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(71) Applicant: Yantai Manoir Heat Resistant Alloys Co., Ltd.
Yantai, Shandong 264000 (CN)

(72) Inventors:

 ZHANG, Minghao Yantai, Shandong 264000 (CN)

 DU, Kun Yantai, Shandong 264000 (CN)

 PEI, Jian Yantai, Shandong 264000 (CN)

 DING, Tianzhen Yantai, Shandong 264000 (CN)

 YE, Guowei Yantai, Shandong 264000 (CN)

(74) Representative: Arnold & Siedsma Bezuidenhoutseweg 57 2594 AC The Hague (NL)

(54) HIGH-ALUMINUM AUSTENITIC ALLOY HAVING EXCELLENT HIGH-TEMPERATURE ANTICORROSION CAPABILITIES AND CREEP RESISTANCE

(57) The present invention provides a high-aluminum austenitic alloy and a high-aluminum austenitic centrifugal casting pipe. The high-aluminum austenitic alloy and the high-aluminum austenitic centrifugal casting pipe have excellent anti-corrosion capabilities and creep resistance at a temperature of 900°C or above, while having required mechanical properties. In weight percentage, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention

is composed of the elements of: C, 0.3-0.7%; Mn, 0-0.5%; Si, 0-0.5%; Cr, 20-26%; Ni, 40-50%; AI, 3.5-5%; Ti, 0.01-0.3%; Zr, 0.01-0.3%; Nb, 0.1-1%; Zr, 0.01-Zr; Zr, 0.01-Zr; Zr, 0.01-Zr; Zr, 0.01-Zr; Zr, 0.01-Zr; Zr, 0.01-Zr; Zr, Z

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to the field of austenitic alloys, specifically to high-aluminum austenitic alloys with excellent high temperature (≥900°C) corrosion resistance and creep resistance.

BACKGROUND

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[0002] Ni-Cr austenitic heat resistant alloy has been widely used in petrochemical industry. On the one hand, the devices used in this industry (such as cracking tubes for steam cracking) have to withstand the combustion near 1100°C outside the furnace tube, and on the other hand, the materials have to withstand the carburization corrosion brought by the hydrocarbon gas inside the furnace tube and the high temperature oxidation of the outer surface, so the materials are required to have good high temperature resistance, corrosion resistance and high temperature mechanical properties, such as creep resistance and high temperature plasticity, in high temperature environment.

[0003] The two most commonly used alloys in Ni-Cr austenitic heat resistant alloys are ZG45Ni35Cr25NbM and ZG50Ni45Cr35NbM (hereinafter, 35/45 is used instead of ZG50Ni45Cr35NbM), with 35/45 alloy being used at higher temperatures and in more severe corrosive environmental conditions. When used, corrosive gas will react with the alloy to undergo high temperature oxidation and corrosion, and a metal oxide layer with a certain thickness will be formed on the inner surface of the furnace tube to protect the material from further oxidation and corrosion. The metal oxide layer formed in 35/45 alloy is mainly $\rm Cr_2O_3 + \rm SiO_2$ composite oxide layer/film. The oxide layer is relatively stable below 1050°C and can effectively prevent oxidation and carburization corrosion of the material. However, when the temperature is higher than 1050°C, the thermal stability of chromium oxide becomes poor, and when the furnace tube is subjected to stress, the oxide layer is prone to crack, resulting in a decrease in its continuity and compactness, which is insufficient to continue protecting the material matrix. This leads to the diffusion of oxidation into the material and acceleration of carburization corrosion, until the oxide layer and the matrix gradually crack and peel off.

[0004] The addition of Al is one way to increase the resistance of the 35/45 Ni-Cr austenitic alloy to oxidation and carburization. When the content of Al is high, a layer of dense aluminum oxide with a certain thickness can be formed on the surface of the alloy, and it also exhibits stability at temperature above 1050°C under the working condition of a cracking furnace, so that the alloy has good carburization resistance and oxidation resistance in a high temperature environment. However, the increase of Al content leads to the decrease of the ductility of the material. Therefore, the heat resistant alloys currently used in the petrochemical industry usually contain little or no aluminum.

[0005] The present invention proposes an austenitic alloy with high aluminum content to ensure high resistance to the environment (such as oxidation and carburization corrosion), while ensuring at least the same high mechanical properties as currently known alloys.

SUMMARY

[0006] The purpose of the present invention is to provide a high-aluminum austenitic alloy and a high-aluminum austenitic centrifugal casting pipe. The high-aluminum austenitic alloy and the high-aluminum austenitic centrifugal casting pipe have excellent anti-corrosion capabilities and creep resistance at a temperature of 900°C or above, while having required mechanical properties. The present invention also relates to a method for manufacturing the high-aluminum austenitic alloy and the high-aluminum austenitic centrifugal casting pipe of the present invention.

[0007] Specifically, in weight percentage, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention is composed of the elements of: C, 0.3-0.7%; Mn, 0-0.5%; Si, 0-0.5%; Cr, 20-26%; Ni, 40-50%; Al, 3.5-5%; Ti, 0.01-0.3%; Zr, 0.01-0.3%; Nb, 0.1-1%; Ta, 0.01-2%; Mo, 0.01-1%; W, 0.01-1.9%; N, 0.001-0.04%; Re, 0.03-0.3%; and a balance of Fe and unavoidable impurities.

[0008] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, the C content ranges from 0.4% to 0.65%.

[0009] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, the Mn content ranges from 0 to 0.4%.

[0010] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, the Si content ranges from 0 to 0.4%.

[0011] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, the Ti content ranges from 0.04% to 0.3%.

[0012] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, the Ta content ranges from 0.07% to 2%, such as 0.2-2%, 0.4-2%.

[0013] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the

present invention, the Mo content ranges from 0.2% to 1%.

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[0014] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, the W content ranges from 0.4% to 1.9%.

[0015] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, the N content ranges from 0.006% to 0.035%.

[0016] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, Re is Y, Hf, and Ce, and the content of each is 0.01-0.1 %.

[0017] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, the total content of Re ranges from 0.08% to 0.3%.

Preferably or alternatively, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention further contains one or more of Cu, V, Co, and B, wherein: Cu, ≤0.1%; V, ≤0.01%; Co, ≤0.03%; B, ≤0.1%.

[0019] The unavoidable impurities include one or more of S, P, and O. Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, $S \le 0.005\%$, $P \le 0.005\%$, and $O \le 0.005\%$.

[0020] Preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention: C, 0.4-0.65%; Mn, 0-0.4%; Si, 0-0.4%; Cr, 20-26%; Ni, 40-50%; Al, 3.5-5%; Ti, 0.04-0.3%; Zr, 0.01-0.3%; Nb, 0.1-1%; Ta, 0.4-2%; Mo, 0.2-1%; W, 0.4-1.9%; N, 0.006-0.035%; Re, 0.08-0.3%; Cu, \leq 0.1%; V, \leq 0.01%; Co, \leq 0.03%; B, \leq 0.1%; and a balance of Fe and unavoidable impurities.

[0021] Preferably, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention has a creep rupture life of \geq 100 hours, preferably \geq 110 hours, and more preferably \geq 115 hours, measured under testing conditions of 1100°C and 17MPa.

[0022] Preferably, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention has an average creep rate of the second stage of creep of $\leq 0.0005\%/h$, preferably $\leq 0.0003\%/h$, measured under testing conditions of 1050°C and 15MPa.

[0023] Preferably, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention has an average creep rate of the second stage of creep of $\leq 0.002\%/h$, preferably $\leq 0.0015\%/h$, measured under testing conditions of 1050°C and 20MPa.

[0024] Preferably, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention has an average creep rate of the second stage of creep of \leq 0.01 %/h, preferably \leq 0.007%/h, measured under testing conditions of 1050°C and 25MPa.

