



(11) **EP 4 148 157 A1**

(12) **EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 153(4) EPC

(43) Date of publication:  
**15.03.2023 Bulletin 2023/11**

(21) Application number: **21800520.5**

(22) Date of filing: **08.05.2021**

(51) International Patent Classification (IPC):  
**C22C 30/00** <sup>(2006.01)</sup> **C22C 1/02** <sup>(2006.01)</sup>  
**C22C 33/04** <sup>(2006.01)</sup> **B22D 27/00** <sup>(2006.01)</sup>  
**C21C 7/10** <sup>(2006.01)</sup> **C21D 8/00** <sup>(2006.01)</sup>  
**C21D 1/00** <sup>(2006.01)</sup> **C22F 1/10** <sup>(2006.01)</sup>

(86) International application number:  
**PCT/CN2021/092505**

(87) International publication number:  
**WO 2021/223760 (11.11.2021 Gazette 2021/45)**

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB  
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO  
PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA ME**  
Designated Validation States:  
**KH MA MD TN**

(30) Priority: **08.05.2020 CN 202010383732**

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(54) **HIGH-STRENGTH HIGH-TEMPERATURE ALLOYS FOR THERMAL POWER UNITS AND PROCESSING TECHNIQUE THEREFOR**

(57) Disclosed are a high-strength superalloy for use in a thermal generating unit and a process of preparing the same, wherein the superalloy comprises by weight percent constituents: C: 0.05%-0.08%, Cr: 14%-17%, Mn: <0.5%, Si: <0.5%, W: 1.0%-2.5%, Mo: 0.3%-2.0%, Ti: 2.0%-2.5%, Al: 1.0%-1.5%, B: <0.003%, Zr: <0.03%, Fe: 37%-48%, balance Ni. The pre-prepared alloy constituents are smelted in an arc furnace under a vacuum

degree up to 0.5Pa; the alloy is cogged with a deformation amount up to 70% at a temperature 200°C ~250°C above the Ni<sub>3</sub>Al ( $\gamma'$ ) precipitation temperature, and hot rolled with a deformation amount up to 80% at a temperature 150°C ~200°C above the  $\gamma'$  precipitation temperature. The resulting alloy has an excellent high-temperature mechanical property at 650°C above.

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## Description

### FIELD

**[0001]** The disclosure relates to the field of materials and material preparation, and more particularly relates to a high-strength superalloy for a thermal generating unit and a process of preparing the same, wherein the resulting high-strength superalloy may satisfy requirements of thick-wall parts such as the main steam pipeline and the header tank of an advanced 700°C ultra-supercritical (A-USC) thermal generating unit with respect to workability and service performance.

### BACKGROUND

**[0002]** Ever-increasing demand on electricity intensifies energy deficiency and environment pollution; therefore, it is pressing to develop an efficient, energy-conservative, environment-friendly means of power generation. Since fossil-fired power generation has always been a leading power generation technology over a long time, it is believed that the most effective means to address the above problems is increase steam parameters of the power generating unit. Substantial practices reveal that service performance of the material for critical components is a primary factor that restricts improvement of boiler unit steam parameters, while the large-diameter, thick-wall pipes such as the main steam pipeline and the header tank, which are essential components operating under the severest conditions in a thermal generating unit, are very demanding on material serviceability. In the industry of thermal power generation, to satisfy significant increase of the main steam parameters of the thermal generating unit, it is needed to develop a superalloy material which may satisfy performance requirements of large-diameter, thick-wall pipes of a 700°C unit with an excellent workability.

**[0003]** Currently, the large-diameter, thick-wall pipes of under-600°C thermal generating units mainly use ferritic heat-resisting steels (Cr: 9 wt. %-12 wt. %) and heat-resistance austenitic steels. Typical ferritic heat-resisting steels include TP91, NF616, E911, and HCM12A, etc., which have excellent durability and corrosion-resistance properties and are thus extensively applied in large-diameter, thick-wall pipes of under-600°C units. Now, TP91 steel has been extensively used in subcritical and supercritical thermal generating units, from which massive service performance data have been accumulated. These data and practices indicate that the ferritic heat-resisting steels can hardly meet serviceability requirements of higher temperature parameters of large-diameter, thick-wall pipes. Compared with ferritic heat-resisting steels, the coarse-grained (TP304H, TP347H), fine-grained (Super304H, TP347HFG), and high-chromium (HR3C, NF709, SAVE25) heat resistant austenitic steels are better in durability, anti-oxidization, and corrosion-resistance. However, the heat resistant austenitic steels

also have issues such as low heat transfer efficiency, high thermal expansion coefficient, and expensiveness. Particularly when the main steam temperature reaches 700°C or above, the strength of heat-resistant austenitic steels cannot satisfy requirements of large-diameter, thick-wall pipes with respect to material serviceability.

