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(54) Scale removing composition and method.

(57) Disclosed is a scale removing composition containing (A) a flux component having a melting point of 1000 °C or lower, (B) a filler comprising one or more selected from the group consisting of alkali metal or alkaline earth metal carbonates, hydroxides and oxides, and (C) a scale-attacking agent comprising one or more selected from the group consisting of halogen-containing compounds, nitrates, nitrites, sulfates, sulfites and phosphates., By applying the composition to the surface of a scale layer-having metal substrate, the scale as formed on the metal substrate to be heat-treated at a high temperature may be removed rapidly and effectively from the surface of the metal substrate by mechanical peeling treatment and/or acid-washing treatment. As a result, the production efficiency of producing steel plates and other metal products may be improved noticeably. The composition may also be applied to heat-treatment of stainless steels from which removal of scale is difficult, so that the time for acid-washing treatment may remarkably be shortened and the production efficiency may thereby be improved noticeably.

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SCALE REMOVING COMPOSITION

The present invention relates to a scale removing composition, which is coated on the surface of a metal substrate during or before heat treatment of the substrate in order that the scale as already formed on the surface of the said substrate is made easily removable due to heat of the heat treatment.

Since a metal substrate such as a high-temperature slab in continuous casting or a high-temperature coil after hot-rolled is always exposed to an aerial atmosphere, the surface thereof is extremely easily oxidized to form a metal oxide scale thereon. The scale as fomed on the surface of a metal substrate is, after cooled, removed by washing with an acid or the like. However, a scale as formed, for example, on the surface of a stainless steel during heating contains a large amount of non-iron components and is therefore dense and hard, so that removal of such a scale is extremely difficult.

Accordingly, in order to completely remove such a scale, a long time is required for washing the metal substrate with an acid to cause a problem that the efficiency of producing metal products noticeably lowers.

The present invention has been accomplished by finding a fact that a composition containing a flux component having a particular melting temperature, a filler comprising particular alkali metal or alkaline metal compounds or salts and an attacking agent comprising particular compounds or salts has a function of making a scale as formed on a metal substrate easily removable therefrom by mecahnical peeling and/or acid washing when coated on the surface of a high-temperature slab or a metal substrate during or before heat treatment thereof.

Specifically, there is provided in accordance with the present invention a scale removing composition containing:

(A) a flux component having a melting point of 1000 ° C or lower;

(B) a filler comprising one or more selected from the group consisting of alkali metal or alkaline earth metal carbonates, hydroxides and oxides; and

(C) a scale-attacking agent comprising one or more selected from the group consisting of halogen-containing compounds, nitrates, nitrites, sulfates, sulfites and phosphates.

Among the three components of constituting the scale removing composition of the present invention, the flux component (A) acts to form a glassy coat layer over the surface of a scale layer-having metal substrate, when coated over the surface of the substrate during heat treatment, due to the heat of the said substrate to rapidly melt the component (A) thereon. It also forms the same glassy coat layer when the composition is coated over a high-temperature slab in continuous casting. When the composition is coated over the surface of a metal substrate before heat treatment, the component (A) is to melt in the subsequent heat-treatment step to also form the same glassy coat layer over the substrate.

The filler component (B) in the composition has a function of an acid-permeation medium, which dissolves in an acid to improve the permeability of the acid, when the heat-treated metal substrate is washed with an acid. Accordingly, the acid as used for acid-washing may penetrate into the scale layer through the coat layer of the composition of the invention via the filler to be able to peel, dissolve and remove the coat layer along with the scale.

The scale-attacking agent (C) in the composition melts or decomposes by heat singly or along with the dissolved flux to thereby attack the scale as formed on the surface of the metal substrate to make it brittle so as to capture the resulting scale as a form of being mechanically easily peelable or of being easily removable by acid washing, such as an iron halide.

Accordingly, by applying the composition of the invention to the surface of a scale layer-having metal substrate, it is possible to rapidly and effectively remove the scale as formed on the surface of a metal substrate of being heat-treated at a high temperature, by mechanical peeling and/or acid-washing means. As a result, it is possible to noticeably improve the production efficiency in the process of producing metal products such as steel plates and the like, by the present invention.

