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(54) HIGH-TEMPERATURE NICKEL-BASED ALLOY FOR 700°C GRADE ULTRA-SUPERCRITICAL COAL-FIRED POWER STATION AND PREPARATION THEREOF

(57) The present invention provides a nickel-based superalloy for a 700°C ultra-supercritical coal-fired power plant and a fabrication method thereof. This nickel-based alloy comprises 0.01~0.07wt% of C, 23~25.5wt% of Cr, 10~14.5wt% of Co, 0.3~3.5wt% of Mo, 0.5~2.5wt% of W, 0.8~2.2wt% of Nb, 1.0~2.5wt% of Ti, 1.0~2.5wt% of Al, 0.001~0.005wt% of B, 0.01~0.3wt% of Zr, 0.002~0.015wt% of Mg, less than or equal to 0.5wt% of V, less than or equal to 0.005wt% of La, and the balance of Ni and the inevitable impurity elements. The present invention can effectively prevent the propagation of intergranular cracks at high temperatures, and can improve the impact toughness and creep-rupture strength of the alloy also.

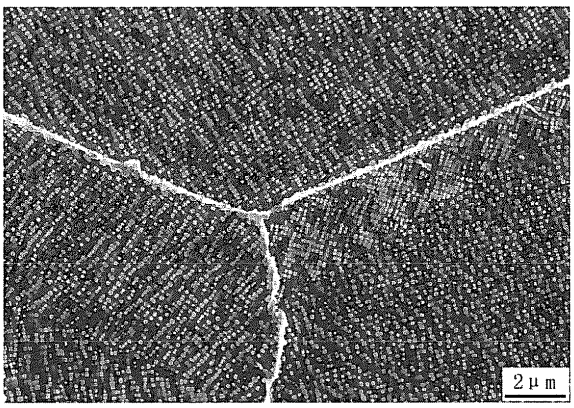

Fig. 2

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Description

Technical Field

[0001] The present invention belongs to the technical field of nickel-based superalloy, in particular to a nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant. This new superalloy can be applied as the high-temperature components in advanced ultra-supercritical coal-fired power plants at the steam temperature rating of 700°C. The highest service temperatures of the new alloy can be reached at 800°C.

Description of the Related Art

[0002] The shortage of energy supply and the deterioration of environment have become the main factors in restraining the sustainable development of the economy, society and the environment throughout the world. Electricity, as secondary energy, will still take a main position in the energy consumption market for a quite long time in the future. In electric power generation structure, thermal power generation occupies a leading position in the majority of countries in the world, which will likewise not be changed for quite a long time in the future. At present, the majority of coal-fired power plants in the world are sub-critical power plants with a steam parameter in the rating of 538°C /18.5MPa. However, from the end of last century, supercritical power plants with a rating of 566°C /24MPa and ultra-supercritical power plants with a rating of 600°C /27MPa take a main position in the development of the coal-fired power plants. The thermal efficiency of the power plants has been enhanced from about 35% for the sub-critical units to about 45% for the ultra-supercritical units. This plays an important role in saving coal and reducing emission of the pollutants such as SOx, NOx and CO_2. Meanwhile, in the recent decades, the major developed countries and country unions in the world, for example, EU, USA and Japan, have implemented research and development of the 700°C (or 760°C) advanced ultra-supercritical coal-fired power generation technologies in succession. EU is the first one that started this project in 1998, enhancing the steam temperature to 700°C /720°C/35MPa, with the expected power generation efficiency increasing from the current 45% to over 50%. USA and Japan then started similar study projects at the beginning of the 21st century. In 2011, China also started to research and develop the 700°C ultra-supercritical coal-fired power generation technologies. In Chinese electrical power generation structure, thermal power units take position up to 80%, while the mean coal consumption of the power plants is far higher than that of the developed countries in the world. To reduce the coal consumption by increasing the steam parameter of the coal-fired power plants, not only will be savings on coal resources and a reduced emission of CO_2, etc, but also will be significant for the sustainable development of the economy, society and the environment.

[0003] As the temperature and pressure of the coal-fired power generation units are increased to the rating of 700°C /720°C /35MPa, higher requirements are imposed on the strength and corrosion resistance of key high-temperature components of the power plants, for example, the HP and IP rotors, cylinders and valve shells in the turbines, superheaters and reheaters in boilers, headers and steam pipes, etc. Generally, the outer wall temperature of the superheater and reheater tubes in the boilers is about 50°C higher than the inner steam temperature. Therefore, when the steam temperature in the superheater and reheater tubes reaches 700°C and 720°C, the maximum temperature of the outer walls of the tubes may reach about 770°C and even higher. At the same time, the steam pressure in the tubes is also increased. With such steam temperature and pressure, the 9~12 Cr% steel and austenitic steels, such as Super304H and HR3C, which are widely applied to the ultra-supercritical coal-fired power plants, fail to meet the requirements for the strength and the corrosion resistance, therefore the nickel-based superalloys must be used.

[0004] At present, for nickel-based alloys used in civil projects (for example the petrochemical industry), the corrosion resistance and high temperature properties are required to be considered in the oxidation or reduction environment. However, for some age-hardening nickel-based alloys applied to the aerospace field, the service duration of the alloys is relative short and the requirements of high-temperature strength are more important. Due to the great difference in the purposes, in particular the prominent characteristics of long operating time (30-40 years) of the ultra-supercritical power plants, the current nickel-based superalloys usually fail to meet the requirements for high-temperature strength, maximum service temperature, structure stability and resistance to oxidation/sulfuration at the same time and thus fail to meet the requirements for long-term use by the high-temperature components of the 700°C ultra-supercritical coal-fired power plants. EU studied nickel-based alloys Inconel 617 and Nimonic 263 in the 700°C ultra-supercritical power generation program, obtained the 617B alloy through optimizing the composition of the 617 alloy and now is optimizing the 263 alloy. Japanese company Sumitomo has developed the Fe-Ni-based alloy HR6W. The Swedish company Sandvik has also developed the Fe-Ni-based Sanicro25 austenitic alloy. Those alloys all fail to meet the requirements of the highest temperature components. For EU's 700°C ultra-supercritical plan, SMC has developed Inconel 740 alloy which possess obvious characteristics of high strength and high corrosion resistance and has thus become the main candidate materials of the high-temperature parts of the power units. China also actively exploits alloys for use at higher temperatures on the basis of the nickel-iron-based alloy GH2984 which is originally used as the superheater of the marine boilers. So far, the above-mentioned alloys are still under development.

[0005] Based on the results of influence of the elements such as Co, Cr, Mo, W, Al, Ti, Nb and C on the structures and properties, a comprehensive consideration of the reasonable combination of the solid solution strengthening and precipitation strengthening of alloys and by means of good grain boundary strengthening, the present invention obtains a nickel-based alloy capable of being used for the long term at a temperature below 800°C. It has the high room temperature and high temperatures tensile properties, creep-rupture properties at high temperatures and excellent corrosion resistance. It has the great prospects in the application of the 700°C-class ultra-supercritical coal-fired power plants.

Contents of the Present Invention

[0006] The objective of the present invention is to provide a nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants and a fabrication method thereof. The new nickel-based superalloy has advantages of reasonable combination of chemical compositions, hot deformation property, excellent high-temperature mechanical properties and corrosion resistance, and good structure stability also.