**[0004]** To satisfy the requirements of large-diameter, thick-wall pipes of a 700°C (A-USC) thermal generating unit boiler with respect to material serviceability, various wrought nickel-based superalloy materials have been developed, e.g., Inconel®740H developed by Special Metals, Haynes®282 developed by Haynes International, CCA 617 developed by Thyssenkrupp, Nimonic 263 developed by Rolls-Royce, and USC41 developed by Hitachi, etc. Despite their excellent high-temperature durability and anti-oxidization property, the above materials are expensive and highly demanding on smelting and hot working techniques with poor weldability, which restrict their rapid promotion and application. Additionally, Sumitomo has developed iron-nickel-based superalloys including HR6W and HR35; Sandvik has developed Sanicro25 iron-nickel-based alloy; CAS IMR (Institute of Metal Research, Chinese Academy of Sciences) and CISRI (China Iron & Steel Research Institute Group) have developed wrought iron-nickel-based superalloys such as GH2984 and GH110, etc., respectively. Compared with wrought nickel-based superalloys, the iron-nickel-based superalloys have a low hot strength, a poor structure stability, and a poor corrosion-resistance property despite their cost advantages. Besides, to achieve a desired structure and performance, they still need deforming processing, resulting in preparation and processing complexity and further incurring a relatively high overall manufacture cost, which renders it difficult for performance improvement.

### SUMMARY

**[0005]** To overcome the above and other features in conventional technologies, a high-strength superalloy for use in a thermal generating unit and a method of preparing the same are provided.

**[0006]** A technical solution adopted by the disclosure is provided below:

**[0007]** A high-strength superalloy for use in a thermal generating unit, comprising, by weigh percent constituents: Carbon (C) between 0.05 and 0.08, Chromium (Cr) between 14 and 17, Manganese (Mn) less than or equal to 0.5, Silicon (Si) less than or equal to 0.5, Tungsten (W) between 1.0 to 2.5, Molybdenum (Mo) between 0.3 and 2.0, Titanium (Ti) between 2.0 and 2.5, Aluminum (Al) between 1.0 and 1.5, Boron (B): less than or equal to 0.003, Zirconium (Zr) less than or equal to 0.03, Iron (Fe) between 37 and 48, balance Ni.

**[0008]** In an aspect, a process of preparing a high-strength superalloy for use in a thermal generating unit is provided, comprising steps of:

(1) smelting and homogenization treating, comprising: taking, by weigh percent constituents: Carbon (C) between 0.05 and 0.08, Chromium (Cr) between 14 and 17, Manganese (Mn) less than or equal to 0.5, Silicon (Si) less than or equal to 0.5, Tungsten (W) between 1.0 to 2.5, Molybdenum (Mo) between 0.3 and 2.0, Titanium (Ti) between 2.0 and 2.5, Aluminum (Al) between 1.0 and 1.5, Boron (B): less than or equal to 0.003, Zirconium (Zr): less than or equal to 0.03, Iron (Fe) between 37 and 48, balance Ni; after the chromium, nickel, tungsten, silicon, manganese, molybdenum and iron are melted and refined under vacuum, adding the aluminum, titanium, boron, zirconium and carbon under argon protection, followed by alloy casting; and after the alloy is solidified, subjecting the solidified alloy to homogenization treatment, followed by air cooling to room temperature;

(2) cogging, comprising: subjecting the smelted and homogenized alloy resulting from step (1) to cogging at a temperature 200°C ~ 250°C above an  $\text{NiAl}$  ( $\gamma'$ ) precipitation temperature, with a deformation amount of each pass being not less than 30% and a final deformation amount in total being not less than 70%;

(3) hot rolling, comprising: subjecting the cogged alloy resulting from step (2) to hot rolling at a temperature 150°C ~ 200°C above the  $\gamma'$  precipitation temperature, with a deformation amount of each pass being not less than 35% and a final deformation amount in total being not less than 80%;

(4) high-temperature solution and aging treatment: subjecting the hot-rolled alloy resulting from step (3) to high-temperature solution and aging treatment.

**[0009]** In a further improvement of the disclosure, the duration of the refining in step (1) ranges from 0.5 hours to 1 hour.

**[0010]** In a further improvement of the disclosure, step (1) specifically comprises: melting the chromium, nickel, tungsten, silicon, manganese, molybdenum and iron when the vacuum degree reaches between 0.3Pa and 0.5Pa, followed by adding coke for deoxidization, the mass of the coke added not exceeding 25% ~ 50% of the mass of carbon, then adding a Ni-Mg alloy for second deoxidization, followed by adding aluminum, titanium, boron, zirconium and carbon, and then stirring for 5~ 10 minutes (min) and discharging liquid alloy for casting, the casting temperature being not lower than 1600°C, and after the liquid alloy is solidified, subjecting the solidified alloy to homogenization treatment, followed by air cooling to room temperature.

**[0011]** In a further improvement of the disclosure, in step (1), a metal mold is used for casting; and a surface of the liquid alloy is covered with an aluminum exothermic

compound upon solidifying.

**[0012]** In a further improvement of the disclosure, in step (1), the homogenization treating specifically comprises: heating from room temperature to 1050°C~1120°C at a heating rate ranging from 10°C/min to 30°C/min, and dwelling at the temperature for 24 hours.

**[0013]** In a further improvement of the disclosure, in step (1), the solidified alloy dwells at a temperature ranging from 900°C to 980°C for 1.0 to 1.5 hours, followed by homogenization treating.

