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(54) **High-nitrogen austenitic stainless steel**

(57) This invention provides a high-nitrogen austenitic stainless steel superior to the conventional one both in the corrosion resistance and strength, despite a low Ni content, characterized in having a Fe content of 50 % by mass or more; containing Cr: 15.0% by mass to 35.0% by mass, Mo: 0.05% by mass to 8.0% by mass %, Mn: 0.2% by mass to 10.0% by mass, Cu: 0.01% by mass to 4.0% by mass and N: 0.8% by mass to 1.5% by mass, both ends inclusive, having a C content of 0.20% by mass or less, a Si content of 2.0% by mass or less, a P content of 0.03% by mass or less, a S content of 0.05% by mass or less, a Ni content of 0.5% by mass or less, an Al content of 0.03% by mass or less, and an O content of 0.020% by mass or less; wherein the contents of Cr, Mo, N and Mn are adjusted so that a compositional parameter  $\eta$  expressed by the equation:

$$\eta = (W_{Cr} + 3.3W_{Mo} + 16W_N) / W_{Mn}$$

where  $W_{Cr}$  is Cr content (% by mass),  $W_{Mo}$  is Mo content (% by mass)  $W_N$  is N content (% by mass) and  $W_{Mn}$  is Mn content (% by mass) has a value of 5 or above. and optionally further containing either one of, or both of:

W: 0.01% by mass to 1.0% by mass; and  
Co: 0.01% by mass to 5.0% by mass,

both ends inclusive ;  
and optionally further containing at least one of:

Ti: 0.01% by mass to 0.5% by mass;  
Nb: 0.01% by mass to 0.5% by mass;  
V: 0.01% by mass to 1.0% by mass; and  
Ta: 0.01% by mass to 0.5% by mass,

both ends inclusive ;  
and optionally further containing at least one of:

B: 0.001 % by mass to 0.01 % by mass;  
Zr: 0.01 % by mass to 0.50% by mass;  
Ca: 0.001% by mass to 0.01% by mass; and  
Mg: 0.001% by mass to 0.01% by mass,

both ends inclusive ;  
and optionally further containing either one of, or both of:

Te: 0.005% by mass to 0.05% by mass; and  
Se: 0.01% by mass to 0.20% by mass,

both ends inclusive.

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**Description**

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

**[0001]** This invention relates to a high-nitrogen austenitic stainless steel.

## 2. Description of related art

**[0002]** Austenitic stainless steel represented by SUS304, SUS316 and so forth are widely used as a steel excellent in corrosion resistance and workability. For purposes demanding particularly excellent corrosion resistance and strength at the same time, SUS316 as an austenitic stainless steel, and SUS329 as a dual-phase stainless steel are generally used. For applications demanding still more excellent corrosion resistance, there is also used SUS836L (also referred to as "super-austenitic stainless steel") having Ni and Mo contents increased therein to a considerable degree.

**[0003]** The above-described austenitic stainless steels, generally believed as highly corrosion resistant, can however show only a limited resistance against local corrosion, and this raises a further demand on still higher strength. Large amounts of use of expensive Ni and Mo also raises another demand on more inexpensive material. In these years, a high-nitrogen austenitic stainless steel is attracting a good deal of attention as a stainless steel further superior to general austenitic stainless steels in strength and corrosion resistance, having a concentration of nitrogen as an interstitial solid solubilized element raised therein to a large extent as compared with that in the general stainless steel, and consequently having a stabilized austenitic phase by virtue of such high concentration of nitrogen. The high-nitrogen austenitic stainless steel is used for versatile applications including air shaft, ball bearing, shaft bush and mold for plastic products, and is also expectant as a biological material as disclosed in Japanese Laid-Open Patent Publication "Tokkaihei" No. 10-183303. The general austenitic stainless steels contain a considerable amount of Ni, which is possibly causative of Ni allergy problem in the field of biological materials, and is understood as one of an undesirable element to human body, whereas the high-nitrogen austenitic stainless steel, using nitrogen as a major austenitic phase stabilizing element, is successful in getting rid of most part of Ni, and is advantageous in keeping the hardness and corrosion resistance at an equivalent or higher level.

**[0004]** The austenitic stainless steel disclosed in Japanese Laid-Open Patent Publication "Tokkaihei" No. 10-183303 is, however, added with a relatively large amount of Mn in order to raise the amount of solubilization of nitrogen (the patent claims a range of Mn content as relatively wide as 2 to 26% by mass, but discloses Mn contents of as relatively high as 11 % by mass and 12% by mass in the embodiments). Adoption of such high Mn composition may result in a degraded corrosion resistance, and also in an insufficient strength.

**[0005]** It is therefore an object of the present invention to provide a high-nitrogen austenitic stainless steel superior to the conventional one both in the corrosion resistance and strength, despite a low Ni content.

## SUMMARY OF THE INVENTION

**[0006]** Aiming at solving the aforementioned problems, a high-nitrogen austenitic stainless steel of this invention has a Fe content of 50% by mass or more, and contains:

Cr: 15.0% by mass to 35.0% by mass;

Mo: 0.05% by mass to 8.0% by mass;

Mn: 0.2% by mass to 10.0% by mass;

Cu: 0.01 % by mass to 4.0% by mass; and

N: 0.8% by mass to 1.5% by mass,

both ends inclusive,

having a C content of 0.20% by mass or less, a Si content of 2.0% by mass or less, a P content of 0.03% by mass or less, a S content of 0.05% by mass or less, a Ni content of 0.5% by mass or less, an Al content of 0.03% by mass or less, and an O content of 0.020% by mass or less;

wherein the contents of Cr, Mo, N and Mn are adjusted so that a compositional parameter  $\eta$  expressed by the equation:

$$\eta \equiv (W_{Cr} + 3.3W_{Mo} + 16W_N) / W_{Mn}$$

where  $W_{Cr}$  is Cr content (% by mass),  $W_{Mo}$  is Mo content (% by mass),  $W_N$  is N content (% by mass) and  $W_{Mn}$  is Mn content (% by mass) has a value of 5 or above.  
and optionally further containing either one of, or both of:

5 W: 0.01% by mass to 1.0% by mass; and  
Co: 0.01% by mass to 5.0% by mass,  
both ends inclusive ;  
and optionally further containing at least one of:  
10 Ti: 0.01% by mass to 0.5% by mass;  
Nb: 0.01% by mass to 0.5% by mass;  
V: 0.01% by mass to 1.0% by mass; and  
Ta: 0.01% by mass to 0.5% by mass,  
both ends inclusive ;  
and optionally further containing at least one of:  
15 B: 0.001 % by mass to 0.01 % by mass;  
Zr: 0.01% by mass to 0.50% by mass;  
Ca: 0.001% by mass to 0.01% by mass; and  
Mg: 0.001% by mass to 0.01% by mass,  
both ends inclusive ;  
20 and optionally further containing either one of, or both of:  
Te: 0.005% by mass to 0.05% by mass; and  
Se: 0.01% by mass to 0.20% by mass,  
both ends inclusive.