[0007] To fulfill the above-mentioned objective, the present invention provides a nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants, characterized by comprising: C 0.01~0.07wt%, Cr 23~25.5wt%, Co 10~14.6wt%, Mo 0.3~3.5wt%, W 0.5~2.5wt%, Nb 0.8~2.2wt%, Ti 1.0~2.5wt%, A1 1.0~2.5wt%, B 0.001~0.005wt%, Zr 0.01~0.3wt%, Mg 0.002~0.015wt%, V 0.01~0.5wt%, La 0.001~0.005wt%, balance of Ni and inevitable impurity elements including S <0.010wt%, P <0.015wt%, Si <0.3wt% and Mn <0.5wt%, wherein the ratio (Al/(Ti+Nb)) of the atomic percentage of A1 to the sum of the atomic percentages of Ti and Nb is in the range of 1.0-1.3; the sum of the atomic percentages of Al, Ti and Nb is 5.5-6.2at%; the ratio (Cr/(Mo+W)) of the atomic percentage of Cr to the sum of the atomic percentages of Mo and W is greater than 12 and the sum of the atomic percentages of Cr, Mo and W is not greater than 30at%.

[0008] Furthermore, the percentage of age-precipitated strengthening phase γ of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants is 14~19wt%.

[0009] The present invention also provides a fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants, characterized by including the following steps of:

Step 1: Put 0.01~0.07wt% of C, 23~25.5wt% of Cr, 10~14.6wt% of Co, 0.3~3.5wt% of Mo,0.5~2.5wt% of W, 0.8~2.2wt% of Nb, 1.0~2.5wt% of Ti, 1.0~2.5wt% of Al, 0.001~0.005wt% of B, 0.01~0.3wt% of Zr, 0.01~0.5wt% of V, 48-58wt% of Ni into a vacuum induction furnace, keeping the ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb in the range of 1.0-1.3, the sum of the atomic percentages of Al, Ti and Nb in the range of 5.5-6.2at %, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr to the sum of the atomic percentage of Mo and W is greater than 12. The sum of the atomic percentages of Cr, Mo and W is not greater than 30at%. Meanwhile, feed 3-6wt% of the dry auxiliary materials with a purity greater than 99.5% into the vacuum induction furnace and the auxiliary materials consisting of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. Melt those raw materials in the vacuum induction furnace at a vacuum condition not lower than 10^{-3} Bar. After the raw materials are completely melted, refine the molten metal for over 30min to remove gases while keeping the vacuum at 10^{-3} Bar. After refining, charge with argon (Ar) protective gas until the pressure reaches 0.4bar, adding 0.3-0.6wt% of Ni-20Ca alloy at the same time to remove the harmful impurity element S, where the temperature of the molten alloy is not lower than 1,500°C. Add 0.01~0.025wt% of Ni-20Mg alloy and 0.001~0.005 wt% of the metal La in turn to perform desulfurization and purification. Fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into mould, the alloy ingot will form at an Argon atmosphere.

Step 2: performing diffusion annealing, billet forging, solid-solution and aging treatment on the alloy to obtain the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants.

[0010] Preferably, in step 2, the temperature of the diffusion annealing is implemented at 1,150~1,220°C, and the duration is 16~48h.

[0011] Preferably, in step 2, the temperature of the billet forging is not lower than 1,050°C.

[0012] Preferably, in step 2, the temperature of the solid solution treatment is implemented at 1,100~1,200°C and the duration is 0.5~2h.

[0013] Preferably, in step 16, the temperature of the aging treatment is implemented at 800°C and the duration is 4~16h.

[0014] Preferably, in step 2, before diffusion annealing, the alloy ingot are refined again by vacuum arc re-melting or by electro-slag re-melting in a protective gas atmosphere.

[0015] More preferably, if the vacuum arc re-melting method is employed in step 2, the re-melting rate shall be strictly controlled to be less than 300kg/h.

[0016] More preferably, when the electro-slag re-melting in a protective gas atmosphere is employed in step 2, a complex quinary slag purified system is used. The complex quinary slag purified system comprises 40~45wt% of CaF_2, 20~30wt% of Al_2O_3, 15~20wt% of CaO, 5~10wt% of MgO and 5-10wt% of TiO_2. The complex quinary slag purified system should be extracted to ensure SiO_2<0.5%, and should be baked for 4h at a temperature of 800°C before usage. Using (40~45%CaF_2 + 20~30%Al_2O_3 + 15~20%CaO + 5~10%MgO + 5~10%TiO_2) can ensure stable Al, Ti and Mg ingredients.

[0017] The chemical composition content ranges of the main alloy elements of the nickel-based high-temperature alloy of the present invention including Ni, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La and some impurity elements S, P, Si, Mn, etc. which are inevitable in the industrial production process mentioned above. Besides, the contents of harmful trace impurity elements such as Pb, Sn, As, Sb and Bi are required to be strictly controlled according to the current industrial protection technologies because those trace elements are harmful to the forging process and the durability as well as the high-temperature plasticity of the alloy.

[0018] The reasons for limiting the chemical composition of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants in the above-mentioned ranges are respectively described below.

[0019] C, as a strengthening element, is good for high-temperature stress-rupture strength of the alloy when $M_{23}C_6$ carbide is formed at grain boundaries and when C with the content of less than 0.01 % is not enough to form a certain amount of $M_{23}C_6$. C together with Ti and Nb can form a primary carbide MC, good for grain size control. In the case of excessive C content, more Ti and Nb will be consumed to form MC, so the C content should be kept below 0.06%. Besides, C also has a function of ensuring mobility of the melted metal during pouring.

[0020] Cr is an important element for enhancing the resistance to oxidation and corrosion and the high-temperature strength of the nickel-based alloy and is also a main element for the formation of the carbides at grain boundaries. Research has shown that, under the condition that the interior of the boiler tubes are full of high temperature steam, in the alloy, Cr with a content greater than 23% can form a protective Cr_2O_3 oxide film on the inner wall of the tube and can ensure that the outer wall of the tube is resistant to flue gas corrosion at the same time. Excessive Cr content will affect the structure stability and workability of the alloy so that the Cr content is required to not exceed 25.5%.

[0021] Co is beneficial to strength of the nickel-based alloy at a high temperature and to the resistance of high-temperature corrosion. Co in the Ni-Cr solid solution can reduce the stacking fault energy and plays a good solid solution strengthening role. When the Co content is lower than 10%, the high-temperature strength is reduced. However, Co is a strategic element with a high price. Excessive Co prompts the formation of η phase in the alloy, which is harmful to the properties of the alloy and affects the forgeability of the alloy. Therefore, the Co content is limited in the range of 10.0~14.6%. For the present invention, it is an important factor for rationally controlling the strengthening elements and reducing the alloy cost.

[0022] Mo entering the γ matrix of the nickel-based alloy plays an important role of solid solution strengthening. In particular, at the condition of reducing Co content to weaken solid solution strengthening, the use of Mo to perform solid solution strengthening is also one of the strengthening element control features of the present invention. However, when excessive Mo is added, it is not only obviously harmful to the resistance of the alloy to the flue gas corrosion in the coal-fired environment but also promotes the formation of σ phase and reduces the hot workability. Therefore the Mo content is controlled to be at 0.3~3.5%.