**[0014]** In a further improvement of the disclosure, in step (2), after each pass of cogging, the ingot is charged back into the furnace to keep temperature, wherein a dwell time  $T$  at the temperature and an out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

**[0015]** In a further improvement of the disclosure, in step (3), after each pass of hot rolling, the ingot is charged back into the furnace to keep temperature, wherein a dwell time  $T$  at the temperature and an out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

**[0016]** In a further improvement of the disclosure, step (4) specifically comprises: first heating to 1100°C ~ 1125°C for solution treating for 3 to 5 hours and then air cooling to room temperature, followed by reheating from the room temperature to 630°C ~ 680°C at a heating rate of 10°C/min to 30°C/min and dwelling at the temperature for 7 to 10 hours, and then air cooling to room temperature, and finally reheating from the room temperature to 740°C to 800°C at a heating rate of 10°C/min to 30°C/min, dwelling at the temperature for 1 to 3 hours, and then air cooling to room temperature.

**[0017]** Compared with conventional technologies, the disclosure offers the following benefits: the alloy provided by the disclosure has a high Fe content but lower contents of precious metals such as W and Nb, thereby having a reduced raw material cost. Meanwhile, the alloy preparing process abandons the conventional triple melting process for superalloys, but adopts a scheme of directly cogging after arc melting, which reduces the preparation composition of the alloy. The smelting process involves second oxidization, reducing the metal liquid solidification rate with an exothermal compound after casting, and then carrying out multiple passes of large-deformation-amount treatment to the alloy, wherein the cogging and rolling temperatures are controlled to 200°C ~ 250°C and 150°C ~ 200°C above the  $\gamma'$  precipitation temperature, respectively, and their single-pass deformation amounts are not less than 30% and 35%, respectively, which ensures enough energy storage for strains during delivery of the alloy. The resulting hot-treated alloy has an excellent high-temperature strength property, a yield strength of not lower than 540MPa and a ductility rate higher than 12% at 700°C.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0018]**

Fig. 1 is an image of an ingot (the oxide scale has been turn-milled) according to example 1;

Fig. 2 is an image of a cogged slab of example 1;

Fig. 3 is an image of a sheet after the first pass of rolling according to example 2; and

Fig. 4 is an image of a rolled sheet according to example 2.

## DETAILED DESCRIPTION

**[0019]** Hereinafter, the present disclosure will be described in further detail with reference to the accompanying drawings.

**[0020]** The disclosure provides a high-strength superalloy for a thermal generating unit, comprising, by weight percent constituents: Carbon (C) between 0.05 and 0.08, Chromium (Cr) between 14 and 17, Manganese (Mn) less than or equal to 0.5, Silicon (Si) less than or equal to 0.5, Tungsten (W) between 1.0 to 2.5, Molybdenum (Mo) between 0.3 and 2.0, Titanium (Ti) between 2.0 and 2.5, Aluminum (Al) between 1.0 and 1.5, Boron (B): less than or equal to 0.003, Zirconium (Zr) less than or equal to 0.03, Iron (Fe) between 37 and 48, balance Ni.

**[0021]** A process of preparing the alloy mainly comprises three steps: alloy smelting, deforming, and heat treating, specifically:

(1) smelting and homogenization treating, comprising: smelting the alloy in an induction arc furnace with a magnesium oxide basic lining, the furnace being rinsed with pure nickel before smelting, and subjecting raw materials of the alloy to shot blasting treatment before addition; refining the raw materials for 0.5h ~ 1h after the Cr, Ni, W, Si, Mn, Mo and Fe are completely melted under a vacuum degree controlled between 0.3Pa and 0.5Pa; then, introducing highly pure argon for protection, followed by adding Al, Ti, B, Zr, and C followed by alloy casting; after the alloy is solidified, subjecting the solidified alloy to homogenization treatment at a temperature ranging from 1050°C to 1120°C for 24h ~ 72h, followed by air cooling to air temperature;

(2) cogging, comprising: subjecting the smelted and homogenized alloy from step (1) at a temperature 200°C ~ 250°C above a  $\gamma'$  precipitation temperature, wherein a deformation amount of each pass is not less than 30%, and a final total deformation amount is not less than 70%;

(3) hot rolling, comprising: subjecting the cogged alloy resulting from step (2) to turn milling of an oxide scale on the surface of the ingot, with a turn-milling depth ranging from 0.5mm to 1mm; after the oxide scale is turn-milled, heating rollers to 500°C above

so as to carry out hot rolling at a temperature 150°C~200°C above a  $\gamma'$  precipitation temperature, wherein the deformation amount of each pass is not less than 35%, and the final deformation amount in total is not less than 80%; and after each pass of cogging and rolling, charging the alloy back to the furnace to keep temperature, wherein a dwell time  $T$  at the temperature and an out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

(4) high-temperature solution and aging treatment: heating the high-temperature rolled ingot resulting from step (3) to 1100°C ~ 1125°C for solution treatment for 3h ~ 5h, followed by air cooling to room temperature, then reheating to 630°C~680°C to dwell at the temperature for 7h ~ 10h, followed by air cooling, finally heating to 740°C~800°C to dwell at the temperature for 1h~3h, followed by air cooling to room temperature.

**[0022]** Preferably, coke is added for deoxidization after the Cr, Ni, W, Si, Mn, Mo and Fe are completely molten, wherein the mass of coke added is not greater than 25%~50% of the mass of carbon in the alloy composition; after the deoxidization, Ni-Mg alloy is added for second deoxidization, and finally, easily burnable elements including Al, Ti, B, Zr, and C are added and stirred for 5min to 10min, and then the melt is discharged, wherein the casting temperature upon discharge is not lower than 1600°C. In addition, a metal mold is used for casting; and the liquid alloy surface is covered with an aluminum exothermic compound during solidification, so as to lower solidification rate and facilitate feeding of the metal liquid.