Additionally, by applying the scale removing composition of the invention to a metal substrate the scale of which is hardly removed, such as a stainless steel under heat treatment, the time necessary for acid-washing of the metal substrate may be shortened and the production efficiency of metal products may remarkably be elevated.

PREFERRED EMBODIMENTS OF THE INVENTION

(A) Flux Components

Examples of the flux component to be in the scale removing composition of the invention include glass

compositions which contain SiO2 as an essential ingredient and additionally other oxide components of Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, B_2O_3, TiO_2, P_2O_5, ZnO, BaO, PbO and others; phosphates or borates of metals such as K, Na, Li, Ca, Mg, Mn, Al, Fe and the like; as well as boric acid and others. The component has a melting point of 1000 ° C or lower, especially falling within the range of from 400 to 800 ° C.

If it has a melting point higher than the defined range, it would hardly form a glassy coat layer on the surface of a metal substrate when the composition has been coated on the surface thereof during heat treatment and, as a result, the effect as the scale-attacking agent would lower.

As mentioned above, the flux component (A) is one to form a glassy coat layer by heat, and the content thereof is preferably from 15 to 98 % by weight, more preferably from 18 to 95 % by weight, on the basis of the three components comprising the component (A) along with the other filler component (B) and scale-attacking agent (C) which will be explained below.

(B) Filler

The filler to be employed in the present invention comprises one or more selected from the group consisting of alkali metal or alkaline earth metal carbonates, hydroxides and oxides, such as Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, $MgCO_3$, $CaCO_3$, MgO, CaO_1 NaOH, $Mg(OH)_2$and the like.

As mentioned above, the filler is employed for the purpose of dissolving in an acid during the procedure of acid-washing so as to improve the permeability of the acid into the scale layer, and the content thereof in the composition is preferably from 0 to 70 % by weight, more preferably from 3 to 68 % by weight, on the basis of the three components comprising the component (B) along with the above-mentioned component (A) and the component (C) which will be explained below.

If the content of the filler is more than the defined range, the effect of the scale attaching agent would be retarded though the acid washability could be improved.

(C) Scale-Attacking Agent

The scale-attacking agent (C) to be in the composition of the invention dissolves or decomposes by heat, as mentioned above, to attack the scale on the surface of a metal substrate to thereby make the scale layer brittle, whereby the resulting scale layer is converted into a form of being mechanically easily peelable or of being easily washed with an acid and, as a result, the layer is to be easily removed. Precisely, the agent (C) comprises one or more selected from the group consisting of halogen-containing compounds, nitrates, nitrites, sulfates, sulfites and phosphates. Examples of halogen-containing compounds include NaCl, NaBr, $CaCl_2$, K_2SIF_6, KBF_4, $Na_3AlF_5$and the like; those of nitrates include $NaNO_3$, KNO_3, $Ca(NO_3)_2$, $Mg(NO_3)_2$and the like; those of nitrites include KNO_2, $NaNO_2$and the like; those of sulfates include K_2SO_4, $KHSO_4$, Na_2SO_4, $NaHSO_4$, $CaSO_4$, $MgSO_4$; those of sulfites include K_2SO_3, $KHSO_3$, Na_2SO_3, $NaHSO_3$and the like; and those of phosphates include P_2O_4, P_2O_5, H_3PO_4, $KH_2PO_4$and the like.

The content of the scale-attacking agent in the composition is preferably from 2 to 80 % by weight, on the basis of the three components (A), (B) and (C). If it is less than 2 % by weight, the composition could not have a sufficient scale-attacking capacity so that the scale would still be tough, even after the composition has been applied thereto, and the scale layer could not be removed after acid-washing for a long period of time. On the contrafy, however, if the content of the scale-attacking agent is more than 80 % by weight, not only the scale layer but also the surface of the metal substrate below the scale layer would be corroded by the composition.

Removal of Scale

Next, the method of removing scale by the use of the above-mentioned scale removing agent of the invention will be explaiend below.

