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(54) **TOOL STEEL FOR HOT WORKING, TOOL FOR HOT WORKING AND PLUG FOR PRODUCING SEAMLESS PIPE**

(57) A hot tool steel, having a favorable adhesion and the lubricity of an oxide scale formed on its surface and having high strength. The hot tool steel consists of C: 0.05 to 0.5%, Si: 0.1 to 1%, Mn: 1.6 to 3.5%, Ni: 0.05 to 0.5%, Mo: 2 to 5%, W: 2 to 5%, Cu: 0.05 to 0.5%, and the balance Fe and impurities. The hot tool steel prefer-

ably contains further one or more of Cr, Co, REM, Ti, Nb, V, Zr and B. The tool made of the hot tool steel is covered on its surface with the oxide scale of 50 to 1500 μm thickness. The typical example of the tool is a piercing plug for manufacturing seamless pipes.

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Description

[Technical Field]

[0001] The present invention relates to a hot tool steel, i.e., a tool steel for use in hot working, and a tool for use in hot working. The tool steel of the present invention is suitable for a material for a plug of a piercing mill, for example, a Mannesmann piercer, which is used in manufacturing seamless pipes or tubes of a high Cr alloy steel and a Ni-based alloy. Typical high Cr alloy steel is a stainless steel containing 13% or more of Cr.

[Background Art]

[0002] A traditional plug that has been used in a rolling mill for manufacturing seamless steel pipes or tubes; specifically, a piercing mill, typically represented by a Mannesmann piercer, is prepared from a steel, which has a basic composition comprised of 3%Cr-1%Ni and the balance Fe. The plug is applied with an oxide scale-formation heat treatment to its surface before being using. The above-mentioned plug is for piercing in manufacture of a seamless pipe or tube of a plain steel.

[0003] However, in a case of piercing in order to produce a seamless pipe or tube of a high Cr alloy steel such as stainless steels containing 13% or more Cr and a Ni-based alloy, the life of the plug is remarkably shortened, because the temperature and the surface pressure increase on the plug surface. For example, the plug is deformed during 1 pass for piercing of a pipe of SUS304, according to JIS.

[0004] During piercing, the main rolls of a piercer are cooled by spraying water on them. The cool water scatters up to the plug, which is heated to a high temperature just after piercing. Therefore, the surface of the plug is abruptly cooled causing partial peeling of an oxide scale on the surface and this peeled portion causes burning in subsequent piercing. Further, after the plug is used, it is usually cooled by dipping it in cool water prior to being used again, and this rapid cooling may sometimes cause a transformation-induced cracking in the base metal of the plug.

[0005] In order to produce seamless pipes or tubes comprised of a high Cr alloy steel such as a stainless steel, which contains 13% or more of Cr, and a Ni-based alloy, the following plugs for the piercer have been proposed.

(a) A plug made of a steel, which has an improved burning resistance by reducing the amount of Cr and an increased high temperature strength and adhesion with the oxide scale by adding Mo or W, etc. (Patent Document 1).

(b) A plug made of a steel which has improved lubricity, peeling resistance, and wear resistance of the oxide scale due to a large addition of Ni, and additional the high temperature strength by adding an excessive amount of Mo and/or W (Patent Document 2).

(c) A plug made of the same steel as in the plug mentioned above (b) and having improved burning resistance and lubricity by restricting the roughness of a base metal at the boundary with the oxide scale (Patent Document 3).

(d) A plug excellent in the wear resistance that is made of a steel containing Cu as an essential ingredient in addition to Ni, Cr, Co, W and/or Mo (Patent Document 4).

(e) A plug made of a steel containing Ti or Zr as an essential ingredient in addition to Cr, Ni, Co, Cu, W and/or Mo and having improved cracking resistance against rapid heating or rapid cooling during the cyclic process (Patent Document 5).

Patent Document 1: Publication of Unexamined Patent Application Sho 63-282241

Patent Document 2: Publication of Unexamined Patent Application Hei 4-74848

Patent Document 3: Publication of Unexamined Patent Application Hei 4-270003

Patent Document 4: Publication of Unexamined Patent Application Sho 57-152446

Patent Document 5: Publication of Unexamined Patent Application Sho 60-208458

[0006] However, the plug (a) has insufficient high temperature strength of the base metal and also insufficient adhesion of the oxide scale. It results in short life in a case of piercing of a long billet, that is, piercing by a long length.

[0007] As for the plugs (a) to (c), the oxide scale at the top end of the plug, where the surface pressure is the highest and the temperature increases, are melted during piercing and, therefore, lose the heat insulation effect and the wear resistance, which tends to cause melting loss and deformation at the top end of the plug.

[0008] The plugs (d) and (e) involve a problem whereby the burning resistance is poor due to an excessive Cr content and, in addition, the top end of the plug tends to cause a melting loss and deformation due to the insufficient high temperature strength.

[Disclosure of the Invention]

[Subject to be solved by the Invention]

[0009] It is the primary objective of the present invention to provide a tool steel having long life, even when it is used for hot working a material of great deformation resistance, as well as a tool manufactured from such a steel.

[0010] It is the second objective of the present invention to provide a plug for use in a piercer for manufacturing seamless pipes or tubes from a material such as a high Cr alloy steel, typically represented by a stainless steel containing 13% or more of Cr, and a Ni-based alloy, having long life and permitting minimal burning.

[Means for Solving the Problems]

[0011] The present inventors have made various studies for attaining the foregoing objectives and obtained the following findings.

(a) In a case of manufacturing a high Cr alloy steel with 13% or more of Cr content, the physical property of the oxide scale formed on the surface of a plug and the strength of the hot tool steel as a material of the plug (hereinafter referred to as "plug material") gives a significant effect on the life of the plug.

