



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 637 241 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
22.03.2006 Bulletin 2006/12

(51) Int Cl.:
B21B 1/02 (1968.09) **B21B 45/00** (1968.09)
C22C 38/00 (1974.07) **C22C 38/18** (2000.01)

(21) Application number: **04734124.3**

(86) International application number:
PCT/JP2004/007223

(22) Date of filing: **20.05.2004**

(87) International publication number:
WO 2004/103589 (02.12.2004 Gazette 2004/49)

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **22.05.2003 JP 2003144557**

(71) Applicant: **SUMITOMO METAL INDUSTRIES, LTD.**
Osaka-shi,
Osaka 541-0041 (JP)

(72) Inventors:
• **HIDAKA, Yasuyoshi;**
Sumitomo Metal Industries, Ltd.
Osaka 5410041 (JP)

• **ANRAKU, Toshiro**
c/o Sumitomo Metal Industries, Ltd
Osaka 5410041 (JP)
• **YAMAKAWA, Tomio**
c/o Sumitomo Metal Industries, Ltd
Osaka 5410041 (JP)
• **KITAMURA, Yasufumi;**
Sumitomo Metal Industries, Ltd.
Osaka 5410041 (JP)

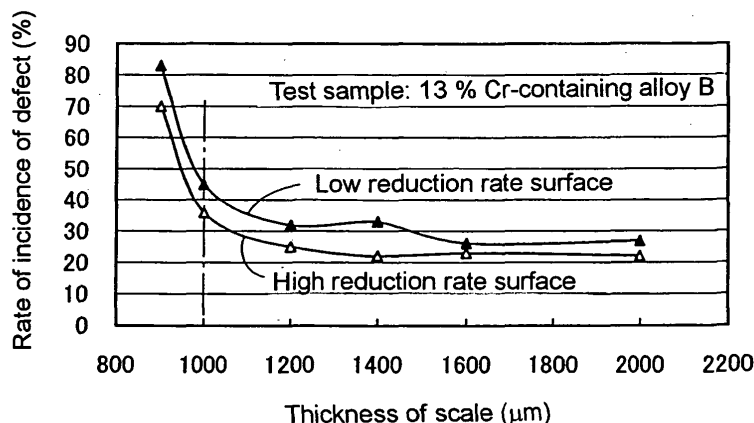
(74) Representative: **Simons, Amanda Louise**
J.A. Kemp & Co.,
14 South Square,
Gray's Inn
London WC1R 5JJ (GB)

(54) **Fe-Cr ALLY BILLET AND METHOD FOR PRODUCTION THEREOF**

(57) Fe-Cr alloy billet manufacturing method according to the present invention, since the blooming is carried out with the high reduction rate surface of the steel strip covered with a scale layer of a large area rate as 70 % or more and without the descaling applied, can reduce the indentation and inclusion of the scale. Thereby, in the case of a billet for use in seamless steel pipes being

manufactured from a steel strip of a Fe-Cr alloy, surface treatment before tube-making can be largely reduced. Thereby, when the Fe-Cr alloy billet is adopted in manufacturing seamless steel pipes, since even the Fe-Cr alloy steel pipe relatively hard to process can be manufactured at low manufacturing cost and efficiently, it can be widely applied in a field of manufacturing hot seamless steel pipes.

FIG.6



EP 1 637 241 A1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to an iron base alloy (in the specification simply referred to as "Fe-Cr alloy") billet containing Cr in the range of 5 to 17 % and a method of manufacturing the same, in more detail, an Fe-Cr alloy billet that can largely reduce a surface treatment of a billet before manufacturing of seamless steel pipes that are manufactured by blooming, and a method of manufacturing the billet.

BACKGROUND ART

[0002] In recent years, for use in oil wells and chemical industries, a demand for steel pipes made of a Fe-Cr alloy is high, and in order to manufacture it efficiently with high quality, the production according to a hot seamless steel pipe manufacturing method is increasing. However, in the manufacture of the Fe-Cr alloy seamless steel pipes, on an external surface of an obtained steel pipe, in some cases, surface defects such as scale flaws are generated.

[0003] Such surface defects, in many cases, are caused owing to scale defects on a billet surface prior to tube-making. That is, owing to descaling failure in a manufacturing process of a billet, scales are left without being removed, the scales are squeezed in or rolled together to be the scale defects, and when the billet is subjected to tube-making with the scale defects remained thereon, the surface defects are caused.

[0004] Accordingly, an improvement in a method of descaling in the manufacturing process of billet is forwarded. However, at present time, it is difficult to assuredly remove scale residue. Accordingly, in order to prevent the surface defects from occurring on a steel pipe after hot tube-making, almost all the billets are subjected to a surface inspection before tube-making, and based on the results, the surface treatment is applied.

[0005] Normally, a billet used for manufacturing the Fe-Cr alloy seamless steel pipe is, as shown in Figs. 1 and 2 that are described later, manufactured by blooming a steel strip made of the same alloy. The steel strip, after being heated to substantially 1200 °C, is processed by the blooming by means of a box type or grooved roll. At that time, with a multi-stage roll, while gradually reducing it and making a diameter of the material smaller, the steel strip is finished into a billet shape.

[0006] In the blooming, in order to remove the scales generated on the steel strip owing to heating, the descaling with high-pressure water is applied. However, frequently, a descaling failure is caused, remaining scales are squeezed in or rolled together with a surface of the steel strip, and thereby the scale defects are caused on the surface of the billet.

[0007] In order to reduce the scale defects, descaling capability, for instance, an increase in a flow rate and ejection pressure of descaling water is enhanced. However, since as the descaling proceeds, a temperature of a bulk material becomes lower, the manufacture of the billet itself is disturbed, that is, also in the enhancement of the descaling capability, there is a limit. From these situations, at present time, it is difficult to assuredly remove the scale residue on the surface of the billet.

[0008] In order to cope with the above problems, there have been proposed various countermeasures of heating equipment. Japanese Patent Application Publication No. 07-258740 proposes, a continuous heating method characterized in that when the steel strip such as a slab or billet is continuously heated with a combustion burner, the generation of oxidation scale is suppressed during heating, the steel strip after the heating is oxidized to generate scales excellent in peelability, and thereby surface defects are removed. However, when the proposed method is applied, a large-scale improvement and remodeling of a continuous heating furnace become necessary.

[0009] Furthermore, in Japanese Patent Application Publication No.57-2831, a method in which before the blooming, SiC is coated to impart oxidizability and thereby to improve the peelability of the scales is disclosed. However, according to the method disclosed here, coating equipment to coat SiC becomes necessary. Furthermore, the coating operation becomes an off-line operation, resulting in lowering the production efficiency.

[0010] Accordingly, either of the countermeasures proposed in Japanese Patent Application Publication Nos. 07-258740 and 57-2831 cannot be brought into actual operation as they are, and also from the capability thereof viewpoint, the complete descaling is difficult. Accordingly, after the manufacture of the billet, the surface treatment prior to tube-making has not yet been omitted.

