(19) Europäisches Patentamt
European Patent Office
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(11) **EP 2 050 526 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
22.04.2009 Bulletin 2009/17

(51) Int Cl.:
B22F 3/10 *(2006.01)* ***C21D 1/76*** *(2006.01)*
C22F 1/02 *(2006.01)*

(21) Application number: **07020457.3**

(22) Date of filing: **18.10.2007**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

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(54) **Atmosphere for sintering, annealing or hardening comprising silane or borane**

(57) The invention relates to a method for sintering or annealing of metal components in a furnace atmosphere comprising nitrogen, hydrogen, argon or any mixture of these gases, each with an addition of a gaseous hydride such as silane or borane.

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Description

[0001] The invention relates to a method for sintering or annealing of metal components in a furnace atmosphere comprising one or more of the gases nitrogen, hydrogen and argon.

[0002] Metal sintering is defined as the thermal treatment of a metal powder or a mixture of metal powders at an enhanced temperature for the purpose of increasing its strength by bonding together of the particles. During sintering atomic diffusion takes place and the powder particles are welded together. The sintering operation has normally to be carried out under a protective atmosphere in order to prevent oxidation and to promote the reduction of surface oxides.

[0003] Annealing is a heat treatment that alters the micro structure of a metal causing changes in properties such as strength and hardness.

[0004] The controlled atmosphere for sintering may be produced by blending pure nitrogen with pure hydrogen. In practice such atmospheres contain about 90% nitrogen and 10% hydrogen, sometimes with small additions of CH_4.

[0005] The controlled atmosphere for annealing may be produced by blending pure nitrogen with pure hydrogen. In practice such atmospheres contain about 95% nitrogen and 5% hydrogen for carbon steel and 75 to 100% hydrogen and rest nitrogen for stainless steel.

[0006] Beside the described synthetic nitrogen-hydrogen atmosphere, today the sintering atmosphere is often produced by the reaction of a hydrocarbon gas with a limited amount of air. Since this reaction is endo-thermic, external heat has to be supplied, and the resulting atmosphere is called endogas. That endogas may contain up to 40% of hydrogen, some carbon monoxide and carbon dioxide with the remainder being nitrogen.

[0007] In the production of metal components of good quality, consistency and properties it is advantageous to use an atmosphere with a very low oxygen content and a low dew point. For high quality applications a controlled atmosphere with an water content or oxygen content below 10 ppm or even less is required. However, the production of such pure atmospheres is elaborate and expensive.

[0008] Thus it is an object of the invention to develop an improved furnace atmosphere for sintering, hardening or annealing of metal components.

[0009] This object is achieved by a method for heat treating of metal components in a furnace atmosphere comprising one or more of the gases nitrogen, hydrogen and argon, which is characterized in that said furnace atmosphere comprises a gaseous hydride.

[0010] Gaseous hydrides such as silane are known to have a very high reactivity with oxygen containing substances or compounds. For example, at room temperature silane or mono silane undergoes a spontaneous reaction with oxygen as well as with air:

$$SiH_4 + O_2 \text{ ----> } SiO_2 + 2\ H_2$$

$$SiH_4 + 2\ H_2O \text{ ----> } SiO_2 + 4\ H_2$$

[0011] By the inventive addition of a gaseous hydride to the furnace atmosphere any oxygen or water vapour in the atmosphere reacts with the gaseous hydride. Thus it is possible to produce atmospheres with an extremely low dew point and low partial pressure of oxygen.

[0012] The invention relates to the heat treatment of metal components. The term "heat treatment" shall mean a method alter the physical or chemical properties of the metal component, in particular sintering, annealing, hardening, tempering and quenching. The term "heat treatment" applies only to processes where the heating and cooling are done for the specific purpose of altering properties intentionally.

[0013] Preferably silanes or boranes are added to the furnace atmosphere. Silanes are chemical compounds of silicon and hydrogen. The lowest silanes, mono silane with the chemical formula SiH_4 and di silane with the chemical formula Si_2H_6, are gaseous and thus are particularly suitable for the invention.

[0014] Boranes are chemical compounds of boron and hydrogen. The two smallest members of the borane group are mono borane or simply borane BH_3 and di borane B_2H_6. All these compounds are known to be very reactive with oxygen and air. Thus, these boranes are also preferably used for reducing the oxygen content in the furnace atmosphere.

[0015] The amount of the gaseous and reactive hydride which is added to the furnace atmosphere is preferably between 0.00001 % and 2 %, most preferably between 0.001 % to 0,05%. The amount of hydride is determined based on one or more of the following factors:

- quality of the atmosphere prior to the addition of the hydride,
- required level of oxygen and water in the furnace atmosphere,
- temperature within the furnace,
- amount of air ingress into the furnace.

[0016] It is advantageous to set the furnace temperature between 300 and 1500 °C for the inventive sintering or annealing application.

[0017] According to the invention it is possible to extremely decrease the oxygen and moisture level in the furnace atmosphere. Thus, it is possible to subject metals to a heat treatment process which could not have been treated in this way before. In particular, the invention allows to sinter or anneal metal components, in particular steel, without getting the material oxidized or/and discouloured.