[0025] Preferably, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention has an average creep rate of the second stage of creep of \leq 0.05%/h, preferably \leq 0.035%/h, measured under testing conditions of 1050°C and 30MPa.

[0026] Preferably, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has a yield strength of \geq 120MPa, preferably \geq 124MPa; a tensile strength of \geq 185MPa, preferably \geq 189MPa; and an elongation of \geq 49%, preferably \geq 50%, measured under a testing condition of 850°C.

[0027] Preferably, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention has a yield strength of \geq 53MPa, preferably \geq 55MPa; a tensile strength \geq 65MPa, preferably \geq 67MPa; and an elongation \geq 59%, preferably \geq 61%, measured under a testing condition of 1050°C.

[0028] Preferably, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention has a carbon increment at a depth of 1mm of 0.5% or less, preferably 0.45% or less, and a carbon increment at a depth of 2mm of 0.05% or less, preferably 0.03% or less, under testing conditions of 1150°C/7 days.

[0029] Preferably, the high-aluminum austenitic alloy centrifugal casting pipe of the present invention has an outer diameter of 60-250mm and a wall thickness of 6-10mm.

[0030] Preferably, the microstructure of the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention comprises columnar grains with a volume fraction of 80% or more and equiaxed grains with a volume fraction of 20% or less, or consists of columnar grains with a volume fraction of 80% or more and equiaxed grains with a volume fraction of 20% or less.

[0031] Preferably, in the wall thickness direction of the high-aluminum austenite centrifugal casting pipe of the present invention, columnar grains are located near the outer wall, and uniform equiaxed grains are located near the inner wall.

[0032] The present invention also provides a method for manufacturing the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention, comprising:

- 1) smelting: smelting chemical components of the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe except AI, Re, Ti and Zr in an intermediate frequency furnace according to the target chemical components to obtain a molten steel;
- 2) deoxidation and deslagging: subjecting the molten steel obtained in step 1) to deoxidation and deslagging;

- 3) adding AI: adding AI to the molten steel treated in step 2), and carrying out deslagging after AI is dissolved;
- 4) modification: adding Re, Ti, and Zr to the steel ladle, introducing the molten steel treated in step 3) into the steel ladle, and carrying out deslagging after Re, Ti, and Zr are dissolved;
- 5) pouring: carrying out deslagging before pouring, and then pouring the molten steel into a metal mold and cooling to obtain the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe.

[0033] Preferably, in step 1), raw materials are selected and prepared according to the target chemical components, and the raw materials are smelted according to a sequence from being difficult to oxidize to being easy to oxidize.

[0034] Preferably, in step 1), Fe, Ni, C, Mn, Cr, Si are smelted in the order of Fe, Ni, C, Mn, FeCr and FeSi.

[0035] Preferably, in step 1), contents of harmful elements such as Pb, Sn, Sb, Zn, As and Bi in the molten steel are controlled to be less than 50 ppm respectively.

[0036] Preferably, in step 1), a sample is collected and sent to a laboratory for testing, and chemical compositions are adjusted based on the laboratory chemical analysis results.

[0037] Preferably, in step 2), after the molten steel is heated to $1650 \pm 50^{\circ}$ C, deoxidation is performed with a deoxidizer and then deslagging is performed.

[0038] Preferably, in step 2), deslagging comprises: covering the molten steel in the furnace with a slagging agent, beginning to blow argon at the bottom of the furnace, and carrying out deslagging after blowing argon. It is preferable to blow argon for 3 ± 1 minutes before deslagging. The floating of oxides, impurities and gases in the molten steel is accelerated by blowing argon from the bottom of the furnace, and the oxides, impurities and gases are removed together after being bonded by the slagging agent, so that the purity of the molten steel is improved.

[0039] Preferably, in step 3), a furnace mouth is covered and protected with argon to block a reaction between air and the surface of the molten steel.

[0040] Preferably, in step 3), blowing argon at the bottom of a furnace and covering and protecting a furnace mouth with argon are performed during the process of adding Al and Al dissolution. The purpose of blowing argon at the bottom of the furnace and covering and protecting the furnace mouth with argon is to ensure that the active elements added subsequently are not burned and oxidized.

[0041] Preferably, in step 3), after the dissolution of AI, the molten steel is heated to $1680 \pm 50^{\circ}$ C, and then a slagging agent is added to form slag and deslagging is performed.

[0042] Preferably, in step 4), Re, Ti, and Zr are added to the steel ladle, the molten steel is introduced into the steel ladle, and the dissolution and homogenization processes of Re, Ti, and Zr are completed through the pouring process of the molten steel; and after the pouring of the molten steel is completed, the surface of the molten steel in the steel ladle is covered by slagging.

[0043] Preferably, in step 5), the molten steel in the steel ladle is rapidly poured into a metal mold rotating at a high speed on a centrifuge, and the molten steel is cooled to obtain the centrifugal casting pipe. The pouring time should be as short as possible.

BRIEF DESCRIPTION OF THE FIGURES

[0044]

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Figure 1 shows average creep rates of the second stage of creep of the alloys of Examples 1, 3, and 4 of the present invention and alloy No. 1 1 (35/45 alloy).

Figure 2 shows cycle oxidation weight gain curves of the alloys of Examples 1, 3, and 4 of the present invention and alloy No.11 (35/45 alloy).

Figure 3 shows high-temperature short-term tensile curves of the alloy of Example 1 of the present invention at 850°C, 950°C, 1050°C, and 1150°C, respectively.

Figure 4 shows high-temperature short-term tensile curves of alloy No.11 (35/45 alloy) at 850 °C, 900°C, 1000°C, and 1050°C, respectively.

Figure 5 shows carbon increment percentages of the alloys of Examples 1-4 of the present invention and alloy No.11 (35/45 alloy) at different depths under testing conditions of 1150°C/7 days.

DETAILED DESCRIPTION

[0045] In order to enable those skilled in the art to understand the characteristics and effects of the present invention, the following is a general explanation and definition of the terms and expressions mentioned in the specification and claims. Unless otherwise indicated, all technical and scientific terms used herein have the ordinary meaning as understood by those skilled in the art with respect to the present invention, and in the event of a conflict, the definition in this specification shall prevail.

[0046] All features defined herein in terms of numerical ranges or percentage ranges, such as values, amounts, contents, and concentrations, are for simplicity and convenience only. Based on this, the description of the numerical range or percentage range should be considered as covering and specifically disclosing all possible secondary ranges and individual values within the range (including integers and fractions).

[0047] When embodiments or examples are described herein, it should be understood that they are not intended to limit the invention to those embodiments or examples. On the contrary, all alternatives, modifications, and equivalents of the methods and materials described herein are intended to be encompassed within the scope specified in the claims. It should be understood that within the scope of the present invention, the above-mentioned technical features and the specific technical features described below (such as embodiments) can be combined with each other to form a preferred technical solution.

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[0048] In the present invention, the effects of various elements in high-aluminum austenitic alloy and centrifugal casting pipe are described as follows.

[0049] C: C is a carbide-forming element. C and medium strong carbide-forming elements (Cr, Mo) or strong carbide-forming elements (Ti, V, Nb) form carbides such as M7C3, M23C6, and MC. During the high-temperature aging process, the supersaturated solid solution carbon in the matrix precipitates in the form of fine and dispersed secondary M23C6, thereby improving the creep rupture properties of the alloy. However, excessive carbon content can reduce the toughness of the alloy, and the content of C needs to be properly selected, so as to ensure the high-temperature creep rupture properties and high-temperature plasticity of the material. The content of C in the alloy of the present invention is controlled at 0.3-0.7%, preferably 0.4-0.65%.

[0050] Mn: Mn can improve welding performance and slow down the diffusion of carbon. The content of Mn in the alloy of the present invention is controlled equal to or below 0.5%. The Mn content is expected to be as low as possible, and the Mn content in the alloy of the present invention is preferably equal to or below 0.4%. In some embodiments, the content of Mn is 0.01-0.4%.

