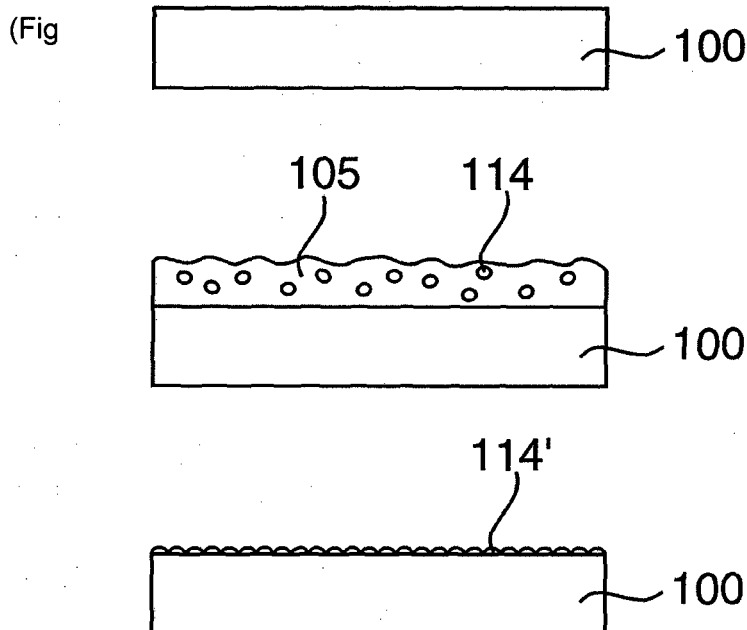


Fig. 1

Description

[0001] The invention relates to a method for the modification of the surface structure of a metal body, more preferably for increasing surface porosity.

[0002] Such a method is known from EP 1 935 508 A1.

[0003] Stainless austenitic steels after their manufacture frequently have a smooth metal surface without structure and can therefore be frequently wetted only with difficulty. This wetting characteristic has e.g. a major influence on the adhesion and durability of paints and coatings, i.e. the application of durable coatings on such surfaces proves difficult.

[0004] In medical technology, biocompatible materials such as for example titanium are used for producing implants. With such implants, too, a surface that is too smooth also results in problems such as poor contact between the implant and the human tissue in which the implant is implanted.

[0005] In the paper "Porous Metal Tubular Support for Solid Oxide Fuel Cell Design", Electrochemical and Solid-State Letters Volume 9, No. 9, Pages A427 to A429, June 2006, a method for the manufacture of a porous nickel tube is described. To this end, the nickel tube is initially oxidized and subsequently reduced in a hydrogen atmosphere.

[0006] The formation of nickel pores at certain temperatures and after certain times is assumed to be due to special relations between the thermal stability of the NiO and the diffusion rates of nickel and oxygen atoms in nickel metal and in NiO.

[0007] Contrary to the oxidation of nickel, in Fe or Co containing metals, not only one oxide but more oxides of the type MO, M₂O₃ and M₃O₄, with M = Fe or Co, with different thermal stabilities are formed depending on the oxidation temperature. In addition, in Fe-based or Co-based alloys, oxides formed by alloying elements such as Cr, Mo, Mn, and Si may be formed which make the picture even more complex. During reduction, the diffusion of Fe or Co and of the alloying elements in the matrix and in the oxides creates an extremely complicated picture.

[0008] The same arguments as for Fe- or Co-based alloys also apply for other metal alloys with additions of Cr, Fe, Cu, Co, Mo, Mn and Si, and for Ta- and Ti-based alloys.

[0009] The object of the present invention therefore is to present a method for increasing the surface porosity of a metal body of a metal or a metal alloy, especially comprising at least one of the metals Fe, Cu, Co, Cr, Ti, Ta, Mo, Mn and Si.

[0010] This object is achieved through a method for the modification of the surface structure of a metal body, comprising the features of claim 1.

[0011] The present invention provides a cost effective way of superseding relatively expensive prior art methods. The method according to the invention provides a simple and highly effective way of modifying the surface

structure of a metal body. Especially, use of a paste makes it possible to apply metal powder, which constitutes a component of such a paste, to complex surface structures. Such a paste can be applied to many internal and external surfaces of components, providing an even distribution of the metal powder.

