A ferritic stainless steel comprising Cr: max 24 mass %, Ti: 200 to 1000 mass ppm, Zr: at least 200 mass ppm, whereby the Zr/Ti ratio is greater than 0.3, O: 10 to 150 mass ppm, N: at least 70 mass ppm, whereby the N/O ratio is greater than 1.5, C: max. 0.03 mass %, and balance Fe and residual elements.
\[ N = 65 \text{ ppm} \ (0.7 \times 10^6 \text{ mm}^{-3}) \]

\[ N = 248 \text{ ppm} \ (1.5 \times 10^6 \text{ mm}^{-3}) \]

\[ N = 490 \text{ ppm} \ (5.3 \times 10^6 \text{ mm}^{-3}) \]

\( D_A \) (mm)

Holding time (min)

( ) - number of inclusions per unit volume

FIG. 2.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Deoxidation</th>
<th>$D_A$ (mm)</th>
<th>REC</th>
<th>$N_r \times 10^6$ (mm$^{-3}$)</th>
<th>$d$ (μm)</th>
<th>T.M.</th>
<th>T.N.</th>
<th>T.O.</th>
<th>T.Ti</th>
<th>T.Zr</th>
<th>T.Ce</th>
<th>$M = \text{Zr or Ce}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIZr-1</td>
<td>0.1% Ti, 0.1% Zr</td>
<td>0.66</td>
<td>0.55</td>
<td>0.45</td>
<td>1.06</td>
<td>0.72</td>
<td>1.45</td>
<td>65</td>
<td>6.0</td>
<td>89</td>
<td>6.5</td>
<td>145</td>
</tr>
<tr>
<td>TIZr-2</td>
<td>0.1% Ti, 0.1% Zr</td>
<td>0.26</td>
<td>0.57</td>
<td>0.85</td>
<td>0.30</td>
<td>0.72</td>
<td>1.45</td>
<td>65</td>
<td>6.0</td>
<td>89</td>
<td>6.5</td>
<td>145</td>
</tr>
<tr>
<td>TIZr-3</td>
<td>0.1% Ti, 0.1% Zr</td>
<td>2.35</td>
<td>1.32</td>
<td>0.44</td>
<td>0.44</td>
<td>0.49</td>
<td>1.44</td>
<td>1.44</td>
<td>0.38</td>
<td>1.27</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>TiCe-1</td>
<td>0.1% Ti, 0.1% Ce</td>
<td>4.05</td>
<td>1.32</td>
<td>0.44</td>
<td>0.44</td>
<td>0.49</td>
<td>1.44</td>
<td>1.44</td>
<td>0.38</td>
<td>1.27</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>TiCe-2</td>
<td>0.1% Ti, 0.1% Ce</td>
<td>2.35</td>
<td>1.32</td>
<td>0.44</td>
<td>0.44</td>
<td>0.49</td>
<td>1.44</td>
<td>1.44</td>
<td>0.38</td>
<td>1.27</td>
<td>0.49</td>
<td>0.49</td>
</tr>
</tbody>
</table>
FERRITIC STAINLESS STEEL, WITH HIGH AND STABLE GRAIN REFINING POTENCY, AND ITS PRODUCTION METHOD

TECHNICAL FIELD

[0001] The present invention relates to a ferritic stainless steel, with high and stable grain refining potency and its production method.

BACKGROUND ART

[0002] In general, steel quality is greatly improved by removing impurities and large inclusions which may adversely affect the properties of the steel. In the production of carbon steels, the fine oxide dispersion technique by the addition of Zr—Mg, Ti—Zr—Ti—Mg or Ti—Mg—Ca is well known as “Oxide Metallurgy”. This technique makes it possible to control the grain size using fine oxide particles, and to develop the high HAZ (heat affected zone) toughness carbon steel plates for pipeline, shipping and construction.

[0003] In the production of ferritic stainless steels, the conventional addition of Al—Ti or Ti causes the formation of larger Al₂O₃ clusters. Consequently, it is difficult to control the grain size using conventional methods for producing ferritic stainless steel and therefore the grain refining level varies widely.

SUMMARY OF THE INVENTION

[0004] It is an aim of the present invention to provide an improved ferritic stainless steel, with high and stable grain refining potency and a method for producing such ferritic stainless steel.