[0051] Si: In the process of molten steel smelting, Si as a strong deoxidizer can reduce the oxygen content in molten steel, thereby improving the purity of molten steel. During the high-temperature service process of the material, an appropriate Si content can enable the material to have good oxidation resistance and anti-carburization performance. The binding force between Si and O is greater than that between Cr and O, and a passive film SiO_2 can be formed in the alloy just like Cr. The oxidation resistance of SiOz is higher than that of Cr_2O_3 , but excessive addition of Si can lead to poor mechanical properties of the alloy, affect its welding performance and reduce its creep rupture life. The Si content in the alloy of the present invention is controlled equal to or below 0.5%, preferably equal to or below 0.4%. In some embodiments, the content of Si is 0.05-0.4%.

[0052] Cr: Cr is the main element that is resistant to high-temperature oxidation and high-temperature corrosion, and can improve the thermal strength of the alloy. When the Cr content is sufficient, an oxide film will form on the surface of the alloy, inhibiting the formation of coke deposition and increasing the carburization resistance of the alloy. The Cr content in the alloy of the present invention is controlled at 20-26%. Excessive Cr content will lead to the rapid or gradual precipitation of ferrite phase in the material, which will reduce the stability of the microstructure of the material under high temperature conditions, and reduce the mechanical properties of the material at high temperature, especially the creep rupture properties. At the same time, it will promote the formation of ferrite phase, and also lead to the decline of the welding performance of the material, resulting in the inability to replace spare parts by welding in the later period.

[0053] Ni: Ni is one of the most important alloy elements in the heat-resistant alloy. The main function of Ni is to stabilize the γ zone, so that the alloy can obtain a complete austenite structure, and then the alloy has a combination of high strength, plasticity and toughness, and ensures that the alloy has good high-temperature strength and creep resistance. The higher price of Ni element directly determines the final price of the product, and the Ni content in the alloy of the invention is controlled to be 40-50% by comprehensively considering the two aspects of cost and performance.

[0054] Al: Al is a necessary element for forming an aluminum oxide layer in the alloy of the present invention under high temperature conditions. The Al content in the alloy of the present invention is relatively high, and is equal to or higher than 3.5%, which can ensure the formation of a continuous and dense alumina layer on the surface of the alloy. Considering that high aluminum content will reduce the toughness of the alloy at room temperature, causing difficulty in machining and increasing machining costs, the Al content in the alloy of the present invention is controlled at 3.5-5%.

[0055] Ti: During the high-temperature aging process of the product, secondary precipitated carbides gradually appear. The addition of Ti element can improve the thermal dynamic stability of the secondary precipitate M23C6, thereby maintaining a uniform dispersion distribution for a long time and improving the high-temperature creep resistance of the alloy; in addition, Ti can inhibit the transformation of the primary precipitate MC into G phase, indirectly improving the stability of the primary precipitate, and also improving the high-temperature creep strength of the alloy. The Ti content in the alloy of the present invention is controlled to be 0.01-0.3%, preferably 0.04-0.3%.

[0056] Zr: As a strong oxidant, the addition of Zr can reduce the oxygen content in molten steel during the smelting process, thereby ensuring the absorption of other core elements. The Zr content in the alloy of the present invention is controlled to be 0.01-0.3%.

[0057] Nb: Nb is one of the precipitation strengthening elements, which can reduce the creep rate and improve the creep resistance. At the same time, Nb is also one of the main forming elements of carbides M7C3, M23C6, and MC, and its carbides are very stable at high temperatures. Nb can also form carbonitrides, change the morphology of carbides, refine M23C6, and make it uniformly dispersed, thereby improving the high-temperature creep strength of the alloy. Considering the high cost of Nb, the content of Nb in the alloy of the present invention is controlled equal to or below 1%, preferably 0.1-1%.

[0058] Ta: Ta plays a role of solid solution strengthening and precipitation strengthening. Ta has a very high affinity with C and other interstitial atoms, and the precipitates formed are very stable at high temperature. Ta also helps to improve the high-temperature instantaneous strength and creep performance of the alloy. The addition of Ta can significantly improve the creep rupture life of the alloy under high temperature and high pressure. The content of Ta in the alloy of the present invention is control to be 0.01-2%, preferably 0.4-2%. In some preferred embodiments, the content of Ta in the alloy of the present invention is 0.07-2%, such as 0.1%, 0.15%, 0.2%, 0.23%, 0.4%, 0.6%, 0.8%, 0.9%, 1%, 1.2%, 1.5% and 1.7%.

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[0059] Mo: Mo atoms are mostly dissolved in the γ matrix, and Mo atoms are larger than Ni and Fe atoms, which can also improve the yield strength. At the same time, the addition of Mo can form M_6C carbides, which is fine and dispersed, and can also play a strengthening role. In addition, Mo can also refine austenitic grains, and fine grains are beneficial for improving the plasticity of the alloy. The content of Mo in the alloy of the present invention is control to be 0.01-1%, preferably 0.2-1%.

[0060] W: W plays a role in solid solution strengthening. W dissolved in γ Matrix. The atomic radius of W is relatively large, which causes obvious lattice expansion in the matrix, prevents dislocation movement, and improves the yield strength. At the same time, W can reduce the stacking fault energy of γ matrix, and the reduction of stacking fault energy can effectively improve the creep performance of high-temperature alloys. The content of W in the alloy of the present invention is control to be 0.01-1.9%, preferably 0.4-1.9%.

[0061] N: N element can form carbonitrides with Nb and C, change the morphology of carbides, refine M23C6, and make it uniformly dispersed, thereby improving the high-temperature creep strength of the alloy. The content of N in the alloy of the present invention is controlled to be 0.001-0.04%, preferably 0.006-0.035%.

[0062] Re (rare earth elements): The rare earth elements in the heat-resistant alloy of the present invention include at least one of Ce, Y, and Hf. The rare earth elements are helpful to refine and stabilize the secondary precipitates, thereby improving the high-temperature mechanical properties of the material. In addition, the rare earth elements also help to promote the compactness of the oxide layer mainly composed of chromium oxide and silicon oxide, thereby improving the high-temperature oxidation resistance of the product. In the alloy of the present invention, the total Re content may be in the range of 0.03-0.3%, preferably 0.08-0.3%, and the addition amounts of Ce, Y, and Hf can each be 0.01-0.1%.

[0063] The high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of the present invention can be manufactured by a method comprising the following steps:

- 1) smelting: smelting chemical components of the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe except Al, Re, Ti and Zr in an intermediate frequency furnace according to the target chemical components to obtain a molten steel;
- 2) deoxidation and deslagging: subjecting the molten steel obtained in step 1)to deoxidation and deslagging;
- 3) adding AI: adding AI to the molten steel treated in step 2), and carrying out deslagging after AI is dissolved;
- 4) modification: adding Re, Ti, and Zr to the steel ladle, introducing the molten steel treated in step 3) into the steel ladle, and carrying out deslagging after Re, Ti, and Zr are dissolved;
- 5) pouring: carrying out deslagging before pouring, and then pouring the molten steel into a metal mold and cooling to obtain the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe.

[0064] In step 1), raw materials can be selected and prepared according to the target chemical composition. The raw materials are preferably smelted according to the sequence from being difficult to oxidize to being easy to oxidize, for example, Fe, Ni, C, Mn, Cr, Si are smelted in the order of Fe, Ni, C, Mn, FeCr and FeSi. In step 1), the content of harmful elements such as Pb, Sn, Sb, Zn, As, Bi in the molten steel can be controlled to be less than 50ppm respectively by optimizing the raw materials. In step 1), a sample can be collected and sent to a laboratory for testing, and chemical compositions can be adjusted based on the laboratory chemical analysis results.