(b) A conventional material for a plug, which is used for production of a stainless steel pipe or tube, contains Cr in order to improve the high temperature strength. However, since Cr has a high affinity with oxygen, when an oxide scale-forming heat treatment for preventing the burning is applied to a plug made of a Cr-containing material, an inner scale layer containing a large amount of spinel type scale with concentrated Cr oxide is formed on the base metal side of the oxide scale. The spinel type oxide is Fe_2CrO_4 . This spinel type scale reaches about 20 to 90 % by mass of the inner layer scale.

[0012] A concentration ratio of the Cr in the inner layer scale increases as the Cr concentration in the base metal increases. In a case where Cr of 0.5% is contained in the base metal, the Cr concentration in the inner layer scale reaches about 1 to 5%.

(c) Generally, the burning tends to occur where the material to be worked and the tool contain identical kind of ingredients. Since the stainless steel contains Cr, the burning during the piercing tends to increase as the concentrated degree of Cr in the inner layer scale of the plug increases. Accordingly, for preventing the burning, it is necessary to suppress an increase of the Cr concentration in the inner layer scale.

[0013] Based on the findings described above, it may be considered that the use of a steel not containing Cr as the plug material is one of means for preventing the burning. However, Cr in the plug material is an ingredient, which is effective in improvement of the structure stability and the high temperature strength of the base metal of the plug, and also effective in improvement of the adhesion and the wear resistance of the formed oxide scale. Accordingly, it was difficult to use a steel with no addition of Cr in the existent plug material.

[0014] In view of the above, the present inventors made an earnest study of the plug, which does not contain Cr as a reinforcing element of a plug material, for use in producing stainless steel pipes and tubes, and have obtained the following findings.

(d) Mn is an element used conventionally for improvement of the structure stability. However, when combined with other alloying elements, it is extremely effective as an ingredient for a material of a plug, which is used for piercing the stainless steel as is described below.

[0015] Mn, as Cr, is an element for stabilizing austenite in order to stabilize the structure at a high temperature and it also improves the high temperature strength. Further, in a case of adding a large amount of Mn to the plug material, a spinel type scale containing Mn oxide, i.e., an inner layer scale with a high Fe_2MnO_4 content, is formed on the base metal side of the oxide scale, which is formed during the oxide scale-forming heat treatment. Fe_2MnO_4 reaches about 20 to 90 % by mass of the inner layer scale.

[0016] Since the inner layer scale comprised mainly of the spinel type scale, i.e., Fe_2MnO_4 , which contains Mn oxides, contains almost no Cr, or contains small amounts of Cr due to dilution with Mn, the burning resistance during piercing of the stainless steel billet is greatly improved. Furthermore, along with concentration of Mn, the wear resistance of the inner layer scale is improved, and wear of the oxide scale layer during piercing is decreased and therefore the life of the plug is improved.

(e) Being different from Cr, Mn is not an element for suppressing the oxidation of steels. Accordingly, an oxide scale layer of a sufficient thickness can be formed on a plug that is made of a steel, which does not contain Cr but does contain Mn as a material, by the oxide scale-forming heat treatment at a low temperature for a short time. Further, since the material tends to be oxidized more easily than the existent plug material containing Cr, the oxide scale is also formed easily on the plug surface during cooling after the completion of the piercing operation and the plug life is improved by the oxide scale.

(f) However, in a case where Mn is added in an excessive amount, the cracking sensitivity of the steel remarkably increases. Therefore it sometimes causes the cracking to the plug surface when cooling water or the like is scattered on the plug surface just after piercing. Accordingly, the content of Mn should be limited. Further, composite addition of W and Mo is necessary as the element for improving high temperature strength.

(g) The inner layer scale, containing the Mn oxide, has a melting point of 1200°C or higher and is not melted during piercing. Accordingly, the oxide does not provide a lubrication effect. Therefore, the piercing operation takes an excess amount of time, and as the surface temperature of the plug becomes higher the plug suffers from the melting loss. Accordingly, for providing the oxide scale with lubricity, optimization of the melting point of the oxide scale is necessary. Eutectic reaction between W oxide and Fe oxide takes place near 1100°C and the melting point of composite oxide of Fe and Si near 1170°C can be utilized for the optimization of the melting point. That is, in a case where the content of W and Si is appropriately controlled, formation of the W oxide and the composite oxide of Fe and Si in the oxide scale can be promoted and the melting point of the oxide scales can be optimized.

(h) The inner layer scale containing a large amount of spinel type scale, Fe_2MnO_4 , which contains Mn oxide, has lower adhesion strength and therefore causes the burning or the melting loss more easily due to the peeling of the oxide scale layer during manufacture of pipes, compared with the spinel type scale having concentrated Cr oxide, that is the inner layer scale containing a large amount of Fe_2CrO_4 .

(i) However, in a case where the metal particles are dispersed in the layer of the inner scale, the deformability of the oxide scale increases. Accordingly, the adhesion strength, which prevents the peeling of the oxide scale during piercing, is improved. In addition, the peeling of the oxide scale during alternating heating and cooling is greatly suppressed and the lubricity and the wear resistance are improved as well.

(j) The metal particles are, for example, particles of Ni, Cu and Co. Since the metal particles are not oxidized even upon applying the oxide scale-forming heat treatment to the plug made of the steel that contains them, they are dispersed and precipitated in the oxide scale layer in the form of metal particles.

(k) However, addition of an excess amount of Ni increases the martensitic transformation temperature of the base metal. Accordingly, transformation-induced cracking occurs when the plug is rapidly cooled by scattering roll cooling water, etc. and sometimes damage the plug. Accordingly, a limit is imposed on the Ni content. However, as the Ni content decreases, the adhesion strength of the oxide scale is lowered accordingly.