The scale removing composition of the invention, which comprises the above-mentioned components, is applied to the surface of a metal substrate already having scale thereon during or before heat treatment. Additionally, the composition may also be applied to a high-temperature slab in continuous casting. Regarding the form of the scale removing composition of the invention when it is actually used as above, the composition of itself may be used as such, or it may be dispersed in a pertinent vehicle to give a coating composition which is used as above.

After the scale removing composition of the invention has been applied to a metal substrate having a scale layer on the surface thereof during heat treatment, the flux component (A) in the composition may rapidly dissolve due to the heat of the substrate to give a glassy coat layer over the scale layer.

Alternatively, the composition may also be applied to an already scale layer-having metal substrate before heat treatment at room temperature. In the latter case, the flux component (A) in the composition coated can dissolve in the subsequent heat-treating step to also give a glassy coat layer over the scale layer.

Accordingly, the scale layer on the metal substrate is thereby made brittle due to the action of the scale-attacking agent component (C) as being in the thus formed molten glassy coat layer and is then captured in the said composition as a form of being easily removable by acid washing, such as an iron halide or the like.

The glassy coat layer of the composition which has captured the scale therein is cracked due to the difference in the thermal expansion between the metal substrate and the glassy coat layer during the cooling step to be effected after heat treatment and, as a result, it becomes easily mechanically peelable. Additionally, since the scale layer on the metal substrate after completion of heat treatment has become brittle and is therefore in the form of being easily peelable due to the action of the scale-attacking agent component (A) as mentioned above, the scale-captured glassy coat layer may be peeled off from the surface of the metal substrate by means of a mechanical scale-peeling treatment, for example, by bending the metal substrate or by roll-brushing the same.

After completion of heat treatment, the metal substrate is generally subjected to washign with a mineral acid such as HCl, H_2SO_4or the like, after the above-mentioned mechanical scale peeling treatment. By the acid-washing treatment, the glassy coat layer may easily be removed along with the scale. Precisely, by the above-mentioned acid-washing, the filler component (B) such as an alkali metal, carbonate which is in the glassy coat layer is attacked by an acid and is dissolved out to the liquid. As a result, the glassy coat layer is made brittle and mechanically easily breakable while the acid used in acid-washing is to penetrate into the inside of the glassy coat layer from the filler-dissolved site. Accordingly, as mentioned above, the scale layer on the surface of the metal substrate is corroded by the scale-attacking agent component (C) and is then made mechanically brittle or is converted into a form of being easily washed with an acid, such as an iron halide, and after all the scale is removed from the surface of the metal substrate along with the above-mentioned glassy coat layer. However, if removal of the scale-captured glassy coat layer may completely be effected by the previous mechanical peeling treatment only, the subsequent acid-washing treatment may be omitted. Alternatively, removal of the scale-captured glassy coat layer may be effected only by the acid-washing treatment without the previous mechanical peeling treatment.

As mentioned above in detail, removal of scale by acid-washing and/or mechanical peeling treatment may efficiently and rapidly be effected by the present invention.

Next, the present invention will be explained in more detail by way of the following examples, which, however, are not intended to restrict the scope of the present invention.

Preparation of Samples

Using three kinds of glass composition (a), (b) and (c) each having the composition as shown in Table 1 below, eleven kinds of samples (Nos. 1 to 11) as shown in Table 2 below were prepared.

Size of Test Sample

A test sample of SUS430 stainless steel sheet (4 mm x 50 mm x 100 mm) was used.

Acid for Acid-Washing Treatment

A 8 wt.% HCl was used as an acid for acid-washing treatment.

Table 1 (wt.%)

Ingredients	a	b	c
SiO_2		40	35
B_2O_3		20	20
Na_2O	10	25	23
K_2O	15		
Li_2O			4
CaO		10	10
P_2O_5	45		3
Al_2O_3	30	5	5

Table 2 (wt.%)

Components	Ingredients	1	2	3	4	5	6	7	8	9	10	11
Scale-Attacking Agent	NaCl	10	10	10	10	5	5		80	10		
	$CaCl_2$			20					2	10		
	NaF						20					
	Na_2SO_4										30	
	KH_2PO_4											50
Filler	$CaCO_3$	10	50	60				10	3	15		20
	MgO		20		15						10	
Flux	H_3BO_3				5							
	$Na_2B_4O_7$	10			20							
	Glass (a)	70		10	50	45			15		60	
	Glass (b)		20			50						
	Glass (c)						75	90		65		30

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EXAMPLE 1:

Ingredients of Fromulation No. 1 of Table 2 above were ground in a ball mill, and 1 g of the resulting powder was coated on the surface of a test sample and heated at 700 °C for 30 minutes. Next, the test sample was cooled and acid-treated at 80 °C for 30 seconds. As a result, the glassy coat layer formed peeled off from the test sample along with the scale to give a scale-free surface.