[0023] The W enters the γ matrix and the γ' strengthening phase by half, respectively. The W has a relatively large atom radius which is greater than the radius of the matrix element Ni by over ten percent and plays an obvious role of solid solution strengthening. In particular, W and Mo added together perform a compound solid solution strengthening. However, W is an element for speeding up thermal corrosion and therefore the W content is controlled to be at 0.5~2.5%.

[0024] The Nb content is controlled to be at 0.8~2.2%. The difference between the radii of the Nb and Ni atoms is greater than that of the W and Ni atoms. Nb is an important precipitation strengthening and solid solution strengthening element in the alloy of the present invention and together with A1 and Ti are strengthening elements of the γ' phase. However, Nb content must be controlled to be appropriate because excessive Nb will promote the formation of the η phase, reduce the protection properties of the oxide film and deteriorate the welding property due to promotion of liquation cracks.

[0025] Ti is controlled to be at 1.0~2.5%. It is an important strengthening element for forming γ' phase. The Ti element is also an important grain size stabilizer, together with the Nb forming primary carbide (Ti, Nb)C. However, an excessive Ti content will promote the formation of the harmful η phase and cause internal oxidation, reducing the plasticity of the alloy.

[0026] A1 is good for resisting oxidation and improving the structure of the oxide film, together with Ti and Nb forming the γ strengthening phase with Ni. Al is an important element for stabilizing the γ' phase and restraining the formation of the η phase. A low A1 content causes undesirable strengthening effect and reduces the high-temperature strength; while a high A1 content obviously reduces the plasticity and toughness of the alloy and narrows the processing temperature scope of the alloy. Meanwhile, in a high-temperature sulfurization environment, a high Al content promotes the internal oxidation and internal sulfurization corrosion. Therefore, A1 is limited in the range of 1.0~2.5%.

[0027] B is a micro-alloying element, rich at grain boundaries, strengthening the bonding force of grain boundaries. Boride at grain boundary can prevent the grain boundary sliding, cavities connection and crack propagation, it has an obvious effect of enhancing the creep property of the alloy. There is an optimum B content. In the present invention, the B content in the alloy is controlled to be at 0.001~0.005%.

[0028] Zr is controlled to be at 0.01-0.3%, good for purifying the grain boundaries and strengthening the bonding force of grain boundaries and together with B is good for keeping the high-temperature strength and endurance plasticity of the alloy. An excessive Zr will reduce the hot workability. Another effect of the Zr is obviously to increase the adhesion property of the protective oxide film on the surface of the alloy.

[0029] Mg is added as a micro-alloying element. Proper Mg is good for improving the creep-rupture life and plasticity of the alloy. Segregation of Mg at the grain boundary and phase boundaries can reduce the grain boundary energy and inter-phase boundary energy, improve the precipitation morphology of the second phase and reduce the local stress concentration. Besides, Mg can also be combined with impurity elements to purify the grain boundaries. Mg is controlled to be at 0.004~0.015%.

[0030] V, when distributed in the γ matrix, can effectively increase the lattice deformation and enhance solid solution strengthening. Meanwhile, a part of the V also enters the strengthening phase γ' to replace Al. V can also easily form precipitates, fine and dispersive VC during solidification, is good for refining grains. Besides, V can improve the thermal working plasticity of the alloy and is controlled to be at 0.001~0.5wt%.

[0031] La is added as a micro-alloying element and can be combined with the impurity elements, in particular the harmful element S, to play the role of purifying and strengthening grain boundaries. Besides, La is good for oxidation resistance. La is controlled to be at 0.001~0.005%.

[0032] S is a harmful impurity element, prompting the segregation of elements and the formation of a harmful phase during solidification. In the alloy, S is segregated at grain boundaries and the inter-phase boundaries, seriously affecting the thermal plasticity and high-temperature creep-rupture properties of the alloy. S is controlled at below 0.010% and should be controlled to be as low as possible.

[0033] P has dual effects, prompting the segregation of elements and the precipitation of harmful phases during solidification. Proper P content can improve creep property. Excessive P is seriously segregated at grain boundaries to reduce the grain boundary strength and affects the toughness. P shall be controlled to be at below 0.015%.

[0034] Si is a common impurity element, rich at the grain boundaries. Si can reduce the grain boundary strength and promote the formation of TCP phase. The research results of the present invention indicate that a high Si content can promote the precipitation of the Si-riched G phase at the grain boundary to obviously affect the plasticity, toughness and workability of the alloy. Thus Si must be controlled below 0.3%.

[0035] Mn, like other impurities, is segregated at grain boundaries. Mn can weaken the grain boundary bonding force, reduce creep strength and promote the formation of the harmful phase at grain boundaries. Mn should be controlled below 0.5%.

[0036] Ni is the most important element of γ matrix and the main formation element of Y precipitation strengthening phase. To ensure the stability of the structure, obtain the high-temperature strength and toughness and ensure that the alloy has good workability, the Ni content must be kept about 50%.

[0037] Figure 1 is a diagram of the research result on the relationship of the precipitation amount and the Al+Ti+Nb content. According to the alloy composition design of the present invention, the principles of controlling the precipitation strengthening phase Al, Ti and Nb focus on: the ratio Al/(Ti+Nb) is in the range of 1.0-1.3, and the sum of Al+Ti+Nb is 5.5~6.2at%, so that the precipitation amount of the strengthening phase is in the range of 14~19wt%. Forming proper precipitation strengthening effect is the first guarantee factor for obtaining a proper high strength and without γ' phase to η phase transformation. The structure of the strengthened precipitation phase of the alloy is stable.

[0038] The γ' phase of this alloy for the present invention is of the Ni_3(Al,Ti,Nb) type. Although the Nb and Ti have good strengthening effects at a temperature of 700-800°C, a large coherent strain field is generated due to a large mismatch degree of γ'/γ, so this γ' phase is metastable. It is also easy to form Ni_3 (Ti,Nb) type η phase. At the condition of reasonable control over the compositions and using the melting technology, billet forging method and heat-treatment method, the present invention ensures that the γ' phase is precipitated at a favorable position in the grains and at grain boundaries during the heat treatment. This results that the characteristics of discontinuous distribution of γ' at grain boundaries, can prevent the crack propagation along the grain boundaries and improves the impact toughness and creep property of the alloy. This is a remarkable characteristic of the structure design of the present invention for improving γ' phase stability and optimizing the γ' phase strengthening effect. Figure 2 is a microstructure diagram of the alloy of the present invention after heat-treatment.

[0039] In the composition design of the alloy of the present invention, the principle of controlling Mo and Cr element is as follows: the atom ratio Cr/(Mo+W) is greater than 12, and the sum of Mo+Cr+W does not exceed 30at%. In a long-term aging process at a temperature of 700-800°C, no σ phase and μ phase is formed in this alloy and the content of the impurity element Si is controlled below 0.3wt% to restrain the precipitation of the G phase. The microstructures at standard heat-treatment state and after long-term aging of the ally can be seen in figure attached to abstract and figure 2, respectively.

