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(54) **A method for making a protective coating on a metal substrate**

(57) The method for making a protective coating on a metal substrate including nickel atoms comprises the steps of : electro-chemical deposition of an aluminum layer on the substrate using a bath consisting of a ionic liquid comprising a chloroaluminate anion and an organic cation, and vacuum heating of said substrate on which

the aluminum layer has been deposited, such that nickel atoms migrate from the substrate to the aluminum layer, with the formation of a nickel-aluminum alloy-based protective coating.

Description

[0001] The present invention relates to a method for making a protective coating on a metal substrate including nickel atoms.

[0002] This metal substrate is particularly a turbine blade for use in the aeronautic field or in gas plants for producing electric power. At the high operating temperatures of the turbines of this kind, said coating acts as a barrier against substrate oxidation, as well as a "bond coat" for any possible subsequent coating of one or more further protective layers.

[0003] Said protective layer is known to be obtained by means of rather complicated and expensive methods, particularly the "chemical vapor deposition" (CVD).

[0004] The object of the present invention is to provide a method as stated in the preamble of the present description, which results in reduced energy consumption and is environment-friendly.

[0005] According to the invention, this object is achieved by means of a method comprising the steps of

- electro-chemical deposition of an aluminum layer on said substrate using a bath consisting of an ionic liquid comprising a chloroaluminate anion and an organic cation, and
- vacuum heating of said substrate on which the aluminum layer has been deposited, such that nickel atoms migrate from said substrate to the aluminum layer, with the formation of a nickel-aluminum alloy-based protective coating.

[0006] The inventive method has the advantages of not requiring high temperatures or the use of dangerous gases and expensive plants, for being implemented.

[0007] The turbines coated by means of the inventive method has an improved energy performance. This improvement - though poor in absolute terms - is nevertheless very significant in view of the long operating life of a gas turbine. For example, an increase as low as 1 % in the performance of a 50 MW turbine may result in about 1000 tons of gas saved per year, which corresponds to about 200.000 Euro saved per year at present prices. The decrease of fuel consumption further results in the additional advantage of reducing the emission of undesired substances, such as nitrogen and carbon dioxide.

[0008] The metal substrate being used preferably contains at least 10% by weight of nickel and can be particularly a nickel-based super-alloy, for example one of those that are commercially known as Hastelloy, Inconel, Waspaloy, Rene (e.g. Rene 41, Rene 80, Rene 95, Rene 104), Haynes, Incoloy, MP98T, TMS and the like.

[0009] The ionic liquid is for example a chloroaluminate of imidazole, pyridinium or ammonium.

[0010] Advantageously, the electrochemical deposition step is carried out at a temperature ranging between 20 and 50 °C using a current density ranging between 0,5 and 2,5 A/dm², whereas the vacuum heating step is

carried out at a temperature ranging between 900 and 1150 °C and at a pressure ranging between $1 \cdot 10^{-5}$ and $133 \cdot 10^{-5}$ Pa.

[0011] Typically, the aluminum layer deposited on the substrate can have a thickness ranging between 10 and 100 μm.

[0012] An exemplary embodiment of the method according to the invention will be now provided by way of non-limiting illustration.

EXAMPLE

[0013] A substrate consisting of a nickel alloy made of Ni 72.0%, Cr 15.5%, Fe 8.0%, Si 0.5%, Mn 1.0%, C 0.15%, Cu 0.5%, S < 0.02% is dipped in a bath of 1-butyl, 3-methyl-imidazole hepta-chloroaluminate, made of AlCl₃ and 1-butyl,3-methyl-imidazole chloride at 1:2 molar ratio. In the bath, in which an anode made of an Al plate with a purity of more than 99% is provided, an electric current is passed with a density of 1 A/dm². This electrochemical treatment is carried out for 2 hours at ambient temperature thereby causing the formation of a 25 μm-thick aluminum coating layer on the substrate.

[0014] Subsequently, the coated substrate is removed from the bath and kept for 2 hours at a temperature of 1120 °C and a pressure of $< 133 \cdot 10^{-5}$ Pa. Thereby, a coating layer made of the Al₃Ni and AlNi compounds is formed by interdiffusion.

[0015] Obviously, the principle of the invention being understood, the implementation details and the embodiments thereof may be widely changed relative to what has been described herein by way of example, without however departing from the scope of the invention as defined in the annexed claims.

Claims

1. A method for making a protective coating on a metal substrate including nickel atoms, comprising the steps of
 - electro-chemical deposition of an aluminum layer on said substrate using an ionic liquid bath comprising a chloroaluminate anion and an organic cation, and
 - vacuum heating of said substrate on which the aluminum layer has been deposited, such that nickel atoms migrate from said substrate to the aluminum layer, with the formation of a nickel-aluminum alloy-based protective coating.
2. The method according to claim 1, wherein said step of electrochemical deposition is carried out at a temperature ranging between 20 and 50 °C.
3. The method according to any preceding claim, wherein said step of electrochemical deposition pro-

vides for the use of a current density ranging between 0.5 and 2.5 A/dm².

4. The method according to any preceding claim, wherein said step of vacuum heating is carried out at a temperature ranging between 900 and 1150 °C and at a pressure ranging between $1 \cdot 10^{-5}$ and $133 \cdot 10^{-5}$ Pa. 5
5. The method according to any preceding claim, wherein said metal substrate contains at least 10% nickel by weight. 10
6. The method according to any preceding claim, wherein said metal substrate is a nickel-based super-alloy. 15
7. The method according to any preceding claim, wherein said ionic liquid is a chloroaluminate of imidazole, pyridinium or ammonium. 20
8. The method according to any preceding claim, wherein said aluminum layer has a thickness ranging between 10 and 100 μm. 25

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EUROPEAN SEARCH REPORT

Application Number
EP 09 42 5494

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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2 The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 21 April 2010	Examiner Gault, Nathalie
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Application Number
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The Hague	21 April 2010	Gault, Nathalie
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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		

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82