[0012] For the purpose of this disclosure, the term "paste" shall especially mean a viscous mixture or suspension of granular material (e.g. metal powder) within a background fluid (or base referred to as binder), preferably showing adhesive characteristics. The term "porosity" shall mean the fraction of the volume of voids over the total volume. Especially, the term "surface porosity" shall mean the fraction of the volume of voids within the surface layer over the total volume of the surface layer.

[0013] Advantageous embodiments of the invention are the subject matter of the dependent claims.

[0014] Advantageously, the first heat treatment, which serves, i.a. to remove the binder from the paste and thus from the surface of the metal body, is effected in such a way that the modified metal body surface has a porosity of 50% - 60%. During this process step the paste loses the binders forming a chemical sponge like solid structure holding the powders together, thereby creating a desired porosity. For many applications, such a porosity is expedient or at least sufficient. As examples for components, for which such a porosity is sufficient, it is referred to e.g. components requiring minimum mechanical strength used for aesthetical purposes.

[0015] According to a preferred embodiment of the invention, at least one further heat treatment of the surface of the metal body is performed, in order to adjust a surface porosity provided by the first heat treatment. Especially, depending on a temperature (sintering temperature) and/or pressure used for the further heat treatment, a surface porosity can be adjusted to for example 10% - 40%. Depending on the temperature of the further process the porosity can be adjusted. As is well known in the powder metal industry, increasing temperature will help particles to move towards the equilibrium therefore finally achieving non porous structures.

[0016] According to a preferred embodiment of the invention, the paste applied to the surface of the metal body is a MIM-paste. MIM-pastes are pastes, in which metal powders are combined with, for example, wax and/or plastics binders to produce a mixture, which, according to previous applications, was used in metal injection molding (MIM) processes, wherein usually such a MIM-paste is injected as a liquid into a hollow mold using plastic injection molding machines. MIM pastes contain chemicals to allow injection and the powders in the required alloy composition such as CATAMOLD® powders developed by BASF containing 0.4%C, 2%Ni and remaining Iron.

[0017] Preferably, the first and/or at least one further heat treatment is provided as a furnace treatment. Such furnace treatments are especially advantageous in connection with removal of binders as used in MIM-pastes,

and also to perform sintering. In sintering, the metal powder provided on the surface of the metal body is heated to temperatures, which are not high enough to melt the metal body, but at which metal particles bind together and to the metal work piece.

[0018] Typically, furnace atmospheres containing nitrogen (or argon) plus hydrogen will be used. A hydrogen content of between 1 and 100% can be required or expedient, depending on the alloy content. E.g. an alloy containing high chromium will need hydrogen contents higher than 75% or alloys containing copper may require as low as 1% hydrogen in the inert mixtures. The temperature ranges used in the process will typically lie between 500 and 1200°C depending on the alloy paste used for the particular application. The temperature can be advantageously determined by taking into consideration the melting point of the alloy being used.

[0019] The method according to the invention provides a low cost surface coating opportunity. By adjusting surfaces to a desired porosity, and thus a higher surface area, it is possible to provide the surfaces of metal bodies with higher heat flux capabilities. Also, increase of nucleation sites will improve the pool boiling effects of the surface compared to untreated materials.

[0020] Also, it is possible to use the method according to the invention in connection with brazing applications for heat exchanger materials. The MIM pastes can actually be used in combination with brazing pastes at reduced brazing temperatures. This will provide proper joining of sheets forming the heat exchangers by employing the proper brazing pastes. These will melt and form the braze joint, whereas MIM pastes will basically sinter at these temperatures on the internal and external surfaces of the heat exchangers. Thus, surfaces with increased porosity and thus increased surface area are formed, whereby the heat exchanging capacity can be significantly enhanced.

[0021] Advantageously, the first and/or at least one further heat treatment are performed in a defined gas atmosphere. The furnace atmosphere will contain reducing agents for metal oxides, thereby facilitating the removal of the oxides and thus assisting pure metal to pure metal powder surface contact and increasing the sintering capability.