[0065] In step 2), the molten steel can be heated, and then deoxidized with a deoxidizer before deslagging. Preferably, the molten steel is heated to $1650 \pm 50^{\circ}$ C, followed by deoxidation and deslagging. In step 2), deslagging preferably comprises: covering the molten steel in the furnace with a slagging agent, beginning to blow argon at the bottom of the furnace, and carrying out deslagging after blowing argon. It is preferable to blow argon for 3 ± 1 minutes before deslagging. In the deslagging process, oxides, impurities and gases in the molten steel are removed by adding slagging agent and blowing argon at the bottom of the furnace, so that the purity of the molten steel is improved. Before deoxidation, the

temperature of the molten steel in the furnace is controlled by controlling the power of the intermediate frequency furnace. **[0066]** In step 3), it is preferable to cover and protect the furnace mouth with argon to block the reaction between air and the surface of the molten steel. In step 3), it is preferable to keep blowing argon at the furnace bottom and covering and protecting the furnace mouth with argon during the process of adding Al blocks and Al dissolution. Blowing argon at the bottom of the furnace is to introduce argon bubbling at the bottom of the furnace to make the oxide slag in the molten steel adhere, which is helpful to remove the oxide slag. Covering and protecting the furnace mouth with argon is to replace the air at the furnace mouth with argon to prevent the added Al from being oxidized by the oxygen in the air. One of the characteristics of the alloy of the present invention is that it contains Al. During adding Al and Al dissolution, the present invention uses blowing argon at the furnace bottom and covering and protecting the furnace mouth with argon to ensure that the added Al is not burned or oxidized. During the Al dissolution process, the temperature of the molten steel in the furnace can be controlled by controlling the power of the intermediate frequency furnace to avoid accidents caused by excessive temperature. In step 3), after the dissolution of Al, the molten steel can be heated up, and then a slagging agent can be added to form slag and deslagging can be performed. Preferably, the molten steel is heated to $1680 \pm 50^{\circ}\text{C}$ then performing deslagging.

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[0067] In step 4), Re, Ti, and Zr can be added to the steel ladle and the molten steel is introduced into the steel ladle. The dissolution and homogenization of raw materials such as Re are completed through the pouring process of the molten steel. After the pouring of the molten steel is completed, the surface of the molten steel in the steel ladle is covered by slagging. One of the characteristics of the alloy of the present invention is that the alloy contains Re, and by adding Re into molten steel, the castability of molten steel is improved, and simultaneously, the performance of the alloy is improved.

[0068] In step 5), deslagging can be carried out when the temperature of the molten steel reaches the pouring temperature. Technicians in this field can determine the pouring temperature based on the amount of steel, mold size, etc. After deslagging, the molten steel in the steel ladle can be poured into a metal mold rotating at a high speed on a centrifuge, and the molten steel is cooled to obtain the centrifugal casting pipe. The casting time should be as short as possible.

[0069] In some embodiments, the high-aluminum austenitic centrifugal casting pipe of the present invention is manufactured using a method comprising the following steps:

Step 1: selecting and preparing raw materials according to the target chemical composition; smelting the raw materials according to the sequence from being difficult to oxidize to being easy to oxidize (for example, Fe, Ni, C, Mn, Cr, Si are smelted in the order of Fe, Ni, C, Mn, FeCr and FeSi); melting the chemical components except Al, Re, Ti and Zr to obtain a molten steel; optimizing raw materials to control the content of harmful elements such as Pb, Sn, Sb, Zn, As, Bi in the molten steel less than 50ppm respectively; collecting chemical composition samples and sending them to the laboratory for testing, and adjusting chemical compositions based on the laboratory chemical analysis results;

Step 2: after verifying the chemical compositions, heating the molten steel to $1650 \pm 50^{\circ}$ C, and then deoxidizing with a deoxidizer before deslagging; using a slagging agent to cover the molten steel in the furnace, and starting blowing argon at the bottom of the furnace; carrying out deslagging after blowing argon for 3 ± 1 minutes;

Step 3: covering and protecting the furnace mouth with argon to block the reaction between air and the surface of the molten steel; adding Al blocks and dissolving Al, wherein the furnace bottom is kept to blow argon and the furnace mouth is covered and protected with argon in the process; after Al is dissolved, heating and stirring the molten steel; and after the molten steel is heated to $1680 \pm 50^{\circ}$ C, adding a slagging agent to form slag and carrying out deslagging, and preparing to discharge;

Step 4: adding rare earths, Ti, and Zr to the steel ladle; introducing molten steel into the steel ladle, wherein the dissolution and homogenization of raw materials such as rare earths are completed through the pouring process of the molten steel; after the pouring of the molten steel is completed, covering the surface of the molten steel in the steel ladle by slagging;

Step 5: transferring the steel ladle to the front of a centrifuge, and after the temperature of the molten steel reaches the pouring temperature, carrying out the final deslagging in the ladle; then, pouring the molten steel in the steel ladle rapidly into a metal mold rotating at a high speed on the centrifuge, and cooling the molten steel to obtain the centrifugal casting pipe.

[0070] The microstructure of the high-aluminum austenitic alloy and the high-aluminum austenitic centrifugal casting pipe of the present invention comprises columnar grains with a volume fraction of 80% or more and equiaxed grains with a volume fraction of 20% or less, or consists of columnar grains with a volume fraction of 80% or more and equiaxed grains with a volume fraction of 20% or less. In a preferred embodiment, in the wall thickness direction of the high-aluminum austenite centrifugal casting pipe of the present invention, columnar grains are located near the outer wall and uniform equiaxed grains are located near the inner wall.

[0071] The outer diameter of the high-aluminum austenitic alloy centrifugal casting pipe of the present invention can be 60-250mm, such as 60-70mm, and the wall thickness can be 6-10mm, such as 7-8mm.

[0072] The high-aluminum austenitic alloy and the high-aluminum austenitic centrifugal casting pipe of the present invention have excellent anti-corrosion capabilities and creep resistance at a temperature of 900°C or above, and at the same time having required mechanical properties.

[0073] Compared with 35/45 alloy, the high-aluminum austenitic alloy and the high-aluminum austenitic centrifugal casting pipe of the present invention have:

- (1) Longer creep rupture life: a creep rupture life measured under the test conditions of 1100 °C and 17MPa is \geq 100 hours, preferably \geq 110 hours, and more preferably \geq 115 hours;
- (2) Smaller creep rate: an average creep rate of the second stage of creep measured under the testing conditions of 1050° C and 15MPa is $\le 0.0005\%$ /h, preferably $\le 0.0003\%$ /h; an average creep rate of the second stage of creep measured under the testing conditions of 1050° C and 20MPa is $\le 0.002\%$ /h, preferably $\le 0.0015\%$ /h; an average creep rate of the second stage of creep measured under the testing conditions of 1050° C and 25MPa is $\le 0.01\%$ /h, preferably $\le 0.007\%$ /h; an average creep rate of the second stage of creep measured under the testing conditions of 1050° C and 30MPa is $\le 0.05\%$ /h, preferably $\le 0.035\%$ /h;
- (3) Better anti-oxidation performance: after 19 cycles of a process of raising the air temperature to 950°C at a rate of 600°C/h, holding for 4 hours, and then cooling to room temperature to measure the weight gain, a weight gain of the alloy is ≤ 0.3 g/m², preferably ≤ 0.15 g/m²;
- (4) Better anti-carburization performance: under the testing conditions of 1150°C/7 days, a carbon increment at the depth of 1 mm is 0.5% or less, preferably 0.45% or less, and a carbon increment at the depth of 2 mm is 0.05% or less, preferably 0.03% or less.

