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#### (54) METHOD FOR CONTROLLING BRIGHT ANNEALING FURNACE

#### (57) Purpose

To establish a method for controlling a bright annealing furnace for reducing the generation of white powder therein.

#### Means

A steam partial pressure of an internal environment within a bright annealing furnace generating a boron ox-

ide is reduced to less than 1 x  $10^{-5}$  by lowering a dew point of the internal furnace environment. The dew point of the heating environment within the bright annealing furnace is lowered by introducing a gas having a hydrocarbon component, or a chemical compound having a carbon component, into the furnace.

# Description

#### **Technical field**

[0001] The present invention relates to method of controlling the generation of white powder within a bright annealing furnace.

#### **Background Art**

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[0002] White ash particles, often referred to as "white powder," are normally generated within a bright annealing furnace, when a heat-treated steel strip, such as stainless steel strip or the like, is heat treated in the internal furnace environment which is not to oxidize the surface of the strip.

**[0003]** A large volume of white powder easily accumulates in the cooling zone of the annealing furnace and inside of a cooler for cooling a furnace environment gas. Continuous operation of the furnace over a long period of time results in making the thermally low conductive white powder accumulate in and adhere to the cooler and/or other related mechanisms, thus inhibiting the performance of the cooler. A large amount of cooling water has been used in an attempt to solve the problem, but has been found not to be the desired solution due to limitations on pump capacity.

**[0004]** Moreover, because the hardness of the white powder is greater than that of the heat treated steel strip, there are cases where the steel strip is damaged as a result of excessive pressure resulting from the accumulation of the white powder on the skin-pass roller. This can adversely affect the quality of the finished product.

**[0005]** Therefore, the white powder adversely affects the cooling performance of the bright annealing furnace and also has the potential to degrade the quality of the finished product. Thus, even though the bright annealing furnace is correctly installed and operated, it has been found necessary to periodically conduct the maintenance by lowering the temperature and opening the furnace for the sole purpose of cleaning out the accumulated white powder.

[0006] The skin-pass rollers must also be removed, polished, and re-installed when this type of maintenance is conducted. Moreover, even though a reducing gas of hydrogen and nitrogen is injected into the internal furnace environment while the furnace is operating, the gradual release of oxygen atoms makes it difficult to set the residual oxygen concentration to the required value when the gas is re-injected into the furnace environment, since the internal environment is oxidized by the opening operation of the furnace for the maintenance. The operating yield of the bright annealing furnace is also significantly reduced because the furnace cannot be operated while the aforesaid maintenance is being conducted.

[0007] As noted above, a conventional bright annealing furnace exhibits the shortcoming of generating a white powder which makes it difficult to maintain the cooling performance of the furnace, reduces production efficiency due to the periodic maintenance required to remove the white powder (during which the furnace may not be operated), and adversely affects the quality of the finished product. As a result of these shortcomings, it is desirable that a method of reducing the generation of white powder is invented.

Reference Document 1 Japanese unexamined patent publication No. 10-72624

#### Disclosure of the Invention

## Shortcomings in the Prior Art

**[0008]** The inventor, having analyzed the composition of the white powder generated within a bright annealing furnace used for mass production annealing (hereafter referred to as a production furnace), bases the present invention on the discovery that the main component of the white powder is a large volume of a boron oxide compound. In regard to the process through which the boron oxide is generated, the inventor concludes, based on his research, that the generation of the boron oxide results from a relationship between the boron in the heat treated steel strip and the residual oxygen and water within the furnace. Therefore, if the generation of boron oxide can be suppressed, the previously noted problems relating to the generation of white powder can be essentially eliminated.

**[0009]** The present invention, which has been made possible as a result of the inventor's study of the prior art technology, has the purpose of suppressing the generation of white powder within a bright annealing furnace.

# Means of Resolving Shortcomings in the Prior Art

**[0010]** The method for controlling bright annealing furnace invention comprises a step that a partial pressure of the steam of the internal environment within the furnace generating the boron oxide is established at less than 1 x  $10^{-5}$ . More specifically, it is preferable that the partial pressure of the steam is established at a value less than 1 x  $10^{-5}$  by lowering a dew point of the internal furnace environment.