[0040] In conclusion: the present invention takes into consideration not only the rational combinations of compound solid solution strengthening of a proper amount of W in the Ni-Cr-Co-Mo matrix combined with Al, Ti and Nb precipitation strengthening, but also the addition of a small amount of vanadium to enhance the strengthening and the optimization of the micro-alloying elements B, Zr and Mg. This invention is to strictly control the contents of the conventional harmful elements S, P, Si and Mn, in particular, and adding a trace of La in the melting process, and thus it plays the role of purifying and strengthening grain boundaries. The chemical composition design of the alloy is more rational; the microstructure has a high stability during long-term aging. The 14~19wt% γ' phase precipitation strengthening is generated, and the precipitation of harmful phases such as the η phase, G phase and σ phase are restrained in the aging process. The γ' phase in the alloy is of the Ni_3 (Al, Ti, Nb) type and the sum of the Al, Ti and Nb, and the ratio Al/(Ti+Nb) are rationally controlled to obtain the proper amount of the stable strengthening phases. Accompany with the corresponding purified melting process, the reasonable billet forging method and the heat treatment process, the Y phases are precipitated in the grains and also at favorable positions of grain boundaries, capable of effectively preventing the propagation of intergranular cracks and improving the impact toughness and creep property thereof.

Description of Several Views of the Attached Drawings

[0041]

Figure 1 is a research result diagram of the relationship between γ' precipitation amount and Al+Ti+Nb content.
Figure 2 is a microstructure diagram of this alloy after long-term aging.
Figure 3 is a TTT diagram of η phase precipitation of the alloy 2 in a comparative example.
Figure 4 is a TTT diagram of σ phase precipitation of the alloy 3 in a comparative example.

[0042] The Figure attached to the abstract is a microstructure diagram of this alloy at standard heat treatment state.

Description of the Preferred Embodiments

[0043] To make the present invention easily understood, the invention is described in detail in combination with the following preferred embodiments and comparative examples as well.

Embodiment 1

[0044] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants comprises with C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical compositions and the weight percentages of the impurities S, P, Si and Mn can be seen in table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of Mo and W atoms, and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1.

[0045] A fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants comprises with the following steps of:

Selecting high quality raw materials, placing 0.05wt% of C, 24.3wt% of Cr, 14.2wt% of Co, 0.32wt% of Mo,1.05wt% of W, 1.48wt% of Nb, 1.52wt% of Ti, 1.61wt% of Al, 0.003wt% of B, 0.02wt% of Zr, 0.18wt% of V, 55wt% of Ni and 5wt% of the dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace, the auxiliary materials consisting of 40wt% of the CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. These raw materials are melted in the vacuum induction furnace under vacuum conditions of 10^{-3} Bar. After the raw materials are completely melted, the molten metal are refined for 10minutes to remove gases while keeping the vacuum at not lower than 10^{-3} Bar. After the refining is complete, charge the Argon gas until the pressure reaches 0.4bar, adding 0.5wt% of Ni-20Ca alloy at the same time to remove the harmful impurity element S. When the temperature of the molten metal is at 1,520°C before pouring; add 0.015wt% Ni-20Mg alloy and 0.005 wt% metal La in turn to perform desulfurization and purification. Fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into moulds, the alloy ingot will form at an Argon atmosphere.

[0046] Perform diffusion annealing for the alloy ingot at a temperature of 1,190°C and billet forging at a temperature of 1,200°C, forging the alloy ingot into ∅15mm bar product through three times reheating, implementing a solid solution treatment on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of the γ' strengthening phase of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants is at 16.8wt%.

Embodiment 2

[0047] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants comprises C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical composition and the weight percentages of the impurities S, P, Si and Mn can be seen in Table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of A1 to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of Mo and W, and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1, too.

[0048] The fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants comprises the following steps:

Select high quality raw materials and place 0.05wt% of C, 24.5wt% of Cr, 10.2wt% of Co, 1.35wt% of Mo,1.05wt% of W, 1.67wt% of Nb, 1.49wt% of Ti, 1.72wt% of Al, 0.003wt% of B, 0.02wt% of Zr, 0.17wt% of V, 57wt% of Ni and 5wt% of the dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace. The auxiliary materials consist of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. Smelt these raw materials in vacuum induction furnace at the vacuum condition of 10^{-3} Bar. After the raw materials are completely melted, refine the metal for 10min to remove gases while keeping the vacuum not lower than 10^{-3} Bar. After refining is complete, charge with Argon gas until the pressure reaches 0.4bar, adding 0.5wt% Ni-20Ca alloy at the same time to remove the harmful impurity element S. When the temperature of the molten metal is at 1,520°C before pouring, add 0.015wt% Ni-20Mg alloy and 0.005 wt% metal La in turn to perform desulfurization and purification. Fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into moulds, the alloy ingot will form in an argon atmosphere.

[0049] Performing diffusion annealing on alloy ingot at a temperature of 1,190°C and billet forging at a temperature of 1,200°C, forging the alloy ingot into ∅15mm bar product through three times reheating, implementing solid solution annealing on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of precipitation strengthening phase γ' of this nickel-based superalloy for the 700°C ultra-supercritical coal-fired power plants is at 18.5wt%.

Embodiment 3

[0050] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises with C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical composition and the weight percentages of the impurities S, P, Si and Mn can be seen in Table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of Mo and W, and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1, too.

[0051] The fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises the following steps:

Select high quality raw materials, placing 0.05wt% of C, 24.7wt% of Cr, 14.5wt% of Co, 2.43wt% of Mo,1.15wt% of W, 1.62wt% of Nb, 1.56wt% of Ti, 1.56wt% of Al, 0.002wt% of B, 0.04wt% of Zr, 0.10wt% of V, 52wt% of Ni and 5wt% of the dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace. The auxiliary materials consist of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. Those raw materials are melted in the vacuum induction furnace at a vacuum condition of 10^{-3} Bar. After the raw materials are completely melted, refine the materials for 10min to remove gases while keeping the vacuum at not lower than 10^{-3} Bar. After refining is completed, charge with Argon gas until the pressure reaches 0.4bar, adding 0.5wt% Ni-20Ca alloy at the same time to remove the harmful impurity element S. When the temperature of the molten metal is at 1,5200□ before pouring; add 0.015wt% Ni-20Mg alloy and 0.005 wt% metal La in turn to perform desulfurization and purification. Fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into the moulds, the alloy ingot will form at an Argon atmosphere.

[0052] Performing diffusion annealing for 24 hr on the alloy ingot at a temperature of 1,190°C and billet forging at a temperature of 1,200°C, forging the alloy ingot into ∅15mm bar product through three times reheating, implementing solid solution treatment on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of precipitation strengthening phase γ' of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants is at 17wt%.

Embodiment 4

[0053] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises with C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical composition and the weight percentages of the impurities S, P, Si and Mn can be seen in Table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of Mo and W atoms and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1, too.

[0054] The fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants comprises the following steps:

Select high quality raw materials and place 0.07wt% of C, 25.0wt% of Cr, 14.6wt% of Co, 2.87wt% of Mo,1.20wt% of W, 1.56wt% of Nb, 1.60wt% of Ti, 1.58wt% of Al, 0.002wt% of B, 0.04wt% of Zr, 0.15wt% of V, 51wt% of Ni and 5wt% of the dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace and the auxiliary materials consisting of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. These raw materials are melted in the vacuum induction furnace at a vacuum condition of 10^{-3} Bar. After the raw materials are completely melted, refine the materials for 10min to remove gases while keeping the vacuum not lower than 10^{-3} Bar. After the refining is completed, charge with Argon gas until the pressure reaches 0.4bar, adding 0.5wt% Ni-20Ca alloy at the same time to remove the harmful impurity element S. When the temperature of the molten metal is at 1,520°C before pouring; add 0.015wt% Ni-20Mg alloy and 0.005 wt% of metal La in turn to perform desulfurization and purification. Fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into the moulds, the alloy ingot will form at an Argon atmosphere.