[0017] Further, in a case where only Cu is added, that is, with no addition of Ni, a Cu metal layer with a low melting point is formed at the boundary between the oxide scale and the base metal, and the Cu-embrittlement is induced to damage the plug surface. However, when Ni and Cu, in an appropriate amount, are added in combination, the metal particles are dispersed in the oxide scale and a metal layer is formed at the boundary between the oxide scale and the base metal forming a Ni-Cu alloy, and the Cu-embrittlement is suppressed. In addition, the adhesion of the spinel type scale containing Mn oxide, that is Fe_2MnO_4 , to the base metal, is improved.

(1) The effect of Co for improving the adhesion strength of the oxide scale is lower than Ni and an excessive additional amount of Co is necessary for improving the adhesion strength of the oxide scale. Also an excessive amount of the Co addition increases the material cost. Accordingly, it is desirable that a steel with composite addition of Ni and Cu is used as the plug material and the additional Co is an option.

[0018] The gist of the present invention accomplished on the basis of the various findings described above resides in a tool steel for use in hot working as described in the following (1), a tool for use in hot working as described in the following (2), and a plug for use in a pierce-rolling mill used for manufacturing seamless pipes to be described in the following (3). In the following description, "%" for the ingredient content represents % by mass.

(1) A hot tool steel consisting of C: 0.05 to 0.5%, Si: 0.1 to 1%, Mn: 1.6 to 3.5%, Ni: 0.05 to 0.5%, Mo: 2 to 5%, W:

2 to 5%, Cu: 0.05 to 0.5%, and the balance Fe and impurities.

(2) A tool for use in hot working made of the hot tool steel according to said (1) above, in which its surface is covered with oxide scales with 50 to 1500 μm thickness formed by the oxide scale-forming heat treatment.

(3) A plug for use in a piercing mill used for manufacturing seamless pipes, comprising the hot tool steel described in (1) above, in which its surface is covered with oxide scales of 50 to 1500 μm thickness formed by the oxide scale-forming heat treatment.

[0019] The hot tool steel described in (1) above may also contain at least one ingredient selected from at least one of the following groups (A) to (D):

(A) Cr: 0.05 to 1%;

(B) Co: 0.05 to 5%;

(C) one or more of Ti, Nb, V, Zr and B: 0.05 to 0.5% in total; and

(D) REM: 0.001 to 0.2%;

wherein REM means 17 elements including 15 lanthanoid elements from La to Lu and also including Sc and Y.

[Best Mode for carrying out the Invention]

[0020] The reasons for defining the hot tool steel, the tool for use in hot working and the plug for use in a piercer used for manufacturing seamless pipes according to the present invention will now be described in detail below.

[0021] 1. Hot tool steel

C: 0.05 to 0.5%

C is effective for improvement of the high temperature strength of steel. However, at a content of less than 0.05%, no sufficient high temperature strength can be obtained. On the other hand, at a content of more than 0.5%, the hardness of the surface of the tool, which is quenched after being used, is excessively high thereby tending to cause a quenching crack. Accordingly, the C content is set to 0.05 to 0.5%. The lower limit is preferably 0.07%, more preferably 0.1%. The upper limit is preferably 0.3%, more preferably 0.2%.

[0022] Si: 0.1% to 1%

Si is effective as a deoxidizing agent of a steel. Further, it is not only effective for making a higher Ac_1 transformation point and densification of oxide scale formed on the surface, but also for formation of fayalite (Fe_2SiO_4), which increases the high temperature deformability of the oxide scale that improves the adhesion. At a content of less than 0.1%, such effects cannot be obtained. On the other hand, at a content of more than 1%, fayalite is excessively formed and it lowers the melting point of the oxide scale and also lowers the high temperature hardness. Due to the reasons described above, the Si content of 0.1 to 1% is appropriate. The lower limit is preferably 0.15%, more preferably 0.2%. Further, the upper limit is preferably 0.6%, more preferably 0.5%.

[0023] Mn: 1.6 to 3.5%

Mn is one of the most important elements of the steel according to the present invention because it controls the shape of the oxide scale formed on the surface of the steel and also improves the high temperature strength of the steel. At a content of less than 1.6%, the effect of improving the adhesion of the oxide scale is not recognized and the effect of improving the high temperature strength is insignificant. Therefore any improvement for the life of the steel cannot be recognized in a case of using the steel as a tool. On the other hand, at a content of more than 3.5%, the quenching crack resistance of the base metal is lowered and cracking, which shortens the life of the tool, occurs on the surface during cooling after being used as the tool. Due to the reasons described above, an appropriate Mn content is 1.6 to 3.5%. The lower limit is preferably 2%, more preferably 2.5%. The upper limit is preferably 3.25%, more preferably 3.2%.

[0024] Ni: 0.05 to 0.5%

Ni is dispersed and precipitated as metal particles in the oxide scale layer, particularly, in the inner scale layer with a high Fe_2MnO_4 content and therefore it is effective for improving the peeling resistance of the oxide scale. This effect is particularly remarkable in a case of adding Ni with Cu to be described later. However, at a content of less than 0.05%, such an effect cannot be obtained. On the other hand, at a content of more than 0.5%, the transformation-induced cracking resistance of the steel is lowered. Accordingly, the Ni content of 0.05 to 0.5% is appropriate. The lower limit is preferably 0.15%, more preferably 0.2%. The upper limit is preferably 0.45%, more preferably 0.4%.

[0025] Mo: 2 to 5%

Mo is an ingredient which is effective for improving not only the high temperature strength of the steel but also the adhesion of the oxide scale when it is added with Ni and Cu. The effect can be obtained at a content of 2% or more but the effect is saturated at 5%. Accordingly, an appropriate Mo content is 2 to 5%. The lower limit is preferably 2.25%,

more preferably 2.5%. The upper limit is preferably 4.5%, and more preferably 4%.