**[0023]** During the temperature rise period of the alloy in the procedures of homogenization treatment, solution treatment, and aging treatment, the heating rate should be controlled within a range from 10°C to 30°C/min, wherein the ingot should dwell at 900°C~980°C for 1.0h to 1.5h before being heated to the homogenization treatment temperature; and then the ingot is heated to 1050°C ~ 1120°C at the heating rate between 10°C/min and 30°C/min.

**[0024]** The hot-treated alloy has an excellent high-temperature strength property, with a yield strength not less than 540MPa and a ductility higher than 12% at 700°C.

## Example 1

**[0025]** This example provides a high-strength superalloy for use in a thermal generating unit, comprising, by weight percent constituents: Carbon (C) 0.06, Chromium (Cr) 16, Manganese (Mn) 0.2, Silicon (Si) 0.15, Tungsten (W) 1.6, Molybdenum (Mo) 1.2, Titanium (Ti) 2.2, Aluminum (Al) 1.4, Boron (B) 0.002, Zirconium (Zr) 0.02, Iron (Fe) 37, balance Ni.

**[0026]** A magnesium oxide basic lining was applied for smelting the alloy, the furnace was rinsed with pure nickel before smelting, and the raw materials of the alloy were

subjected to shot blasting treatment before addition. The alloy was smelted with an induction arc furnace, with the vacuum degree being controlled at 0.35Pa. The elements including Cr, Ni, and W were completely molten and then refined for 40min, and before adding Al, Ti, B, Zr, and C, highly pure argon was introduced for protection. After the alloy composition including Cr, Ni, and W were completely molten, coke was added for deoxidization, wherein the mass of coke added does not exceed 50% of the carbon content in the alloy composition; upon completion of deoxidization, the Ni-Mg alloy was added for second deoxidization; finally, easily burnable elements including Al, Ti, B, Zr, and C were added; the melt was stirred for 5min and then discharged for casting, wherein the casting temperature was 1630°C. A metal mold was used for the casting; after casting, the liquid alloy surface was covered with a sodium nitrate + aluminum oxide exothermic compound so as to reduce the solidification rate and facilitate feeding of the metal liquid.

**[0027]** After the liquid alloy was solidified into an ingot, the ingot was heated to 1020°C at a rate of 10°C/min and dwelled at the temperature for 1.0h; then, the temperature rose up to 1160°C, followed by homogenization treatment for 24h, and then air cooled to room temperature. After the oxide scale was turn-milled, the alloy was cogged at a temperature 220°C above a  $\gamma'$  precipitation temperature, the deformation amount of each pass being 30% and the final deformation amount in total being 70%. Afterwards, the alloy was subjected to hot rolling at a temperature 160°C above the  $\gamma'$  precipitation temperature, with the deformation amount of each pass being 35% and the final deformation amount in total being 80%. Before rolling of the alloy, the rollers were heated to 500°C above, and after each pass of cogging and rolling, the alloy was charged back to the furnace to keep the temperature for 30min. The rolled alloy was reheated to 1120°C for solution treatment for 4h and then air cooled to room temperature, followed by reheating to 650°C and holding at the temperature for 8h, and then air cooled to room temperature; finally, the alloy was reheated to 760°C and dwelled at the temperature for 2h, followed by air cooling, wherein the heating rate during the procedures of homogenization treatment, solution treatment, and aging treatment was 10°C/min, and the ingot should dwell at 950°C for 1.0h before being heated to the homogenization treatment temperature.

**[0028]** Figs. 1 and 2 are images of the ingot and the forged alloy slab according to example 1, where no noticeable cracks are found in their surface, which indicates that the alloy smelting and processing solution is reasonable. The alloy performance testing result indicates that the alloy has a yield strength of 582MPa and a ductility of 14.2% at 700°C, showing that the alloy has an excellent high-temperature strength property.

#### Example 2

**[0029]** This example provides a high-strength super-

alloy for use in a thermal generating unit, comprising, by weigh percent constituents: Carbon (C) 0.07, Chromium (Cr) 15, Manganese (Mn) 0.2, Silicon (Si) 0.15, Tungsten (W) 2.2, Molybdenum (Mo) 0.4, Titanium (Ti) 2.2, Aluminum (Al) 1.4, Boron (B) 0.002, Zirconium (Zr) 0.02, Iron (Fe) 47, balance Ni. A magnesium oxide basic lining was applied for smelting the alloy, the furnace was rinsed with pure nickel before smelting, and the raw materials of the alloy were subjected to shot blasting treatment before addition. The alloy was smelted with an induction arc furnace, with the vacuum degree being controlled at 0.35Pa. The elements including Cr, Ni, and W were completely molten and then refined for 40min, and before adding Al, Ti, B, Zr, and C, highly pure argon was introduced for protection. After the alloy constituents including Cr, Ni, and W were completely molten, coke was added for deoxidization, wherein the mass of coke added does not exceed 40% of the carbon content in the alloy composition; upon completion of deoxidization, the Ni-Mg alloy was added for second deoxidization; finally, easily burnable elements including Al, Ti, B, Zr, and C were added; the melt was stirred for 5min and then discharged for casting, wherein the casting temperature was 1650°C. A metal mold was used for the casting; after casting, the liquid alloy surface was covered with a sodium nitrate + aluminum oxide exothermic compound so as to reduce the solidification rate and facilitate feeding of the metal liquid. The proportion between sodium nitrate and aluminum oxide exothermic compound was known to those skilled in the art.