[0074] Meanwhile, the high-aluminum austenitic alloy and the high-aluminum austenitic centrifugal casting pipe of the present invention have good strength and elongation at high temperatures: a yield strength measured at 850°C is \geq 120MPa, such as \geq 124MPa; a tensile strength measured at 850°C is \geq 185MPa, such as \geq 189MPa; an elongation measured at 850°C is \geq 49%, for example \geq 50%; a yield strength measured at 1050°C is \geq 53MPa, such as \geq 55MPa; a tensile strength measured at 1050°C is \geq 65MPa, for example \geq 67MPa; an elongation measured at 1050°C is \geq 59%, for example \geq 61%.

[0075] The present invention will be further explained with Examples and drawings.

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[0076] The high-aluminum austenitic centrifugal casting pipes of Examples 1-7, Comparative Examples 8-10, Comparative Examples 13-16, and Examples 17-20 are manufactured by the following method:

Step 1: selecting and preparing raw materials according to the target chemical composition; smelting the raw materials according to the sequence from being difficult to oxidize to being easy to oxidize; melting the chemical components except AI, Re, Ti and Zr to obtain a molten steel, wherein Fe, Ni, C, Mn, Cr, Si are smelted in the order of Fe, Ni, C, Mn, FeCr and FeSi; controlling the content of harmful elements such as Pb, Sn, Sb, Zn, As, Bi in molten steel to be below 50ppm, respectively; collecting chemical composition samples and sending them to the laboratory for testing, and adjusting the chemical compositions based on the laboratory chemical analysis results;

Step 2: after verifying the chemical compositions, heating the molten steel to 1650°C, and then deoxidizing with a deoxidizer before deslagging; using a slagging agent to cover the molten steel in the furnace, and starting blowing argon at the bottom of the furnace; performing deslagging after blowing argon for 3 minutes;

Step 3: covering and protecting the furnace mouth with argon to block the reaction between air and the surface of the molten steel; adding Al blocks and dissolving Al, wherein the furnace bottom is kept to blow argon and the furnace mouth is covered and protected with argon in the process; after Al is dissolved, heating and stirring the molten steel; and after the molten steel is heated to 1680°C, adding a slagging agent to form slag and carrying out deslagging, and preparing to discharge;

Step 4: adding rare earths, Ti, and Zr to the steel ladle; introducing molten steel into the steel ladle, wherein the dissolution and homogenization of raw materials such as rare earths are completed through the pouring process of the molten steel; after the pouring of the molten steel is completed, covering the surface of the molten steel in the steel ladle with slag;

Step 5: transferring the steel ladle to the front of a centrifuge, and after the temperature of the molten steel reaches the pouring temperature, carrying out the final deslagging in the ladle; then, pouring the molten steel in the steel ladle rapidly into a metal mold rotating at a high speed on the centrifuge, and cooling the molten steel to obtain the centrifugal casting pipe.

[0077] The outer diameter of the centrifugal casting pipes in the Examples of the present invention is 66mm, and the wall thickness is 7mm. The microstructure of the centrifugal casting pipes in the Examples of the present invention

consists of columnar grains with a volume fraction of $\ge 80\%$ and equiaxed grains with a volume fraction of $\le 20\%$, and in the direction of wall thickness, columnar grains are located near the outer wall, while uniform equiaxed grains are located near the inner wall.

[0078] The chemical compositions and contents of the centrifugal casting pipes of the Examples and Comparative Examples of the present invention are shown in Table 1. Herein, alloys No.1-7 respectively correspond to Examples 1-7; alloys No.8-10 respectively correspond to Comparative Examples 8-10; alloy No.11 is an existing alloy material ZG50Ni45Cr35NbM (35/45 alloy) having a C content of 0.44%; alloy No. 12 is an existing alloy material ZG50Ni45Cr35NbM (35/45 alloy) with a C content of 0.45%; alloys No.13-16 respectively correspond to Comparative Examples 13-16; alloys No.17-20 respectively correspond to Examples 17-20.

Table 1: Compositions of the alloys of Examples and Comparative Examples (weight%, with a balance of Fe)

								•			•			
Allo y	С	Mn	Si	Cr	Ni	Al	Ti	Zr	Nb	Та	Мо	W	N	Re
1	0.4	0.3 3	0.0 7	24	48	4. 5	0.2	0.2 4	0. 5	0.4	0.5	0.8	0.03 4	0.08
2	0.32	0.2 5	0.2 6	25	40	4	0.2 7	0.2 5	0. 9	0.9	0.6	0.4	0.00 6	0.18
3	0.63	0.2 8	0.4	24	50	3. 5	0.08	0.1	1	1.2	1	1. 5	0.02 4	0.22
4	0.52	0.0 4	0.3 4	26	47	4. 3	0.2	0.2 3	0. 7	0.6	0.2	1. 9	0.00 9	0.08
5	0.47	0.2 1	0.1	20	44	3. 8	0.1	0.0 9	0. 1	2	0.8	1. 1	0.01 2	0.29
6	0.7	0.1 1	0.4	22	44	5	0.3	0.2 8	0. 3	1.7	0.6	0. 9	0.03 4	0.15
7	0.45	0.1 5	0.2 6	23	42	4. 9	0.0 4	0.0 2	1	0.8	0.3	0.6	0.01 7	0.24
8	0.4	0.4 3	0.0 5	29	48	4. 6	0.2	0.2 3	0. 5	0.4	0.5 1	0.8	0.03 3	0.05
9	0.5 2	0.3 9	0.3 4	26	47	6	0.2	0.2 4	0. 7	0.6	0.2	1. 9	0.00 8	0.08
10	0.4 7	0.2 1	0.1	20	44	7. 5	0.1	0.9	0. 1	2	0.8	1. 1	0.01 2	0.29
11	0.4 4	1.2	1.4	35	45	-	0.1	-	0. 7	-	į	0.8	0.00 3	ı
12	0.4 5	1.1	1.3	35	45	-	0.08	-	0. 6	-	ı	0.7	0.00 3	ı
13	0.4 1	0.7 4	0.9 1	23	35	4. 1	0.1	0.0 3	1. 2	-	0.0 3	0.7	0.01 1	0.07
14	0.4 2	0.7 5	0.8 2	23	35	3. 9	0.0 3	0.0 3	1. 3	-	0.0 3	0.5	0.01	0.05
15	0.3 9	0.7 5	0.9 1	24	36	4. 0	0.0 7	0.0 4	1. 3	-	0.0 4	0.8	0.01 2	0.08
16	0.4 1	0.7 7	0.9 5	24	36	4. 1	0.08	0.0 5	1. 2	-	0.0 3	0.5	0.11	0.07
17	0.4 6	0.3 0	0.0 9	24	45	4. 1	0.1	0.1 2	0. 7	0.1	0.5	0.8	0.03 3	0.05
18	0.5 1	0.2 5	0.2 1	25	44	4. 0	0.2 1	0.2 4	0. 9	0.0 7	0.7	0.4	0.01 2	0.14
19	0.4 3	0.2 8	0.3 2	24	45	3. 9	0.1 1	0.1 0	1. 0	0.15	0.9	1. 0	0.02 2	0.23
20	0.4 9	0.0 4	0.0 3	26	46	4. 3	0.2 1	0.2 1	0. 6	0.2 3	0.3	0.7	0.01 1	0.01 2

[0079] Creep rupture life: According to ASTM E139-11, the creep rupture life of the alloys was measured under the testing conditions of 1100°C/17MPa, and the results are shown in Table 2.

[0080] It can be seen from Table 2 that the creep rupture life at 1100°C/17MPa of the alloys of Examples of the present invention is generally superior to that of the alloys of Comparative Examples (alloys No.8-10 and alloys No.13-16) and alloy No.11 and alloy No.12 of the prior art. Alloys No.13-16 do not contain Ta and have a much lower creep rupture life than the alloys of the present invention.