25 **[0007]** The high-nitrogen austenitic stainless steel of this invention makes it possible to attain a good balance between the strength and corrosion resistance, by allowing a large amount of N (nitrogen) to solubilize while limiting Ni content, and by optimizing contents of the essential elements which comprise Cr, Mo, N and Mn within ranges specific to this invention. This consequently makes it possible to realize a high-nitrogen austenitic stainless steel superior to conventional one both in the corrosion resistance and strength, despite a low Ni content. For example, it is no more impossible to  
30 achieve both of high corrosion resistance equivalent to that of SUS836L which is a super-austenitic stainless steel, and strength higher than that of SUS329J4L which is a dual-phase stainless steel, after being subjected to solution heat treatment.

**[0008]** The following paragraphs will describe reasons for the compositional limitations of the individual elements in the high-nitrogen austenitic stainless steel of this invention.

35 (1) Cr: 15.0% by mass to 35.0% by mass

**[0009]** Cr functions to distinctively increase N solubility in the molten metal, largely contributes to the corrosion resistance and strength, and also effectively suppresses generation of nitrogen blow holes. A Cr content of less than 15.0%  
40 by mass results in only an insufficient N solubility in the molten metal, and this makes it difficult to ensure satisfactory levels of corrosion resistance and strength, and makes the nitrogen blow holes more likely to occur. On the other hand, the Cr content exceeding 35.0% by mass may destabilize the austenitic phase and may fail in keeping non-magnetism of the material due to ferrite-forming nature of Cr. It is also anticipated that  $\sigma$  phase causative of degradation in the toughness and ductility becomes more likely to precipitate. It is therefore preferable to adjust the Cr content within a  
45 range from 24.0% by mass to 32.0% by mass, and more preferably from 25.0% by mass to 30.0% by mass.

(2) Mo: 0.05% by mass to 8.0% by mass

**[0010]** Similarly to Cr, also Mo distinctively increases N solubility in the molten metal, but can exhibit a larger effect  
50 of improving the corrosion resistance than Cr can only with a smaller amount, and is successful in obtaining an effect of improving the strength through solid solution strengthening. An amount of Mo addition of less than 0.05% by mass results in only a poor effect, whereas the amount of addition exceeding 8.0% by mass induces nitrogen blow holes and destabilizes the austenitic phase, and thereby makes it difficult to keep the non-magnetism. Formation of an embrittled phase degrades the toughness and ductility, and it becomes hazardous during the hot working. This also raises a problem  
55 of increasing insoluble Cr nitride during the solution heat treatment, and of considerably degrading the corrosion resistance. The amount of Mo addition is therefore more preferably adjusted to 0.05% or more and less than 5.0% by mass, and still more preferably to 0.10% by mass or more and less than 2.5% by mass.

(3) Mn: 0.2% by mass to 10.0% by mass

**[0011]** Mn is an austenite forming element, and contributes to stabilization of the austenitic phase and to lowering of the solid solution temperature of the Cr nitride described later. Also, Mn distinctively increases N solubility in the molten metal, it is effective in improving the strength and suppressing generation of the nitrogen blow holes. It is also effective as a deoxidation element or desulfurizing element. A Mn content of less than 0.2% by mass results in only an insufficient N solubility in the molten metal, and this makes it difficult to ensure a satisfactory level of strength, and tends to cause nitrogen blow holes. On the other hand, the Mn content exceeding 10.0% by mass degrades the corrosion resistance. The Mn content is therefore more preferably adjusted within a range from 0.2% by mass to 6.0% by mass, and still more preferably from 0.2% by mass to 2.0% by mass, both ends inclusive.

(4) Cu: 0.01% by mass to 2.0% by mass

**[0012]** Cu is an austenite forming element, and contributes to stabilization of the austenitic phase and to improvement in the corrosion resistance. An amount of Cu addition of less than 0.01% by mass results in only a poor effect, and the addition exceeding 2.0% by mass raises a problem of lowering in the hot workability. This also increases residual amount of insoluble Cr nitride after the solution heat treatment, and undesirably degrades the corrosion resistance. The amount of Cu addition is therefore more preferably adjusted within a range from 0.02% by mass to 1.8% by mass, and still more preferably from 0.05% by mass to 1.5% by mass, both ends inclusive.

(5) N: 0.8% by mass to 1.5% by mass

**[0013]** N is an interstitial solid solution element into the austenitic phase, and is a basic additive element contributes all of improvement in the strength, stabilization of the austenitic phase, and improvement in the corrosion resistance. The amount of N addition exceeding 1.5% by mass makes the nitrogen blow holes more likely to generate, allows a large amount of insoluble Cr nitride or other transition metal nitrides (e.g., nitrides of Ti, Nb, V and so forth, described later) to remain in the steel after the solution heat treatment, to thereby raise a problem of a considerable degradation in the corrosion resistance. The amount of N addition is therefore more preferably adjusted within a range from 0.8% by mass to 1.4% by mass, both ends inclusive.

(6) Fe: 50% by mass or more

**[0014]** Fe is a major component (i.e., 50% by mass or more) of the steel, and basically composes the residual portion of the steel other than five above-described essential additive elements, optional elements described below, and inevitable impurities. It is to be understood that this invention is not precluded from containing any side components not specifically mentioned in the specification, so far as the above-described effects of this invention will not be ruined.

(7)  $\eta$ : 5 or above

**[0015]**  $\eta$  is a compositional parameter expressed by:

$$\eta \equiv (W_{Cr} + 3.3W_{Mo} + 16W_N) / W_{Mn}$$

where  $W_{Cr}$  is Cr content (% by mass),  $W_{Mo}$  is Mo content (% by mass),  $W_N$  is N content (% by mass) and  $W_{Mn}$  is Mn content (% by mass). Of additive elements relevant to  $\eta$ , N, Cr and Mo function to improve the corrosion resistance, but Mn tends to degrade the corrosion resistance although it is an essential element for increasing the amount of N solubility. The numerator of  $\eta$  is obtained by quantifying effects of improving the corrosion resistance by Mo and N converted on the basis of Cr equivalent. All of N, Cr and Mo contribute to improvement in the corrosion resistance, wherein the effect of improving the corrosion resistance by N measures surprisingly 16 times as large as that of Cr. It is finally indispensable to add Mn in order to dramatically increase the amount of N solubility in the austenitic phase, but excessive addition of Mn seems to partially cancel the net improvement in the corrosion resistance ascribable to thus-increased N, because Mn functions to degrade the corrosion resistance. The  $\eta$  value, having a numerator as a result of positive contribution by N, Cr and Mo to the corrosion resistance, and having a denominator as a result of negative contribution by Mn to the corrosion resistance, can be an effective parameter for generally predicting the corrosion resistance of the finally-obtained steel.

**[0016]** The present inventors found out, after extensive investigations, that the effect of improving the corrosion re-

sistance could distinctively be optimized, and that it was even possible to ensure a level of corrosion resistance equivalent to, or superior to that of super-austenitic stainless steel SUS836L, by balancing the amounts of addition of N, Cr, Mo and Mn so as to adjust  $\eta$  to 5 or above.