[0011] It is preferably to include a process wherein a gas having a hydrocarbon component is introduced into the

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internal environment of the bright annealing furnace to reduce a water vapor pressure to a value of less than  $1 \times 10^{-5}$  by lowering the dew point of the internal environment within the furnace.

**[0012]** It is preferably to include another process wherein a chemical compound having a carbon component is introduced into the internal environment of the bright annealing furnace to reduce the water vapor pressure to a value of less than  $1 \times 10^{-5}$  by lowering the dew point of the internal environment within the furnace.

#### Effect of the Invention

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**[0013]** The present invention provides a method through which the generation of boron oxide may be suppressed, the boron oxide being the causative agent of the white powder.

#### **Best Mode for Carrying out the Invention**

**[0014]** The following describes various embodiments of the bright annealing furnace control method invention with reference to the attached drawings. The invention has resulted from an understanding of the reasons for the generation of large amounts of white powder that collect and adhere to inside of a bright annealing furnace of the type where stainless steel and other like substances are heat treated in a internal environment which is not to oxidize surfaces of the substances, and is thus able to effectively suppress generation of the white power.

**[0015]** Analysis of the components of the white powder that has collected in production furnaces up to the present time has determined that the main component of the white powder is a large amount of boron oxide component. In pursuing the source of the boron generating the boron oxide, it became apparent that the volume of boron in a steel strip before heat-treating was different than the volume after heat-treating. In other words, it was observed that there was a reduction in the amount of boron in the steel strip after the heat treating process was completed in the furnace.

**[0016]** In order to determine the release and dispersion tendencies of boron in steel sheet, it was conducted a test to heat the steel sheet to 1,000°C in a hydrogen environment. In case hydrogen obtained from a hydrogen cylinder was introduced to this environment, no release or dispersion of boron was observed. The dew point of the heating environment in a general bright annealing furnace extends from -30°C to -40°C. Using the hydrogen from the hydrogen cylinder resulted in the dew point falling below -60°C, thus a temperature was much lower than that encountered in a production furnace.

[0017] The results of this test demonstrated that (1) steam partial pressure was lowered due to the low dew point, and (2) there was no oxygen source from which the boron could be oxidized. There are not any residual water component and oxygen to react with the boron in the heat-treated steel strip, thus resulting in no release and dispersion of boron.

[0018] Current production furnaces do not meet these conditions. In other words, the inventor has determined that the internal environment of a commonly used bright annealing furnace has a high dew point and residual water and

oxygen component within the furnace, factors which result in the oxygen reacting with the boron within the heat treated steel strip. Boron oxide, which is the base substance of the white powder, is thus generated.

**[0019]** Taking these facts into consideration, the inventor was able to create the invention by deducing that it would be advantageous to lower the dew point in the internal furnace environment. In other words, it would be beneficial to lower the partial pressure of the steam within the internal furnace environment.

**[0020]** Although the invention proves effective by simply lowering the dew point, there are two methods by which this can be achieved; (1) introducing a gas having a hydrocarbon component or (2) adding a chemical compound having a carbon component, to the internal furnace environment.

**[0021]** Due to the fluid state of the gas having a hydrocarbon component, the gas may be easily injected into the internal furnace environment without regard as to the type of furnace being used, thus making the invention appropriate and applicable to various types of bright annealing furnaces. In cases where a solid chemical compound having a carbon component is used, the chemical compound may simply be placed in the heating region of the bright annealing furnace when inspection or maintenance work is conducted. The methods specified by the invention are thus easily applied to a bright annealing furnace.

**[0022]** Fig. 1 is an Ellingham graph showing the Gibbs standard generated free energy  $\Delta G^{\circ}$  of the boron oxide which is the main component of the white powder. Fig. 2 is a logarithmic graph of a first embodiment below showing the relationship between the partial pressures of methane, carbon monoxide, and steam at 1,400K.