[0055] Performing diffusion annealing for 24 hr for the alloy ingot at a temperature of 1,190°C and billet forging at a temperature of 1,200°C, forging the alloy ingot into ∅15mm bar product through three times reheating, implementing solid solution treatment on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of γ' precipitation strengthening phase of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant is at 17.3wt%.

Embodiment 5

[0056] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises with C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical composition and the weight percentages of the impurities S, P, Si and Mn can be seen in table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of the Mo and W, and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1, too.

[0057] The fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants comprises the following steps:

Selecting high quality raw materials and place 0.06wt% of C, 24.4wt% of Cr, 13.6wt% of Co, 3.04wt% of Mo,1.16wt% of W, 1.51wt% of Nb, 1.51wt% of Ti, 1.51wt% of Al, 0.003wt% of B, 0.05wt% of Zr, 0.16wt% of V, 52wt% of Ni and 0.5wt% of the dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace with the auxiliary materials consisting of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. Smelt those raw materials in the vacuum induction furnace under vacuum condition of 10^{-3} Bar. After the raw materials are completely smelted, refine the materials for 10 minutes for removing gases while keeping the vacuum not lower than a 10^{-3} Bar. After the refining is completed, charge with Argon gas until the pressure reaches 0.4 bar, adding 0.5wt% o Ni-20Ca alloy at the same time to remove the harmful impurity element S. When the temperature of the molten metal is at 1,520°C before pouring, add 0.020wt% of the Ni-20Mg alloy and 0.005 wt% metal La in turn to perform desulfurization and purification; Fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into moulds, the alloy ingot will form at an Argon atmosphere.

[0058] Remelt the alloy ingot melted by the vacuum induction furnace by vacuum arc remelting. Annealing the electrode for 1h at a temperature of 900°C; removing the oxide scale on the surface; welding the electrode at a vacuum of 10^{-3}mmHg; smelting at a voltage of 25V; controlling the vacuum to be 10^{-3}mmHg; keeping the melting rate at 250kg/h; and finally stress release annealing alloy ingot for 1h at a temperature of 900°C; performing diffusion annealing on the re-melted alloy ingot at a temperature of 1,190°C and billet forging at a temperature of 1,200°C, forging the alloy ingot into ∅15mm bar product through three times reheating, implementing solid solution treatment on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of γ' precipitation strengthening phase of the nickel-based superalloy for 700□ ultra-supercritical coal-fired power plant is at 15wt%.

Embodiment 6

[0059] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises with C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical composition and the weight percentages of the impurities S, P, Si and Mn can be seen in Table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of Mo and W atoms, and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1, too.

[0060] The fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises the following steps:

Selecting high quality raw materials and place 0.06wt% of C, 24.7wt% of Cr, 12.9wt% of Co, 0.53wt% of Mo,2.23wt% of W, 1.59wt% of Nb, 1.62wt% of Ti, 1.54wt% of Al, 0.004wt% of B, 0.005wt% of Zr, 0.15wt% of V, 54wt% of Ni and 5wt% of the dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace and the auxiliary materials consisting of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. Those raw materials are melted in the vacuum induction furnace under vacuum conditions of 10^{-3} Bar. After the raw materials are completely melted, refine the molten metal for 10 min to remove gases while keeping the vacuum not lower than 10^{-3} Bar. After the refining is completed, charge with argon gas until the pressure reaches 0.4bar, adding 0.5wt% Ni-20Ca alloy at the same time to remove the harmful impurity element S. When the temperature of the molten metal is at 1,520°C before pouring, add 0.025wt% Ni-20Mg alloy and 0.005 wt% of metal La in turn to perform desulfurization and purification. Fully melting the materials, mixing the molten metal well, filtering the mixed materials and pouring the molten metal into moulds, the alloy ingot will form at an Argon atmosphere.

[0061] Remelt the alloy ingot by electroslag remelting under a protective atmosphere. Remove the oxide scale from the surface of the alloy ingot, then being welded with the electrode, Perform electroslag remelting by using (40% CaF_2 + 25%Al_2O_3 + 15%CaO + 10%MgO + 10%TiO_2) complex quinary slag purified system, wherein the slag is extracted while the SiO_2 is ensured to be less than 0.5%. The electroslag ingot are baked for 4h at a temperature of 800°C, keeping the smelting voltage of ESR furnace at 50V and the smelting at remelting rate of 250kg/h; and finally annealing the electro-slag remelted ingot for 1h at a temperature of 900°C. Performing diffusion annealing on ESR re-melted alloy ingot at a temperature of 1,190°C and billet forging at a temperature of 1,200°C, forging the ESR alloy ingot into ∅15mm bar product through three times reheating, implementing solid solution treatment on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of γ' precipitation strengthening phase of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants is at 17.2wt%.

Comparative example 1

[0062] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises with C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical compositions and the weight percentages of the impurities S, P, Si and Mn can be seen in Table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of Mo and W atoms, and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1, too.

[0063] The fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises the following steps:

Selecting high quality raw materials and place 0.05wt% of C, 24.98wt% of Cr, 14.6wt% of Co, 1.36wt% of Mo,1.19wt% of W, 1.54wt% of Nb, 1.53wt% of Ti, 1.51wt% of Al, 0.002wt% of B, 0.04wt% of Zr, 53wt% of Ni and 0.5wt% of the dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace and the auxiliary materials consisting of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. Smelt these raw materials in the vacuum induction furnace at vacuum condition of 10^{-3} Bar. After the raw materials are completely melted, refine the materials for 10min to remove gases while keeping the vacuum not lower than 10^{-3} Bar. After the refining is completed, charge with Argon gas until the pressure reaches 0.4bar, adding 0.5wt% Ni-20Ca alloy at the same time to remove the harmful impurity element S When the temperature of the molten metal is at 1,520°C before pouring; add 0.015wt% Ni-20Mg alloy and 0.015 wt% metal La in turn to perform desulfurization and purification. Fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into moulds, the alloy ingot will form at an argon atmosphere;

[0064] Remelt the VIM alloy ingot by means of vacuum arc remelting (VAR). Annealing the electrode for 1h at a temperature of 900°C, removes the oxide scale from the surface; welding the electrode of the alloy ingots at a vacuum of 10^{-3}mmHg; then melting both of them at a voltage of 25V; controlling the vacuum at 10^{-3}mmHg; keeping the melting rate 250kg/h; and finally annealing the VAR alloy ingot for 1h at a temperature of 900°C; perform diffusion annealing on the re-melted VAR alloy ingot at a temperature of 1,190°C and forging the alloy ingot at 1,200°C, into ∅15mm bar product through three times reheating, implementing solid solution annealing on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of Y precipitation strengthening phase of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant is at 16wt%.

Comparative example 2

[0065] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises with C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical composition and the weight percentages of the impurities S, P, Si and Mn can be seen in Table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of Mo and W atoms, and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1, too.