**[0017]** The following paragraphs will describe reasons for the compositional limitations of minor elements (intentionally added elements and inevitable impurities).

(8) C: 0.20% by mass or less

**[0018]** C is an interstitial solid solution element, contributes to improvement in the strength, and is effectively functions, as an austenite forming element, to suppress formation of nitrogen blow holes. The amount of addition thereof exceeding 0.20% by mass lowers the N solubility, decreases Cr content in the austenite phase through formation of Cr carbide, and thereby results in degradation in the corrosion resistance. Although being an optional element, C is preferably added in an amount of 0.005% by mass or more in view of making the effect of intentional addition thereof distinct. The C content is preferably adjusted within a range from 0.005% by mass to 0.15% by mass, and more preferably from 0.01% by mass to 0.10% by mass, both ends inclusive.

(9) Si: 2.0% by mass or less

**[0019]** Si is an effective deoxidizing element. Al is known as a deoxidizing element stronger than Si in the general steels, but in the high-nitrogen steel, it is causative of formation of AlN which considerably degrades the high-temperature strength, toughness and ductility. It is therefore preferable to use Si, together with the essential element Mn, as the major deoxidizing element. The deoxidizing effect of Si becomes distinct when it is added in an amount of 0.01% by mass or more. The amount of Si addition exceeding 2.0% by mass makes the steel more likely to cause undesirable as crack or something during the hot working, and also degrades the toughness and ductility. The amount of Si addition is therefore more preferably adjusted within a range from 0.01% by mass to 1.0% by mass, and still more preferably from 0.01% by mass to 0.5% by mass, both ends inclusive.

(10) P: 0.03% by mass or less

**[0020]** P is one of hazardous impurities, and the content exceeding 0.03% by mass results in degradation of the hot workability, and also in degradation of the toughness and ductility due to lowered strength at the grain boundary. It is therefore preferable that P is not contained as possible, and the lower limit thereof is appropriately determined taking the cost balance into account.

(11) S: 0.05% by mass or less

**[0021]** S is one of hazardous impurities, and the content exceeding 0.05% by mass results in degradation of the hot workability, and also tends to degrade the corrosion resistance due to formation of MnS. It is therefore preferable that S is not contained as possible, and the lower limit thereof is appropriately determined taking the cost balance into account. It is preferably adjusted to 0.01% by mass or less.

(12) Ni: 0.5% by mass or less

**[0022]** Ni is intentionally suppressed in this invention in order to reduce the cost and to avoid adverse influences such as Ni allergy when applied to human body. It is therefore preferable that Ni is not contained as possible, but a content to as much as 0.5% by mass is allowable, because an unnecessarily high level of reduction undesirably increases the cost. The Ni content is preferably limited to 0.3% by mass or less, and more preferably to 0.1 % by mass or less.

(13) Al: 0.03% by mass or less

**[0023]** As described in the above, Al is effective as a deoxidizing element, but considerably lowers the corrosion resistance through formation of AlN in the high-nitrogen steel, even under a slight excess of the Al content. In this invention, the Al content is limited to 0.03% by mass or less, in view of avoiding the nonconformity and of raising the amount of N solubilization into the austenite phase as possible. The Al content is preferably limited to 0.025% by mass or less, and more preferably to 0.020% by mass or less.

(14) O: 0.020% by mass or less

**[0024]** The O content is limited to 0.020% by mass or less, because an excess content lowers the cleanliness of the steel, and thereby degrades the corrosion resistance. The O content is preferably limited to 0.015% by mass or less, and more preferably 0.010% by mass or less.

**[0025]** The following paragraphs will describe still other elements which can be added to the high-nitrogen austenitic stainless steel of this invention.

(15) W: 0.01% by mass to 1.0% by mass

**[0026]** W not only contributes to improvement in the corrosion resistance, but also to improvement in the strength as a solid solution strengthening element. An amount of addition of less than 0.01% by mass results in only a poor effect, whereas the amount of addition exceeding 1.0% by mass degrades the toughness and ductility due to formation of an embrittled phase, and thereby induces a nonconformity which is hazardous for the hot working. This also increases insoluble Cr nitride during the solution treatment, and thereby considerably lowers the corrosion resistance. The W content is preferably adjusted within a range from 0.05% by mass to 0.9% by mass, and more preferably from 0.1% by mass to 0.8% by mass, both ends inclusive.

(16) Co: 0.01% by mass to 5.0% by mass

**[0027]** Co contributes to improvement in the corrosion resistance and strength. An amount of addition of less than 0.01% by mass results in only a poor effect, whereas the amount of addition exceeding 5.0% by mass increases the cost, and undesirably increases insoluble Cr nitride during the solution heat treatment, and thereby considerably lowers the corrosion resistance. The Co content is preferably adjusted within a range from 0.05% by mass to 4.5% by mass, and more preferably from 0.1% by mass to 4.0% by mass, both ends inclusive.

**[0028]** In view of improving the strength and corrosion resistance, either one of, or both of W and Co can be added within the above-specified ranges.

(17) Ti: 0.01% by mass to 0.5% by mass

(18) Nb: 0.01 % by mass to 0.5% by mass

(19) V: 0.01 % by mass to 1.0% by mass

(20) Ta: 0.01% by mass to 0.5% by mass

**[0029]** All of Ti, Nb, V and Ta can bind with C and N, allow carbides or carbonitrides to precipitate, and thereby contribute to improvement in the strength. The precipitation can suppress growth of the austenitic grain by the pinning effect, and consequently contribute to improvement in the strength and toughness through refinement of the grain.

Amounts of addition of these elements of less than 0.01 % by mass result only in poor effects, whereas the amounts of addition exceeding the respective upper limits considerably degrade the corrosion resistance through formation of hazardous oxides or nitrides in the steel, and also undesirably make the strength more likely to degrade through lowering of an effective amount of N solubility. The Ti content is preferably adjusted within a range from 0.02% by mass to 0.4% by mass, and more preferably from 0.03% by mass to 0.3% by mass, both ends inclusive. The Nb content is preferably adjusted within a range from 0.02% by mass to 0.4% by mass, and more preferably from 0.03% by mass to 0.3% by mass, both ends inclusive. The V content is preferably adjusted within a range from 0.02% by mass to 0.9% by mass, and more preferably from 0.03% by mass to 0.8% by mass, both ends inclusive. The Ta content is preferably adjusted within a range from 0.02% by mass to 0.4% by mass, and more preferably from 0.03% by mass to 0.3% by mass, both ends inclusive.

**[0030]** It is allowable to add only a single element selected from Ti, Nb, V and Ta, or two or more elements in combination.

(21) B: 0.001 % by mass to 0.01 % by mass

**[0031]** B is an element effective for improving the strength and hot workability. An amount of addition of less than 0.001% by mass results in only a poor effect, whereas the content exceeding 0.01% by mass adversely affects the hot workability and also degrades the corrosion resistance. The B content is preferably adjusted within a range from 0.001 % by mass to 0.008% by mass, and more preferably from 0.001 % by mass to 0.005% by mass, both ends inclusive.