#### **First Embodiment**

**[0023]** The following will explain the method through which the gas having a hydrocarbon component is introduced to the internal oven environment. A reaction similar to that noted below is thought to occur as a result of the hydrocarbon reacting with a minute amount of water  $(H_2O)$  and oxygen  $(O_2)$  residing within the bright annealing furnace. Explaining the reaction with methane  $(CH_4)$  as an example, decomposed  $CH_4$  becomes carbon (C), and the  $H_2O$  is converted into

carbon monoxide (CO) and hydrogen (H<sub>2</sub>) as a result of an oxidation and reduction reaction. **[0024]** [Formula 1]

$$C H_4 + \frac{1}{2} O_2 \rightarrow C O + 2 H_2 \quad K_1 = \frac{[C O][H_2]^2}{[C H_4][O_2]^{1/2}} = \frac{P (C0) \cdot P (H_2)^2}{P (CH_4) \cdot P (O_2)^{1/2}} \cdots (1)$$

$$H_{2} + \frac{1}{2} O_{2} \rightarrow H_{2} O \qquad K_{2} = \frac{[H_{2}O]}{[H_{2}][O_{2}]^{1/2}} = \frac{P(H_{2}O)}{P(H_{2}) \cdot P(O_{2})^{1/2}} \cdots (2)$$

$$C H_4 + H_2 O \rightarrow C O + 3 H_2$$
 ... (1) – (2)

In this reaction,  $K_1$  and  $K_2$  are equilibrium constants. Moreover, partial pressure P ( $H_2$ ) is unrestricted at a value near 1 due the approximately 100% concentration of  $H_2$  in the internal environment of the bright annealing furnace. Even if the furnace operates with an internal environment other than pure  $H_2$  (75%  $H_2$ , 25 %  $N_2$ , for example), the nitrogen ( $N_2$ ) is not involved in the reaction. Also, of all components, the  $H_2$  component comprises almost the entire environment. Thus, if error is taken into consideration, partial pressure P ( $H_2$ ) may be considered as 1 (as in the following).

[0025] With partial pressure P (H<sub>2</sub>) being 1, converting equations (1) and (2) in Formula 1 above results in Formula 2 below.

[0026] [Formula 2]

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# [Formula 2]

 $K_1 = \frac{P(C0)}{P(CH_4) \cdot P(O_2)^{1/2}} \setminus K_2 = \frac{P(H_20)}{P(O_2)^{1/2}}$ 

from which the following is derived.

[0027] [Formula 3]

[Formula 3]

$$\frac{K_1}{K_2} = \frac{P(C0)}{P(CH_4) \cdot P(H_20)} = const(at constant temperature) \cdots (3)$$

**[0028]** For a typical temperature up to 1,120°C in a production furnace (reference taken as the highest temperature of the material in the furnace in Fig. 1), the Gibbs standard generated free energy  $\Delta G^{\circ}$  of the boron oxide shown in the Fig. 1 Ellingham diagram demonstrates that it possible to effectively suppress the generation of boron oxide if P (H<sub>2</sub>)/P (H<sub>2</sub>O), which is steam partial pressure P (H<sub>2</sub>O) in a 1 to 1 ratio with the dew point, is above approximately 1 x 10<sup>5</sup>. Therefore, equation 3 shows that, in regard to random methane partial pressure P (CH<sub>4</sub>) as shown in Fig. 2, the reduction of carbon monoxide partial pressure P (CO) has the effect of reducing steam partial pressure P (H<sub>2</sub>O) to a point below 1 x 10<sup>-5</sup> which thus makes it possible to suppress the generation of boron oxide.

**[0029]** Therefore, by lowering the dew point through the introduction of a hydrocarbon-containing gas into the internal environment of a bright annealing furnace, it thus becomes possible to essentially suppress the generation of the causative agent of the white powder.

#### **Second Embodiment**

**[0030]** The following will describe a method of introducing a chemical compound having a carbon component into the annealing furnace. The reaction is described using a solid state carbon (C) as the chemical compound. A carbonate, such as barium carbonate (BaCO<sub>3</sub>), and a solid carbon are placed in the annealing furnace to induce a reaction similar to a solid state carburizing process.