COMPARATIVE EXAMPLE 1:

1 g of a powder obtained by grinding the ingredients of Formulation No. 2 was coated on a test sample and heated at 750 °C for 20 minutes. The formed glassy coat layer was in the form of a semi-molten state. Next, after cooled, it was acid-treated in the same manner as in Example 1. However, only the glassy coat layer dissolved in the acid but almost all the scale layer remained.

COMPARATIVE EXAMPLE 2:

1 g of a powder obtained by griding the ingredients of Formulation No. 3 was coated on a test sample and heated at 800 °C for 20 minutes. The formed glassy coat layer was in the form of a semi-molten state. Next, after cooled, it was acid-treated in the same manner as in Example 1. However, only the glassy coat layer dissolved in the acid but almost all the scale layer remained.

EXAMPLE 2:

A test sample was first heated at 900 °C for 30 minutes, and, while hot, 0.8 to 1.0 g of a powder as obtained from Formulation No. 4 was coated over the surface scale layer of the hot sample by the use of a spraying gum. Thereafter the coated sample was spontaneously cooled to room temperature in air. After thus cooled, the surface of the test sample was observed and it was found that the formed glassy coat layer peeled off from the test sample along with the scale and therefore the scale was completely removed.

EXAMPLE 3:

1 g of a powder obtained by grinding the ingredients of Formulation No. 5 was coated on a test sample and heated at 700 °C for 30 minutes. Next, the test sample was cooled and then acid-treated at 80 °C for one minutes, whereby the formed glassy coat layer was peeled off from the surface of the test sample along with the scale to give a scale-free surface.

EXAMPLE 4:

1 g of a powder obtained by grinding the ingredients of Formulation No. 6 was coated on a test sample and heated at 800 °C for 30 minutes. Next, after cooled, the coated sample was acid-treated in the same manner as in Example 1. As a result, the glassy coat layer was completely dissolved to give a scale-free surface.

COMPARATIVE EXAMPLE 3:

1 g of a powder obtained by griding the ingredients of Formulation No. 7 was coated on a test sample and heated at 700 °G for 30 minutes. Next, the coated sample was then acid-treated in the same manner as in Example 1. As a result, almost all the glassy coat layer was dissolved in the acid, but the scale layer was not removed.

COMPARATIVE EXAMPLE 4:

1 g of a powder obtained by grinding the ingredients of Formulation No. 8 was coated on a test sample and heated at 900 °C for 30 minutes. The thus formed glassy coat layer was a semi-molten state. Next, the test sample was mechanically bend to peel the glassy coat layer and the surface of the test sample was observed. It was found that the surface was free from scale but was corroded into the inside of the steel

substrate.

EXAMPLE 5:

1 g of a powder obtained by grinding the ingredients of Formulation No. 9 was coated on a test sample and heated at 700 °C for 30 minutes. After cooled, the surface of the test sample was observed and it was found that a part of the formed glassy coat layer peeled off. The coat layer was removed by the use of a steel wool to give a substrate surface having little scale.

EXAMPLE 6:

1 g of a powder obtained by grinding the ingredients of Formulation No. 10 was coated on a test sample and heated at 650 °C for one hour. Next, after cooled, the coated sample was acid-treated in the same manner as in Example 1. As a result, the formed classy coat layer was peeled off from the metal substrate along with scale to give a scale-free surface.