[0026] W: 2 to 5%

W improves the high temperature strength of the steel. Further, W is an extremely important element for controlling the lubricity of the oxide scale. Accordingly, a content of at least 2% is necessary. On the other hand, at a content of more than 5%, the melting point of the oxide scale is excessively lowered and the oxide scale layer has a tendency to peel off during use and this causes burning. Accordingly, an appropriate W content is 2 to 5%. The lower limit is preferably 2.5%, more preferably 3%, and the upper limit is preferably 4.5%, more preferably 4%.

[0027] Cu: 0.05 to 0.5%

Cu is one of the most important elements as well as Ni, in the steel of the present invention for improving the adhesion and the lubricity of the oxide scale. Particularly, it greatly improves the adhesion and the lubricity of the oxide scale by the addition with Ni as described above.

[0028] It has been explained that Cu improves the adhesion of scale in Patent Documents 4 and 5 above. However, any of the steels disclosed in these Patent Documents is a steel with a Mn content of 1.5 or less. Further, the steel disclosed in Patent Document 5 has a Cr content as high as 1 to 3%. On the other hand, in the steel according to the present invention, Mn is 1.6 to 3.5% and the Cr content, even when it is added, is 0.05 to 0.5%.

[0029] As described above, in the steel with an increased Mn content, the inner layer scale containing a large amount of spinel type scale, Fe_2MnO_4 , which contains Mn oxide, is formed. While the scale has a remarkable effect of preventing the burning as described above, they are poor in adhesion compared with the scale in which Cr is concentrated. Cu serves for improving the adhesion. However, at a content of less than 0.05%, no such effect can be obtained. On the other hand, at a content of more than 0.5%, a soft alloy layer with a high Cu content is formed at the boundary between the oxide scale and the base metal. Accordingly, the peeling resistance of the oxide scale is lowered and the oxide scale transits from the base metal to the material to be worked during a piercing operation, and the burning tends to occur. Due to the reasons described above, an appropriate range of the Cu content is 0.05 to 0.5%. The lower limit is preferably 0.07%, more preferably 0.075%, and the upper limit is preferably 0.4%, more preferably 0.3%.

[0030] The foregoing are essential ingredients for the tool steel of the present invention. One of the tool steels according to the present invention consists of the ingredients described above and the balance Fe and impurities.

The other tool steel according to the present invention comprises the ingredients described above and, in addition, at least one ingredient selected from the ingredients to be described below, and the balance Fe and impurities.

[0031] Cr: 0.05 to 0.5%

While it is not necessary to add Cr, Cr may be optionally added since this is an element effective for improving the adhesion of the oxide scale. However, at a content of less than 0.05%, such an effect cannot be obtained. On the other hand, at a content of more than 0.5%, the quenching cracking tends to occur. Further, in a case where the Cr content is excessive, the spinel type scale, in which Cr is concentrated, is formed and the burning upon working of a stainless steel tends to occur as described above. With the reasons described above, the Cr content, if added, is preferably 0.05 to 0.5%.

[0032] Co: 0.05 to 5%

While it is not necessary to add Co, Co is an element effective for improving the toughness. Co is an element effective for improving the peeling resistance of the oxide scale by being dispersed and precipitated as metal particles in the oxide scale layer, as well as Ni described above. Accordingly, Co may be optionally added. However, at a content of less than 0.05%, such an effect cannot be obtained. On the other hand, at a content of more than 5%, the metal particles become excessive tending to cause the burning and the heat fatigue characteristic of the tool deteriorates tending to cause the cracking on its surface due to heat fatigue when the tool is put under repetitive heating and cooling. Further, excessive Co suppresses formation of the oxide scale. Accordingly, the Co content, if added, is preferably 0.05 to 5%.

[0033] Ti, Nb, V, Zr, B: 0.05 to 0.5% each or a total of two or more

While it is not necessary to add these elements, since any of them has an effect of refining grains and is effective for improving the toughness, one or more of them may be optionally added. However, in a case where the content of each of the elements or the content of a total of the elements is less than 0.05%, such an effect cannot be obtained. On the other hand, at a content of more than 0.5%, a brittle phase appears in the base metal and its strength is lowered. Accordingly, the content of each of the elements or the content of a total of the elements, if added, is preferably 0.05 to 0.5%.

[0034] REM: 0.001 to 0.2%

While it is not necessary to add REM, i.e., 17 elements including 15 lanthanide elements from La to Lu, Sc and Y; since, each of the elements is an ingredient that is effective for improving the adhesion of the oxide scale, one or more of them may be optionally added. However, in a case where the content of each of the elements or the content of a total of the elements is less than 0.001%, such an effect cannot be obtained and, at a content of more than 0.2%, a brittle phase, which lowers the strength of the steel, appears. Accordingly, the content of each of the elements or the content of a total of the elements, if added, is preferably 0.001 to 0.2%.

[0035] The balance of the hot tool steel of the present invention comprises Fe and impurities. The content of P and

S as impurities causes no particular problems as long as they are at a usual level to be contained as impurities in the steel of this type. However, since P and S may sometimes lower the adhesion of the oxide scale, it is preferred to restrict each of them to 0.01% or less.

2. Thickness of the oxide scale of the tool for use in hot working and plug for use in piercer

[0036] According to the present invention, a tool for use in hot working and the plug for use in a piercer for manufacturing seamless pipes are made of the hot tool steel, which has the chemical composition described above. It is also necessary that its surface is covered with an oxide scale layer of 50 to 1500 μm thickness formed by "oxide scale-forming heat treatment". The reason for this is described below.

[0037] If the thickness of the oxide scale layer is less than 50 μm , the heat insulating effect is insufficient and a temperature rise of a base metal cannot be sufficiently suppressed. Further the oxide scale layer is rapidly worn and consumed to bring about early deformation of the tool, and also the lubricity decreases, which causes burning.