[0066] The fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises the following steps:

Select high quality raw materials and place 0.05wt% of C, 24.4wt% of Cr, 13.6wt% of Co, 1.19wt% of Mo,1.06wt% of W, 1.81wt% of Nb, 1.73wt% of Ti, 1.14wt% of Al, 0.003wt% of B, 0.05wt% of Zr, 0.16wt% of V,54wt% of Ni and 0.5wt% of the dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace and the auxiliary materials consisting of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. Melting those raw materials in the vacuum induction furnace under vacuum conditions of 10^{-3} Bar. After the raw materials are completely melted, refine the materials for 10min to remove gases while keeping the vacuum not lower than 10^{-3} Bar. After refining is completed, charge with Argon gas until the pressure reaches 0.4bar, adding 0.5wt% Ni-20Ca alloy at the same time to remove the harmful impurity element S. When the temperature of the molten metal is at 1,520°C before pouring, add 0.020wt% Ni-20Mg alloy and 0.005wt% metal La in turn to perform desulfurization and purification. Fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into moulds, the alloy ingot will form at an Argon atmosphere.

[0067] Remelt the VIM alloy ingot by means of vacuum arc re-melting. Annealing the VIM electrode for 1h at a temperature of 900°C, removes the oxide scale from the surface; welding the VIM electrode with auxiliary electrode at a vacuum of 10^{-3} mmHg; smelting both of them at a voltage of 25V; controlling the vacuum to be 10^{-3}mmHg; keeping the melting rate 250kg/h; and finally annealing the VAR alloy ingot for 1h at a temperature of 900°C; performing diffusion annealing on the VAR re-melted alloy ingot at a temperature of 1,190°C and forging the VAR alloy ingot at 1,200°C into ∅15mm bar product through three times reheating, implementing solid solution treatment on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of γ' precipitation strengthening phase of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant is at 13.4wt%.

Comparative example 3

[0068] A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant comprises with C, Cr, Co, Mo, W, Nb, Ti, Al, B, Zr, Mg, V, La, Ni and the inevitable impurity elements. The actually tested weight percentages of chemical composition and the weight percentages of the impurities S, P, Si and Mn can be seen in Table 1. The ratio (Al/(Ti+Nb)) of the atomic percentage of Al to the sum of the atomic percentage of Ti and Nb, the sum (Nb+Ti+Al) of the atomic percentages of Al, Ti and Nb, the ratio (Cr/(Mo+W)) of the atomic percentage of Cr and the sum of Mo and W atoms, and the sum (Cr+Mo+W) of the atomic percentages of Cr, Mo and W can be seen in Table 1, too.

[0069] The fabrication method of this nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants comprises the following steps:

Select high quality raw materials and place 0.06wt% of C, 24.4wt% of Cr, 12.91wt% of Co, 3.41wt% of Mo,2.33wt% of W, 1.59wt% of Nb, 1.63wt% of Ti, 1.53wt% of Al, 0.004wt% of B, 0.005wt% of Zr, 0.15wt% of V,51wt% of Ni and 5wt% of dry auxiliary materials with a purity of 99.5% into a vacuum induction furnace and the auxiliary materials consisting of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3. Those raw materials are melted in the vacuum induction furnace at vacuum condition of 10^{-3} Bar. After the raw materials are completely melted, refine the materials for 10min to remove gases while keeping the vacuum not lower than 10^{-3} Bar. After refining is completed, charge with Argon gas until the pressure reaches 0.4bar, adding 0.5wt% Ni-20Ca alloy at the same time to remove the harmful impurity element S. When the temperature of the molten metal is at 1,520°C before pouring, add 0.025wt% Ni-20Mg alloy and 0.005wt% metal La in turn to perform desulfurization and purification. Fully melt the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into moulds, the alloy ingot will form at an Argon atmosphere.

[0070] Remelt the VIM alloy ingot by means of electro-slag re-melting under a protective argon atmosphere. Remove the oxide scale from alloy ingot surface, being welded it with the auxiliary electrode. Perform electro-slag re-melting by using (40% CaF_2 + 25%Al_2O_3 + 15%CaO + 10%MgO + 10%TiO_2) complex quinary slag purified system, wherein the slag is extracted while the SiO_2 is ensured to be less than 0.5%, and the electro-slag ingot are baked for 4h at a temperature of 800°C; keeping the ESR smelting voltage at 50V and the smelting rate 250kg/h. Finally anneal the electro-slag ingot for 1h at a temperature of 900°C; performing diffusion annealing on the ESR re-melted alloy ingot at a temperature of 1,190°C and billet forging at a temperature of 1,200°C, forging the alloy ingot into ∅15mm bar product through three times reheating, implementing solid solution treatment on the bar product for 1h at a temperature of 1,150°C, water cooling and aging the bar product for 16h at a temperature of 800°C, air cooling. Thus, the weight fraction of γ' precipitation strengthening phase of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants is at 18.2wt%.

Table 1. Chemical compositions of the alloys in embodiments 1-6 and of the alloy in comparative examples 1-3

	Heat	wt%																		Atomic ratio			
		C	Cr	Co	Mo	W	Nb	Ti	Al	B	Zr	Mg	V	La	S	P	Si	Mn	Ni	Al/ (Ti+Nb)	Nb+Ti +Al(%)	Cr/ (Mo+W)	Cr+Mo +W (%)
Embodiment	1	0.032	24.10	14.00	0.32	1.02	1.42	1.46	1.55	0.003	0.02	0.003	0.18	0.003	0.0005	0.005	0.05	0.05	Bal	1.257	5.831	52.12	26.718
	2	0.034	24.33	10.13	1.34	1.05	1.61	1.43	1.63	0.003	0.02	0.003	0.17	0.003	0.0004	0.005	0.05	0.05	Bal	1.282	6.100	23.80	27.672
	3	0.030	24.46	14.40	2.41	1.14	1.55	1.50	1.50	0.002	0.04	0.003	0.15	0.003	0.0005	0.005	0.05	0.05	Bal	1.160	5.907	15.03	28.641
	4	0.05	24.73	14.50	2.84	1.18	1.50	1.54	1.52	0.002	0.04	0.003	0.15	0.003	0.0005	0.005	0.05	0.05	Bal	1.168	5.968	13.22	29.215
	5	0.04	24.14	13.50	3.01	1.15	1.45	1.45	1.45	0.003	0.05	0.004	0.16	0.003	0.0006	0.004	0.09	0.05	Bal	1.173	5.693	12.34	28.713
	6	0.04	24.50	12.78	0.52	2.21	1.53	1.56	1.48	0.004	0.05	0.005	0.15	0.003	0.0005	0.005	0.07	0.05	Bal	1.120	5.923	26.61	27.470
Comparative example	1	0.03	24.73	14.50	1.35	1.18	1.48	1.47	1.45	0.002	0.04	0.003	-	-	0.0020	0.005	0.05	0.05	Bal	1.154	5.756	23.22	28.486
	2	0.03	24.14	13.50	1.18	1.05	1.79	1.66	1.09	0.003	0.05	0.004	0.16	0.003	0.0006	0.004	0.06	0.05	Bal	0.750	5.376	25.78	27.519
	3	0.04	24.12	12.78	3.38	2.31	1.53	1.56	1.51	0.004	0.05	0.005	0.15	0.003	0.0005	0.005	0.07	0.05	Bal	1.142	6.053	9.71	29.524

[0071] The chemical compositions of the alloys in embodiments 1-6 are fully in accordance with the composition scope of the alloy of the present invention and within the requirements of the limiting conditions. The alloy in the comparative example 1 is not added with V and La during smelting. The atom ratio of Al/(Ti+Nb) and the sum of the Nb+Ti+Al of the alloy in comparative example 2 do not conform to the limiting conditions of the alloy of the present invention. The atomic ratio Cr/(Mo+W) in comparative example 3 does not conform to the limiting conditions of the alloy of the present invention.