[0018] In general, the invention is useful for the heat treatment of all kind of metals. Examples for preferred metals and metal powders to be used with the inventive method are iron, low alloyed steel, austenitic, ferritic and duplex stainless steel, copper and copper alloys, nickel and nickel alloys.

[0019] In the prior art the controlled atmosphere for annealing may be produced by blending pure nitrogen with pure hydrogen. In practice such atmospheres contain about 95% nitrogen and 5% hydrogen for carbon steel and 75 to 100% hydrogen and rest nitrogen for stainless steel.

[0020] According to a preferred embodiment of the invention a little amount of silane is added to the furnace atmosphere. In this case the hydrogen content of the atmosphere can be essentially reduced. For heat treating carbon steel the atmosphere will preferably contain pure nitrogen with addition of silane, and for the heat treatment of stainless steel the furnace atmosphere will consist of about 5-10% hydrogen, a small amount of silane and the remainder being nitrogen.

[0021] The inventive furnace atmosphere is either plain nitrogen, plain hydrogen, plain argon or a mixture of these gases blended with a gaseous hydride. Preferred furnace atmospheres are

- plain nitrogen,
- a mixture of an inert gas and hydrogen,
- a mixture of nitrogen and hydrogen,
- a mixture of argon and hydrogen,
- a mixture of nitrogen, argon and hydrogen,

wherein to each of the above atmospheres a gaseous hydride, especially silane, is added.

[0022] The mixture of nitrogen and hydrogen or the mixture of argon and hydrogen are preferably produced by blending pure nitrogen with hydrogen or pure argon with hydrogen, respectively. Nitrogen/hydrogen mixtures may also be produced by endothermic generators or ammonia dissociation.

[0023] The invention is particularly advantageous for the production of a controlled atmosphere in industrial furnaces, for example in a continuous furnace for heat treatment of metals. In such furnaces there is always some leak air entering the furnace increasing the oxygen and water vapour content of the furnace atmosphere. By the inventive addition of a gaseous reactive hydride any ingress of air and moisture reacts with the hydride so that within the furnace a high quality atmosphere is permanently guaranteed.

[0024] The inventive method is not only useful to decrease the oxygen and water vapour content in a furnace atmosphere but can also be used as a reducing agent to react with other impurities in the atmosphere, for example organic compounds.

[0025] Annealing of steel in the inventive atmosphere is a good alternative to pickling of stainless steel. By using the inventive atmosphere the amount of oxides on the surface of the steel can be essentially reduced.

[0026] Another preferred application of the invention is sintering of powder containing easily oxidised elements like chromium, manganese and silicon.

Claims

1. Method for heat treatment of metal components in a furnace atmosphere comprising one or more of the gases nitrogen, hydrogen and argon, **characterized in that** said furnace atmosphere comprises a gaseous hydride.

2. Method according to claim 1 **characterized in that** said furnace atmosphere comprises silane or borane.

3. Method according to any of claims 1 or 2 **characterized in that** the concentration of said gaseous hydride in said furnace atmosphere is between 0.00001 % and 2 %, preferably between 0.001% to 0,05%.

4. Method according to any of claims 1 to 3 **characterized in that** said sintering or annealing is carried out at a temperature between 300 and 1500 °C.

5. Method according to any of claims 1 to 4 **characterized in that** said sintering or annealing is carried out in an industrial furnace.

6. Method according to any of claims 1 to 5 **characterized in that** said furnace atmosphere essentially consists of

- nitrogen and said gaseous hydride or of
- argon, hydrogen and said gaseous hydride or of
- an inert gas and hydrogen and said gaseous hydride.

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EUROPEAN SEARCH REPORT

Application Number
EP 07 02 0457

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 5 543 127 A (KARINTHI PIERRE [FR] ET AL) 6 August 1996 (1996-08-06) * the whole document * -----	1-6	INV. B22F3/10 C21D1/76 C22F1/02

TECHNICAL FIELDS SEARCHED (IPC)

B22F
C21D
C22F

~~The present search report has been drawn up for all claims~~

Place of search	Date of completion of the search	Examiner
Munich	2 June 2008	von Zitzewitz, A

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

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EPO FORM 1503 03.82 (P04C01)

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Application Number
EP 07 02 0457

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

see annex

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 07 02 0457

The Search Division considers that the present European patentapplication does not comply with the requirements of unity of invention and relates to severalinventions or groups of inventions, namely:

1. claims: 1-6 partially

nitrogen
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2. claim: 1 partially

hydrogen
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3. claim: 1 partially

argon

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 07 02 0457

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.

02-06-2008

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5543127 A	06-08-1996	DE 69418085 D1	02-06-1999
		DE 69418085 T2	02-09-1999
		EP 0614991 A1	14-09-1994
		ES 2130373 T3	01-07-1999
		FR 2702495 A1	16-09-1994
		JP 7048102 A	21-02-1995

EPO FORM P0459

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