[0011] As a method of surface treatment of the billet before tube-making, there is a conventional method in which flaws are detected by ultrasonic defect detection or the like and portions in concern are externally ground by use of a grinder or a peeler. However, since locations where the flaws occur and the frequency thereof are different from one billet to another billet, automated operation is difficult; as a result, the surface treatment before tube-making normally becomes an off-line operation. Accordingly, the manufacture of the seamless steel pipes from the billet is low in the production efficiency and a work environment of the billet treatment is bad.

[0012] In the case of the treatment of the billet being automated, irrespective of locations and rate of incidence of flaws, in some cases, whether flaws are present or not, it is necessary to uniformly grind all billet surfaces to remove

and treat. In this case, the yield of the billet is remarkably deteriorated.

[0013] In place of the uniform grinding of the surface of the billet like this, as to an automated treatment that specifies positions of flaws, for instance, Japanese Patent Application Publication No. 10-277912 proposes a method of treating surface flaws characterized in that after marking on a steel strip, image data thereof is collected, and from the image data, surface flaw data is extracted. However, according to the proposed method of treating surface flaws, a lot of equipment and expenses are necessary; accordingly, it is not suitable for a method of treating the billet.

[0014] As mentioned above, in manufacturing the billet for use in the manufacture of the seamless steel pipe, in order to prevent the scale defect from occurring on the surface thereof, various proposals have been submitted. However, the complete descaling is difficult, that is, the surface treatment after the manufacture of the billet has not yet been omitted.

[0015] Furthermore, in surface treatment of the billet, the operation is usually performed off-line, the production efficiency is low and work environment is bad. Even when the treatment is automated, the production yield is lowered and huge equipment expense is necessary.

[0016] Accordingly, a manufacturing method that can omit or reduce the surface treatment of the billet, in particular, a manufacturing method that can largely reduce the surface treatment of the billet after blooming for use in the manufacture of Fe-Cr alloy seamless steel pipes is demanded to be developed.

SUMMARY OF THE INVENTION

[0017] The present invention is carried out in accordance with the abovementioned problems of conventional technologies and a demand for development of a manufacturing method, and intends to provide a Fe-Cr alloy billet that can largely reduce the treatment of the billets before tube-making in the case of seamless steel pipe, being manufactured from a Fe-Cr alloy steel strip by means of the blooming, and a method of manufacturing the billet.

[0018] In view of that the descaling methods that have been used and proposed so far cannot completely remove the scale defects generated on a surface of the billet, the present inventors hit on an idea of not removing the scales, but positively covering the billet surface with the scale, thereby suppressing the surface defects.

[0019] In order to embody the idea in the Fe-Cr alloy billet, the blooming of the steel strip adopted in the process of manufacturing the Fe-Cr alloy billet was studied in detail.

[0020] Figs. 1(a) through 1(c) are diagrams for explaining a blooming process of the steel strip in a manufacturing process of the billet, and situations of change in cross section of the steel strip accompanying the blooming process. Fig. 1(a) shows a cross section of the steel strip before the blooming, Fig. 1(b) showing a cross section of the steel strip in the middle process of the blooming, and Fig. 1(c) showing a cross section of the billet after the blooming. The blooming is performed at both first and second stand. In the first stand, with a grooved roll, for instance, a box type roll and in the second stand with a grooved roll, reverse rolling is respectively carried out.

[0021] A steel strip 1 in the blooming, after being heated to substantially 1200 °C, is gradually reduced for every reduction surface at the first stand. As shown in Fig. 1(b), it is processed into the steel strip 1 having a rectangular cross section. In the next place, the steel strip 1 having a rectangular cross section is charged at the second stand, rolled so as to gradually make the cross section smaller and, as shown in Fig. 1(c), finished in a shape like a final billet 2.

[0022] Fig. 2 is a diagram of one example for explaining in detail situations of change in a shape of the cross section of the steel strip in the blooming process in the manufacture of the billet. In the blooming process shown in Fig. 2, the cross section of the steel strip 1 is gradually reduced and finally finished to a billet 2 after rolling ten passes. In the rolling process, the steel strip 1 before the blooming is placed so as being laid on the shorter side (corresponding to Fig. 1(a)), and processed so as to be the steel strip 1 having a rectangular cross section after the rolling of a seven pass at the first stand (corresponding to Fig. 1(b)). Next, the steel strip having the rectangular cross section is subjected to the eighth through tenth rolling at the second stand and finished into the final billet 2 (corresponding to Fig. 1(c)).

[0023] In a page shown in Fig. 2, the first, second, fourth, sixth, eighth and tenth passes show the rolling in the vertical reduction direction, and the third, fifth, seventh and ninth passes show the rolling in the horizontal reduction direction. In an actual rolling, the steel strip is rotated 90° to change a rolling reduction direction.

[0024] The steel strip 1 shown in Fig. 1(a) is divided into a high reduction rate surface 3 and a low reduction rate surface 4, the high reduction rate surface 3 showing a surface that becomes higher in the reduction rate in the blooming, the low reduction rate surface 4 showing other surface thereof. In the ordinary blooming, as shown in Fig. 2, the steel strip before the blooming is disposed in the longitudinal direction; accordingly, the high reduction rate surface 3 becomes a surface of shorter side in the slab-shaped steel strip, the low reduction rate surface 4 becoming a surface of longer side.

[0025] However, when by the blooming process shown in Figs. 1(a) through 1(c) and Fig. 2, the steel strip 1 is reduced for every reducing surfaces at the first stand and further rolled at the second stand to be finished into the billet 2, and, in an external surface of the billet 2, an area ratio of a portion that was the high reduction rate surface 3 to a portion that was the low reduction rate surface 4 in the steel strip 1 becomes almost the same.

[0026] That is, a cross section of the billet 2 after the blooming shown in Fig. 1(c) is equally divided into four portions of two high reduction rate surfaces 3' (portion reduced with high reduction rate of the steel strip 1) and two low reduction

rate surfaces 4' (portion reduced with low reduction rate of the steel strip 1) and a central angle θ (an angle occupying in a surface portion of the billet 2) of the high reduction rate surface 3' shown in the same drawing becomes 90° .

[0027] Fig. 3 is a perspective view showing an entire configuration of the billet after the blooming. In the rolling with the grooved roll at the first stand, a center portion of the low reduction rate surface 4 is not directly restrained by a reduction roll, or, even when restrained, is only slightly restrained compared to other portions. Accordingly, in the billet 2 after the blooming, as shown in Fig. 3, wrinkles 5 are generated in the longitudinal direction of the billet.

[0028] As the grooved roll that is used in the blooming, a box type roll, a diamond type roll or an oval type roll can be illustrated. However, the box type roll is effective in preventing the steel strip from inclining/falling. Accordingly, in view of the stability of the blooming, the box type roll is adopted in many cases.

[0029] Accordingly, on the basis of the wrinkles 5 of the billet 2 after the blooming, the high reduction rate surface 3' can be specified in a range of a central angle of $\pm 45^\circ$ ($\theta/2$) with a surface h that is orthogonal to the wrinkles 5 as a center of the billet 2.

[0030] Based on the knowledge of the high reduction rate surface of the steel strip and the billet, the manufacturing process of the Fe-Cr alloy billet was further studied in more detail and the following findings (a) through (e) were obtained.

(a) In order to prevent the scale defects from occurring on the surface of the Fe-Cr alloy billet, it is difficult to completely remove the scales generated on the steel strip before the blooming.

