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(54) **CAST IRON-BASED AUSTENITE CREEP-RESISTANT STEEL, AND PREPARATION METHOD
AND USE THEREFOR**

(57) The present invention belongs to the technical field of austenitic creep-resistant steel, in particular to a cast iron-based austenitic creep-resistant steel and preparation method and application thereof. The austenitic creep-resistant steel according to the present invention comprises, by mass percentage, the following components: C: 0.2 to 0.5; Si: 0.5 to 2.0; Mn<0.5; Cr: 20 to 28; Ni: 8 to 13; P≤0.04; S≤3; W: 0.5 to 2; N: 0.2 to 0.4; with the balance being iron and other unavoidable impurities.

The austenitic creep-resistant steel prepared according to the present invention suppresses the high-temperature ferrite phase and thus eliminating the defects of precipitated nitrogen porosity, reduces the processing cost of castings as compared with the ordinary Cr-Ni-based austenitic heat-resistant steel by optimizing the range of addition of nitrogen and carbon elements, and offers excellent mechanical properties at high temperature and long creep fracture time.

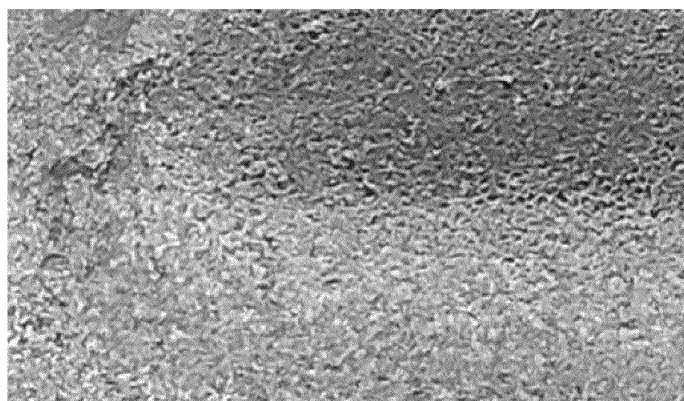


FIG. 1

Description**Technical Field**

5 **[0001]** The present invention belongs to the technical field of austenitic creep-resistant steel, in particular to a cast iron-based austenitic creep-resistant steel and preparation method and application thereof.

Background

10 **[0002]** Austenitic steel is a steel with austenitic structure after normalizing. The alloying elements (Ni, Mn, N, Cr, etc.) added to the steel can give the metal a stable austenitic structure after normalizing.

15 **[0003]** The iron-based austenitic creep-resistant steel refers to a heat-resistant steel with an austenitic structure at room temperature and special requirements for high-temperature creep properties of the material. The steel, based on Fe, comprises about 20% to 25% of Cr, about 9% to 40% of Ni, about 0.3% to 0.5% of C, about 0.5% to 2% of Nb and a certain amount of Mo, W, and B elements. Among the three austenitic matrix heat-resistant steels (superalloys) of Fe, Co, and Ni, the cost of iron-based heat-resistant raw materials is the lowest, but the thermal stability of the austenitic matrix is the worst, the TCP phase precipitates the fastest when used at high temperature for a long time, therefore the creep resistance is the worst.

Summary

20 **[0004]** The present invention provides a cast iron-based austenitic creep-resistant steel and preparation method and application thereof.

25 **[0005]** To solve the above described technical problems, the present invention provides an austenitic creep-resistant steel, comprising, by mass percentage, the following components: C: 0.2 to 0.5; Si: 0.5 to 2.0; Mn<0.5; Cr: 20 to 28; Ni: 8 to 13; P≤0.04; S≤0.3; W: 0.5 to 2; N: 0.2 to 0.4; with the balance being iron and other unavoidable impurities.

30 **[0006]** In another aspect, the present invention provides a preparation method of austenitic creep-resistant steel, comprising adding the foresaid raw materials into an intermediate frequency furnace for smelting and casting the melt into a mould, whereby the austenitic creep-resistant steel is obtained.