[0031] [Formula 4]

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# [Formula 4]

B a CO<sub>3</sub>
$$\stackrel{\Delta}{\rightarrow}$$
 B a O + CO<sub>2</sub>

C (solid) + CO<sub>2</sub> $\rightarrow$  2 CO

CO +  $\frac{1}{2}$  O<sub>2</sub> $\rightarrow$  CO<sub>2</sub>

... (4)

[Formula 5]

[0032] The following (equation 5) is derived from equation 4.

C (solid) 
$$+\frac{1}{2} O_2 \rightarrow CO \quad K_3 = \frac{P(C0)}{P(O_2)^{1/2}} \quad \cdots (5)$$

[Formula 6]

[0033] Equation 6 is derived from equation 5 and the previously noted K<sub>2</sub> to obtain

$$\frac{K_3}{K_2} = \frac{P(C0)}{P(H_20)} = 2.65 \times 10^2$$
 (temperature at 1400K) ...(6)

[0034] For a typical bright annealing furnace temperature up to 1,120°C, the Gibbs standard generated free energy  $\Delta G^{\circ}$  of the boron oxide shown in the Fig. 1 Ellingham diagram shows that it is possible to effectively suppress the generation of boron oxide if P (H<sub>2</sub>)/P (H<sub>2</sub>O), which is steam partial pressure P (H<sub>2</sub>O) in a 1 to 1 ratio with the dew point, is above approximately 1 x 10<sup>5</sup>. Therefore, equation 6 demonstrates that the reduction of carbon monoxide partial pressure P (CO) has the effect of reducing steam partial pressure P (H<sub>2</sub>O) to a point below 1 x 10<sup>-5</sup>, thus making it possible to suppress the generation of boron oxide.

**[0035]** Therefore, by lowering the dew point through the introduction of a chemical compound having a carbon component into the internal environment of a bright annealing furnace, it becomes possible to essentially control the generation of the causative agent of the white powder.

### **Brief Description of the Drawings**

[0036]

Fig. 1 is an Ellingham diagram showing the Gibbs standard generated free energy  $\Delta G^{\circ}$  of the boron oxide, the

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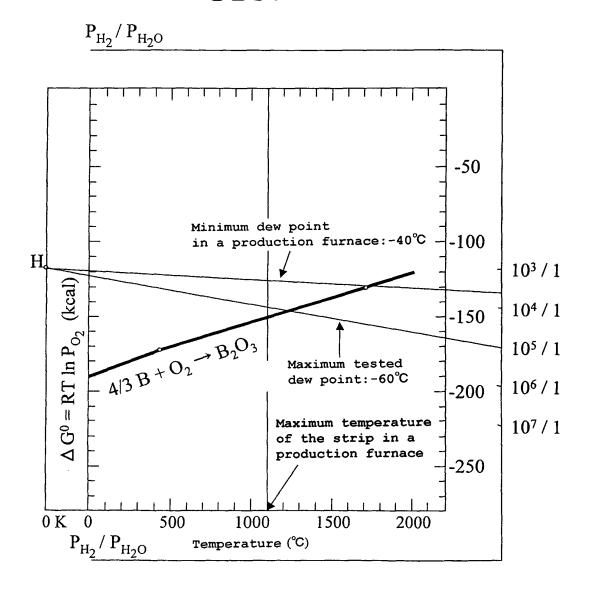
causative agent of the white powder.