(22) Zr: 0.01% by mass to 0.50% by mass

**[0032]** Zr is an additive element effective for improving the strength. An amount of addition of less than 0.01% by mass results in only a limited effect, whereas the amount of addition exceeding 0.50% by mass degrades the toughness and ductility. The Zr content is preferably adjusted within a range from 0.03% by mass to 0.40% by mass, and more preferably from 0.05% by mass to 0.30% by mass, both ends inclusive.

(23) Ca: 0.001% by mass to 0.01% by mass

(24) Mg: 0.001% by mass to 0.01% by mass

**[0033]** Both of Ca and Mg are additive elements effective for improving the hot workability. Excessive addition of the both degrades the corrosion resistance, toughness, ductility and hot workability. They are also effective in view of improving the machinability. Amounts of addition of the both less than 0.001% results in only poor effects, whereas the amounts of addition exceeding 0.01% by mass undesirably degrade the hot workability. Each of the Ca and Mg contents is preferably adjusted within a range from 0.001% by mass to 0.008% by mass, and more preferably from 0.001% by mass to 0.005% by mass, both ends inclusive.

**[0034]** It is allowable to add only a single element selected from B, Zr, Ca and Mg, or two or more elements in combination.

(25) Te: 0.005% by mass to 0.05% by mass

(26) Se: 0.01% by mass to 0.20% by mass

**[0035]** Both of Te and Se are additive elements effective for improving the machinability. Amounts of addition of the both less than the lower limits result in only poor effects, and the amounts of addition exceeding the upper limits undesirably degrade the corrosion resistance, toughness, ductility and hot workability. The Te content is preferably adjusted within a range from 0.01% by mass to 0.04% by mass, both ends inclusive. The Se content is preferably adjusted within a range from 0.02% by mass to 0.18% by mass, and more preferably from 0.05% by mass to 0.15% by mass, both ends inclusive.

**[0036]** The high-nitrogen austenitic stainless steel of this invention is preferably subjected to solution treatment at 1,100°C to 1,250°C, both ends inclusive (typically for 0.1 hours to 2 hours, both ends inclusive). For example, by subjecting the steel of this invention after being melted so as to have the above-described composition to hot-forging or rolling, and further by subjecting the product to solution treatment within the above-described temperature range, the precipitated Cr nitride can be dissolved, and this successfully makes the structure uniform, and makes it possible to distinctively improve the corrosion resistance. According to the investigations by the present inventors, the Cr nitride particularly having a diameter (expressed in this patent specification by a diameter of a circle having an area same as that of the projected area of the nitride grain (referred to as circle-converted diameter, hereinafter)) of 2  $\mu\text{m}$  or larger remaining in the steel was found to largely affect the corrosion resistance. In order to ensure a desirable corrosion resistance, it is of course preferable that no Cr-base nitride having a diameter of 2  $\mu\text{m}$  or larger is observed in the sectional structure of the steel. It is to be noted herein that the solution heat treatment carried out within a temperature range from 1,100°C to 1,250°C does not always ensure disappearance of the Cr-base nitride of 2  $\mu\text{m}$  or larger in diameter, and that the hazardous Cr-base nitride of 2  $\mu\text{m}$  or larger in diameter can be suppressed to a satisfactory degree, only when an optimum solution heat treatment temperature is selected depending on steel composition within the above-described temperature range, which will be described later in Examples.

**[0037]** The steel of this invention can realize a strength of as large as 1,000 MPa on the tensile strength basis, after being subjected to the solution treatment carried out to an extent not causative of observable Cr-base nitride having a diameter of 2  $\mu\text{m}$  or larger.

**[0038]** The high-nitrogen austenitic stainless steel of this invention can be worked so as to produce wire product or sheet product. In this case, a more distinct level of strengthening is available by carrying out the area-reducing process at the final stage of the wire making or sheet making by cold wire drawing or cold rolling. After such process, Cr-base nitride having a diameter of 2  $\mu\text{m}$  or larger is observed neither in the section of a wire product 100, shown in FIG. 1, normal to the axis thereof, nor in the section of a sheet product 150, shown in FIG. 2, normal to the drawing direction thereof, and it is made possible to obtain the wire product or sheet product as having a mean grain size (in circle-converted diameter) of the austenitic matrix phase of 100  $\mu\text{m}$  or smaller. The refinement of the mean grain size of the austenitic matrix phase makes it possible to obtain the wire product or sheet product having an extremely high strength and an excellent corrosion resistance. A specific attainable level of strength may be 1,500 MPa or more, or may be even 2,000 MPa or more (strengthening up to 2,500 MPa or around, for example, is attainable, with the upper limit value not

specifically limited).

**[0039]** The finally-obtained grain size of the austenitic matrix phase of the wire product or sheet product is adjustable by working ratio (reduction of area for the wire product, and draft for the sheet product) in cold working which precedes the solution heat treatment. The mean grain size exceeding 100  $\mu\text{m}$  results in only a limited effect of improvement in the strength, whereas reduction in the mean grain size to as small as 2  $\mu\text{m}$  or smaller is technically difficult, considering that re-crystallization can proceed to a certain degree during the solution heat treatment within the above-described temperature range. Refinement of the structure may be more distinctive when any one or more of Ti, Nb, V and Ta, all of which being known to be effective in suppressing growth of the grain, are added within the above-described compositional ranges.

**[0040]** As has been described in the above, the high-nitrogen austenitic stainless steel of this invention is successful in achieving both of high corrosion resistance equivalent to that of SUS836L which is a super-austenitic stainless steel, and strength higher than that of SUS329J4L which is a dual-phase stainless steel, after being subjected to solution heat treatment. The steel can realize a strength of as high as 1,500 MPa or more (or even as high as 2,000 MPa or more), when cold-worked in a form of wire product or sheet product after the solution heat treatment.

**[0041]** The high-nitrogen austenitic stainless steel of this invention can be processed into various forms of wire product, rod steel, sheet steel, plate product, pipe, forged product and shape steel. Specific applications will be listed below.

**[0042]** Applications demanding consideration on biological contact are exemplified by those brought into direct contact with human body, and preferable examples include accessories such as necklace, pierce and ring; watch components such as back lid of wrist watch and band of wrist watch; spectacle components such as frame of a pair of spectacles; metal components for furniture or building interior such as door knob; cutlery and kitchen tools such as spoon, fork and ladle; metal components for home appliances; dental materials such as dental floss, artificial root and orthodontic wire; biological implant materials such as plate, bolt, nut, spring, screw, wire, electrode, artificial bone and artificial joint; and medical tools such as syringe needle, surgical knife, scalpel, saw, forceps and surgical drill.