35 **[0007]** In a third aspect, the present invention also provides an application of the foresaid austenitic creep-resistant steel in an automobile engine exhaust manifold or a turbocharger housing.

40 **[0008]** The present invention is advantageous in that the austenitic creep-resistant steel prepared according to the present invention suppresses the high-temperature ferrite phase and thus eliminating the defects of precipitated nitrogen porosity; in that it reduces the processing cost of castings as compared with the ordinary Cr-Ni-based austenitic heat-resistant steel by optimizing the range of addition of nitrogen and carbon elements; and in the excellent mechanical properties at high temperature and long creep fracture time. With the reduction in cost of the raw materials by more than 60%, the high temperature creep fracture time, the thermal conductivity and the linear expansion coefficient reach the level of 1.4849 heat-resistant steel.

45 **[0009]** Other features and advantages of the present invention will be described in the following description, and will become apparent in part from the description, or will be understood by implementing the invention. The objects and other advantages of the present invention are achieved and obtained by means of the structures particularly indicated in the description as well as in the accompanying drawings.

50 **[0010]** In order to make the above objects, features and advantages of the present invention more obvious and understandable, detailed description will be given below based on preferred embodiments in conjunction with the drawings.

Description of the Drawings

55 **[0011]** In order to more clearly illustrate the embodiments of the present invention or the technical solutions in the prior art, the accompanying drawings to be used in the description of the embodiments or prior art will be briefly described below. It is obvious that the accompanying drawings in the following description are only some of the embodiments recorded in the present invention, and other accompanying drawings can be obtained according to these accompanying drawings without creative work for those of ordinary skill in the art.

FIG. 1 is a sample drawing of an austenitic creep-resistant steel prepared according to Example 1 of the present invention.

FIG. 2 is a sample drawing of an austenitic creep-resistant steel prepared according to Comparative Example 1 of the present invention.

Description of the Embodiments

[0012] In order to make the objects, technical solutions and advantages of the embodiments of the present invention clearer, the technical solutions of the present invention will be described clearly and completely in conjunction with the accompanying drawings, and it is clear that the described embodiments are a part of the embodiments of the present invention, and not all of them. Based on the embodiments in the present invention, all other embodiments obtained by those skilled in the art without making creative efforts fall within the scope of protection of the present invention. In iron-based austenitic steel, nickel is the main austenitizing element, whose main role is to form and stabilize austenite, making austenitic steels obtain good high-temperature mechanical properties and oxidation and corrosion resistance, both to avoid phase transformation when cooled to room temperature and to inhibit the precipitation of TCP phase during prolonged use at high temperatures. Nickel is a precious metal element and is a strategic resource. The production of austenitic creep-resistant steel consumes a large amount of nickel, resulting in high prices of its products. The development of low-nickel austenitic creep-resistant steel that replaces nickel in whole or in part with other cheap alloying elements is conducive to reducing costs and improving the market competitiveness of heat-resistant steel products.

[0013] As strong austenite-forming elements, when used as interstitial solid solution elements, the effect of nitrogen and carbon on stabilizing austenite is about 30 times that of nickel, which can greatly reduce the amount of nickel used in austenitic creep-resistant steel, thereby reducing the costs of raw materials. However, in actual production, the addition of nitrogen often makes the castings produce nitrogen porosity defects, and seriously affect the machining and cutting performance of materials. Carbon in excess will also form carbide thus increasing the cost of machining tools, resulting in an increase in the overall cost of production, which is not worth the candle.

[0014] To solve the above described technical problems, the present invention provides an austenitic creep-resistant steel, comprising, by mass percentage, the following components: C: 0.2 to 0.5; Si: 0.5 to 2.0; Mn<0.5; Cr: 20 to 28; Ni: 8 to 13; P≤0.04; S≤0.3; W: 0.5 to 2; N: 0.2 to 0.4; with the balance being iron and other unavoidable impurities.