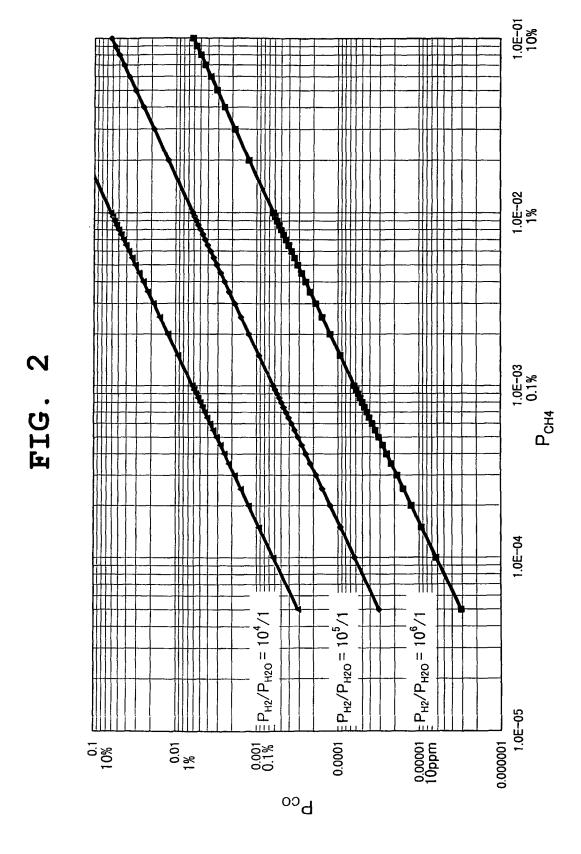
Fig. 2 is a logarithmic graph showing the relationship between the partial pressure of methane, carbon monoxide, and steam at 1,400K.

#### Claims

- 1. A method for controlling bright annealing furnace comprising a step that a partial pressure of steam within the internal environment of said furnace generating a boron oxide is reduced to a value less than 1 x 10<sup>-5</sup>.
- 2. A method for controlling bright annealing furnace according to claim 1 wherein said step of reducing the partial pressure of steam to a value less than 1 x 10<sup>-5</sup> is conducted by lowering a dew point of the internal environment within said furnace by means of an insertion of a gas having a hydrocarbon component to the internal furnace environment.
- **3.** A method for controlling bright annealing furnace according to claim 1 wherein said step of reducing the partial pressure of steam to a value less than 1 x 10<sup>-5</sup> is conducted by lowering a dew point of the internal environment within said furnace by means of an addition of a chemical compound having a carbon component to the internal furnace environment.

FIG. 1





# INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/015025

	101/012	004/013023
A. CLASSIFICATION OF SUBJECT MATTER Int.Cl <sup>7</sup> C21D1/76, C21D9/46		
According to International Patent Classification (IPC) or to both national	l classification and IPC	
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification system) Int.Cl <sup>7</sup> C21D1/76, C21D6/00, C21D9/46	assification symbols)	
Kokai Jitsuyo Shinan Koho 1971-2005 Ji	roku Jitsuyo Shinan Koho tsuyo Shinan Toroku Koho	1994-2005 1996-2005
Electronic data base consulted during the international search (name of d WPI, ELSEVIER, JOIS	data base and, where practicable, search te	erms used)
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category* Citation of document, with indication, where app	propriate, of the relevant passages	Relevant to claim No.
Y JP 10-72624 A (Nisshin Steel 17 March, 1998 (17.03.98), Par Nos. [0001] to [0004] (Family: none)	Co., Ltd.),	1-3
Y JP 2003-247787 A (Chugai Ro 0 05 September, 2003 (05.09.03) Par No. [0006] & EP 1338659 A1		1-3
Y JP 11-158559 A (Sumitomo Metaltd.), 15 June, 1999 (15.06.99), Claims; drawings (Family: none)	al Industries,	1-3
Y   Further documents are listed in the continuation of Box C.   See patent family annex.		
* Special categories of cited documents:  "A" document defining the general state of the art which is not considered to be of particular relevance  "E" earlier application or patent but published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means "p" document published prior to the international filing date but later than the priority date claimed  Date of the actual completion of the international search  "O" January, 2005 (07.01.05)	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  "&" document member of the same patent family  Date of mailing of the international search report  25 January, 2005 (25.01.05)	
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	
Facsimile No.	Telephone No.	

Form PCT/ISA/210 (second sheet) (January 2004)

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# INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/015025

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No	
Y	JP 57-35620 A (Oriental Engineering Kabushiki Kaisha), 26 February, 1982 (26.02.82), Detailed Explanation of The Invention (Family: none)	1-3	
Y	JP 53-110909 A (Oriental Engineering Kabushiki Kaisha), 28 September, 1978 (28.09.78), Detailed Explanation of The Invention (Family: none)	1-3	
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