**[0030]** After the liquid alloy was solidified into an ingot, the ingot was heated to 1020°C at a rate of 10°C/min and dwelled at the temperature for 1.0h; then, the temperature rose up to 1160°C, followed by homogenization treatment for 24h, and then air cooled to room temperature. After the oxide scale was turn-milled, the alloy was cogged at a temperature 240°C above a  $\gamma'$  precipitation temperature, the deformation amount of each pass being 30% and the final deformation amount in total being 70%. Afterwards, the alloy was subjected to hot rolling at a temperature 180°C above the  $\gamma'$  precipitation temperature, with the deformation amount of each pass being 35% and the final deformation amount in total being 80%. Before rolling of the alloy, the rollers were heated to 500°C above, and after each pass of cogging and rolling, the alloy was charged back to the furnace to keep the temperature for 30min. The rolled alloy was reheated to 1120°C for solution treatment for 4h and then air cooled to room temperature, followed by reheating to 650°C and holding at the temperature for 8h, and then air cooled to room temperature; finally, the alloy was reheated to 760°C and held at the temperature for 2h, followed by air cooling, wherein the heating rate during the procedures of homogenization treatment, solution treatment, and aging treatment was 10°C/min, and the ingot should dwell at 950°C for 1.0h before being heated to the homogenization treatment temperature.

**[0031]** Figs. 3 and 4 are images of the alloy subjected

to the first pass of rolling and the rolled alloy, respectively, where no noticeable cracks are found in their surface, which indicates that the alloy processing solution is reasonable. The alloy performance testing result indicates that the alloy has a yield strength of 543MPa and a ductility of 16.1% at 700°C, showing that the alloy has an excellent high-temperature strength property.

#### Example 3

##### [0032]

(1) smelting and homogenization treating, comprising: taking, by weigh percent constituents: Carbon (C) 0.05, Chromium (Cr) 14, Manganese (Mn) 0.5, Silicon (Si) 0.1, Tungsten (W) 1.0, Molybdenum (Mo) 2.0, Titanium (Ti) 2.0, Aluminum (Al) 1.0, Boron (B) 0.003, Zirconium (Zr) 0.01, Iron (Fe) 37, balance Ni; After the Cr, Ni, W, Si, Mn, Mo and Fe were completely molten under a vacuum degree reaching 0.3Pa~0.5Pa, coke was added for deoxidization, wherein the mass of coke added was not greater than 25% of the mass of carbon; and then a Ni-Mg alloy was added for second deoxidization, and finally, Al, Ti, B, Zr, and C were added and stirred for 5min, and then the melt was discharged for casting, wherein a metal mold was used for the casting, the casting temperature being not lower than 1600°C, followed by solidification, with the liquid alloy surface being covered with an aluminum exothermic compound, dwelling at 900°C for 1.5h, and finally, the solidified alloy was heated from room temperature to 1120°C at a heating rate of 10°C/min, followed by homogenization treating for 24h, and then the homogenized alloy was air cooled to room temperature.

(2) cogging: the smelted and homogenized alloy resulting from step (1) was cogged at a temperature 200°C above the  $\gamma'$  precipitation temperature, with the deformation amount of each pass being not less than 30%, and the final deformation amount in total being not less than 70%; the alloy was charged back to the furnace to keep temperature after completion of each pass of cogging, wherein the dwell time  $T$  at the temperature and the out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

(3) hot rolling: subjecting the cogged alloy resulting from step (2) to hot rolling at a temperature 150°C above the  $\gamma'$  precipitation temperature, the deformation amount of each pass being not less than 35%, and the final deformation amount in total being not less than 80%; the alloy after each pass of hot rolling was charged back to the furnace to keep temperature, wherein the dwell time  $T$  at the temperature and the out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

(4) high-temperature solution and aging treatment:

the alloy resulting from step (3) was first heated to 1100°C for solution treating for 5h and then air-cooled to room temperature, followed by being reheated to 630°C from the room temperature at a heating rate of 10°C/min and dwelling at the temperature for 10h, then air-cooled to room temperature, followed by being reheated to 740°C from the room temperature at a heating rate of 10°C/min and dwelling at the temperature for 3h, and then air-cooled to room temperature.

#### Example 4

##### [0033]

(1) smelting and homogenization treating: comprising: taking, by weigh percent constituents: Carbon (C) 0.08, Chromium (Cr) 15, Manganese (Mn) 0.2, Silicon (Si) 0.5, Tungsten (W) 2.5, Molybdenum (Mo) 1.0, Titanium (Ti) 2.0, Aluminum (Al) 1.5, Boron (B) 0.001, Zirconium (Zr) 0.02, Iron (Fe) 48, balance Ni; After the Cr, Ni, W, Si, Mn, Mo and Fe were completely molten under a vacuum degree reaching 0.3Pa~0.5Pa, coke was added for deoxidization, wherein the mass of coke added was not greater than 35% of the mass of carbon; and then a Ni-Mg alloy was added for second deoxidization, and finally, Al, Ti, B, Zr, and C were added and stirred for 7min, and then the melt was discharged for casting, wherein a metal mold was used for the casting, the casting temperature being not lower than 1600°C, followed by solidification, with the liquid alloy surface being covered with an aluminum exothermic compound, dwelling at 980°C for 1h, and finally, the solidified alloy was heated from room temperature to 1100°C at a heating rate of 20°C/min, followed by homogenization treating for 24h, and then the homogenized alloy was air cooled to room temperature.