Room-temperature and high-temperature tensile tests:

[0072] The nickel-based superalloys for 700°C ultra-supercritical coal-fired power plant in embodiments 1-6 and comparative examples 1-3 are forged to round bars for implementation of the tensile tests at room temperature and at 700°C and 800°C, respectively. The tensile test results can be seen in Table 2.

Table 2. Room-temperature and high-temperature tensile performance of the nickel-based alloys of the embodiments and comparative examples

Test temperature	Alloy		Mechanical property			
			Yield strength $R_{p0.2}$/MPa	Tensile strength R_m/MPa	Elongation A/%	Area reduction Z/%
Room temperature	Embodiments	1	796.9	1225.8	32.4	38.9
		2	824.7	1239.7	30.0	37.2
		3	788.1	1214.9	28.0	33.0
		4	814.2	1233.1	27.6	32.5
		5	795.6	1218.3	24.2	32.3
		6	804.1	1209.3	24.9	31.1
	Comparative examples	1	708.4	1119.5	18.1	22.3
		2	652.9	1010.2	30.7	39.6
		3	813.9	1219.4	23.5	32.1
700°C	Embodiments	1	646.0	1008.0	27.2	31.3
		2	666.8	1023.0	24.8	32.4
		3	645.3	986.0	27.2	31.4
		4	662.1	1020.2	23.8	31.4
		5	650.9	1006.9	23.9	30.5
		6	645.2	1012.4	24.7	30.0
	Comparative examples	1	561.8	886.2	14.9	19.0
		2	519.5	822.6	22.5	30.4
		3	659.3	978.0	20.2	26.1

(continued)

Test temperature	Alloy		Mechanical property			
			Yield strength $R_{p0.2}$/MPa	Tensile strength R_m/MPa	Elongation A/%	Area reduction Z/%
800°C	Embodiments	1	611.2	841.3	19.8	25.5
		2	628.3	849.1	20.8	27.5
		3	602.1	809.3	18.0	25.6
		4	622.9	845.0	18.0	25.6
		5	619.5	815.6	20.1	28.2
		6	615.2	816.8	19.1	27.2
	Comparative examples	1	540.3	708.9	9.8	14.4
		2	491.7	642.2	16.3	24.0
		3	616.1	837.5	14.9	24.1

[0073] From the data in Table 2, it can be seen that the room temperature tensile test shows that the yield strength of the nickel-based alloys of the embodiments and comparative examples is greater than 780MPa, the tensile strength is greater than 1,200MPa, the elongation is greater than 24.0%, and the area reduction is greater than 32.0%. In the case of a 700°C tensile test, the yield strength is greater than 640MPa, the tensile strength is greater than 980MPa, the elongation is greater than 23.0%, and the area reduction is greater than 30.0%. In the case of an 800°C tensile test, the yield strength is greater than 600MPa, the tensile strength is greater than 800MPa, the elongation is greater than 17.0%, area reduction is greater than 25.0%; the alloys have high tensile strength and tensile ductility at both room temperature and high temperatures.

[0074] Comparatively, for the alloy of comparative example 1 without V and La, not only the tensile strength decreases, but also the tensile ductility reduces by 35%~50% in comparison with the embodiment, in particular to the alloy with high S content. The alloy of the compositions Nb, Ti and Al in comparative example 2 do not conform to the restriction conditions, shows relatively low strength and the tensile strength reduced by 15%~20% in comparison with the embodiment, besides the equilibrium phase this alloy contains η phase, as shown in figure 3. The alloy of the compositions Cr, Mo and W in comparative example 3 do not conform to the restriction conditions, shows that the strength and toughness are affected, and moreover there is a harmful brittle σ phase as the equilibrium phase of the alloy, as shown in Figure 4. These results indicate that the scopes and the restriction conditions of chemical composition limited by the present invention are strong guarantee for good tensile properties of the alloy.

High-temperature stress-rupture tests:

[0075] The nickel-based superalloys for 700°C ultra-supercritical coal-fired power plant in embodiments 1-6 is forged into bar product for stress-rupture tests at 750°C, 800°C and 850°C, respectively.

[0076] At the condition of 750°C /205MPa, the stress-rupture life of the alloy in embodiments 1-6 is greater than 5,000h, the elongation is greater than 12.0%, the area reduction is greater than 16.0%; at the condition of 800°C /125MPa the stress-rupture life is greater than 5,000h, the elongation is greater than 14.0%, the area reduction is greater than 18.0%; at the condition of 850°C /100MPa, the stress-rupture life is greater than 1,500h, the elongation is greater than 20.0%, and the area reduction is greater than 25.0%.

[0077] At the condition of 750°C/205MPa, the stress-rupture life of the alloy in comparative examples 1-3 is less than 3,000h, the elongation is less than 8.0%, the area reduction is less than 11.0%; at the condition of 800°C /125MPa the stress-rupture life is less than 2,500h, the elongation is less than 10.0%, the area reduction is less than 14.0%; at the condition of 850°C /100MPa, the stress-rupture life is less than 750h, the elongation is less than 12.0%, and the area reduction is less than 17.0%.

[0078] The nickel-based alloy of the present invention characterizes with high forgeability, can be used to manufacture the highest-temperature parts of the turbines and boilers of the 700°C ultra-supercritical coal-fired power plants and also can be applied to other fields where it needs a material with high ability of oxidation resistance, corrosion resistance, and with high tensile strength and creep strength as well.

Claims

1. A nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant, **characterized by** comprising : C 0.01~0.07wt%, Cr 23~25.5wt%, Co 10~14.6wt%, Mo 0.3~3.5wt%, W 0.5~2.5wt%, Nb 0.8~2.2wt%, Ti 1.0~2.5wt%, A1 1.0~2.5wt%, B 0.001~0.005wt%, Zr 0.01~0.3wt%, Mg 0.002~0.015wt%, V 0.01~0.5wt%, La 0.001~0.005wt%, the balance of Ni and the inevitable impurity elements including S <0.010wt%, P <0.015wt%, Si <0.3wt% and Mn <0.5wt%; wherein the ratio of the atomic percentage of Al to the sum of the atomic percentages of Ti and Nb is in a range of 1.0-1.3; the sum of the atomic percentages of Al, Ti and Nb is 5.5-6.2at%; the ratio of the atomic percentage of Cr to the sum of the atomic percentages of Mo and W is greater than 12, and the sum of the atomic percentages of Cr, Mo and W is not greater than 30at%.