(b) Complete removal of the scales generated on the steel strip was given up and generation pattern of the scales which are unlikely to be squeezed in or rolled together during the blooming was studied. As a result, scales generated and adhered to the steel strip over a large covering area were found unlikely to be squeezed in or rolled together during the blooming.

(c) Specifically, in the process of manufacturing the billet, there is no need for descaling with a high-pressure water descaler.

(d) Furthermore, as the rolling of a first pass in the blooming (first stand) is begun from the high reduction rate surface of the steel strip, the generated scales can be more closely adhered to the steel strip.

(e) Still furthermore, as heating conditions (atmosphere, heating temperature and holding time) of the steel strip were adjusted, the scales are unlikely to exfoliate during the blooming and can be generated over a larger covering area of the steel strip.

[0031] The present invention was achieved based on the above findings and a Fe-Cr alloy billet according to the (1) below and methods of manufacturing the Fe-Cr alloy billet according to (2) through (4) below are gist of the invention.

(1) An Fe-Cr alloy billet, characterized in that a high reduction rate surface is covered with a scale layer with an area ratio of 70 %, 80 %, 90 % or more.

(2) A manufacturing method of the Fe-Cr alloy billet, the manufacturing method of the Fe-Cr alloy billet by the blooming, without applying the descaling of the steel strip.

(3) A manufacturing method of the Fe-Cr alloy billet, wherein in a manufacturing method of a Fe-Cr alloy billet by the blooming, after a scale having a thickness of 1000 μm or more is formed on the steel strip, without applying the descaling, the blooming is performed.

(4) In the manufacturing method of the Fe-Cr alloy billet according to (3), it is preferable to firstly reduce the high reduction rate surface of the steel strip. Furthermore, the steel strip is preferably held in an atmosphere containing 2.5 % by volume or more of steam, and at a temperature of 1200 $^\circ\text{C}$ or more for 2 hr or more to generate the scale.

[0032] In the present invention, the "Fe-Cr alloy" means an iron base alloy containing 5 to 17 % of Cr and, whereby necessary, other alloy elements such as Ni and Mo may be contained.

[0033] The "high reduction rate surface" according to the invention means, in the steel strip, a surface where when the blooming is applied to form into a billet shape, the reduction rate becomes higher, and, in the billet, a portion that was the high reduction rate surface in the steel strip before the rolling. Normally, in the steel strip having a slab shape, the high reduction rate surface becomes a shorter side surface.

[0034] The "high reduction rate surface" in the billet, as shown in Fig. 3, simply on the basis of the wrinkles, can be specified in a range where a central angle is $\pm 45^\circ$ ($\theta/2$) with a central surface orthogonal to the wrinkles with respect to a center of the billet. In order to more accurately specify the "high reduction rate surface" in the billet, results of macro-observation of a cross section of the billet can be used.

[0035] Fig. 4 is a diagram showing one example of observation results of macro-photographs of the billet cross section. In the center portion of the macro-observation, as shown with an elliptic of dotted line, segregation correlated with a direction of the cross section of the steel strip before the blooming can be observed. That is, since a position where the segregation occurs coincides with a final solidifying position of the steel strip, the final solidifying position depends on a shape of cross section made of a longer side surface 4 and a shorter side surface 3 of the steel strip.

[0036] From the observation results of the macro-photograph of the cross section shown in Fig. 4, a surface approximately in parallel with the elliptic of dotted line is the longer side surface 4, the "lower reduction rate surface", and a surface orthogonal to the elliptic of dotted line is the shorter side surface 3, the "higher reduction rate surface". Accordingly, since, in the billet, even after the rolling, the segregation correlated with a direction of cross section of the steel strip before the blooming remains, from a distribution of the segregation shown by the elliptic dotted line, the "high reduction rate surface" in the billet can be specified.

[0037] As mentioned above, the area ratios of the high reduction rate surface and the low reduction rate surface on an external surface of the billet after the manufacture become almost the same, and the cross section of the billet is equally divided into four portions of two high reduction rate surfaces and two low reduction surfaces. Accordingly, a value of an "area rate of the high reduction rate surface" (a ratio of area of scales in the high reduction rate surface) stipulated according to the invention, when multiplied by 1/2, can be replaced by a "total area rate (of billet)" (a ratio of area of scales in an entire area of the billet).

[0038] That is, in the invention, "70 % or more in the area rate of the high reduction rate surface" can be stipulated in other words as "35 % or more of total area rate", "80 % or more in the area rate of the high reduction rate surface" can be stipulated in other words as "40 % or more of total area rate", and "90 % or more in the area rate of the high reduction rate surface" can be stipulated in other words as "45 % or more of total area rate".

BRIEF DESCRIPTION OF THE DRAWINGS

[0039] Figs 1(a) through 1(c) are diagrams for explaining a blooming process of a steel strip in a manufacturing step of a billet, and situations of a change in a cross section of the steel strip accompanying therewith.

[0040] Fig. 2 is a diagram of one example for explaining in detail situations of a change in a shape of the cross section of the steel strip in the blooming process in manufacture of the billet.

[0041] Fig. 3 is a perspective view showing an entire constitution of the billet after the blooming.

[0042] Fig. 4 is a diagram showing one example of observation results of macro-photographs of the cross section of the billet.

[0043] Fig. 5 is a diagram showing relationship between a rate of incidence of defects on a surface of a billet that uses a test sample A and a thickness of scale of the steel strip.

[0044] Fig. 6 is a diagram showing relationship between a rate of incidence of defects of a surface of a billet that similarly uses a test sample B and a thickness of scale on the steel strip.

[0045] Fig. 7 is a diagram showing relationship between a rate of incidence of defects of a surface of a billet that similarly uses a test sample C and a thickness of scale of the steel strip.

[0046] Fig. 8 is a diagram showing relationship between a thickness of scale of the steel strip and a holding temperature when an amount of steam in an atmosphere of a heating furnace is varied.

BEST MODE FOR CARRYING OUT THE INVENTION

[0047] In a Fe-Cr alloy billet according to the present invention, a high reduction rate surface thereof is covered with a scale layer at an area rate of 70 %, 80 %, 90 % or more. In other words, it is covered with the scale layer at a total area rate of 35 % or more, 40 % or more or 45 % or more.

[0048] As shown in examples described later, in the case of the high reduction rate surface being covered with the scale layer at an area rate of 70 % or more, a surface treatment rate can be reduced by substantially 50 % in comparison with comparative examples where the descaling is applied.

[0049] In the Fe-Cr alloy billet according to the invention, there is tendency that the higher the area rate for the high reduction rate surface is, the lower the surface treatment rate of the billet is. For instance, in the case of the high reduction rate surface being covered with the scale layer at the area rate of 80 % or more, the treatment rate becomes substantially 30 % of that of a comparative example, and similarly in the case of being covered with the scale layer at the area rate of 90 % or more, the treatment rate becomes substantially 20 % of that of the comparative example. Accordingly, the area rate of the high reduction rate surface covered by the scale correlates well with the rate of incidence of defects on a surface of the billet.