[0005] This aim is achieved by a ferritic stainless steel comprising Cr: max 24 mass %, Ti: 200 to 1000 mass ppm, Zr: at least 200 mass ppm, whereby the Zr/Ti ratio is greater than 0.3, O: 10 to 150 mass ppm, N: at least 70 mass ppm, whereby the N/O ratio is greater than 1.5, C: max. 0.03 mass %, and balance Fe and residual elements.

[0006] According to an embodiment of the invention the ferritic stainless steel comprises Ti and/or Zr oxides/nitrides (i.e. oxides and/or nitrides containing Titanium, oxides and/or nitrides containing Zirconium, and oxides and/or nitrides containing both Titanium and Zirconium) with a maximum diameter of 5 μm. It should be noted that the expression “diameter” is intended to mean the diameter of an equivalent spherical volume corresponding to the volume of the oxide/nitride. For the observation of oxide/nitride particles, a metal sample was dissolved by using the potentiostatic electrolytic extraction method with an electrolyte of 10% acetylated—1% tetramethylammonium chloride—methanol (150 mV, 40-50 mA, 300 Coulombs). After extraction, the electrolyte was filtered using a polycarbonate membrane (PC) filter with an open-pore size of 50 nm. The particle observation and the composition analysis on film filters were made using SEM and by using EPMA. Essentially more than 200 particles for each sample were measured to obtain a representative particle size distribution.

[0007] According to another embodiment of the invention the ferritic stainless steel comprises a total number of more than 1x10⁶ Ti and/or Zr oxides/nitrides per mm² of the steel.

[0008] The present invention also concerns a method for producing of a ferritic stainless steel, which may be used to produce a ferritic stainless steel according to the present invention. The method compromises comprises the step of adding deoxidizers Si, Mn, Ti and Zr to the melt in the order of weak deoxidizer to strong deoxidizer, i.e. firstly Si and Mn are added to the melt either at the same time or separately, then Ti is added to the melt, and finally Zr is added to the melt, i.e. the deoxidizers are preferably added to the melt in the following order: Si—Mn, Ti, Zr.

[0009] According to an embodiment of the invention the method comprises the step of deoxidizing a melt with the deoxidizers Ti and Zr in said order with an interval of 1 to 5 minutes between additions, holding the melt for at least one minute and casting the melt.

[0010] The method according to the present invention may be used to produce ferritic stainless steel suitable, such as AISI 430, 434, 436 or 444 for many applications with weldability and workability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] TABLE 1 is the content of main elements and characteristics of particles and microstructure in Fe-20 mass % Cr experiments.

[0012] FIG. 1 shows the size distributions of oxide/nitride particles with different compositions in Ti—Zr addition experiments at different N contents, and

[0013] FIG. 2 shows the average grain size in specimens of Ti—Zr addition experiments with different N content as a function of holding time at 1200 and 1400°C.

DETAILED DESCRIPTION OF EMBODIMENTS

[0014] The inventors performed experiments concerning the addition of Ti, Zr, Ce, and examined the distribution characteristics of oxides/nitrides produced, and the consequent microstructure, for stably enhancing the grain refining potency in ferritic stainless steel with higher N content and lower C content. Especially, the inventors focused on the selection of oxides/nitrides and the fine particle dispersion technique (with high amount and uniform space-distribution) fit to the above objective. It was found that Ti—Zr oxides/nitrides, i.e. oxides/nitrides containing both Titanium and Zirconium and Zirconium nitrides were the most promising particles with following grain refining potencies:

[0015] (a) Ti—Zr oxides/nitrides have a high potency as ferrite solidification nucleants, and enhance equiaxed grain zone ratio and equiaxed grain refining in as-cast structure.

[0016] b) Zr nitrides have a thermal-stable potency as pinning particles on ferrite grain growth in reheated structure.

[0017] The present invention which was based on the outcome from the above examinations, provides a new “Oxide Metallurgy” technique with effective application of nitrides, in other words, an “Oxide/Nitride Metallurgy” technique for the production of ferritic stainless steel with higher N content specification and lower C content specification.