[0038] On the other hand, in a case where the thickness of the oxide scale layer exceeds 1500 μm , many voids and micro cracks are formed in the scale layer, and the adhesion with the base metal decreases, so that the scale tends to peel during handling before use, as well as interlayer peeling, which tends to be caused between the inner and outer layer scales during use, and this causes flaws in the products. These flaws are those on the inner surface of a pipe after piercing in the case of piercing using the plug. Accordingly, an appropriate thickness of the oxide scale layer is 50 to 1500 μm .

[0039] The thickness of the oxide scale layer means a total of the thickness of both the inner layer scale and the outer layer scale formed thereon. The outer layer scale is mainly comprised of FeO and Fe_3O_4 in which the outer most layer is Fe_2O_3 .

3. Manufacture of tool steel for use in hot working, the tool for use in hot working, and the plug for use in a piercer

[0040] The hot tool steel of the present invention is manufactured by melting a raw material by a known process such as an atmospheric melting method, the AOD method, or the VOD method, and then casting the obtained molten steel into an ingot or a billet by the ingot making method or the continuous casting method, and then forming the ingot or billet into a predetermined shape optionally by hot working, such as hot rolling. In this case, there is no particular restriction on the manufacturing conditions.

[0041] The tool for use in hot working and the plug for use in a piercer for manufacturing seamless pipes or tubes can be manufactured by casting the molten steel, obtained as described above, directly into the shape of a predetermined tool or plug, or forming the ingot or billet steel pipe into a predetermined shape of the tool or the plug by applying hot forging. There is also no particular restriction on the manufacturing conditions in this case. However, the heat treatment for forming the oxide scale is preferably conducted under the following conditions.

4. Condition for oxide scale-forming heat treatment

(1) Heating Atmosphere

[0042] In the scale-forming treatment, steams contained in a heating atmosphere are important and the concentration of the steams in a furnace has to be kept at 5% or more by volume. This condition is attained by mixing a fuel such as LNG, LPG, C-gas, and butane with air and burning them.

(2) Heating Temperature

[0043] The thickness of the scale depends on the heating temperature and the heating time. For forming the spinel type scale, which contains a large amount of Mn oxides, at a uniform thickness, the treatment is preferably conducted at 800°C or higher. In a case where the heating temperature exceeds 1200°C the formed scale is melted. Therefore, the heating temperature is desirably 1200°C or lower.

(3) Heating Time

[0044] The heating time may be determined depending on the heating temperature so that the predetermined scale thickness is obtained.

[Example]

[0045] Sixty kinds of alloy steels which have the chemical compositions shown in Table 1 and Table 2 were melted by an atmospheric melting, the obtained ingots were hot forged and then externally ground and finished into plugs for use in a piercer for manufacturing seamless pipes.

[0046] The plugs, each finished into a predetermined shape, were heated in an LNG combustion atmosphere (10%CO₂, 2%O₂, 20%H₂O and the balance N₂ on the basis of % by volume) at various temperatures and times shown in Table 3 and Table 4 in order to form an oxide scale layer with various thickness also shown in Table 3 and Table 4.

[0047] By using each of the obtained plugs, piercing was conducted. In the piercing process, a round billet made of SUS304 of the following size was pierced and formed into a hollow shell of the following size. The plug was continuously served for piercing a number of billets. The piercing conditions are as described below.

[0048] Size for billet and hollow shell.

For parallel piercing

Billet: 70 mm diameter × 1000 mm length

Hollow shell: 72 mm diameter × 2200 mm length

For expanding piercing

Billet: 65 mm diameter × 1000 mm length

Hollow shell: 93 mm diameter × 2200 mm length

Heat temperature for billet: 1200°C

Cross angle: 15°

Feed angle: 10°

Plug size:

For parallel piercing : 54 mm diameter

For expanding piercing: 75 mm diameter

[0049] "Parallel piercing" means that the diameter of the billet and the outer diameter of the hollow shell after piercing are substantially equal to each other. The "expanding piercing" means that the outer diameter of the hollow shell is larger than the diameter of the billet.

[0050] The frequency of use limit of a plug (the number of pierced pipes) and the surface of the plug after piercing were examined. It was judged whether a plug was usable or not, by observing the state of the peeling or the wear exhaustion of the oxide scale of the plug, occurrence of the cracking or the burning of the plug, and the melting loss or the deformation at the top end of the plug.

[0051] The results of the examination are shown in Table 3 and Table 4 together with the conditions for the oxide scale-forming heat treatment, the thickness of the oxide scale layer, and the tensile strength (TS: N/mm²) at 1000°C of the material steel.

[0052] As can be seen in Table 3 and Table 4, the plugs made of the tool steel, according to the present invention (indicated by reference numerals 1 to 31), could be used for eight times or more of piercing, and the surface of the plugs after piercing was also excellent enough.

[0053] On the contrary, each of the plugs made of the steels indicated by reference numerals 32 and 33, in which the content of Cu was insufficient, was low in the adhesion strength of the oxide scale and the oxide scale on the plug peeled during piercing, and it resulted in the melting loss. As for the plug made of the steel indicated by reference numeral 34, in which the Cu content was excessive, the base metal just below the oxide scale was deformed during piercing, and it resulted in the burning at the top end of the plug.

[0054] The plug made of the steel indicated by reference numeral 35, in which the Mn content was insufficient, lacked the high temperature strength and its top end was deformed during piercing of three pipes. As for the plug made of the steel indicated by reference numeral 36, in which the Mn content was excessive, the quenching crack occurred at the body of the plug during piercing.

[0055] The plug made of the steel indicated by reference numeral 37, in which the Ni content was insufficient, was poor in the adhesion of the oxide scale, and the melting loss occurred at the top end in piercing of four pipes. As for the plug made of the steel indicated by reference numeral 38, in which the Ni content was excessive, the quenching crack occurred during water cooling after piercing.