[0015] In particular, the austenitic creep-resistant steel according to the present invention eliminates the defects of precipitated nitrogen porosity by suppressing the high-temperature ferrite phase, reduces the processing cost of castings as compared with the ordinary Cr-Ni-based austenitic heat-resistant steel by optimizing the range of addition of nitrogen and carbon elements and by adding an appropriate amount of easy-cutting elements, and offers better creep fracture time than 1.4849 heat-resistant steel at 1000°C and 35 MPa while greatly reducing the cost of raw materials. In the austenitic creep-resistant steel of the present invention, C can form carbides having high thermal stability with Cr and W elements at grain boundaries, which play a role in precipitation strengthening of grain boundaries to reduce the rate of creep at grain boundaries, thereby improving the service life of the parts. Also, in the present invention, C and N together replace the precious metal Ni to play the role of stabilizing the austenite matrix and reducing the cost of raw materials. Under the composition of the present invention, when C is less than 0.2%, the as-cast matrix contains about 3% (volume percentage) of TCP phase. After aging treatment at 900°C to 1000°C, more TCP phases will be precipitated (>5%), which shortened the creep fracture time of the material at 1000 °C by about 80%. When the C content exceeds 0.4%, carbides appear inside the grain, as a result, the machining performance deteriorates seriously and the machining tool cost increases by 100% to 900%. Based on this, the mass percentage of C in the austenitic creep-resistant steel according to the present invention is controlled to 0.2% to 0.5%.

[0016] In the austenitic creep-resistant steel of the present invention, the role of Si is to assist deoxidation during smelting to improve the fluidity of molten steel, reduce defects of casting slag holes, and slightly improve high-temperature oxidation resistance and corrosion resistance. When Si is > 2.0% or < 0.5%, the fluidity of molten steel drops sharply while the defects of casting slag holes increase sharply. Si is the main ferrite forming element. Too high Si content leads to appearance of the ferrite phase in the as-cast state, and reduces the high temperature stability of the austenite matrix and carbides, reducing the service life of the parts. In the austenitic creep-resistant steel according to the present invention, the mass percentage of Si is controlled at 0.5% to 2.0%.

[0017] In the austenitic creep-resistant steel according to the present invention, the content of Mn needs to be controlled <0.5%. Generally, Mn can replace Ni to reduce the cost of raw materials, and can also react with S to form spherical MnS, reducing the hot brittleness of grain boundary FeS. In the present invention, however, when the mass percentage of Mn is greater than 0.5%, the defects of precipitated porosity increase significantly, and the absorption rate of N during smelting decreases significantly. Since the N element is added to the molten steel through the N-containing alloy, other alloying elements will be brought in. The decrease in the N absorption rate will lead to an increase in the amount of N-containing alloy added, and the amount of other alloying elements brought in also increases, making the adjustment of the composition of the molten steel more difficult. In mass production, as the casting rework also contains N, when the Mn content is too high, the N in the rework in the steel melting process is also lost seriously. Since the lost N needs to be supplemented by N-containing alloy, the proportion of casting rework used is reduced. Therefore, when the yield of the actual process is low, this will cause a backlog of casting rework, making recycling impossible. According to Pauling's theory, the electron vacancy number of Mn is 3.66, the highest among the austenite-forming elements. In iron-based austenitic creep-resistant steels with low nickel equivalents, Mn significantly promotes the formation of TCP phase,

decreasing the stability of the austenitic matrix and making the creep rate increase. Therefore, it is necessary to use low-Mn raw materials to reduce the Mn content.

[0018] In the austenitic creep-resistant steel according to the present invention, the main role of Cr is to provide oxidation resistance and corrosion resistance from 900 to 1050°C, as well as to increase the solubility of N in the molten steel, thereby improving the absorption rate of N when N-containing alloys are added, reducing boiling of the molten steel at high temperatures, and reducing the defects of casting porosity. However, Cr is a ferrite forming element. Too high Cr content leads to appearance of the ferrite phase in the as-cast state. At a temperature above 900°C, the tensile strength of ferrite is less than one-tenth of that of austenite, seriously reducing the high-temperature mechanical properties of the parts. Cr is also a TCP phase forming element and has an electron vacancy number of 4.66. When the Cr mass percentage is less than 20%, the solubility of N in the molten steel is less than 0.3%, resulting in the appearance of the sigma phase in the as-cast structure and increasing the defects of casting porosity. When the Cr mass percentage is greater than 28%, the ferrite phase also appears in the as-cast state when the content of other alloying elements meets the requirements. Based on this, the mass percentage of Cr in the technical solution according to the present invention is controlled to 20% to 28%.