EXAMPLE 7:

1 g of a powder obtained by grinding the ingredients of Formulation No. 11 was coated on a test sample and heated at 700 °C for 30 minutes. Next, after cooled, the coated sample was acid-treated in the same manner as in Example 1. As a result, the formed glassy coat layer was dissolved in the acid to give a clean surface having little scale.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A scale removing composition, which is characterized by containing:
   (A) a flux component having a melting point of 1000 °C or lower;
   (B) a filler comprising one or more selected from the group consisting of alkali metal or alkaline earth metal carbonates, hydroxides and oxides; and
   (C) a scale-attacking agent comprising one or more selected from the group consisting of halogen-containing compounds, nitrates, nitrites, sulfates, sulfites and phosphates.

2. The composition as claimed in claim 1, in which the flux component (A) comprises one or more selected from the group consisting of glass compositions which contain SiO_2 as a main component and additionally other oxide components of Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, B_2O_3, TiO_2, P_2O_5, ZnO, BaO, PbO and the like, phosphates or borates of metals of K, Na, LI, Ca, Mg, Mn, Al, Fe and the like, and boric acid, the materials of the group having a melting point of 1000 °C or lower.

3. The composition as claimed in claim 1, in which the filler (B) comprises one or more selected from the group consisting of Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, $MgCO_3$, $CaCO_3$, MgO, CaO, NaOH, $Mg(OH)_2$ and the like.

4. The composition as claimed in claim 1, in which the scale-attacking agent (C) comprises one or more selected from the group consisting of halogen-containing compounds such as NaCl, NaBr, $CaCl_2$, K_2SiF_6, KBF_4, Na_3AlF_5 and the like, nitrates such as $NaNO_3$, KNO_3, $Ca(NO_3)_2$, $Mg(NO_3)_2$ and the like, nitrites such as KNO_2, $NaNO_2$ and the like, sulfates such as K_2SO_4, $KHSO_4$, $NaSO_4$, $NaHSO_4$, $CaSO_4$, $MgSO_4$ and the like, sulfites such as K_2SO_3, $KHSO_3$, Na_2SO_{31} $NaHSO_3$ and the like, and phosphoric acid compounds such as P_2O_4, P_2O_5, H_3PO_4, KH_2PO_4 and the like.

5. The composition as claimed in claim 1, in which the content of the flux component (A) is from 15 to 98 % by weight, that of the filler (B) is from 0 to 70 % by weight and that of the scale attacking agent (C) is from 2 to 80 % by weight, on the basis of the total weight of the three components (A) , (B), (C).

6. A metal coated structure, which is composed of a metal substrate and a glassy coat layer derived from

a scale removing composition as claimed in claim 1, the glassy coat layer being formed on the surface of the substrate.

7. A method of removing scale from the surface of a metal substrate, in which a scale removing composition as claimed in claim 1 is applied to a metal substrate during or before heat treatment thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 11 2692

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 415 691 (RAMESH VYAS) * Claims 1,2,4,5; examples *	1-4	C 23 G 5/00 C 21 D 1/70
X	CHEMICAL ABSTRACTS, vol. 94, no. 13, 1981, page 276, abstract no. 107545z, Columbus, Ohio, US; & JP-A-80 125 283 (NIPPON STEEL CORP.) 26-09-1980 * Abstract *	1-7	
X	CHEMICAL ABSTRACTS, vol. 92, no. 20, May 1980, page 230, abstract no. 167493z, Columbus, Ohio, US; & JP-A-79 36 901 (NIPPON STEEL CORP.) 12-11-1979 * Abstract *	1,3,4,6,7	
X	SOVIET INVENTIONS ILLUSTRATED, week 8503, section chemistry, 27th Febraury 1985, accession no. 85-017874/03, Derwent Publications Ltd, London, GB; & SU-A-1097 714 (CEMENT IND. RES. INST.) 01-11-1982 * Abstract *	1-4,6,7	
A	CHEMICAL ABSTRACTS, vol. 83, no. 1, 14th July 1975, page 256, abstract no. 14313e, Columbus, Ohio, US; & JP-A-74 122 436 (MITSUBISHI HEAVY INDUSTRIES, LTD) 22-11-1974		TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 23 G C 21 D
A	GB-A-1 061 806 (THE BABCOCK & WILCOX CO.)		

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	04 March 91	LANDAIS A.M-R.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
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