[0056] The plug made of the steel indicated by reference numeral 39, in which the Mo content was insufficient, lacked the high temperature strength and the deformation occurred at the top end during piercing of four pipes. The plug made of the steel indicated by reference numeral 40, in which the content of Ni and Mo was excessive, lacked the transformation-induced cracking resistance and the transformation-induced cracking occurred during piercing of three pipes.

[0057] The plug made of the steel indicated by reference numeral 41, in which the W content was insufficient, lacked the high temperature strength, and the deformation occurred at the top end during piercing of three pipes. On the other

hand, in the plug made of the steel indicated by reference numeral 42, in which the W content was excessive, the oxide scale was softened during piercing and the melting loss occurred during piercing of four pipes.

[0058] The plug made of the steel indicated by reference numeral 43, in which the C content was insufficient, lacked the high temperature strength, and the top end was deformed during piercing of four pipes. On the other hand, in the plug made of the steel indicated by reference numeral 44, in which the C content was excessive, the cracking occurred in the body of the plug during water cooling after piercing.

[0059] The plug made of the steel indicated by reference numeral 45, in which the Si content was insufficient, lacked the adhesion strength of the oxide scale, and the burning occurred at the top end during piercing of three pipes. On the other hand, in the plug made of the steel indicated by reference numeral 46, in which the Si content was excessive, the oxide scale was softened during piercing and the deformation occurred at the top end during piercing of four pipes.

[0060] In the plug made of the steel indicated by reference numeral 47, in which the Cr content was excessive, the cracking occurred in the body during water cooling after piercing. In the plugs made of the steel indicated by reference numerals 48 and 49, in which the Co content was excessive, defects occurred at the top end during piercing.

[0061] In the plugs made of the steels indicated by reference numerals 50 to 54, in which the content of one or more of Ti, Nb, V, Zr and B was excessive, the defects occurred at the top end during piercing. In the plugs made of the steels indicated by reference numerals 55 to 58, in which the REM content was excessive, the defects occurred at the top end during piercing.

[0062] In each of the plugs made of the steels indicated by reference numerals 59 and 60, the chemical composition of the base metal was within the range defined in the present invention. However, the plug made of the steel 59 scarcely had the heat insulating effect since the thickness of the oxide scale layer was as thin as 45 μm , and its top end was deformed during piercing of two pipes. On the other hand, in the plug made of the steel 60, in which the thickness of the oxide scale layer was as thick as 1600 μm and porous, the adhesion strength was low and, as a result of early peeling and detaching of the oxide scale layer at the top end, its top end was lost by melting during piercing of four pipes.

Table 1

Section	Steel No.	Chemical Composition (% by mass, bal.: Fe and Impurities)									
		C	Si	Mn	Ni	Mo	W	Cu	Cr	Co	others
Inventive Example	1	0.15	0.28	2.90	0.32	2.95	3.90	0.05	-	-	.
	2	0.13	0.29	3.10	0.32	3.30	4.15	0.10	-	-	-
	3	0.15	0.30	2.85	0.25	3.00	3.60	0.30	-	-	-
	4	0.14	0.28	2.95	0.30	2.95	4.20	0.48	-	-	-
	5	0.06	0.29	1.75	0.20	2.85	4.12	0.20	-	-	-
	6	0.20	0.35	3.04	0.30	3.00	4.13	0.15	-	-	-
	7	0.30	0.25	3.20	0.07	2.87	3.89	0.30	0.10	-	-
	8	0.35	0.45	2.98	0.20	3.21	4.02	0.10	0.20	-	-
	9	0.36	0.32	3.25	0.45	3.11	3.98	0.12	-	-	-
	10	0.35	0.65	3.20	0.10	3.10	2.55	0.09	-	0.50	-
	11	0.10	0.85	3.45	0.23	3.30	3.00	0.12	-	0.30	-
	12	0.20	0.20	2.50	0.30	2.90	4.25	0.22	-	4.50	-
	13	0.25	0.55	2.22	0.25	2.40	3.55	0.33	0.40	3.50	-
	14	0.30	0.25	3.20	0.07	2.05	3.89	0.28	-	-	Ti:0.30
	15	0.35	0.30	3.11	0.45	4.21	3.25	0.19	-	-	Nb:0.40
	16	0.48	0.40	2.89	0.30	3.21	3.65	0.07	-	-	V:0.10
	17	0.35	0.25	3.11	0.45	3.33	3.90	0.36	-	-	Zr:0.45
	18	0.25	0.60	3.45	0.50	4.25	3.99	0.40	-	-	B:0.20
	19	0.15	0.30	3.00	0.29	3.33	3.25	0.36	-	-	Ti+Nb:0.36
	20	0.30	0.30	3.20	0.20	4.80	3.89	0.28	0.40	-	V:0.10

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Table continued

Section	Steel No.	Chemical Composition (% by mass, bal.: Fe and Impurities)									
		C	Si	Mn	Ni	Mo	W	Cu	Cr	Co	others
	21	0.35	0.25	3.11	0.45	3.33	3.25	0.19	0.43	-	Nb+B:0.23
	22	0.35	0.25	2.22	0.25	2.40	3.55	0.19	-	2.00	Ti+V:0.35
	23	0.15	0.30	3.00	0.33	3.00	3.33	0.07	-	4.50	Zr:0.25
	24	0.15	0.30	3.20	0.20	4.80	3.89	0.36	0.38	3.70	Tr+V+Nb 0.35
	25	0.35	0.25	2.95	0.30	2.95	4.20	0.36	-	-	REM:0.02
	26	0.25	0.95	3.10	0.45	3.33	3.25	0.40	-	-	REM:0.01
	27	0.30	0.30	3.20	0.20	4.80	3.89	0.36	-	-	REM:0.005
	28	0.30	0.30	2.50	0.30	3.09	3.55	0.19	0.49	-	REM:0.10
	29	0.35	0.25	3.11	0.30	2.95	4.20	0.07	-	4.50	REM:0.15
	30	0.15	0.30	3.00	0.20	4.80	3.89	0.07	0.10	0.09	REM:0.13
	31	0.35	0.25	3.11	0.45	3.33	3.25	0.19	0.10	0.09	Zr:0.25, REM:0.15