**[0043]** The steel is applicable to general high-strength, high-corrosion-resistant materials, and preferable examples of the applications include bolt, nut, cylinder liner, shaft, hub, connector, bearing, lathe, rail, gear, pin, screw, roll, turbine blade, mold, die, drill, valve, valve sheet, cutting edge, nozzle, gasket, ring, spring, ocean beach environmental components, industrial furnace components, chemical plant components, oil drilling components, oil refining plant components, waste incinerator components, steam turbine components, gas turbine components, nuclear reactor components (e.g., secondary cooling water piping components for pressurized water reactor), aircraft components, structural components for construction and civil engineering (e.g., bridge components such as bridge pier and suspension bridge components, electric pole and steel tower for power cable), and decorative components.

**[0044]** The steel is also effectively applicable to high-strength, high-corrosion-resistant components which are necessarily non-magnetic, and examples of which include spring, shaft, bearing, lathe, pin, die and rail for precision electronic components; wire used for components for printed board production; mesh; biological implant electrode; MRI component; drug production components; hanger components; linear motor car components; components for semiconductor production apparatus; forceps, bearing; saw; and cutting edge.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0045]**

FIG. 1 is a drawing for explaining a definition of grain size of a wire product; and  
FIG. 2 is a drawing for explaining a definition of grain size of a sheet product.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0046]**

Table 1

|                        | C      | Si    | Mn    | P    | S    | Cu    | Ni    | Cr     | Mo     | Co   | W    | V     | Al     | Ti   | Nb   | O       | N     |
|------------------------|--------|-------|-------|------|------|-------|-------|--------|--------|------|------|-------|--------|------|------|---------|-------|
| Example 1              | 0.04   | 0.15  | 0.2   | 0.01 | 0.01 | 0.01  | 0.16  | 0.21   | 30.0   | 1.00 | 0.15 | 0.20  | 0.008  | 0.01 |      | 0.002   | 1.38  |
| Example 2              | 0.03   | 0.20  | 1.5   | 0.02 | 0.01 | 0.05  | 0.20  | 24.0   | 6.02   | 1.52 |      | 0.46  | 0.007  |      | 0.05 | 0.003   | 1.20  |
| Example 3              | 0.10   | 0.31  | 1.0   | 0.02 | 0.01 | 0.20  | 0.01  | 27.0   | 1.87   |      |      |       | 0.006  |      |      | 0.002   | 1.05  |
| Example 4              | 0.03   | 0.50  | 7.0   | 0.01 | 0.01 | 0.51  | 0.10  | 18.0   | 4.03   | 0.26 | 0.10 | 0.21  | 0.006  | 0.09 | 0.04 | 0.002   | 1.07  |
| Example 5              | 0.02   | 0.11  | 9.0   | 0.02 | 0.01 | 0.32  | 0.30  | 26.0   | 2.50   | 0.98 |      | 0.48  | 0.005  | 0.06 |      | 0.002   | 1.33  |
| Example 6              | 0.03   | 0.19  | 2.0   | 0.02 | 0.01 | 0.16  | 0.20  | 25.0   | 1.50   | 0.34 | 0.14 | 0.01  | 0.006  |      |      | 0.001   | 1.20  |
| Example 7              | 0.05   | 0.16  | 3.0   | 0.01 | 0.01 | 1.50  | 0.08  | 26.0   | 2.01   |      | 0.13 | 0.004 |        |      |      | 0.003   | 0.84  |
| Example 8              | 0.03   | 0.22  | 1.5   | 0.02 | 0.01 | 0.16  | 0.07  | 25.0   | 2.45   | 0.47 | 0.15 |       | 0.005  |      |      | 0.001   | 1.12  |
| Example 9              | 0.05   | 0.21  | 1.8   | 0.02 | 0.01 | 0.16  | 0.40  | 25.1   | 0.10   | 0.20 |      | 0.02  | 0.006  | 0.02 | 0.01 | 0.003   | 1.17  |
| Example 10             | 0.06   | 0.20  | 1.5   | 0.02 | 0.01 | 0.97  | 0.07  | 32.0   | 0.51   | 0.31 | 0.05 | 0.32  | 0.005  | 0.15 | 0.05 | 0.003   | 1.21  |
| Example 11             | 0.01   | 0.28  | 5.0   | 0.01 | 0.01 | 0.10  | 0.09  | 28.0   | 0.54   | 0.29 | 0.16 | 0.12  | 0.010  |      | 0.07 | 0.002   | 0.98  |
| Example 12             | 0.03   | 0.01  | 2.0   | 0.02 | 0.01 | 0.16  | 0.03  | 28.4   | 0.52   |      | 0.15 | 0.01  | 0.007  |      |      | 0.005   | 1.22  |
| Example 13             | 0.03   | 0.20  | 1.8   | 0.02 | 0.01 | 0.19  | 0.02  | 26.0   | 1.99   |      |      |       | 0.008  |      |      | 0.001   | 1.14  |
| Comparative Example 1  | * 0.31 | 0.24  | 4.0   | 0.01 | 0.01 | 0.14  | 0.31  | 26.8   | 0.54   |      |      | 0.20  | 0.006  |      |      | 0.002   | 1.11  |
| Comparative Example 2  | 0.06   | *2.51 | 2.0   | 0.01 | 0.01 | 0.16  | 0.06  | 23.9   | 1.97   |      |      | 0.15  | 0.008  | 0.03 | 0.05 | 0.004   | *0.74 |
| Comparative Example 3  | 0.04   | 0.19  | *12.2 | 0.02 | 0.01 | 0.14  | 0.16  | * 13.0 | 7.99   |      |      | 0.51  | 0.009  |      | 0.05 | 0.002   | 1.21  |
| Comparative Example 4  | 0.05   | 0.14  | 8.0   | 0.02 | 0.01 | *4.98 | 0.10  | 20.1   | 0.98   |      |      | 0.11  | 0.009  |      |      | 0.005   | 0.99  |
| Comparative Example 5  | 0.04   | 0.12  | * 0.1 | 0.02 | 0.01 | 0.21  | *6.01 | 29.5   | 0.56   | 0.05 | 0.05 | 0.31  | 0.007  |      |      | 0.003   | 1.31  |
| Comparative Example 6  | 0.05   | 0.15  | 2.0   | 0.02 | 0.01 | 0.19  | 0.20  | * 37.0 | 0.51   |      |      |       | 0.009  |      |      | 0.002   | 1.02  |
| Comparative Example 7  | 0.05   | 0.20  | 6.0   | 0.01 | 0.01 | 0.15  | 0.07  | 19.2   | *12.02 |      |      |       | 0.008  | 0.05 |      | 0.003   | 1.08  |
| Comparative Example 8  | 0.07   | 0.21  | 4.0   | 0.02 | 0.01 | 0.15  | 0.17  | 20.9   | 4.02   | 0.51 |      |       | *0.060 |      |      | 0.002   | 0.99  |
| Comparative Example 9  | 0.03   | 0.16  | 1.5   | 0.02 | 0.01 | 0.18  | 0.16  | 24.0   | 0.52   | 0.15 | 0.05 |       | 0.010  |      |      | * 0.031 | 1.20  |
| Comparative Example 10 | 0.08   | 0.23  | 1.0   | 0.01 | 0.01 | 0.14  | 0.24  | 29.1   | 1.01   |      |      |       | 0.009  | 0.11 |      | 0.004   | *1.80 |
| Comparative Example 11 | 0.07   | 0.15  | *12.0 | 0.01 | 0.01 | 0.20  | 0.01  | 17.5   | 2.01   |      |      |       | 0.012  |      |      | 0.003   | 1.01  |
| Comparative Example 12 | 0.02   | 0.17  | 0.8   | 0.02 | 0.01 | 0.92  | *25.1 | 20.2   | 6.27   |      |      |       | 0.009  |      |      | 0.040   | *0.14 |
| Comparative Example 13 | 0.02   | 0.21  | 0.9   | 0.02 | 0.01 |       | * 6.4 | 24.9   | 3.98   |      |      |       | 0.010  |      |      | 0.004   | *0.19 |
| Comparative Example 14 | 0.04   | 0.34  | 1.1   | 0.03 | 0.01 | 0.15  | *11.8 | 17.5   | 2.12   |      |      |       | 0.025  |      |      | 0.005   | *0.03 |