Ferritic Stainless Steel According to an Embodiment of the Present Invention

(A) Oxides/Nitrides and Particle Characteristics

[0018] The oxides/nitrides according to the present invention consist of Ti—Zr oxides/nitrides and Zr nitrides. The above selection of the oxide/nitride was performed considering the following points:
[0019] (1) ZrN has a high potency as a ferrite solidification nucleant like that of TiN and VN, from the point of lattice registry, and enhances the equiaxed grain zone ratio and equiaxed grain refining in the as-cast structure. Of course, both Ti—Zr oxides/nitrates and Zr nitrates have a partial or complete ZrN surface.

[0020] (2) ZrN has a thermal-stable potency as pinning particles on ferrite grain growth, in comparison to TiN, in reheated structure. Of course, Zr nitrates include a little TiN, because ZrN is mainly precipitated in the melt and TiN might be precipitated on ZrN surface in the solidification/cooling.

[0021] Thus, “—Zr oxides/nitrates” means a mainly Ti(O,N) core covered partially or completely by Zr oxide, Zr nitrates or their complexes (for example, ZrO_2—ZrN with a low content of Ti(O,N)). “Zr—oxide” means mainly ZrN including TiN (for example, ZrN—TiN). This naming due to the content of Ti, Zr, O and N was done for convenience.

[0022] In the case of excess Ti content, there are comparatively larger Ti oxides, besides Ti—Zr oxides/nitrates. On the other hand, in the case of small Ti content, there are comparatively larger Zr oxides besides Ti—Zr oxides/nitrates. Thus, the Zr/Ti ratio should be controlled to be over 0.3, and the N/O ratio should be controlled to be over 1.5.

(B) Chemical Composition

[0023] The ferritic stainless steel according to the present invention has a chemical composition recited in claim 1.

[0024] O is an essential element for producing Ti—Zr oxides/nitrates by Ti and Zr addition. In order to obtain a sufficient number of Ti—Zr oxide/nitride particles to achieve a noticeable effect, the O content is set to 10 to 150 mass ppm.

[0025] N is an essential element for producing Ti—Zr oxides/nitrates and Zr nitrates by Ti and Zr addition. In order to obtain a sufficient number of Ti—Zr oxides/nitrates and Zr nitrates to achieve a noticeable effect, the N content is set over 70 mass ppm. In addition, from the view point of priority formation of Zr nitrides, the N/O ratio is over 1.5.

[0026] Excessive C content causes the deterioration of toughness characteristics by carbide formation and the remarkable narrowing ferrite region by γ loop movement. Therefore, the C content is set below 0.03 mass%.

[0027] Ti contributes the primary formation of Ti(O,N) core and then the consequent formation of fine Ti—Zr oxides/nitrates which act as nucleants for ferrite solidification in the melt, when the Al content is very low. In addition, Ti contributes the formation of fine TiN in the solidification/cooling which acts as pinning particles for ferrite grain growth in the reheating. At least, the Ti content: 200 mass ppm is necessary to achieve the above effect. However, excessive Ti content causes the deterioration of toughness characteristics by carbide formation. Therefore, the Ti content is set below 1000 mass ppm to avoid/reduce the deterioration of toughness characteristics.

[0028] In order to obtain a sufficient number of Ti—Zr oxides/nitrates and Zr nitrates to achieve a noticeable effect, the Zr content is set over 200 mass ppm under the C-less condition. In addition, from the view point of priority formation of Zr nitride, the Zr/Ti ratio is over 0.3.

[0029] Excessive Cr content causes the formation of brittle a phase. Therefore, the Cr content is set below 24 mass%.

[0030] Residual elements: Si and Mn are essential elements as first deoxidizers for producing ferritic stainless steel. In addition, one or more ferrite stabilizing elements such as Mo, Nb and V, which then constitute residual elements in the ferritic stainless steel, can also be added. Furthermore, one or more corrosion resistance elements such as Ni and Cu, which then constitute residual elements in the ferritic stainless steel, can also be added.

Method for Producing a Ferritic Stainless Steel

According to an Embodiment of the Present Invention

[0031] A method recited in claim 4 for controlling the fine particle dispersion (with a high number of particles and uniform space-distribution) of Ti—Zr oxides/nitrates and Zr nitrides, has a deoxidation order characterized by the following: The deoxidation operation of the steel is based on Ti and Zr addition in the melt after Si—Mn deoxidation. The melt is deoxidized with Ti and then Zr, using 1 to 5 minutes intervals between additions. Thereafter, the melt is cast after at least 1 minute holding. That is, all deoxidizers should be added in the order of weak deoxidizer to strong deoxidizer, i.e. Si and Mn, then Ti and finally Zr.