Table 2

Section	Steel No.	Chemical Composition (% by mass, bal: Fe and Impurities)									
		C	Si	Mn	Ni	Mo	W	Cu	Cr	Co	others
Comparative Example	32	0.15	0.30	3.00	0.29	3.00	4.10	-*	-	-	-
	33	0.12	0.31	3.20	0.21	3.20	4.20	0.003*	-	-	-
	34	0.16	0.31	3.12	0.40	3.00	3.98	1.00*	-	-	-
	35	0.15	0.31	1.50*	0.15	2.96	4.20	0.30	-	-	-
	36	0.22	0.28	4.00*	0.29	3.12	3.85	0.40	-	-	-
	37	0.45	0.34	2.00	0.01*	3.12	4.12	0.20	-	-	-
	38	0.30	0.28	2.88	0.60*	3.00	4.25	0.26	-	-	-
	39	0.32	0.32	2.50	0.25	1.80*	4.20	0.23	-	-	-
	40	0.31	0.40	3.20	0.55*	5.50*	3.50	0.33	-	-	-
	41	0.29	0.51	2.60	0.30	4.00	1.75*	0.45	-	-	-
	42	0.28	0.28	2.33	0.20	3.20	5.20*	0.22	-	-	-
	43	0.01*	0.20	1.80	0.50	4.50	3.20	0.06			- - -
	44	0.55*	0.15	2.00	0.20	2.80	4.20	0.12	-	-	-
	45	0.30	0.08*	3.10	0.10	2.80	3.65	0.25	-	-	-
	46	0.40	1.20*	3.50	0.05	3.80	4.25	0.30	-	-	-
	47	0.25	0.50	3.20	0.08	4.00	3.22	0.44	0.53*	-	-
	48	0.25	0.95	3.10	0.10	2.55	3.55	0.36	-	5.20*	-
	49	0.15	0.30	3.00	0.33	3.00	3.33	0.45	0.25	6.00*	-

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Table continued

Section	Steel No.	Chemical Composition (% by mass, bal: Fe and Impurities)									
		C	Si	Mn	Ni	Mo	W	Cu	Cr	Co	others
	50	0.35	0.25	2.95	0.20	3.31	4.00	0.26	-	-	V+B: 0.58*
	51	0.35	0.30	3.11	0.45	4.21	3.25	0.33	-	-	Nb: 0.60*
	52	0.20	0.33	3.10	0.20	2.55	3.55	0.36	0.20	-	Ti:0.55*
	53	0.15	0.28	2.90	0.32	2.95	-*	0.36	-	3.20	Zr+V: 0.52*
	54	0.14	0.28	3.10	0.32	3.30	4.15	0.19	0.18	1.89	Zr: 0.56*
	55	0.35	0.25	3.11	0.45	3.33	3.25	0.19	-	-	REM: 0.22*
	56	0.25	0.30	2.65	0.10	3.00	4.20	0.11	0.21	-	REM: 0.25*
	57	0.20	0.33	3.10	0.10	2.55	3.55	0.36	-	3.10	REM: 0.21*
	58	0.15	0.28	2.90	0.45	3.33	3.25	0.11	0.43	1.39	REM: 0.28*
	59	0.13	0.29	3.10	0.32	2.95	3.90	0.05	-	-	-
	60	0.15	0.28	2.90	0.32	2.95	3.90	0.05	-	-	-
Remarks: Symbol " *" means to be out of the range defined in the present invention.											

Table 3

Section	Steel No.	H ₂ O concentration in atmosphere (Vol.%)	Heating temperature (°C)	Heating time (h)	Tensile strength at 1000°C (N/mm ²)	Oxide scale thickness (μm)	Plug life (Number of pipe/plug)	Damaged state of Plug
Inventive Example	1	20	1050	6	120	800	9	Good
	2	20	1100	4	115	800	8	Good
	3	20	1050	6	120	800	8	Good
	4	20	1050	6	100	800	9	Good
	5	20	1050	6	105	800	8	Good
	6	20	1050	6	120	800	9	Good
	7	20	1050	6	115	800	10	Good
	8	20	1050	6	115	800	11	Good
	9	20	1050	6	120	800	10	Good
	10	20	1050	6	122	800	9	Good
	11	20	1050	6	124	800	10	Good
	12	20	1050	6	121	800	10	Good
	13	20	1100	6	118	1200	10	Good
	14	20	1050	6	110	800	10	Good
	15	20	1050	6	105	800	10	Good
	16	20	1050	6	104	800	10	Good
	17	20	1050	4	121	900	11	Good
	18	20	1050	6	110	800	10	Good
	19	20	1050	6	105	800	10	Good
	20	20	1050	6	104	800	10	Good
	21	20	1050	8	110	970	10	Good
	22	20	1050	6	112	800	10	Good
	23	20	1050	8	108	970	10	Good
	24	20	1050	6	120	800	10	Good
	25	20	1050	6	118	800	10	Good
	26	20	1050	6	121	800	10	Good
	27	20	1050	8	108	970	10	Good
	28	20	1000	6	111	900	10	Good
	29	20	1050	6	110	800	10	Good
	30	20	1050	6	105	800	10	Good
	31	20	1050	6	105	800	10	Good