[0050] In the manufacturing method according to the invention, in the blooming of the steel strip, in order to remove scales generated during heating of the steel strip, the descaling with a high pressure water descaler is not applied. The reason for this is that as mentioned above, since a technology for completely removing the scale has not yet been established, it is intended to avoid that the scale remains incompletely or irregularly and is squeezed in and rolled together to cause the scale flaw.

[0051] In the manufacturing method according to the invention, although whether the blooming of the steel strip is started from a high reduction rate surface or from a low reduction rate surface is not speculated, it is preferably started from the high reduction rate surface of the steel strip. This is because when the high reduction rate surface is rolled at

the first pass of the blooming, the scale generated on the steel strip can be press-bonded sufficiently onto the high reduction rate surface.

[0052] Furthermore, a reason for press-bonding the scale onto the high reduction rate surface is because when the scale is squeezed in the high reduction rate surface with the scale insufficiently remained, the scale flaw is likely to be caused. In the invention, when the scale is closely attached at the area rate of 70 % or more, in a process of the blooming after that, the scale becomes unlikely to be squeezed in a matrix of the steel strip. The tendency becomes more remarkable as the higher the area rate with which the scale covers becomes higher.

[0053] In a manufacturing method according to the invention, the scale having a thickness of 1000 μm or more that becomes a defect with difficulty in the blooming and is unlikely in causing a defect on the surface of the billet after the manufacture is generated on the steel strip. The thickness of the scale can be obtained by controlling heating conditions (atmosphere, heating temperature and holding time) of the steel strip.

[0054] Figs. 5 through 7 are diagrams showing relationship, in the case of the descaling being not applied, between the rate of incidence of defects on a surface of a Fe-Cr alloy billet and a thickness of the scale of the steel strip. As test samples, 5 to 17 % Cr-containing alloys A, B and C shown in Table 1 are used. Fig.5 shows relationship with test sample A, Fig. 6 showing relationship with test sample B, and Fig. 7 showing relationship with test sample C, respectively.

Table 1

Test sample	Content of chemical component (mass %)								
	C	Si	Mn	P	S	Cr	Ni	Mo	Fe
A	0.18	0.25	0.5	0.015	0.007	5.0	-	-	Bal.
B	0.18	0.25	0.5	0.015	0.008	13.0	-	-	Bal.
C	0.18	0.25	0.5	0.014	0.008	17.0	-	-	Bal.

[0055] As specific conditions, test samples A, B and C are heated at a temperature of 1200 °C in an air atmosphere heating furnace with a holding time varied to alter the thicknesses of a high reduction rate surface and a low reduction rate surface of the steel strip. The test samples each are measured for the rate of incidence of defects on a surface of the billet. The reason for the air atmosphere heating furnace being set at a temperature of 1200 °C is due to the fact that the heating temperature is appropriate for reducing the deformation resistance in the blooming.

[0056] Furthermore, the measurement of the rate of incidence of defects on the surface of the billet is carried out by detecting the surface defects, after removing the scale on the billet surface by means of shot blasting, by use of a flaw detecting method with a leak detector of magnetic flux. The rate of incidence of defects is expressed in terms of a number ratio (number of billets where defects are detected/total billets number).

[0057] From results shown in Figs. 5 through 7, it is found that as the scale becomes thicker, the rate of incidence of defects decreases. When the thickness of the scale of the high reduction rate surface is 1000 μm or more, the rate of incidence of defects becomes 35 % or less, and furthermore when it is 1200 μm or more, the rate of incidence of defects becomes 25 % or less. The results, as explained in examples described later, show that the rate of incidence of defects is reduced to one half, furthermore substantially to one third that of the comparative example that is reproduced by a conventional method.

[0058] From this, in the invention, before the blooming, the thickness of the scale on the steel strip is necessarily 1000 μm or more, and furthermore desirably 1200 μm or more.

[0059] A detail of the mechanism is not clear; however, it is assumed that when the rate of incidence of defects on the billet surface is intended to be suppressed, in order to cover the billet surface stretched by the blooming with the scale layer having an area rate as large as possible, a certain amount of scale, that is, a scale thickness is effective to be secured.

[0060] Fig. 8 is a diagram showing relationship between the thickness of the scale on the steel strip and a holding temperature when an amount of steam in an atmosphere of a heating furnace is varied. In the drawing, an amount of steam contained in an atmosphere gas was varied as 0, 2.5, 10 and 20 % by volume %.

[0061] With 13 % Cr-containing alloy B shown in the Table 1 as a test sample and with an atmosphere gas of 10 % CO_2 -5 % O_2 -Bal. N_2 as a basis, a concentration of steam contained in the atmosphere gas was varied in the range of 0 to 20 %. At this time, the steel strip was heated at a temperature of 1200 °C and a holding time was varied, and a thickness of the scale generated on the steel strip was measured.

[0062] The thickness of the scale was measured by, after the steel strip was oxidized at a holding time between 1 to 6 hr, cutting a test sample followed by processing to a micro-sample further followed by observing a cross section. Furthermore, scale structures at this time are shown in Table 2.

[0063] From results shown in Fig. 8, in order to obtain a scale having a thickness of 1000 μm or more in an atmosphere

that does not contain steam, heating of substantially 6 hr is necessary. The atmosphere that does not contain steam is substantially the same as air atmosphere.

[0064] On the other hand, by allowing containing 2.5 % or more of steam in the atmosphere, an oxidation speed can be very much improved. In order to effectively obtain a thickness of 1200 μm or more, in an atmosphere containing 2.5 % or more of steam, the steel strip has only to be held for 2 hr or more at a temperature of 1200 °C.

Table 2

Steam in atmosphere (%)	Structure of scale	
	External layer scale	Internal layer scale
0 (not containing)	Fe_2O_3	FeCr_2O_4
	Fe_3O_4	Fe_3O_4
2.5 to 20	Fe_2O_3	FeCr_2O_4
	Fe_3O_4	FeO
	FeO	

[0065] As shown in Table 2, scale structures of all are constituted of two-layered structure including an external layer scale and an internal layer scale. In the invention, the external layer scale is a scale generated outside of a surface of an original steel strip and the internal layer scale is a scale generated inside of the surface of the original steel strip.

[0066] In a scale formed in an atmosphere that contains 2.5 % or more of steam, the external layer scale is made of Fe_2O_3 , Fe_3O_4 and FeO and the internal layer scale is made of FeCr_2O_4 and FeO. On the other hand, in a scale generated in an atmosphere that does not contain steam, the external layer scale is made of Fe_2O_3 and Fe_3O_4 and the internal layer scale is made of FeCr_2O_4 and Fe_3O_4 .

[0067] Although the scale structure may be any of the above modes, as a scale structure that the scale defect cannot generate more easily, ones containing FeO are preferable. This is because, owing to high deformability of FeO itself, the FeO is not likely to cause destruction such as crack even under a large pressure, and furthermore, since the high temperature hardness thereof is lower than that of the steel strip, the squeezing flaw is not likely to be caused.

[0068] For instance, Fe_2O_3 is hardly deformed, and furthermore, Fe_3O_4 , when it is deformed by stretching experimentally at a very low speed at a temperature of 800 °C or more, can be stretched but cannot cope with a deformation speed during the rolling, resulting in causing crack and peeling off. On the other hand, FeO can deform in conformity with a deformation speed during the rolling and does not cause crack.