[0019] In the austenitic creep-resistant steel according to the present invention, Ni is the primary austenite-forming element and has an electron vacancy number of 0.66, and is the strongest element to inhibit the TCP phase in the main alloying elements of iron-based heat-resistant steel. Ni is the alloying element with the highest proportion in raw material cost. Ni also reduces the solubility of N, which increases casting porosity defects at higher levels of both elements. In the case that the content of other alloying elements meets the requirements, when the mass percentage of Ni is less than 8%, the material matrix contains about 1% (volume percentage) of TCP phase in the as-cast state. After aging treatment at 900°C to 1000°C, more TCP phases will be precipitated (>3%), which will shorten the creep fracture time of the material at 1000 °C by about 60%. However, when the Ni content exceeds 13%, the creep rupture time begins to decrease when the Ni content continues to increase. Based on this, the mass percentage of Ni in the technical solution according to the present invention is controlled to 8% to 13%.

[0020] In the austenitic creep-resistant steel according to the present invention, the main role of W is to form carbides with C for precipitation strengthening, and the W dissolved in the matrix can play the effect of solid solution strengthening, improving creep rupture time and inhibiting the defects of nitrogen porosity. Compared with Mo, which has a similar effect, the chromium equivalent factor of W is smaller and has fewer side effects on the stability of the austenite matrix. When the addition of W exceeds 2%, the continuous increase of W will not increase the creep fracture time, but the material chromium equivalent and the average electron vacancy number increase. Based on this, in the technical solutions described in the present invention the mass percentage of W is controlled to 0.5% to 2%.

[0021] In the austenitic creep-resistant steel according to the present invention, N is the main austenite-forming element and solid solution N can replace about 30 times Ni. However, when the mass percentage of N is >0.4%, the addition of >25% Cr and >2% W cannot suppress the defects of precipitated nitrogen porosity, while the processing properties deteriorate. Based on this, the mass percentage of N in the technical solution according to the present invention is controlled to 0.2% to 0.4%.

[0022] The austenitic creep-resistant steel has a tensile strength of not less than 110 MPa at 1000°C, a yield strength of not less than 40 MPa, and an elongation after fracture of not less than 15%.

[0023] The austenitic creep-resistant steel has a creep fracture time of not less than 77h at 1000°C and 35 MPa.

[0024] The austenitic creep-resistant steel has a thermal conductivity of 22 to 24 W/(m·K) at 800°C and 26 to 27 W/(m·K) at 1000°C.

[0025] The austenitic creep-resistant steel has an average linear expansion coefficient of $(17-18) \times 10^{-6}$ at 25 to 800°C and $(17-19) \times 10^{-6}$ at 25 to 1000°C.

[0026] In another aspect, the present invention provides a preparation method of austenitic creep-resistant steel, comprising adding the foresaid raw materials into an intermediate frequency furnace for smelting and casting the melt into a mould, whereby the austenitic creep-resistant steel is obtained.

[0027] The present invention also provides an application of the foresaid austenitic creep-resistant steel in an automobile engine exhaust manifold or a turbocharger housing.

[0028] The austenitic creep-resistant steel has an operating temperature of up to 1050°C.

[0029] The austenitic creep-resistant steel is prepared with reference to the components and proportions in Table 1.