Table 4

Section	Steel No.	H ₂ O concentration in atmosphere (Vol.%)	Heating temperature (°C)	Heating time (h)	Tensile strength at 1000°C (N/mm ²)	Oxide scale thickness (μm)	Plug life (Number of pipe/plug)	Surface state of Plug
Compa- rative Example	32	20	900	3	105	600	2	Melting loss
	33	20	1050	6	110	800	3	Melting loss
	34	20	1050	6	105	800	3	Top end deformation
	35	20	1050	6	50	800	3	Melting loss at top end
	36	20	1050	6	110	800	4	Body cracking
	37	20	1000	8	110	800	4	Melting loss at top end
	38	20	1050	6	115	800	5	Body cracking
	39	20	1050	6	60	800	4	Top end deformation
	40	20	1050	6	111	800	3	Good
	41	20	1050	6	74	800	3	Top end deformation
	42	20	1050	6	110	800	4	Melting loss
	43	20	1050	6	105	800	5	Top end deformation
	44	20	1050	6	110	800	3	Body cracking
	45	20	1050	6	112	800	3	Top end burning
	46	20	1050	6	105	800	4	Top end deformation
	47	20	1050	6	120	800	3	Body cracking
	48	20	1050	6	115	800	3	Top end defect
	49	20	850	2	105	300	7	Burning
	50	20	1050	6	104	800	3	Top end defect
	51	20	1050	6	103	800	3	Top end defect
	52	20	1050	6	112	800	4	Top end defect
	53	20	1050	6	103	900	3	Top end defect
	54	20	1050	6	100	800	2	Top end defect
	55	20	1050	6	120	800	3	Top end defect
	56	20	1050	6	111	800	4	Top end defect
	57	20	1050	6	121	800	3	Top end defect
	58	20	1100	6	120	970	3	Top end defect
	59	20	700	1	110	45*	2	Melting loss
	60	20	1050	15	111	1600*	4	Melting loss
Remarks: Symbol "*" indicates to be out of the range as defined in the present invention								

[Industrial Applicability]

[0063] The hot tool steel, according to the present invention, is excellent in high temperature strength. Further, an oxide scale formed on its surface by an oxide scale-forming heat treatment has high adhesion with its base metal and is also excellent in burning resistance and the lubricity when working with high Cr content steel. Accordingly, the tool for hot working, according to the present invention, whose surface is covered with an oxide scale of a predetermined thickness which is provided by the oxide scale-forming heat treatment, not only has a long working life, but also is free from the possibility of causing surface defects, such as burning flaws to the products. The tool steel, according to the present invention, is particularly suitable material for a piercer plug used for manufacturing a seamless pipe or tube made of high Cr alloy steel, such as stainless steel with Cr content of 13% or more and Ni-based alloy. The plug has a long working life and contributes to the manufacturing of seamless pipes with less inner surface flaws at a reduced expenditure.

Claims

1. A hot tool steel consisting of, % by mass, C: 0.05 to 0.5%, Si: 0.1 to 1%, Mn: 1.6 to 3.5%, Ni: 0.05 to 0.5%, Mo: 2 to 5%, W: 2 to 5%, Cu: 0.05 to 0.5%, and the balance Fe and impurities.
2. A hot tool steel consisting of, % by mass, C: 0.05 to 0.5%, Si: 0.1 to 1%, Mn: 1.6 to 3.5%, Ni: 0.05 to 0.5%, Mo: 2 to 5%, W: 2 to 5%, Cu: 0.05 to 0.5%, and at least one of the elements described below, and the balance Fe and impurities;
Cr: 0.05 to 0.5%
REM: 0.001 to 0.2%
wherein REM means 17 elements including lanthanide elements and Sc and Y.
3. A hot tool steel consisting of, % by mass, C: 0.05 to 0.5%, Si: 0.1 to 1%, Mn: 1.6 to 3.5%, Ni: 0.05 to 0.5%, Mo: 2 to 5%, W: 2 to 5%, Cu: 0.05 to 0.5%, from 0.05 to 5% of Co, and the balance Fe and impurities.
4. A tool steel for use in hot working comprising, % by mass, C: 0.05 to 0.5%, Si: 0.1 to 1%, Mn: 1.6 to 3.5%, Ni: 0.05 to 0.5%, Mo: 2 to 5%, W: 2 to 5%, Cu: 0.05 to 0.5%, Co: 0.05 to 5%, and at least one of the elements described below, and the balance Fe and impurities;
Cr: 0.05 to 0.5%
REM: 0.001 to 0.2%
wherein REM means 17 elements including lanthanide elements, and Sc and Y.
5. The tool steel for use in hot working according to any one of claims 1 to 4, further comprising at least one element selected from Ti, Nb, V, Zr, and B of 0.05 to 0.5 % by mass for each or a total of two or more of them, and the balance Fe and impurities.
6. A tool for use in hot working comprising the hot tool steel according to any one of claims 1 to 5, wherein the surface thereof is covered with oxide scale of 50 to 1500 μm thickness formed by an oxide scale-forming heat treatment.
7. A plug for use in a piercer used for manufacturing seamless pipes, made of the hot tool steel according to any one of claims 1 to 5 wherein the surface is covered with an oxide scale of 50 to 1500 μm thickness formed by an oxide scale-forming heat treatment.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/006373

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl⁷ C22C38/00, B21B25/00

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.Cl⁷ C22C38/00-38/60, B21B25/00

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)
JICST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 8-193241 A (Kawasaki Steel Corp.), 30 July, 1996 (30.07.96), Claims (Family: none)	1-7
A	JP 8-206709 A (Sumitomo Metal Industries, Ltd.), 13 August, 1996 (13.08.96), Claims (Family: none)	1-7
A	JP 58-123859 A (Daido Steel Co., Ltd.), 23 July, 1983 (23.07.83), Claims (Family: none)	1-7

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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Date of the actual completion of the international search
03 August, 2004 (03.08.04)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/006373

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 4-270003 A (Sumitomo Metal Industries, Ltd.), 25 September, 1992 (25.09.92), Claims (Family: none)	1-7

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