[0032] For controlling the fine particle dispersion, the Al-less condition should also be carefully kept for preventing particle agglomeration. The ferritic stainless steel might be contaminated unavoidably with Al in its production process, although it is essentially an Al-less material. Therefore, the Al content might be set below 0.01 mass%, and preferably 0.005 mass%.

Example 1

[0033] Fe—20 mass % Cr ferritic stainless steels, having chemical compositions shown in Table 1 were melted at 1600°C. in a MgO crucible under an Ar gas atmosphere in a high frequency induction furnace. The process of sample making was based on melting a Fe—20 mass % Cr alloy with constant free 0 content: 150 mass ppm, and with different N contents: 65 mass ppm, 250 mass ppm and 500 mass ppm. Thereafter, the melt was deoxidized with Ti (0.1 mass %) and Zr or Ce (0.1 mass %) using 60 s interval between additions and then after 30 s cooled to 1400°C. After that, the ingot sample was quenched in water. The final chemical compositions, the as-cast structure in ingot (the ratio of equiaxed grain zone to columnar grain zone. REC, and the mean equiaxed grain size, D_β, and the particle characteristics (total number of particles per unit volume, Nv, and median diameter of particles, d) are shown in Table 1.

[0034] The size distributions of particles with different compositions are shown in FIG. 1 for Ti—Zr deoxidation experiments with different N contents. TiZr-1 to TiZr-3 samples correspond to Ti—Zr addition experiments, and TiCe-1 and TiCe-2 samples correspond to Ti-Ce addition experiments. In the case of Ti—Zr addition, it is clear that grain refining in as-cast structure can be generally promising. Especially, TiZr-2 and TiZr-3 samples produced according to the present invention have an as-cast structure with the ratio of equiaxed grain zone to columnar grain zone, REC: over 50% and the mean equiaxed grain size, D_β below 300 micron. On the other hand, grain refining in as-cast structure was not confirmed in TiZr-1 sample with the lack of N and Zr content.

Example 2

[0035] New specimens were cut from the equiaxed grain zones of TiZr-1 to TiZr-3 samples with Ti—Zr addition, and
then were reheated at 1200° C. and 1400° C. during 60 min under an Ar atmosphere by using a Confocal Scanning Laser Microscope (CSLM). By in-situ observation the grain growth behavior in each reheated specimen was investigated. The change of the average equiaxed grain size of each specimen during heat treatment is shown in FIG. 2.

TiZr-2 and TiZr-3 samples produced according to the present invention could keep the perfect pinning effect on ferrite grain growth during 60 min reheating at 1200° C. Especially, the TiZr-3 sample could keep the perfect pinning effect on ferrite grain growth for a few minutes of reheating at 1400° C.

On the other hand, a clear pinning effect was not confirmed in TiZr-1 sample with the lack of N and Zr contents.

Further modifications of the invention within the scope of the claims would be apparent to a skilled person.

1. A ferritic stainless steel, wherein it comprises
   Cr: max 24 mass %,
   Ti: 200 to 1000 mass ppm,
   Zr: at least 200 mass ppm,
   whereby the Zr/Ti ratio is greater than 0.3,
   O: 10 to 150 mass ppm,
   N: at least 70 mass ppm
   whereby the N/O ratio is greater than 1.5,
   C: max. 0.03 mass %, and
   balance Fe and residual elements.

2. A ferritic stainless steel according to claim 1, wherein it comprises Ti and/or Zr oxides/nitrides with a maximum diameter of 5 μm.

3. A ferritic stainless steel according to claim 1, wherein it comprises a total number of more than $1 \times 10^5$ Ti and/or Zr oxides/nitrides per mm³ of the steel.

4. A method for producing of a ferritic stainless steel according to claim 1, wherein the method comprises the step of adding deoxidizers Si, Mn, Ti and Zr to a melt in the order of weak deoxidizer to strong deoxidizer, i.e. firstly Si and Mn, then Ti, and finally Zr.

5. A method according to claim 4, wherein the method comprises the step of deoxidizing a melt with said deoxidizers in said order with an interval of 1 to 5 minutes between additions, holding the melt for at least one minute and casting the melt.

* * * * *