[0022] Advantageous applications for the method according to the invention are, for example, heat exchangers, boilers and medical implants.

[0023] Advantageously, the metal body comprises at least one of the metals Fe, Cu, Co, Cr, Ti, Ta, Mo, Mn and Si.

[0024] The invention will now be further explained referring to the accompanying figures. Herein,

Figure 1 schematically shows the application of the invention to a metal body made of steel, and Figure 2 shows a diagram according to a preferred embodiment of the method according to the invention.

[0025] In Figure 1, a metal body (especially made of steel) is shown in various states, and designated 100. Initially, (see upper image) the metal body is its uncoated state. Herein, a surface porosity is typically too low for numerous applications.

[0026] In the middle image, a paste 105 has been applied to the surface of the metal body, comprising a binder 110 and metal particals 114.

[0027] In the lower image, the metal body 100 is shown after a heat treatment according to the invention, i.e. wherein the binder 110 has been removed by means of a heat treatment such as a furnace operation, and the metal particals 114 have sintered onto the surface of the metal body 100, here designated 114'.

[0028] A flow diagram of a preferred embodiment of the method of the invention is shown in Figure 2. Here, in a step 200 a metal body is provided, and coated with a paste comprising a binder and a metal powder, preferably an MIM-paste (step 210).

[0029] In a subsequent step 220, the metal body together with the paste is subjected to a first heat treatment, wherein the binder is removed from the paste and thus from the surface of the metal body, and the metal powder contained in the paste is sintered onto the surface of the metal body to provide a modified metal body surface.

[0030] Preferably, after step 220, the modified metal body surface has a porosity of 50% - 60%.

[0031] In a subsequent step 230 the metal body is subjected to a further heat treatment, by means of which the porosity of the surface of the metal body is modified to 10% - 40%.

Claims

1. Method for modifying the surface structure of a metal body (100), comprising the following steps:
 - application of a paste (110), comprising a binder (112) and a metal powder (114) to a surface of the metal body (100),
 - subjecting the metal body (100) to a first heat treatment to remove the binder from the paste and to sinter the metal powder onto the surface of the metal body (100) to provide a modified metal body surface.
2. Method according to claim 1, wherein the first heat treatment is effected in such a way that the modified metal body surface has a porosity 50% - 60%.
3. Method according to claim 1 or claim 2, comprising at least one further heat treatment of the surface of the metal body (100) in order to adjust a surface porosity generated by the first heat treatment.
4. Method according to claim 3, wherein the at least one further heat treatment, especially one second

heat treatment, is effected in such a way that the modified surface of the metal body has a porosity of 10% - 40%.

5. Method according to any one of the preceding claims, wherein the paste (110) applied to the surface of the metal workpiece (100) is a MIM-paste. 5
6. Method according to any one of the preceding claims, wherein the first and/or the at least one further heat treatment is are furnace treatments. 10
7. Method according to any one of the preceding claims, wherein the first and/or the at least one further heat treatment is are performed in a defined gas atmosphere. 15