Table 2: Creep rupture life of various alloys at 1100°C/17MP

Alloy	Creep rupture life (h)
1	127
2	131
3	138
4	118

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(continued)

Alloy	Creep rupture life (h)
5	154
6	123
7	126
8	86
9	104
10	97
11	108
12	100
13	18
14	15
15	22
16	19
17	89
18	96
19	112
20	104

[0081] Creep rate: At 1050°C, different stresses were applied to the alloy, and its length at different times was measured with an extensometer. The deformation amount is differentiated with respect to time to obtain the deformation rate. The average results of the deformation rate in the second stage of creep are shown in Table 3. For the convenience of comparison, after taking the logarithm of the average creep rate of the second stage of creep and pressure, Figure 1 is obtained. The 35/45 alloy in Table 3 and Figure 1 is alloy No.11.

[0082] It can be seen from Table 3 and Figure 1 that at the same pressure and temperature, the average creep rate of the second stage of creep of the alloys of the present invention is significantly lower than that of the comparative alloy, so the creep resistance of the alloys of the present invention is significantly better than that of the comparative alloy 35/45.

Table 3: Average creep rate of the second stage of creep of alloys under different pressures at 1050 °C

		na stage of or cop of a							
Pressure (MPa)	Average creep rate of the second stage of creep (%/h)								
i ressure (ivii a)	Example 1	Example 3	Example 4	35/45 alloy					
35	0.0201837	-	-	0.1896310					
30	0.0123634	0.0316228	0.0079433	0.0701448					
25	0.0034995	0.0064565	0.0025119	0.0216346					
20	0.0010276	0.0013646	0.0007943	0.0051277					
15	0.0001754	0.0002630	0.0000883	0.0008014					
10	0.0000141	-	-	0.0000586					

[0083] Cyclic oxidation: In order to simulate the actual conditions of the alloy during use, the cyclic oxidation test was carried out on the alloy. The air temperature was raised to 950°C at a rate of 600 °C, and held for 4 hours. Then, it was cooled to room temperature to measure the weight gain. This process is repeated. The test results are shown in Table 4 and Figure 2. The 35/45 alloy in Table 4 and Figure 2 is alloy No.11.

[0084] It can be seen from Table 4 and Figure 2 that the oxidation resistance of the alloys of the present invention is significantly better than that of the 35/45 alloy.

Table 4: Weight gain of alloys after cyclic oxidation

Tuble 4	. Weight gain	veight gain of alloys after cyclic oxidation						
Number of cycles		Weight g	ain (g/m²)					
Number of cycles	Example 1	Example 3	Example 4	35/45 alloy				
0	0	0	0	0				
1	0.01	0.01	0	0.26				
2	0.02	0.01	0.01	0.35				
3	0.02	0.03	0.02	0.35				
4	0.04	0.02	0.09	0.3				
5	0.18	0.11	0.07	0.51				
6	0.11	0.17	0.09	0.41				
7	0.15	0.06	0.08	0.62				
8	0.05	0.08	0.1	0.51				
9	0.04	0.06	0.05	0.68				
10	0.1	0.11	0.07	0.51				
11	0.17	0.1	0.08	0.48				
12	0.11	0.07	0.12	0.48				
13	0.08	0.11	0.06	0.62				
14	0.06	0.07	0.1	0.42				
15	0.1	0.06	0.1	0.62				
16	0.08	0.1	0.08	0.51				
17	0.12	0.13	0.07	0.51				
18	0.11	0.11	0.06	0.62				
19	0.09	0.1	0.14	0.68				

[0085] High-temperature short-term tensile test: Yield, tensile, and elongation tests of the alloy were measured at 850°C, 950°C, 1050°C, and 1150°C according to ASTM E21-05. The results are shown in Table 5, Figure 3, and Figure 4. The alloy in Figure 3 is alloy No.1. The alloy in Figure 4 is alloy No. 11.

[0086] By comparing the alloy of Example 1 with the 35/45 alloy, it can be seen that the alloy of Example 1 has good strength and elongation at high temperatures even though it contains a relatively high amount of aluminum.

Table 5-1: High-temperature short-term tensile test results of alloys of Examples and Comparative Examples at different temperatures

			· · · · · · · · · · · · · · · · · · ·			
		850°C			950°C	
Alloy	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
1	124	192	50	89	106	61
2	125	198	50	92	108	60
3	131	201	49	93	106	60
4	124	189	52	89	104	62
5	120	195	51	90	106	61
6	124	190	51	91	110	61
7	126	200	50	94	113	59

(continued)

		850°C			950°C	
Alloy	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
11	121	205	27.5	-	-	-

Table 5-2: High-temperature short-term tensile test results of alloys of Examples and Comparative Examples at different temperatures

		1050°C			1150°C	
Alloy	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%s)
1	55	67	61	32	40	72
2	58	68	60	32	39	72
3	53	65	63	31	38	74
4	54	65	61	35	40	70
5	59	69	59	33	41	71
6	56	67	61	32	41	72
7	55	67	62	32	40	71
11	55	61	36.2	-	-	-

[0087] Carburization test: A solid carburizing agent was placed into the test pipe section, and after drying treatment, the test pipe section was welded, sealed, and placed in an environment of 1150°C. After heat preservation for 7 days, carbon content increment per millimeter from the inner surface to the outer surface of the alloy was measured. The results are shown in Table 6 and Figure 5. The 35/45 alloy in Figure 5 is alloy No.11.

[0088] It can be seen from Table 6 and Figure 5 that the carbon increments of the alloys of the present invention are significantly lower than that of the comparative alloy, indicating that the alloys of the present invention have good carburization resistance.

Table 6: carburization text results (%) of alloys of Example and Comparative Examples at 1150°C for 7 days

Alloy	Carbon increment at the depth of 1mm (%)	Carbon increment at the depth of 2mm (%)	Carbon increment at the depth of 3mm (%)	Carbon increment at the depth of 4mm (%)
1	0.35	0.01	0	0
2	0.39	0.03	0.01	0
3	0.44	0.01	0	0
4	0.31	0.02	0	0
5	0.37	0.02	0.01	0
6	0.29	0	0	0
7	0.3	0.01	0	0
11	1.12	0.3	0.04	0.01

Claims

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1. A high-aluminum austenitic alloy or a high-aluminum austenitic centrifugal casting pipe, wherein in weight percentage, the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe is composed of the

elements of: C, 0.3-0.7%; Mn, 0-0.5%; Si, 0-0.5%; Cr, 20-26%; Ni, 40-50%; Al, 3.5-5%; Ti, 0.01-0.3%; Zr, 0.01-0.3%; Nb, 0.1-1%; Ta, 0.01-2%; Mo, 0.01-1%; W, 0.01-1.9%; N, 0.001-0.04%; Re, 0.03-0.3%; and a balance of Fe and unavoidable impurities.

The high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of claim 1, wherein the elemental composition of the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has one or more of the following characteristics:

the content of C is 0.4-0.65%;
the content of Mn is 0-0.4%;
the content of Si is 0-0.4%;
the content of Ti is 0.04-0.3%;
the content of Ta is 0.07-2%, such as 0.4-2%;
the content of Mo is 0.2-1%;
the content of W is 0.4-1.9%;
the content of N is 0.006-0.035%;
the content of Re is 0.08-0.3%; and
Re is Y, Hf, and Ce, and the content of each of Y, Hf and Ce is 0.01-0.1%.

- 20 3. The high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of claim 1, wherein the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe further comprises one or more of Cu, V, Co and B.
 - **4.** The high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of claim 3, wherein the elemental composition of the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has one or more of the following characteristics:

the content of Cu is \le 0.1%; the content of V is \le 0.01%; the content of Co is \le 0.03%; and the content of B is \le 0.1%.