\* out of inventive range

Table 2

|                        | B     | Mg    | Ca    | Ta   | Zr   | Te   | Se   | (Cr+3.3Mo+16N)/Mn |
|------------------------|-------|-------|-------|------|------|------|------|-------------------|
| Example 1              |       |       |       |      |      |      |      | 251.7             |
| Example 2              |       |       |       |      | 0.09 |      |      | 42.0              |
| Example 3              |       |       | 0.003 |      |      |      |      | 50.0              |
| Example 4              |       | 0.003 |       |      |      |      |      | 6.9               |
| Example 5              | 0.003 | 0.003 | 0.002 | 0.09 | 0.10 | 0.03 |      | 6.2               |
| Example 6              |       |       |       |      |      |      |      | 24.7              |
| Example 7              |       |       |       |      |      | 0.03 | 0.10 | 15.4              |
| Example 8              |       |       |       |      |      |      |      | 34.0              |
| Example 9              |       |       |       |      |      |      |      | 24.5              |
| Example 10             | 0.003 |       |       | 0.09 |      |      |      | 35.4              |
| Example 11             | 0.002 |       | 0.002 | 0.09 |      |      |      | 9.1               |
| Example 12             | 0.002 | 0.003 |       |      |      |      |      | 24.8              |
| Example 13             |       |       |       |      |      |      |      | 28.2              |
| Comparative Example 1  |       |       |       |      |      |      |      | 11.6              |
| Comparative Example 2  |       |       |       |      |      | 0.03 | 0.10 | 21.1              |
| Comparative Example 3  |       |       |       |      |      |      | 0.09 | * 4.8             |
| Comparative Example 4  | 0.003 |       |       |      |      |      |      | * 4.9             |
| Comparative Example 5  |       |       |       |      |      | 0.02 | 0.10 | 475.5             |
| Comparative Example 6  |       | 0.003 |       | 0.11 |      |      | 0.11 | 27.5              |
| Comparative Example 7  | 0.002 |       | 0.003 | 0.10 |      |      |      | 12.7              |
| Comparative Example 8  |       |       |       | 0.11 | 0.09 |      |      | 12.5              |
| Comparative Example 9  |       | 0.003 |       |      | 0.11 |      |      | 29.9              |
| Comparative Example 10 |       |       | 0.002 |      |      |      |      | 61.2              |
| Comparative Example 11 |       |       |       |      |      |      |      | * 3.4             |
| Comparative Example 12 |       |       |       |      |      |      |      | 57.5              |
| Comparative Example 13 |       |       |       |      |      |      |      | 45.6              |
| Comparative Example 14 |       |       |       |      |      |      |      | 22.7              |

\* out of inventive range

Table 3

|                        | N blow holes<br>Yes/No | Solution heat treatment temperature<br>°C | Mean grain size<br>μm | Tensile strength<br>MPa | Pitting corrosion potential<br>V vs SCE |
|------------------------|------------------------|-------------------------------------------|-----------------------|-------------------------|-----------------------------------------|
| Example 1              | No                     | 1250                                      | 163                   | 1184                    | >0.90                                   |
| Example 2              | No                     | 1200                                      | 97                    | 1147                    | >0.90                                   |
| Example 3              | No                     | 1200                                      | 102                   | 1115                    | >0.90                                   |
| Example 4              | No                     | 1150                                      | 74                    | 1120                    | >0.90                                   |
| Example 5              | No                     | 1100                                      | 54                    | 1171                    | >0.90                                   |
| Example 6              | No                     | 1200                                      | 105                   | 1140                    | >0.90                                   |
| Example 7              | No                     | 1200                                      | 99                    | 1075                    | >0.90                                   |
| Example 8              | No                     | 1200                                      | 93                    | 1130                    | >0.90                                   |
| Example 9              | No                     | 1200                                      | 97                    | 1141                    | >0.90                                   |
| Example 10             | No                     | 1250                                      | 159                   | 1146                    | >0.90                                   |
| Example 11             | No                     | 1150                                      | 78                    | 1102                    | >0.90                                   |
| Example 12             | No                     | 1200                                      | 96                    | 1146                    | >0.90                                   |
| Example 13             | No                     | 1200                                      | 104                   | 1133                    | >0.90                                   |
| Comparative Example 1  | No                     | 1200                                      | 110                   | 1122                    | 0.69                                    |
| Comparative Example 2  | No                     | 1200                                      | 98                    | 1039                    | 0.75                                    |
| Comparative Example 3  | No                     | 1100                                      | 55                    | 1144                    | 0.63                                    |
| Comparative Example 4  | No                     | Forging crack                             | Forging crack         | Forging crack           | Forging crack                           |
| Comparative Example 5  | No                     | 1300                                      | 588                   | 1162                    | >0.90                                   |
| Comparative Example 6  | No                     | 1300                                      | 473                   | 1103                    | >0.90                                   |
| Comparative Example 7  | No                     | 1300                                      | 643                   | 1118                    | >0.90                                   |
| Comparative Example 8  | No                     | 1200                                      | 105                   | 1097                    | 0.77                                    |
| Comparative Example 9  | No                     | 1200                                      | 100                   | 1140                    | 0.60                                    |
| Comparative Example 10 | Yes                    |                                           |                       |                         |                                         |
| Comparative Example 11 | No                     | 1100                                      | 58                    | 1094                    | 0.49                                    |
| Comparative Example 12 | No                     | 1150                                      | 92                    | 690                     | >0.90                                   |
| Comparative Example 13 | No                     | 1100                                      | 55                    | 702                     | >0.90                                   |
| Comparative Example 14 | No                     | 1100                                      | 43                    | 591                     | 0.39                                    |

Table 4

|           | Product form | Cold working ratio % | Tensile strength Mpa | Mean grain size μm |
|-----------|--------------|----------------------|----------------------|--------------------|
| Example 5 | sheet        | 50                   | 2178                 | 44                 |
|           |              | 70                   | 2455                 | 26                 |