Table 1 Element composition and proportion of austenitic creep-resistant steel in Examples and Comparative Examples

	C	Si	Mn	P	S	W	Ni	N	Cr
Example 1	0.33	1.3	0.2	0.015	0.012	0.6	12.5	0.39	23.9
Example 2	0.25	0.53	0.21	0.013	0.01	1.9	8.1	0.26	20.5
Example 3	0.49	1.98	0.21	0.016	0.013	2.9	12.8	0.26	27.9

(continued)

	C	Si	Mn	P	S	W	Ni	N	Cr
Comparative Example 1	0.42	1.2	1.1	0.018	0.011	0.02	38.7	0.03	19.2
Comparative Example 2	0.35	1.2	0.21	0.014	0.01	0	11.2	0.26	24.2
Comparative Example 3	0.36	1.1	0.25	0.014	0.009	1.4	14	0.27	23.9
Comparative Example 4	0.34	1.3	0.24	0.011	0.012	1.3	7.8	0.28	24.1
Comparative Example 5	0.1	0.9	0.24	0.010	0.012	1.5	9.9	0.27	23.8

[0030] The data are summarized in Table 2 after the performance test of the Examples and Comparative Examples in Table 1.

Table 2 Performance data of austenitic creep-resistant steel in Examples and Comparative Examples

	Mechanical properties at 1000°C			Creep rupture time (h) at 1000°C and 35 MPa	Average linear expansion coefficient (10 ⁻⁶ /K)		Thermal conductivity W/(m·K)	
	Tensile strength (MPa)	Yield strength (MPa)	Elongation (%)		25°C to 800°C	25°C to 1000°C	800°C	1000°C
Example 1	121	85	25	79	17.1	17.5	23	26.5
Example 2	130	88	26	77	17	17.2	22.9	26.3
Example 3	135	91	25	79	17.6	18.1	23.9	27.2
Comparative Example 1	98	66	38	49	17	17.6	23.3	26.6
Comparative Example 2	105	78	26	61	17.8	18.2	22.8	26.9
Comparative Example 3	125	78	32	55	17.1	17.5	23.4	26.5
Comparative Example 4	130	85	26	28	18.6	19.4	25.9	29.1
Comparative Example 5	120	79	19	18	17.1	17.4	26.3	29.3

[0031] According to data shown in FIGS. 1-2 and Table 2, the austenitic creep-resistant steel prepared according to the present invention suppresses the high-temperature ferrite phase and thus eliminating the defects of precipitated nitrogen porosity, reduces the processing cost of castings as compared with the ordinary Cr-Ni-based austenitic heat-resistant steel by optimizing the range of addition of nitrogen and carbon elements, and offers excellent mechanical properties at high temperature and long creep fracture time.

[0032] In summary, the austenitic creep-resistant steel prepared according to the present invention suppresses the high-temperature ferrite phase and thus eliminating the defects of precipitated nitrogen porosity, reduces the processing cost of castings as compared with the ordinary Cr-Ni-based austenitic heat-resistant steel by optimizing the range of addition of nitrogen and carbon elements, and offers excellent mechanical properties at high temperature and long creep fracture time. With the reduction in cost of the raw materials by more than 60%, the high temperature creep fracture time, the thermal conductivity and the linear expansion coefficient reach the level of 1.4849 heat-resistant steel.

[0033] Inspired by the above ideal embodiments of the present invention, those skilled in the art can make various

changes and modifications without deviating from the technical idea of the present invention. The technical scope of the present invention is not limited to the contents of the description, and must be determined according to the scope of the claims.