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- 5. The high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of claim 1, wherein the unavoidable impurities comprise one or more of S, P and O; preferably, in the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe, the content of S is ≤0.005%, the content of P is ≤0.005%, and the content of O is ≤0.005%.
- **6.** The high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of claim 1, wherein the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has one or more of the following properties:

the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has a creep rupture life of \geq 100 hours, preferably \geq 110 hours, and more preferably \geq 115 hours, measured under testing conditions of 1100°C and 17MPa:

the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has an average creep rate of the second stage of creep of $\leq 0.0005\%/h$, preferably $\leq 0.0003\%/h$, measured under testing conditions of 1050° C and 15MPa;

the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has an average creep rate of the second stage of creep of $\le 0.002\%/h$, preferably $\le 0.0015\%/h$, measured under testing conditions of $1050^{\circ}C$ and 20MPa;

the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has an average creep rate of the second stage of creep of $\le 0.01\%/h$, preferably $\le 0.007\%/h$, measured under testing conditions of 1050°C and 25MPa:

the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has an average creep rate of the second stage of creep of $\leq 0.05\%/h$, preferably $\leq 0.035\%/h$, measured under testing conditions of 1050° C and 30MPa;

the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has a yield strength of \geq 120MPa, a tensile strength of \geq 185MPa, and a enlongation of \geq 49%, measured at 850°C;

the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has a yield strength of \geq 53MPa, a tensile strength of \geq 65MPa, and a enlongation of \geq 59%, measured at 1050°C; and the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe has a carbon increment of 0.5% or less at a depth of 1mm and a carbon increment of 0.05% or less at a depth of 2mm under the testing conditions of 1150°C/7 days.

- 7. The high-aluminum austenitic centrifugal casting pipe of claim 1, wherein the high-aluminum austenitic alloy centrifugal casting pipe has an outer diameter of 60-250mm and a wall thickness of 6-10mm.
- 8. The high-aluminum austenitic centrifugal casting pipe of claim 1, wherein the microstructure of the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe comprises columnar grains with a volume fraction of 80% or more and equiaxed grains with a volume fraction of 20% or less; preferably, in the wall thickness direction of the high-aluminum austenite centrifugal casting pipe, columnar grains are located near the outer wall and uniform equiaxed grains are located near the inner wall.

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- **9.** A method for manufacturing the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe of any one of claims 1-8, comprising the following steps:
 - 1) smelting: smelting chemical components of the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe except Al, Re, Ti and Zr in an intermediate frequency furnace according to the target chemical components to obtain a molten steel;
 - 2) deoxidation and deslagging: subjecting the molten steel obtained in step 1) to deoxidation and deslagging;
 - 3) adding Al: adding Al to the molten steel treated in step 2), and carrying out deslagging after Al is dissolved;
 - 4) modification: adding Re, Ti, and Zr to the steel ladle, introducing the molten steel treated in step 3) into the steel ladle, and carrying out deslagging after Re, Ti, and Zr are dissolved;
 - 5) pouring: carrying out deslagging before pouring, and then pouring the molten steel into a metal mold, and cooling to obtain the high-aluminum austenitic alloy or the high-aluminum austenitic centrifugal casting pipe.
- 10. The method of claim 9, wherein the method has one or more of the following characteristics:
 - in step 1), contents of Pb, Sn, Sb, Zn, As and Bi in the molten steel are controlled to be less than 50 ppm respectively;
 - in step 2), after the molten steel is heated to 1650 \pm 50°C, deoxidation is performed with a deoxidizer and then deslagging is performed;
 - in step 2), deslagging comprises: covering the molten steel in the furnace with a slagging agent, beginning to blow argon at the bottom of the furnace, and carrying out deslagging after blowing argon, wherein the time for blowing argon is preferably 3 ± 1 minutes;
 - in step 3), the furnace mouth is covered and protected with argon to block the reaction between air and the surface of the molten steel;
 - in step 3), blowing argon at the bottom of the furnace and covering and proctecting the furnace mouth with argon are performed in the process of adding Al and Al dissolution;
 - in step 3), after the dissolution of AI, the molten steel is heated to 1680 \pm 50°C, and then a slagging agent is added to form slag and deslagging is carried out.