(2) cogging: the smelted and homogenized alloy resulting from step (1) was cogged at a temperature 220°C above the  $\gamma'$  precipitation temperature, with the deformation amount of each pass being not less than 30%, and the final deformation amount in total being not less than 70%; the alloy was charged back to the furnace to keep temperature after completion of each pass of cogging, wherein the dwell time  $T$  at the temperature and the out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

(3) hot rolling: subjecting the cogged alloy resulting from step (2) to hot rolling at a temperature 200°C above the  $\gamma'$  precipitation temperature, the deformation amount of each pass being not less than 35%, and the final deformation amount in total being not less than 80%; the alloy after each pass of hot rolling was charged back to the furnace to keep temperature, wherein the dwell time  $T$  at the temperature and

the out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

(4) high-temperature solution and aging treatment: the alloy resulting from step (3) was first heated to 1120°C for solution treating for 3h and then air-cooled to room temperature, followed by being reheated to 650°C from the room temperature at a heating rate of 20°C/min and dwelling at the temperature for 8h, then air-cooled to room temperature, followed by being reheated to 800°C from the room temperature at a heating rate of 20°C/min and dwelling at the temperature for 1h, and then air-cooled to room temperature.

#### Example 5

#### [0034]

(1) smelting and homogenization treating: comprising: taking, by weigh percent constituents: Carbon (C) 0.06, Chromium (Cr) 17, Manganese (Mn) 0.1, Silicon (Si) 0.3, Tungsten (W) 2.0, Molybdenum (Mo) 0.3, Titanium (Ti) 2.1, Aluminum (Al) 1.3, Zirconium (Zr) 0.01, Iron (Fe) 42, balance Ni;

After the Cr, Ni, W, Si, Mn, Mo and Fe were completely molten under a vacuum degree reaching 0.3Pa~0.5Pa, coke was added for deoxidization, wherein the mass of coke added was not greater than 50% of the mass of carbon; and then a Ni-Mg alloy was added for second deoxidization, and finally, Al, Ti, B, Zr, and C were added and stirred for 10min, and then the melt was discharged for casting, wherein a metal mold was used for the casting, the casting temperature being not lower than 1600°C, followed by solidification, with the liquid alloy surface being covered with an aluminum exothermic compound, dwelling at 950°C for 1h, and finally, the solidified alloy was heated from room temperature to 1050°C at a heating rate of 30°C/min, followed by homogenization treating for 24h, and then the homogenized alloy was air cooled to room temperature.

(2) cogging: the smelted and homogenized alloy resulting from step (1) was clogged at a temperature 250°C above the  $\gamma'$  precipitation temperature, with the deformation amount of each pass being not less than 30%, and the final deformation amount in total being not less than 70%; the alloy was charged back to the furnace to keep temperature after completion of each pass of cogging, wherein the dwell time  $T$  at the temperature and the out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

(3) hot rolling: subjecting the clogged alloy resulting from step (2) to hot rolling at a temperature 170°C above the  $\gamma'$  precipitation temperature, the deformation amount of each pass being not less than 35%, and the final deformation amount in total being not

less than 80%; the alloy after each pass of hot rolling was charged back to the furnace to keep temperature, wherein the dwell time  $T$  at the temperature and the out-of-furnace time  $t$  satisfy  $5t \leq T \leq 10t$ .

(4) high-temperature solution and aging treatment: the alloy resulting from step (3) was first heated to 1115°C for solution treating for 4h and then air-cooled to room temperature, followed by being reheated to 680°C from the room temperature at a heating rate of 30°C/min and dwelling at the temperature for 7h, then air-cooled to room temperature, followed by being reheated to 770°C from the room temperature at a heating rate of 30°C/min and dwelling at the temperature for 2h, and then air-cooled to room temperature.

**[0035]** The high-temperature superalloy according to the present disclosure comprises, by weigh percent constituents: Carbon (C) between 0.05 and 0.08, Chromium (Cr) between 14 and 17, Manganese (Mn) less than or equal to 0.5, Silicon (Si) less than or equal to 0.5, Tungsten (W) between 1.0 to 2.5, Molybdenum (Mo) between 0.3 and 2.0, Titanium (Ti) between 2.0 and 2.5, Aluminum (Al) between 1.0 and 1.5, Boron (B): less than or equal to 0.003, Zirconium (Zr) less than or equal to 0.03, Iron (Fe) between 37 and 48, balance Ni. The pre-prepared alloy constituents are smelted in an electric arc furnace under a vacuum degree not higher than 0.3Pa; the alloy was clogged with a deformation amount up to 70% at a temperature 200°C ~ 250°C above the  $\text{Ni}_3\text{Al}$  ( $\gamma'$ ) precipitation temperature, and hot rolled with a deformation amount up to 80% at a temperature 150°C ~ 200°C above the  $\gamma'$  precipitation temperature. The alloy preparing process according to the disclosure has a low manufacture cost, and the alloy prepared according to the method has an excellent high-temperature mechanical property at 650°C above.