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Claims

1. An austenitic creep-resistant steel comprising, by mass percentage, the following components: C: 0.2 to 0.5; Si: 0.5 to 2.0; Mn<0.5; Cr: 20 to 28; Ni: 8 to 13; P≤0.04; S≤0.3; W: 0.5 to 2; N: 0.2 to 0.4, wherein the creep rupture time of the austenitic creep-resistant steel at 1000°C and 35MPa is not less than 77h, the thermal conductivity of the austenitic creep-resistant steel at 800°C is 22 to 24W/(m·K), the thermal conductivity at 1000°C is 26 to 27W/(m·K), the average linear expansion coefficient of the austenitic creep-resistant steel at 25°C to 800°C is $(17-18) \times 10^{-6}/K$, and the average linear expansion coefficient at 25°C to 1000°C is $(17-19) \times 10^{-6}/K$.
2. The austenitic creep-resistant steel according to claim 1, wherein the austenitic creep-resistant steel has a tensile strength of not less than 110 MPa at 1000°C, a yield strength of not less than 40 MPa, and an elongation after fracture of not less than 15%.
3. A preparation method of austenitic creep-resistant steel, comprising adding the raw materials according to claim 1 into an intermediate frequency furnace for smelting and casting the melt into a mould, whereby the austenitic creep-resistant steel is obtained.
4. Application of the austenitic creep-resistant steel according to claim 1 in an automobile engine exhaust manifold or a turbocharger housing.

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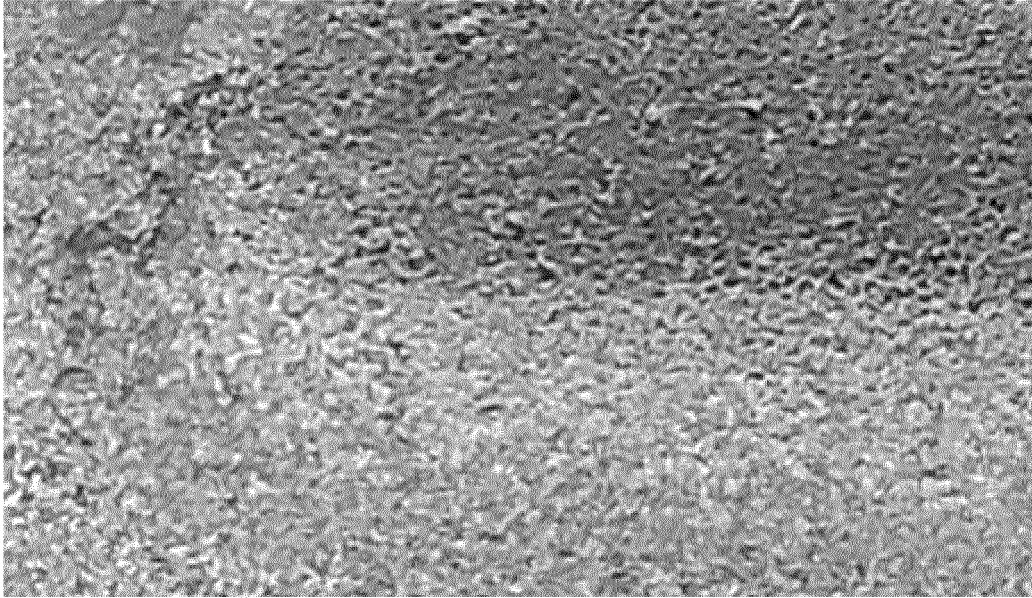