[0069] In the case of FeO being present, FeO is preferably contained 30 % or more as a thickness in the external layer scale when a cross section is subjected to micro-observation. The thickness of FeO can be measured by observing a color tone by means of the cross section micro-observation, by mapping O_2 (oxygen) by use of EPMA or by identifying in advance a structure of the whole scale by use of X-ray diffraction.

[0070] Furthermore, when the steam concentration becomes more than 20 %, effects of a rise of the scale generation speed and an increase in FeO ratio are gradually saturated. Accordingly, in consideration of damage of a furnace wall and the like of the heating furnace, the upper limit of the steam concentration is desirably set at substantially 25 %.

[0071] In the invention, in order to secure a scale thickness on the steel strip of 1000 μm or more, a heating temperature of the steel strip is desirably set at 1200 °C or more. Furthermore, the heating temperature, from viewpoints not only of scale generation but also of processability during the blooming, is desirably set at 1200 °C or more. On the other hand, the upper limit of the heating temperature, similarly, in consideration of the damage and the like of the equipment, is desirably set at 1300 °C or less.

[0072] In the invention, in order to secure the scale thickness on the steel strip of 1000 μm or more, in the case of the heating temperature of the steel strip being set at 1200 °C or more, a holding time is preferably set at 2 hr or more.

(Example 1)

[0073] Effects that a manufacturing method of a Fe-Cr alloy billet stipulated by the present invention exhibits will be explained with reference to specific Example 1 and Example 2. Test materials were 5 to 17 % Cr-containing alloys A, B and C, and as a steel strip of starting material, a bloom CC material having a short side of 280 mm x long side of 600 mm x length of 7400 mm was used. The steel strip was subjected to heating at 1200 °C for 6 hr in an atmospheric heating furnace (not containing steam). Furthermore, after the heating of the steel strip, the manufacture was carried out under two conditions, that is, in one, the descaling was applied with a high-pressure water descaler having a pressure of 100 kg/cm^2 and in the other, the descaling was not applied.

[0074] The blooming of the steel strip was performed at the first and second stand respectively by reverse rolling. The first pass of the rolling at the first stand was differentiated by whether the high reduction rate surface was reduced or the low reduction rate surface was reduced. Thereafter, at the first stand, the steel strip was reduced to a cross sectional shape of substantially short side of 250 mm x long side of 400 mm, followed by finishing, at the second stand, into a

billet of a final size of a diameter of 225 Ø.
[0075] After the billet was manufactured, a surface scale was removed by shot blasting and flaw detection was performed by use of an NDI flaw detector due to magnetic leakage flux flaw detecting method. Here, flaws having a depth of 0.5 mm or more were detected. The flaw having a depth of 0.5 mm or more, when subjected to rolling and tubing as it is without treating, becomes a flaw on a surface of a steel tube; accordingly, it is necessary to treat a surface. A criterion was not determined on a length of defect. However, in consideration of being stretched to a final product, a defect having a small length such as several tens millimeters was checked.

[0076] The rate of incidence of defects was evaluated in terms of number ratio (number of generated defects/total number). At the last, an area rate with which the scale covers a surface of the billet was investigated. The area rate of the scale was measured in such a manner that a cross section observation sample was sampled from the high reduction rate surface of the billet for each 1 m, a length of peeled scale was observed by micro-observation, and {(average length of peeled scale in a vertical direction x average length of peeled scale in a horizontal direction) / total area} was calculated as an area rate. As the area rate of the scale, an average value of the area rates of all samples in the respective billets was used.

[0077] The frequencies of incidence of defects and the area rates of scales that cover the high reduction rate surface of the billet at this time are shown in Tables 3 through 5. Table 3 shows results of 5 % Cr-containing alloy A was used as a test sample; Table 4 shows results of 13 % Cr-containing alloy B was used as a test sample; and Table 5 shows results of 17 % Cr-containing alloy C was used as a test sample.

[0078] In Example 1, in each case where any of the test samples was used, thicknesses of scales formed on steel strips immediately after taking out of a heating furnace were substantially 1000 µm, and the scale structure was made of an external layer scale of Fe₂O₃ and Fe₃O₄ and an internal layer scale of FeCr₂O₄ and Fe₃O₄. Furthermore, thicknesses of scales covering surfaces of the billets immediately after the manufacture were 150 µm or more.

Table 3

Test No.	Blooming		State of billet			Group
	Descaling	Rolled surface at the first pass	Rate of incidence of defects (%)	Scale area rate (%)		
				High reduction rate surface	All surface of billet	
A1	Applied	Low reduction rate surface	92	50	25	Comparative example
A2	Applied	High reduction rate surface	97	48	24	
A3	Not applied	Low reduction rate surface	47	73	36.5	Inventive example
A4	Not applied	High reduction rate surface	35	83	41.5	
Note) Test sample: 5 % Cr-containing alloy A						

EP 1 637 241 A1

Table 4

Test No.	Blooming		State of billet			Group
	Descaling	Rolled surface at the first pass	Rate of incidence of defects (%)	Scale area rate (%)		
				High reduction rate surface	All surface of billet	
B1	Applied	Low reduction rate surface	97	49	24.5	Comparative example
B2	Applied	High reduction rate surface	93	47	23.5	
B3	Not applied	Low reduction rate surface	45	71	35.5	Inventive example
B4	Not applied	High reduction rate surface	33	82	41	
Note) Test sample: 13 % Cr-containing alloy B						

Table 5

Test No.	Blooming		State of billet			Group
	Descaling	Rolled surface at the first pass	Rate of incidence of defects (%)	Scale area rate (%)		
				High reduction rate surface	All surface of billet	
C1	Applied	Low reduction rate surface	94	50	25	Comparative example
C2	Applied	High reduction rate surface	98	45	22.5	
C3	Not applied	Low reduction rate surface	44	70	35	Inventive example
C4	Not applied	High reduction rate surface	32	80	40	
Note) Test sample: 17 % Cr-containing alloy C						

[0079] As shown in Tables 3 through 5, in the case of the descaling being applied in the blooming as comparative examples, the scale coverage was in the range of 45 to 50 % by the area rate of the high reduction rate surface (22.5 to 25 % in terms of the total area), the rate of incidence of defects was nearly the total number, and with the number rate of 92 to 98 % surface treatment was necessary

[0080] On the other hand, in the case of, among the inventive examples, the low reduction rate surface being rolled in the first pass, the scale coverage of the high reduction rate surface was such high as in the range of 70 to 73 % by the area rate of the high reduction rate surface (35 to 36.5 % in terms of the total area), the rate of incidence of defects were dropped as much as 44 to 47 %. That is, one half that of the comparative examples. Furthermore, when the high reduction rate surfaces were rolled at the first pass in the inventive examples, the scale coverage was such high as in the range of 80 to 83 % in the area rate of the high reduction rate surface (40 to 41.5 % in terms of the total area), and at the same time, the rate of incidence of defects was reduced to substantially one third that of the comparative examples, that is, 32 to 35 %.