#### Claims

1. A high-strength superalloy for use in a thermal generating unit, comprising, by weigh percent constituents: Carbon (C) between 0.05 and 0.08, Chromium (Cr) between 14 and 17, Manganese (Mn) less than or equal to 0.5, Silicon (Si) less than or equal to 0.5, Tungsten (W) between 1.0 to 2.5, Molybdenum (Mo) between 0.3 and 2.0, Titanium (Ti) between 2.0 and 2.5, Aluminum (Al) between 1.0 and 1.5, Boron (B): less than or equal to 0.003, Zirconium (Zr) less than or equal to 0.03, Iron (Fe) between 37 and 48, balance Ni.
2. A process of preparing a high-strength superalloy for use in a thermal generating unit, comprising:

(1) smelting and homogenization treating, com-

- prising: taking, by weigh percent constituents: Carbon (C) between 0.05 and 0.08, Chromium (Cr) between 14 and 17, Manganese (Mn) less than or equal to 0.5, Silicon (Si) less than or equal to 0.5, Tungsten (W) between 1.0 to 2.5, Molybdenum (Mo) between 0.3 and 2.0, Titanium (Ti) between 2.0 and 2.5, Aluminum (Al) between 1.0 and 1.5, Boron (B): less than or equal to 0.003, Zirconium (Zr): less than or equal to 0.03, Iron (Fe) between 37 and 48, balance Ni; after the chromium, nickel, tungsten, silicon, manganese, molybdenum and iron are melted and refined under vacuum, adding the aluminum, titanium, boron, zirconium and carbon under argon protection, followed by alloy casting; and after the alloy is solidified, subjecting the solidified alloy to homogenization treatment, followed by air cooling to room temperature; (2) cogging, comprising: subjecting the smelted and homogenized alloy resulting from step (1) to cogging at a temperature 200°C ~ 250°C above an Ni<sub>3</sub>Al ( $\gamma'$ ) precipitation temperature, with a deformation amount of each pass being not less than 30% and a final deformation amount in total being not less than 70%; (3) hot rolling, comprising: subjecting the cogged alloy resulting from step (2) to hot rolling at a temperature 150°C ~ 200°C above the  $\gamma'$  precipitation temperature, with a deformation amount of each pass being not less than 35% and a final deformation amount in total being not less than 80%; (4) high-temperature solution and aging treatment: subjecting the hot-rolled alloy resulting from step (3) to high-temperature solution and aging treatment.
3. The process of preparing a high-strength superalloy for use in a thermal generating unit according to claim 2, wherein a duration of the refining in step (1) ranges from 0.5 hours to 1 hour.
  4. The process of preparing a high-strength superalloy for use in a thermal generating unit according to claim 2, wherein step (1) specifically comprises: melting the chromium, nickel, tungsten, silicon, manganese, molybdenum and iron when the vacuum degree reaches between 0.3Pa and 0.5Pa, followed by adding coke for deoxidization, the mass of the coke added not exceeding 25% ~ 50% of the mass of carbon, then adding a Ni-Mg alloy for second deoxidization, followed by adding aluminum, titanium, boron, zirconium and carbon, and then stirring for 5~ 10 minutes (min) and discharging liquid alloy for casting, the casting temperature being not lower than 1600°C, and after the liquid alloy is solidified, subjecting the solidified alloy to homogenization treatment, followed by air cooling to room temperature.
  5. The process of preparing a high-strength superalloy for use in a thermal generating unit according to claim 2, wherein in step (1), a metal mold is used for casting; and a surface of the liquid alloy is covered with an aluminum exothermic compound upon solidifying.
  6. The process of preparing a high-strength superalloy for use in a thermal generating unit according to claim 2, wherein in step (1), the homogenization treating specifically comprises: heating from room temperature to 1050°C~1120°C at a heating rate ranging from 10°C/min to 30°C/min, and dwelling at the temperature for 24 hours.
  7. The process of preparing a high-strength superalloy for use in a thermal generating unit according to claim 2, wherein in step (1), the solidified alloy dwells at a temperature ranging from 900°C to 980°C for 1.0 to 1.5 hours, followed by homogenization treating.
  8. The process of preparing a high-strength superalloy for use in a thermal generating unit according to claim 2, wherein in step (2), after each pass of cogging, the ingot is charged back into the furnace to keep temperature, wherein a dwell time T at the temperature and an out-of-furnace time t satisfy  $5t \leq T \leq 10t$ .
  9. The process of preparing a high-strength superalloy for use in a thermal generating unit according to claim 2, wherein in step (3), after each pass of hot rolling, the ingot is charged back into the furnace to keep temperature, wherein a dwell time T at the temperature and an out-of-furnace time t satisfy  $5t \leq T \leq 10t$ .
  10. The process of preparing a high-strength superalloy for use in a thermal generating unit according to claim 2, wherein step (4) specifically comprises: first heating to 1100°C ~ 1125°C for solution treating for 3 to 5 hours and then air cooling to room temperature, followed by reheating from the room temperature to 630°C ~ 680°C at a heating rate of 10°C /min to 30°C /min and dwelling at the temperature for 7 to 10 hours, and then air cooling to room temperature, and finally reheating from the room temperature to 740°C to 800°C at a heating rate of 10°C /min to 30°C /min, dwelling at the temperature for 1 to 3 hours, and then air cooling to room temperature.