Table continued

|    | Product form             | Cold working ratio % | Tensile strength Mpa | Mean grain size $\mu\text{m}$ |
|----|--------------------------|----------------------|----------------------|-------------------------------|
| 5  | wire                     | 50                   | 2188                 | 49                            |
|    |                          | 70                   | 2461                 | 25                            |
| 10 | Example 6<br>sheet sheet | 50                   | 2151                 | 54                            |
|    |                          | 70                   | 2389                 | 33                            |
|    | wire                     | 50                   | 2156                 | 63                            |
|    |                          | 70                   | 2377                 | 35                            |
| 15 | Example 13<br>sheet      | 50                   | 2162                 | 59                            |
|    |                          | 70                   | 2392                 | 36                            |
|    | wire                     | 50                   | 2158                 | 60                            |
|    |                          | 70                   | 2403                 | 30                            |

**[0047]** Each of steels having chemical compositions listed in Table 1 and Table 2 was melted under a pressurized atmosphere having a nitrogen partial pressure of 50 atm or less during melting in a pressurizable high-frequency induction furnace, and then cast to produce a 50-kg steel ingot. A test piece was cut out from the bottom portion of the steel ingot, and visually observed for presence or absence of nitrogen blow holes. The steel ingot was then homogenized under heating, and hot-forged to thereby produce a 24-mm-diameter round rod. A rod was heated at a varied temperature from 1,100°C to 1,300°C for one hour, and water-cooled so as to accomplish the solution heat treatment. The sectional structure was then observed under an optical microscope (400x magnification) to thereby confirm whether the Cr-base nitride having a diameter of 2  $\mu\text{m}$  or larger on the circle-converted diameter basis has been produced or not. A minimum temperature not causative of the Cr-base nitride was determined as the solution heat treatment temperature. A test sample was then collected from a steel product processed at thus-determined solution heat treatment temperature, and subjected to each of the measurements listed below (Comparative Examples 12 to 14 correspond to SUS836L, SUS329J4L and SUS316, respectively):

(1) Mean Grain Size

Twenty fields of view in the sectional structure were randomly observed under an optical microscope (100x magnification), to thereby measure the mean grain size, conforming to JIS G0551.

(2) Tensile Strength

Measured by a method conforming to JIS Z2241.

(3) Pitting Corrosion Potential

Measured by a method conforming to JIS G0577.

**[0048]** In each of Examples 5, 6 and 13, the 50-kg steel ingot was homogenized under heating, then hot-forged, and hot-rolled so as to obtain a 12.5-mm-diameter wire product, subjected to solution heat treatment under the condition determined in the above, and cold-drawn with reductions of area of 50% and 70% so as to obtain wire products of 8.8 mm in diameter and 6.8 mm in diameter, respectively. These wire products were also subjected to measurements of tensile strength and mean grain size, similarly to as described in the above. Again in each of Examples 5, 6 and 13, the 50-kg steel ingot was homogenized under heating, then hot-forged, and hot-rolled so as to obtain a 5-mm-thick sheet product, subjected to solution heat treatment under the condition determined in the above, and cold-rolling with drafts of 50% and 70% so as to obtain sheet products of 2.5 mm thick and 1.5 mm thick, respectively. These sheet products were also subjected to measurements of tensile strength and mean grain size, similarly to as described in the above. Results are shown in Table 3 and Table 4.

**[0049]** It was found from the results shown in Table 3 that the steels of Examples 1 to 13 were very excellent in both of the tensile strength after the solution heat treatment and corrosion resistance indicated by the pitting corrosion potential, and were successful in attaining higher levels of strength and corrosion resistance as compared with those of ever-known austenitic stainless steels SUS836L, SUS329J4L and SUS316, shown in Comparative Examples 12 to 14, respectively. It was also found from the results shown in Table 4 that the steels of this invention, cold-processed into forms of wire product and sheet product, successfully achieved a super-high strength of as high as 2,000 MPa or above.

## Claims

1. A high-nitrogen austenitic stainless steel having a Fe content of 50% by mass or more, and containing:

Cr: 15.0% by mass to 35.0% by mass;  
 Mo: 0.05% by mass to 8.0% by mass;  
 Mn: 0.2% by mass to 10.0% by mass;  
 Cu: 0.01 % by mass to 4.0% by mass; and  
 N: 0.8% by mass to 1.5% by mass,  
 both ends inclusive,  
 having a C content of 0.20% by mass or less, a Si content of 2.0% by mass or less, a P content of 0.03% by mass or less, a S content of 0.05% by mass or less, a Ni content of 0.5% by mass or less, an Al content of 0.03% by mass or less, and an O content of 0.020% by mass or less;

wherein the contents of Cr, Mo, N and Mn are adjusted so that a compositional parameter  $\eta$  expressed by the equation:

$$\eta \equiv (W_{Cr} + 3.3W_{Mo} + 16W_N) / W_{Mn}$$

where  $W_{Cr}$  is Cr content (% by mass),  $W_{Mo}$  is Mo content (% by mass),  $W_N$  is N content (% by mass) and  $W_{Mn}$  is Mn content (% by mass) has a value of 5 or above ;  
 and optionally further containing either one of, or both of:

W: 0.01% by mass to 1.0% by mass; and  
 Co: 0.01% by mass to 5.0% by mass,  
 both ends inclusive ;  
 and optionally further containing at least one of:  
 Ti: 0.01% by mass to 0.5% by mass;  
 Nb: 0.01% by mass to 0.5% by mass;  
 V: 0.01% by mass to 1.0% by mass; and  
 Ta: 0.01% by mass to 0.5% by mass,  
 both ends inclusive ;  
 and optionally further containing at least one of:  
 B: 0.001 % by mass to 0.01 % by mass;  
 Zr: 0.01% by mass to 0.50% by mass;  
 Ca: 0.001% by mass to 0.01% by mass; and  
 Mg: 0.001% by mass to 0.01% by mass,  
 both ends inclusive ;  
 and optionally further containing either one of, or both of:  
 Te: 0.005% by mass to 0.05% by mass; and  
 Se: 0.01% by mass to 0.20% by mass,  
 both ends inclusive.

2. The high-nitrogen austenitic stainless steel as claimed in Claims 1, having no Cr-base nitride having a diameter of 2  $\mu\text{m}$  or larger observed in the sectional structure thereof after being subjected to solution heat treatment at 1,100°C to 1,250°C, both ends inclusive.
3. The high-nitrogen austenitic stainless steel as claimed in Claim 2, having a tensile strength of 1,000 MPa or more after being subjected to the solution heat treatment.
4. The high-nitrogen austenitic stainless steel as claimed in any one of Claims 1 to 2, being cold-worked in a form of wire product, having no Cr-base nitride having a diameter of 2  $\mu\text{m}$  or larger observed in the structure thereof which appears in a section normal to the axis of the wire product, and having a mean grain size of the austenitic matrix phase of 100  $\mu\text{m}$  or smaller.
5. The high-nitrogen austenitic stainless steel as claimed in any one of Claims 1 to 2, being cold-worked in a form of sheet product, having no Cr-base nitride having a diameter of 2  $\mu\text{m}$  or larger observed in the structure thereof which

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appears in a section normal to the drawing direction of the sheet product, and having a mean grain size of the austenitic matrix phase of 100  $\mu\text{m}$  or smaller.