20

25

30

35

40

45

50

55

(Fig

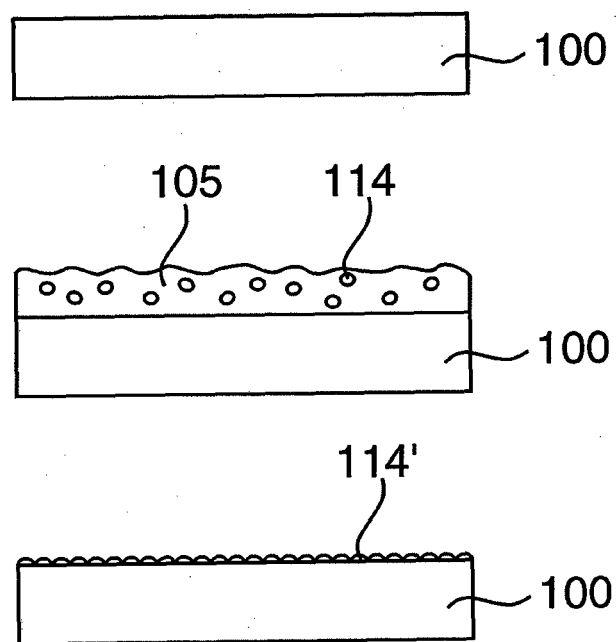


Fig. 1

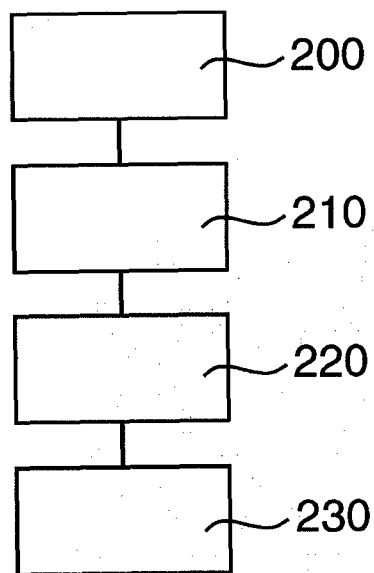


Fig. 2



EUROPEAN SEARCH REPORT

Application Number
EP 13 00 5046

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 3 855 638 A (PILLIAR R) 24 December 1974 (1974-12-24) * column 7, line 29 - line 45 * * column 8, line 15 - line 20 * * examples *	1-7	INV. B22F3/11 B22F3/22 B22F7/04 C23C24/00
X	US 2001/033804 A1 (AN JUNG SOO [KR]) 25 October 2001 (2001-10-25) * example 1 *	1,5-7	
A		2-4	
X	EP 1 229 599 A2 (SANYO ELECTRIC CO [JP]) 7 August 2002 (2002-08-07) * example 1 *	1,5-7	
A		2-4	
X	US 2004/124231 A1 (HASZ WAYNE CHARLES [US] ET AL) 1 July 2004 (2004-07-01) * paragraph [0016] * * paragraph [0036] * * examples *	1,5-7	
A		2-4	
A,D	EP 1 935 508 A1 (LINDE AG [DE]) 25 June 2008 (2008-06-25) * the whole document *	1-7	TECHNICAL FIELDS SEARCHED (IPC) B22F C23C B23K
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 28 March 2014	Examiner Morra, Valentina
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

1
EPO FORM 1503 (03.02) (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 13 00 5046

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-03-2014

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3855638	A	24-12-1974	CA 962806 A1	18-02-1975
			CH 540044 A	15-08-1973
			DE 2127843 A1	16-12-1971
			FR 2095854 A5	11-02-1972
			US 3855638 A	24-12-1974

US 2001033804	A1	25-10-2001	JP 2001252873 A	18-09-2001
			KR 20000053707 A	05-09-2000
			TW 499348 B	21-08-2002
			US 2001033804 A1	25-10-2001

EP 1229599	A2	07-08-2002	CN 1369924 A	18-09-2002
			EP 1229599 A2	07-08-2002
			JP 2002231252 A	16-08-2002
			KR 20020064193 A	07-08-2002
			TW 541748 B	11-07-2003
			US 2002150821 A1	17-10-2002

US 2004124231	A1	01-07-2004	EP 1516942 A1	23-03-2005
			JP 2005133715 A	26-05-2005
			US 2004124231 A1	01-07-2004
			US 2007017958 A1	25-01-2007

EP 1935508	A1	25-06-2008	AT 491526 T	15-01-2011
			BR PI0705913 A	22-07-2008
			CA 2613079 A1	05-06-2008
			CN 101195916 A	11-06-2008
			DE 102007018062 A1	23-10-2008
			EP 1935508 A1	25-06-2008
			EP 1941950 A1	09-07-2008
			KR 20080052454 A	11-06-2008
			MY 144909 A	30-11-2011
			TW 200844261 A	16-11-2008
			US 2008131584 A1	05-06-2008

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1935508 A1 [0002]

Non-patent literature cited in the description

- Porous Metal Tubular Support for Solid Oxide Fuel Cell Design. *Electrochemical and Solid-State Letters*, June 2006, vol. 9 (9), A427-A429 [0005]