[0081] From results shown in Tables 3 through 5, it is found that when the scale coverage is substantially 70 % (35 % in terms of total area rate) in the area rate of the high reduction rate surface, the rate of incidence of defects is reduced to substantially 50 % compared to the comparative example where the descaling is applied, and furthermore, when the scale coverage is substantially 80 % (40 % in terms of total area rate) in the area rate of the high reduction rate surface, the rate of incidence of defects is reduced to substantially one third compared to that of the comparative example.

[0082] This is assumed that although a detail of the mechanism is not clear, when the scale is adhered with a certain area rate close to an entire area or more, uneven scales that cause indentations or inclusions can be inhibited from

occurring.

(Example 2)

5 **[0083]** Steel strips obtained with test samples and steel strip of starting materials under the same conditions as example 1 were heated in a heating furnace. At this time, a moistening device was connected to the atmospheric furnace to vary an atmosphere in the furnace, and heating was carried out at 1200 °C for 6 hr.

10 **[0084]** The conditions of the blooming after the heating and measurement conditions of the rate of incidence of defects and area rate with which scales cover after the manufacture of billets were set as the same as that of (Example1), and thereby an influence that the heating atmosphere affects on the rate of incidence of defects of the billet was investigated. Results of investigation are shown in Tables 6 through 8.

15 **[0085]** In results of investigation, Table 6 shows results when 5 % Cr-containing alloy A was used as a test sample, Table 7 shows results when 13 % Cr-containing alloy B was used as a test sample, and Table 8 shows results when 17 % Cr-containing alloy A was used as a test sample. In each of cases where the above test samples were used in Example 2, a thickness of the scale that covers the surface of the billet was 150 μm or more.

20

25

30

35

40

45

50

55

Table 6

Test No.	Blooming			State of billet			Group
	Descaling	Surface rolled at the first pass	Steam in atmosphere (%)	Rate of incidence of defect (%)	Area rate of scale (%)		
					High reduction rate surface	All surface of billet	
A5	Not applied	High reduction rate surface	0	35	83	41.5	Inventive example
A6	Not applied	High reduction rate surface	2.5	22	90	45	
A7	Not applied	High reduction rate surface	5	21	92	46.5	
A8	Not applied	High reduction rate surface	10	19	95	47.5	
A9	Not applied	High reduction rate surface	20	20	93	46.5	
A10	Not applied	Low reduction rate surface	0	47	73	36.5	
A11	Not applied	Low reduction rate surface	2.5	31	81	40.5	
A12	Not applied	Low reduction rate surface	20	30	83	41.5	
A13	Applied	High reduction rate surface	0	97	48	24	\$

Note) Test material: 5 % Cr-containing alloy A.
 \$ denotes Comparative example.

Table 7

Test No.	Blooming			State of billet			Group
	Descaling	Surface rolled at the first pass	Steam in atmosphere (%)	Rate of incidence of defect (%)	Area rate of scale (%)		
					High reduction rate surface	All surface of billet	
B5	Not applied	High reduction rate surface	0	33	82	41	Inventive example
B6	Not applied	High reduction rate surface	2.5	24	90	45	
B7	Not applied	High reduction rate surface	5	21	90	45	
B8	Not applied	High reduction rate surface	10	22	94	47	
B9	Not applied	High reduction rate surface	20	22	93	46.5	
B10	Not applied	Low reduction rate surface	0	45	71	35.5	
B11	Not applied	Low reduction rate surface	2.5	30	81	40.5	
B12	Not applied	Low reduction rate surface	20	30	83	41.5	
B13	Applied	High reduction rate surface	0	93	47	23.5	

Note) Test material: 13 % Cr-containing alloy B.

\$ denotes Comparative example.

Table 8

Test No.	Blooming			State of billet			Group
	Descaling	Surface rolled at the first pass	Steam in atmosphere (%)	Rate of incidence of defect (%)	Area rate of scale (%)		
					High reduction rate surface	All surface of billet	
C5	Not applied	High reduction rate surface	0	32	80	40	Inventive example
C6	Not applied	High reduction rate surface	2.5	22	90	45	
C7	Not applied	High reduction rate surface	5	21	92	46.5	
C8	Not applied	High reduction rate surface	10	19	95	47.5	
C9	Not applied	High reduction rate surface	20	20	93	46.5	
C10	Not applied	Low reduction rate surface	0	44	70	35	
C11	Not applied	Low reduction rate surface	2.5	31	81	40.5	
C12	Not applied	Low reduction rate surface	20	30	83	41.5	
C13	Applied	High reduction rate surface	0	98	45	22.5	\$

Note) Test material: 17 % Cr-containing alloy C
\$ denotes Comparative example.

[0086] As shown in Tables 6 through 8, it is found that in the inventive examples, as the concentration of steam in the atmosphere increases, the area rate with which the scale covers the high reduction rate surface increases and at the same time the rate of incidence of defects of the billet decreases. This is because a content of steam increases, the scale grows thicker on the steel strip and at the same time FeO that is unlikely to be squeezed in a mother material during the blooming is much generated.

[0087] Among the inventive examples that use the respective test samples, as shown in test Nos. A8 and A9, B8 and B9 and C8 and C9, when the steel strip before the blooming was held in an atmosphere containing 10 % or more of steam in the concentration at a heating temperature of 1200 °C or more for 2 hr or more to generate the scale, the area rate of the high reduction rate surface that the scale covers can be more increased to 93 % or more, and can be reduced the rate of incidence of defects of the billet 22 % or less.

INDUSTRIAL APPLICABILITY

[0088] According to a Fe-Cr alloy billet manufacturing method of the present invention, since the blooming is carried

out with the high reduction rate surface of the steel strip covered with the scale layer having a large area rate, the indentation and inclusion of the scale can be reduced. Thereby, in the case of a billet for use in seamless steel pipes being manufactured from a steel strip of a Fe-Cr alloy, surface treatment before tube-making can be largely reduced.

[0089] Accordingly, when the Fe-Cr alloy billet is adopted for tube-making of seamless steel pipes, even the Fe-Cr alloy steel pipe relatively hard to process, being able to manufacture at low manufacturing costs and with efficiently, can be widely applied in a field of manufacturing of hot seamless steel pipes.

Claims

1. A Fe-Cr alloy billet, **characterized by** a scale layer covers a high reduction rate surface with an area rate of 70 % or more.
2. A Fe-Cr alloy billet, **characterized by** a scale layer covers a high reduction rate surface with an area rate of 80 % or more.
3. A Fe-Cr alloy billet, **characterized by** a scale layer covers a high reduction rate surface with an area rate of 90 % or more.
4. A method of manufacturing a Fe-Cr alloy billet where a steel strip is subjected to blooming to manufacture the billet, **characterized in that** the blooming is applied without applying descaling of the steel strip.
5. A method of manufacturing a Fe-Cr alloy billet where a steel strip is subjected to blooming to manufacture the billet, **characterized in that** the blooming is applied without applying descaling after a scale having a thickness of 1000 μm or more is generated on the steel strip.
6. A method of manufacturing a Fe-Cr alloy billet where a steel strip is subjected to blooming to manufacture the billet, **characterized in that** a high reduction rate surface of the steel strip is firstly reduced without applying descaling after a scale having a thickness of 1000 μm or more is generated on the steel strip.
7. The method of manufacturing a Fe-Cr alloy billet according to claims 5 and 6, **characterized in that** the steel strip is held in an atmosphere containing 2.5 or more of steam by volume % at a heating temperature of 1200 °C or more for 2 hr or more to generate the scale.