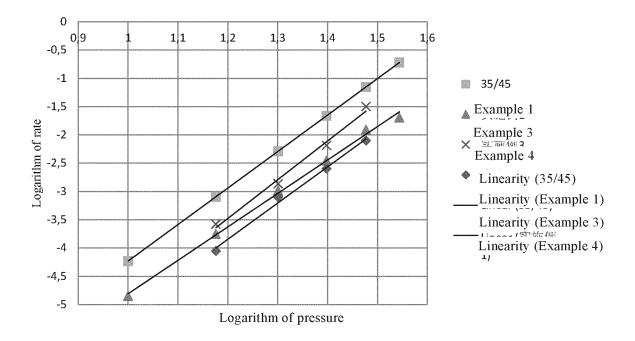


Figure 1

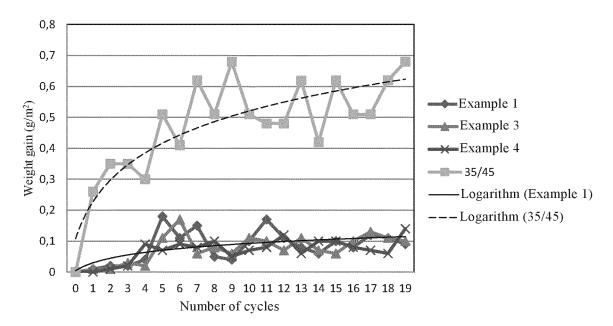


Figure 2

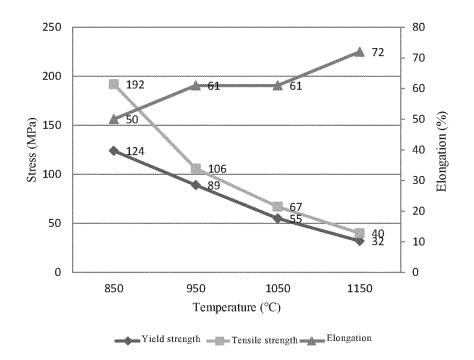


Figure 3

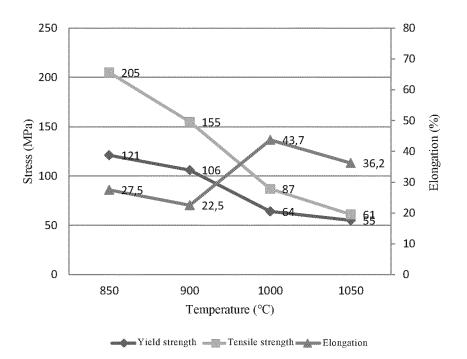


Figure 4

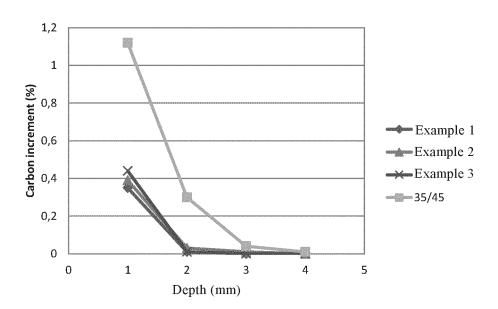


Figure 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2022/07060

			PCT/CN	2022/070698
5		SSIFICATION OF SUBJECT MATTER)/2004 01);	
	C22C	19/05(2006.01)i; C22C 1/02(2006.01)i; C22C 30/00	0(2000.01)1; B 22D 13/02(2000.01)1	
		International Patent Classification (IPC) or to both na	tional classification and IPC	
		DS SEARCHED	1 1 '6" (' 1 1)	
10		ocumentation searched (classification system followed 19/-;C22C1/-;C22C30/-;B22D13/-	by classification symbols)	
	Documentati	on searched other than minimum documentation to the	e extent that such documents are included in	n the fields searched
15	Electronic da	ata base consulted during the international search (nam	e of data base and, where practicable, search	ch terms used)
	铝, 钛 carbor	T; CNABS; CJFD; VEN; WOTXT; USTXT; EPTXT, , 锆, 铌, 钽, 钼, 钨, 氮, 钇, 铪, 铈, 蠕变, 脱氧, 打渣 ı, niobium, "Ti", zirconium, molybdenum, "C", auster m, centrifug+, creep, cast	, "Ce", "Ta", "Al", cerium, titanium, "Y",	"W", tungsten, yttrium,
20	C. DOC	UMENTS CONSIDERED TO BE RELEVANT		
	Category*	Citation of document, with indication, where a	appropriate, of the relevant passages	Relevant to claim No.
	PX	CN 112853155 A (YANTAI MANOIR HEAT RESI: 2021 (2021-05-28) claims 1-10	STANT ALLOYS CO., LTD.) 28 May	1-10
25	Y	CN 110023526 A (KUBOTA CORPORATION) 16 description, paragraphs 9-32	July 2019 (2019-07-16)	1-10
	Y	CN 102187003 A (SCHMIDT & CLEMENS GMBF (2011-09-14) claim 1, description paragraphs 6-20	I. & CO. KG.) 14 September 2011	1-10
30	Y	CN 109112327 A (BEIJING CISRI-GAONA TECH (2019-01-01) description, paragraphs 14-31	NOLOGY CO., LTD.) 01 January 2019	9-10
	A	JP 2014012877 A (NIPPON STEEL CORP.) 23 January entire document	uary 2014 (2014-01-23)	1-10
35	A	US 5316721 A (KUBOTA KK.) 31 May 1994 (1994 entire document	1-05-31)	1-10
		locuments are listed in the continuation of Box C.	See patent family annex.	
40	"A" document to be of p	ategories of cited documents: t defining the general state of the art which is not considered particular relevance plication or patent but published on or after the international	 "T" later document published after the intern date and not in conflict with the application principle or theory underlying the inventing the document of particular relevance; the comment of particular relevance; 	on but cited to understand the ion
	filing dat "L" documen	e t which may throw doubts on priority claim(s) or which is	considered novel or cannot be considered when the document is taken alone	I to involve an inventive step
	special re	establish the publication date of another citation or other cason (as specified) t referring to an oral disclosure, use, exhibition or other	"Y" document of particular relevance; the considered to involve an inventive st combined with one or more other such d	ep when the document is
45		t published prior to the international filing date but later than ty date claimed	being obvious to a person skilled in the a "&" document member of the same patent far	ırt
	Date of the ac	tual completion of the international search	Date of mailing of the international search	report
		03 March 2022	06 April 2022	
50		ling address of the ISA/CN	Authorized officer	
	CN)	tional Intellectual Property Administration (ISA/ ucheng Road, Jimenqiao, Haidian District, Beijing hina		
	l´ ⁻			

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Telephone No.

INTERNATIONAL SEARCH REPORT Information on patent family members

International application No.
PCT/CN2022/070698

								FC1/CN2022/0/0098
5		nt document n search report		Publication date (day/month/year)	Pat	ent family memb	per(s)	Publication date (day/month/year)
	CN	112853155	A	28 May 2021		None		
	CN	110023526	A	16 July 2019	CA	3049514	A1	09 May 2019
					CA	3049514	C	09 November 2021
10					EP	3683325	A1	22 July 2020
10					EP	3683325	A4	20 January 2021
					JP	6422608	B1	14 November 2018
					JР	2019085638	A	06 June 2019
					US	2019345592	A1	14 November 2019
					US	11136655	В2	05 October 2021
15					JP	2019085643	A	06 June 2019
					JP	6934462	В2	15 September 2021
					TW	201936936	A	16 September 2019
					TW	1737940	В	01 September 2021
					KR	20200070152	. A	17 June 2020
20					KR	102303628	B1	17 September 2021
					WO	2019088075	A1	09 May 2019
					SG	11201904858	A1	27 June 2019
					IN	201927021097	' A	01 May 2020
					IN	380253	В	29 October 2021
25	CN	102187003	A	14 September 2011	KR	20190112208	A	02 October 2019
				•	KR	102064375	B1	09 January 2020
					JP	2017128815	A	27 July 2017
					JP	6320590	B2	09 May 2018
					ES	2661333	Т3	28 March 2018
30					BR	122016030244	A2	29 August 2017
					UA	109631	C2	25 September 2015
					HU	E037289	T2	28 August 2018
					ZA	201102259	В	30 November 2011
					JP	2012505314	A	01 March 2012
35					PL	2350329	T3	30 May 2018
33					TR	201802979	T4	21 March 2018
					PT	2350329	Т	08 March 2018
					Π L	212098	D0	30 June 2011
					IL	212098	A	31 October 2017
					US	2016108501	A1	21 April 2016
40					US	1005375€	B2	21 August 2018
					EP	3550045	A1	09 October 2019
					HU	E046718	T2	30 March 2020
					PL	3330390	T3	18 May 2020
					WO	2010043375	A1	22 April 2010
45					KR	20110079881	A	11 July 2011
					KR	101738390		22 May 2017
					ES	2747898	T3	12 March 2020
					EP	3330390		06 June 2018
					EP	3330390		28 August 2019
50					EA	201170560		30 December 2011
					EA	020052		29 August 2014
					CA	2740160		22 April 2010
					CA	2740160		12 July 2016
					KR	20190137965	A	11 December 2019

Form PCT/ISA/210 (patent family annex) (January 2015)

	nt document n search report		Publication date (day/month/year)	Pa	tent family membe	Publication date (day/month/year)		
Cited ii	n scaren report		(day/month/year)	KR	102080674	B1	24 February 2020	
				BR	PI0920279	B1	15 September 202	
				JP	2018131690	A	23 August 2018	
				JP	6486532	B2	20 March 2019	
				US	2011272070	A1	10 November 201	
				US	9249482	B2	02 February 2016	
				CN	102187003	В	06 November 201	
				PT	3330390	T	24 October 2019	
				JP	2014185397	A	02 October 2014	
				DE	102008051014	A1	22 April 2010	
				MX	2011003923	A	03 May 2011	
				EP	2350329	A1	03 August 2011	
				EP	2350329	В1	20 December 201	
				KR	20170058442	A	26 May 2017	
				KR	102029019	В1	07 October 2019	
				MY	160131	A	28 February 2017	
				SG	170388	A 1	30 May 2011	
				ID	514093	Α	08 September 201	
				SG	170388	В	08 October 2014	
				MX	333881	В	08 October 2015	
				BR	200920279	A2	22 August 2017	
				IN	315306	В	05 July 2019	
CN	109112327	Α	01 January 2019	WO	2020093783	A1	14 May 2020	
011	10,11202.	••	01 bandary 2017	CA	3115366	A1	14 May 2020	
				US	2022018005	A1	20 January 2022	
				SG	11202012154 W	A	28 January 2021	
				ES	2891575	Т3	28 January 2022	
				RU	2760223	C 1	23 November 202	
				JP	2021526593	A	07 October 2021	
				BR	112021008637	A2	10 August 2021	
				DK	3650560	Т3	20 September 202	
				KR	20200126001	A	05 November 202	
				IL	283000	D0	30 June 2021	
				CN	109112327	В	03 September 201	
JP	2014012877	Α	23 January 2014	JP	5857894	B2	10 February 2016	
US	5316721	Α	31 May 1994	CA	2058576	A1	01 July 1993	
03	3310721	А	31 Way 1994	CA	2058576	C	04 February 1993	
				EP	0548405	A1	30 June 1993	
				EP	0548405	B1	11 June 1997	
				JP	H0593239	A	16 April 1993	
				DE	69126531	D1	17 July 1997	
				DE	69126531	T2	05 February 1998	

Form PCT/ISA/210 (patent family annex) (January 2015)