FIG. 1

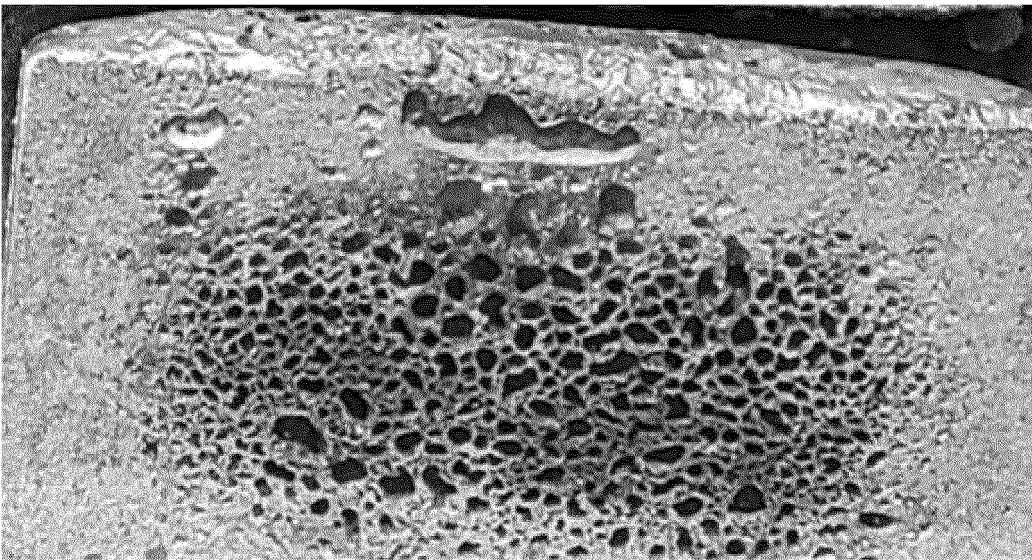


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2022/131885

A. CLASSIFICATION OF SUBJECT MATTER C22C38/02(2006.01)i;C22C38/04(2006.01)i;C22C38/44(2006.01)i;C22C38/34(2006.01)i;C22C33/04(2006.01)i;F01N13/16(2010.01)i;F04D29/02(2006.01)i 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) IPC:C22C38/, C22C33/04, F01N13/16, F04D29/02																					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI; CNABS; CNTXT; CNKI: 奥氏体, 蠕变, 碳, 硅, 锰, 铬, 镍, 钨, 氮, austenite, creep, carbon, C, silicon, Si, manganese, Mn, chromium, Cr, nickel, Ni, nitrogen, N, tungsten, W																					
C. DOCUMENTS CONSIDERED TO BE RELEVANT																					
<table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>PX</td> <td>CN 114086077 A (KEHUA HOLDINGS CO., LTD.) 25 February 2022 (2022-02-25) claims 1-7</td> <td>1-4</td> </tr> <tr> <td>X</td> <td>CA 1070528 A (ARMCO STEEL CORP.) 29 January 1980 (1980-01-29) claims 2 and 12, and description, page 9, lines 19-30, page 10, lines 26-28 and page 22, lines 12-30</td> <td>1-4</td> </tr> <tr> <td>X</td> <td>CN 102712975 A (SUMITOMO METAL INDUSTRIES, LTD.) 03 October 2012 (2012-10-03) description, paragraphs 87-117</td> <td>1-4</td> </tr> <tr> <td>X</td> <td>CN 103620078 A (NIPPON STEEL & SUMITOMO METAL CORP.) 05 March 2014 (2014-03-05) description, paragraphs 65-105</td> <td>1-4</td> </tr> <tr> <td>X</td> <td>US 2007217941 A1 (HITACHI METALS LTD.) 20 September 2007 (2007-09-20) description, paragraphs 21-22 and 34-77</td> <td>1-4</td> </tr> <tr> <td>X</td> <td>CN 101946018 A (HITACHI METALS, LTD.) 12 January 2011 (2011-01-12) description, paragraphs 18-62</td> <td>1-4</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	PX	CN 114086077 A (KEHUA HOLDINGS CO., LTD.) 25 February 2022 (2022-02-25) claims 1-7	1-4	X	CA 1070528 A (ARMCO STEEL CORP.) 29 January 1980 (1980-01-29) claims 2 and 12, and description, page 9, lines 19-30, page 10, lines 26-28 and page 22, lines 12-30	1-4	X	CN 102712975 A (SUMITOMO METAL INDUSTRIES, LTD.) 03 October 2012 (2012-10-03) description, paragraphs 87-117	1-4	X	CN 103620078 A (NIPPON STEEL & SUMITOMO METAL CORP.) 05 March 2014 (2014-03-05) description, paragraphs 65-105	1-4	X	US 2007217941 A1 (HITACHI METALS LTD.) 20 September 2007 (2007-09-20) description, paragraphs 21-22 and 34-77	1-4	X	CN 101946018 A (HITACHI METALS, LTD.) 12 January 2011 (2011-01-12) description, paragraphs 18-62	1-4
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PCT/CN2022/131885

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