6. The high-nitrogen austenitic stainless steel as claimed in Claim 4 or 5, having a tensile strength of 1,500 MPa or more.

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FIG.1

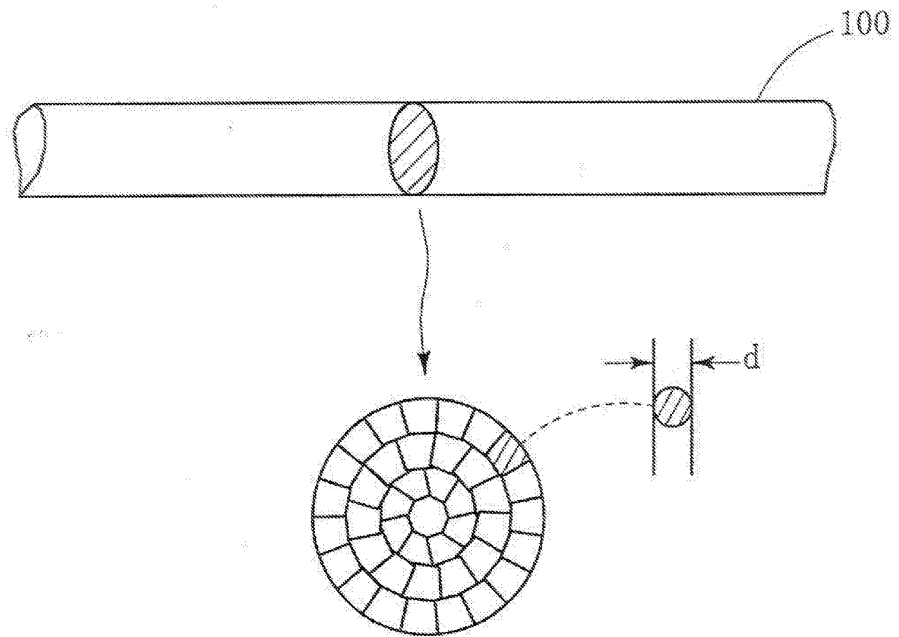
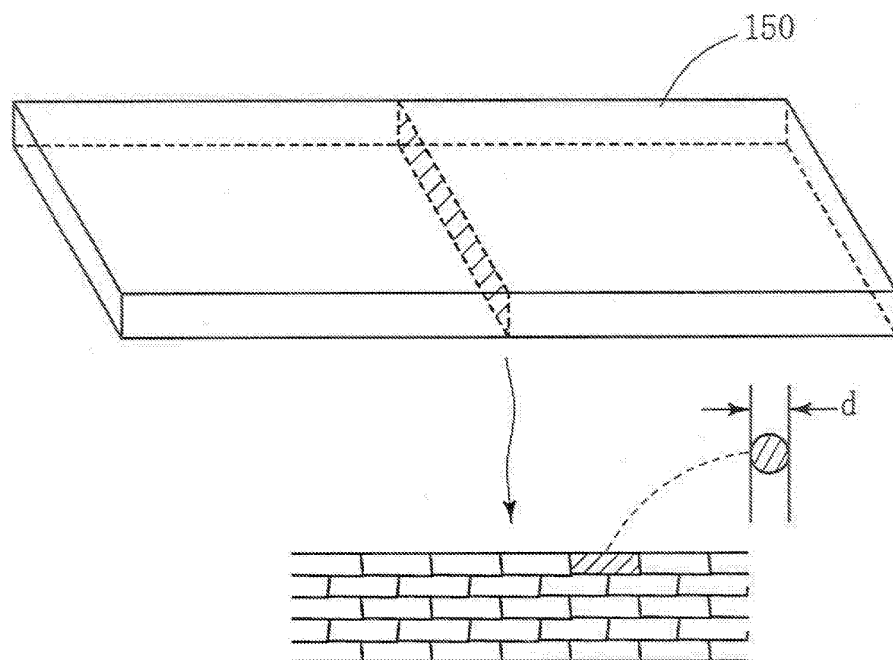


FIG.2





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 05 10 7313

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                        |                                                      |                                                 |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|-------------------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Citation of document with indication, where appropriate, of relevant passages                                                                                                                                          | Relevant to claim                                    | CLASSIFICATION OF THE APPLICATION (IPC)         |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | EP 1 229 142 A (DAIDO TOKUSHUKO KABUSHIKI KAISHA) 7 August 2002 (2002-08-07)<br>* page 3, line 5 - page 5, line 43 *<br>* claims 1-7 *<br>* tables 1-1-2-2 *                                                           | 1-6                                                  | C22C38/20<br>C22C38/22<br>C22C38/38<br>C21D6/00 |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | DE 196 07 828 A1 (VSG ENERGIE + SCHMIEDETECHNIK GMBH, 45143 ESSEN, DE; VSG ENERGIE- UND) 17 October 1996 (1996-10-17)<br>* claims 1-11 *<br>* page 2, line 1 - page 3, line 20 *<br>* examples 1,2 *<br>* tables 1,2 * | 1-6                                                  |                                                 |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | CH 688 862 A (BASF AKTIENGESELLSCHAFT) 30 April 1998 (1998-04-30)<br>* claims 1-7 *<br>* page 2, line 1 - page 5, line 18 *                                                                                            | 1-6                                                  |                                                 |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | CH 688 914 A5 (BASF AKTIENGESELLSCHAFT) 29 May 1998 (1998-05-29)<br>* claims 1-7 *<br>* page 2, line 1 - page 5, line 18 *                                                                                             | 1-6                                                  | TECHNICAL FIELDS SEARCHED (IPC)<br>C22C<br>C21D |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US 5 714 115 A (SPEIDEL ET AL) 3 February 1998 (1998-02-03)<br>* claims 1-20 *<br>* column 1, line 1 - column 3, line 56 *<br>* examples 1,2 *                                                                         | 1-6                                                  |                                                 |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US 6 682 581 B1 (SPEIDEL MARKUS) 27 January 2004 (2004-01-27)<br>* claims 1-7 *<br>* column 3, line 64 - column 5, line 39 *                                                                                           | 1-6                                                  |                                                 |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | EP 0 422 360 A (VEREINIGTE SCHMIEDWERKE GMBH) 17 April 1991 (1991-04-17)<br>* claims 1-6 *                                                                                                                             | 1-6                                                  |                                                 |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                        | -/--                                                 |                                                 |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                        |                                                      |                                                 |
| Place of search<br>The Hague                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                                                                                                        | Date of completion of the search<br>24 November 2005 | Examiner<br>Vlassi, E                           |
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