Fig. 1

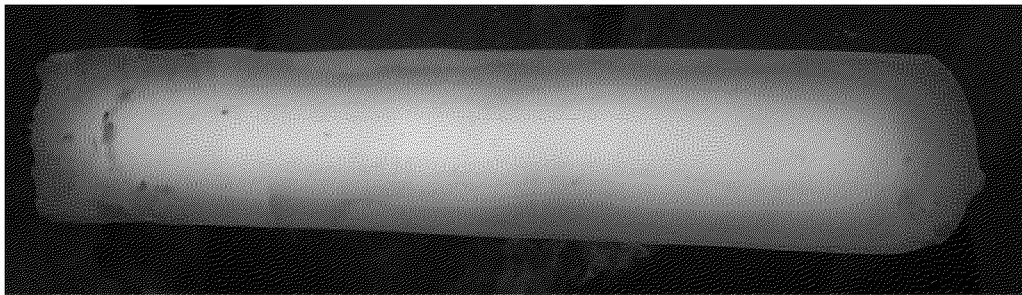


Fig. 2

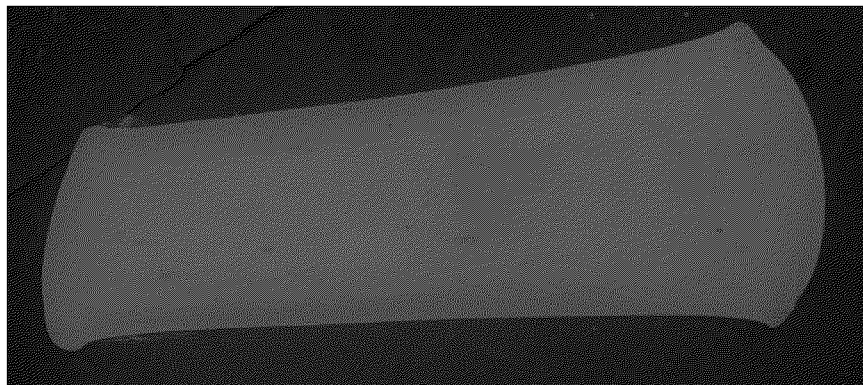


Fig. 3



Fig. 4

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/092505

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> C22C 30/00(2006.01)i; C22C 1/02(2006.01)i; C22C 33/04(2006.01)i; B22D 27/00(2006.01)i; C21C 7/10(2006.01)i; C21D 8/00(2006.01)i; C21D 1/00(2006.01)i; C22F 1/10(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC															
<b>B. FIELDS SEARCHED</b>															
Minimum documentation searched (classification system followed by classification symbols) C22C; B22D; C21C; C21D; C22F															
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) CNABS; CNTXT; DWPI; SIPOABS; CNKI; USTXT; EPTXT; WOTXT; ISI Web of Knowledge: 华能国际, 镍, 铁, 铬, 钨, 钼, 钽, 钛, 碳, 开坯, 屈服强度, Ni, nickel, Fe, iron, ferrum, Cr, chrome, chromium, W, tungsten, Mo, molybdenum, Al, aluminium, aluminum, Ti, titanium, C, carbon, yield strength															
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>															
<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 111394638 A (HUANENG POWER INTERNATIONAL INC. et al.) 10 July 2020 (2020-07-10) claims 1-10</td> <td>1-10</td> </tr> <tr> <td>X</td> <td>CN 110952016 A (HUANENG POWER INTERNATIONAL INC. et al.) 03 April 2020 (2020-04-03) description, paragraphs 0006-0022</td> <td>1-10</td> </tr> <tr> <td>A</td> <td>CN 110863099 A (HBIS COMPANY LIMITED) 06 March 2020 (2020-03-06) entire document</td> <td>1-10</td> </tr> <tr> <td>A</td> <td>CN 103556073 A (XI'AN THERMAL POWER RESEARCH INSTITUTE CO., LTD.) 05 February 2014 (2014-02-05) entire document</td> <td>1-10</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	PX	CN 111394638 A (HUANENG POWER INTERNATIONAL INC. et al.) 10 July 2020 (2020-07-10) claims 1-10	1-10	X	CN 110952016 A (HUANENG POWER INTERNATIONAL INC. et al.) 03 April 2020 (2020-04-03) description, paragraphs 0006-0022	1-10	A	CN 110863099 A (HBIS COMPANY LIMITED) 06 March 2020 (2020-03-06) entire document	1-10	A	CN 103556073 A (XI'AN THERMAL POWER RESEARCH INSTITUTE CO., LTD.) 05 February 2014 (2014-02-05) entire document	1-10
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<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.															
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Date of the actual completion of the international search <b>01 July 2021</b>	Date of mailing of the international search report <b>22 July 2021</b>														
Name and mailing address of the ISA/CN <b>China National Intellectual Property Administration (ISA/ CN)  No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088  China</b> Facsimile No. (86-10)62019451	Authorized officer  Telephone No.														

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INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.  
**PCT/CN2021/092505**

5	Patent document cited in search report		Publication date (day/month/year)		Patent family member(s)		Publication date (day/month/year)	
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	CN	110952016	A	03 April 2020	CN	110952016	B	30 March 2021
10	CN	110863099	A	06 March 2020	None			
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