FIG.1

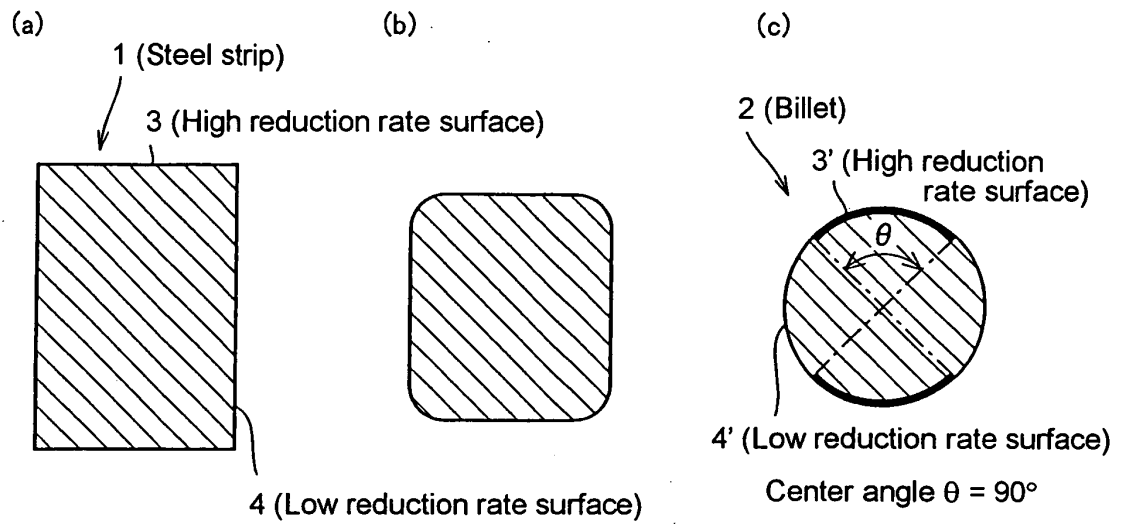


FIG.2

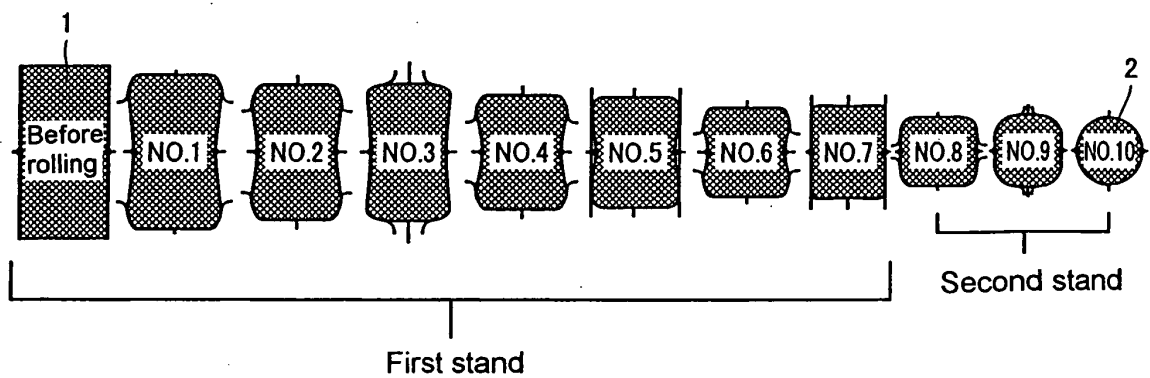


FIG.3

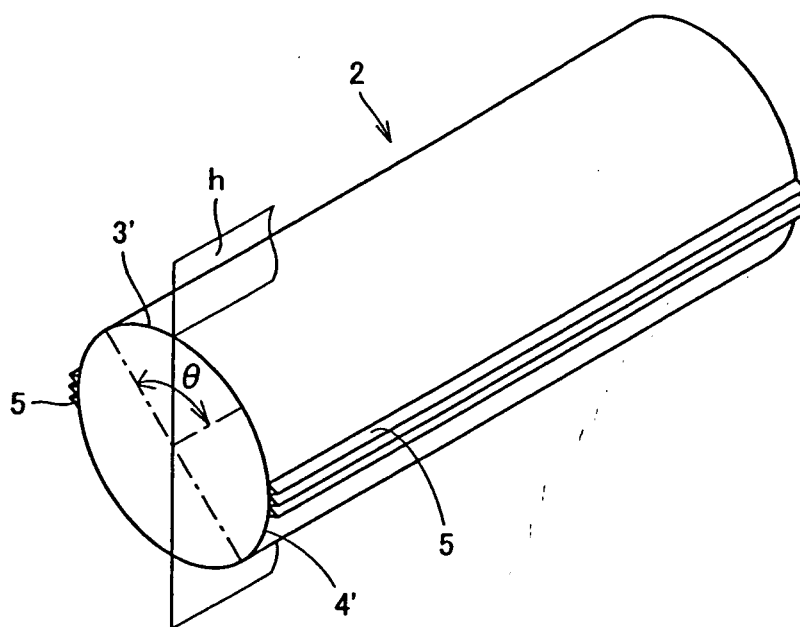


FIG.4

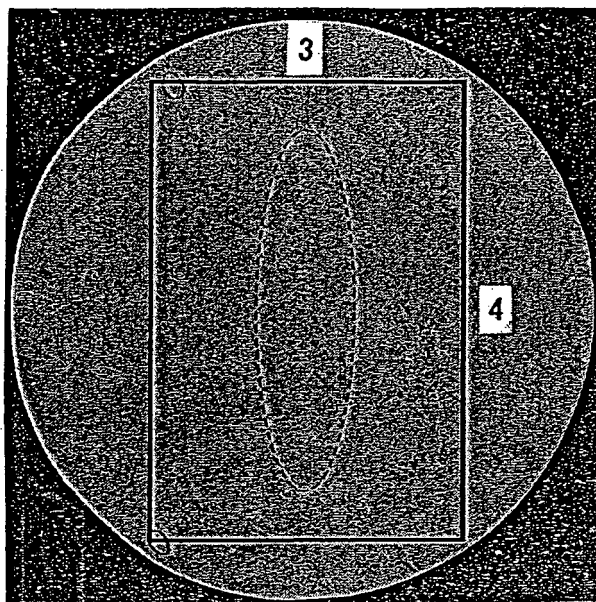


FIG.5

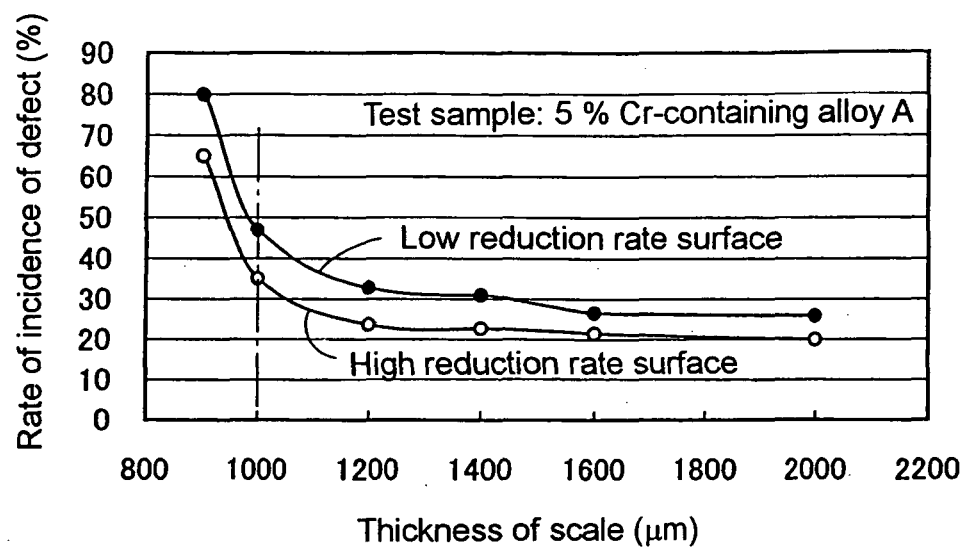


FIG.6

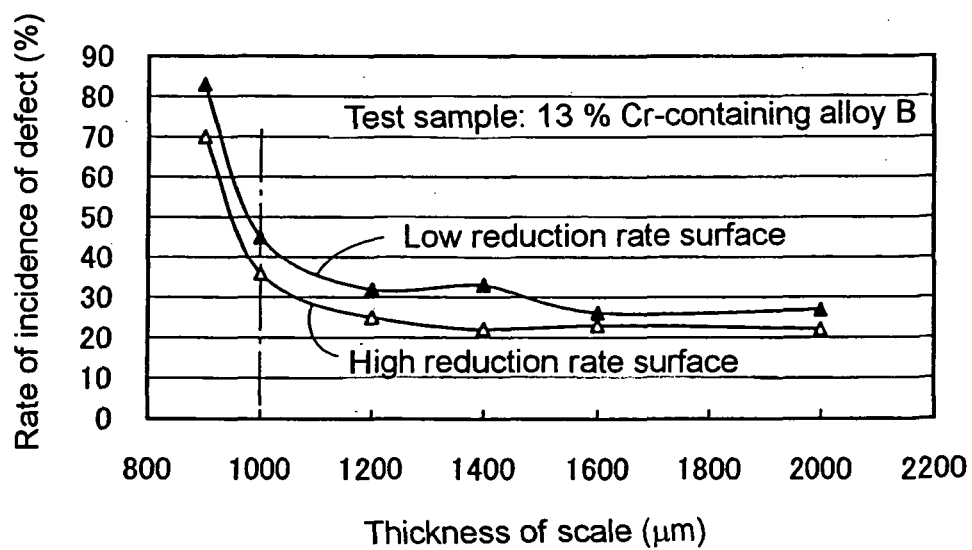


FIG. 7

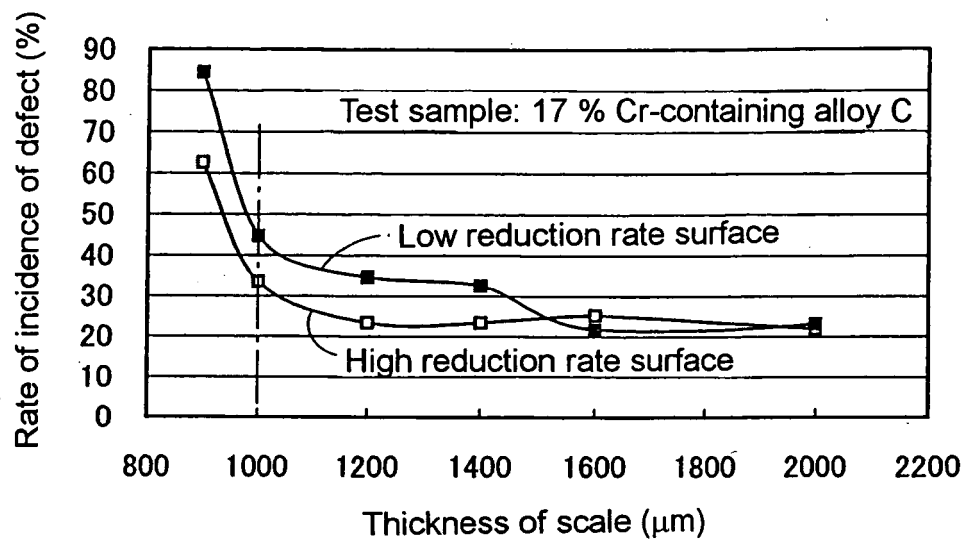
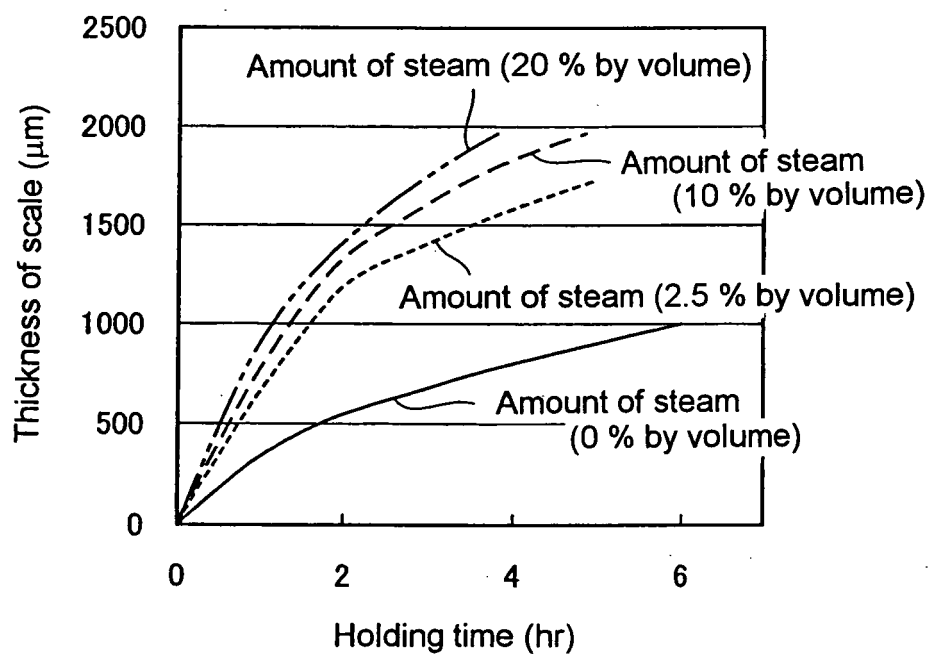


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/007223

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.⁷ B21B1/02, 45/00, C22C38/00, 38/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.⁷ B21B1/02, 45/00, C22C38/00, 38/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2004

Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 5-228507 A (Sumitomo Metal Industries, Ltd.), 07 September, 1993 (07.09.93), (Family: none)	1-7
A	JP 6-100931 A (Kawasaki Steel Corp.), 12 April, 1994 (12.04.94), (Family: none)	1-7

☐ 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

"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 the actual completion of the international search
21 September, 2004 (21.09.04)Date of mailing of the international search report
05 October, 2004 (05.10.04)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.