2. A fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant according to claim 1, **characterized by** comprising the following steps:

   Step 1: placing 0.01-0.07wt% of C, 23~25.5wt% of Cr, 10~14.6wt% of Co, 0.3~3.5wt% of Mo,0.5~2.5wt% of W, 0.8~2.2wt% of Nb, 1.0~2.5wt% of Ti, 1.0~2.5wt% of Al, 0.001~0.005wt% of B, 0.01~0.3wt% of Zr, less than 0.5wt% of V, 48~58wt% of Ni and 3~6wt% of the dry auxiliary materials with a purity greater than 99.5% into a vacuum induction furnace and the auxiliary materials consisting of 40wt% of CaF_2, 40wt% of CaO and 20wt% of Al_2O_3, these raw materials being melted in the vacuum induction furnace under vacuum condition no lower than 10^{-3} Bar, after the raw materials are completely melted, refining the metal for 30min to remove gases while keeping the vacuum not lower than 10^{-3} Bar, after refining is completed, charging with argon gas until the pressure reaches 0.4bar, adding 0.3~0.6wt% of Ni-Ca alloy at the same time to remove the harmful impurity element S, when the temperature of the molten metal is not less than 1,500°C before pouring; adding 0.01~0.025wt% Ni-Mg alloy and 0~0.005wt% metal La in turn to perform desulfurization and purification, fully melting the materials, mixing the molten metal well, filtering the molten metal and pouring the molten metal into moulds, the alloy ingot forming in an argon atmosphere;
   Step 2: performing diffusion annealing, billet forging, solid solution and aging treatment for alloy ingot to obtain the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plants.

3. The fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant according to claim 2, **characterized in that**, in step 2, the temperature of the diffusion annealing is implemented at 1,150~1,220°C, and the duration is 16~48h.

4. The fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant according to claim 2, **characterized in that**, in step 2, the temperature of billet forging is not lower than 1,050°C.

5. The fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant according to claim 2, **characterized in that**, in step 2, the temperature of the solid solution treatment is implemented at 1,100~1,200°C, and the duration is 0.5~2h.

6. The fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant according to claim 2, **characterized in that**, in step 2, the temperature of the solid solution treatment is implemented at 800°C and the duration is 4~16h.

7. The fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant according to claim 2, **characterized in that**, in step 2, before diffusion annealing, the alloy ingot is refined again by vacuum arc re-melting or by electro-slag re-melting in a protective gas atmosphere.

8. The fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant according to claim 7, **characterized in that**, if the vacuum arc re-melting method is adopted in step 2, the re-melting rate shall be strictly controlled at less than 300kg/h.

9. This fabrication method of the nickel-based superalloy for 700°C ultra-supercritical coal-fired power plant according to claim 7, **characterized in that**, when the electro-slag re-melting at a protective gas atmosphere is adopted in step 2, a complex quinary slag purified system is used; the complex quinary slag purified system comprises 40~45wt% of CaF_2, 20~30wt% of Al_2O_3, 15~20wt% of CaO, 5~10wt% of MgO and 5-10wt% of TiO_2; before using, the complex quinary slag purified system should be extracted to ensure SiO_2<0.5%, and should be baked for 4h at a temperature of 800°C.

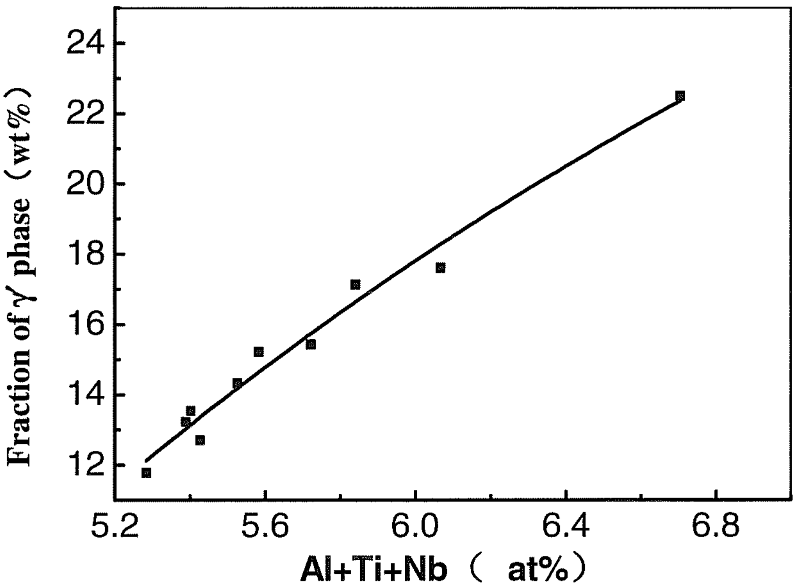
Fraction of γ′ phase (wt%)
24
22
20
18
16
14
12
5.2
5.6
6.0
6.4
6.8
Al+Ti+Nb (at%)

Fig.1

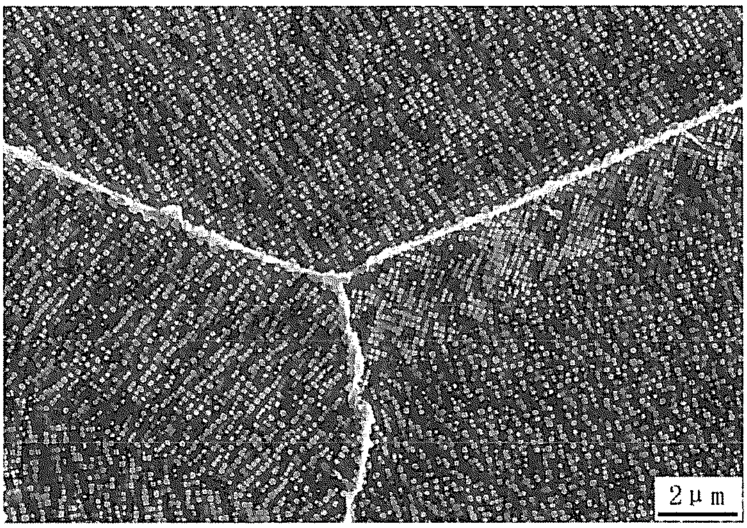
2μm

Fig. 2

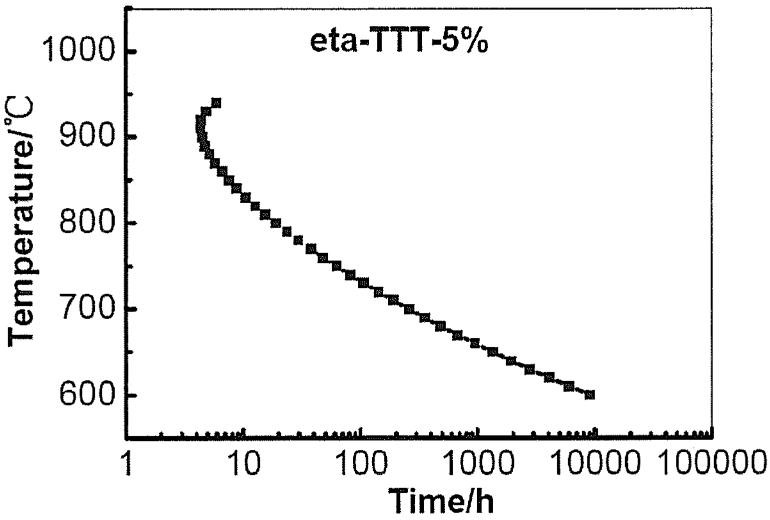
eta-TTT-5%
Temperature/°C
1000
900
800
700
600
1
10
100
1000
10000
100000
Time/h

Fig. 3

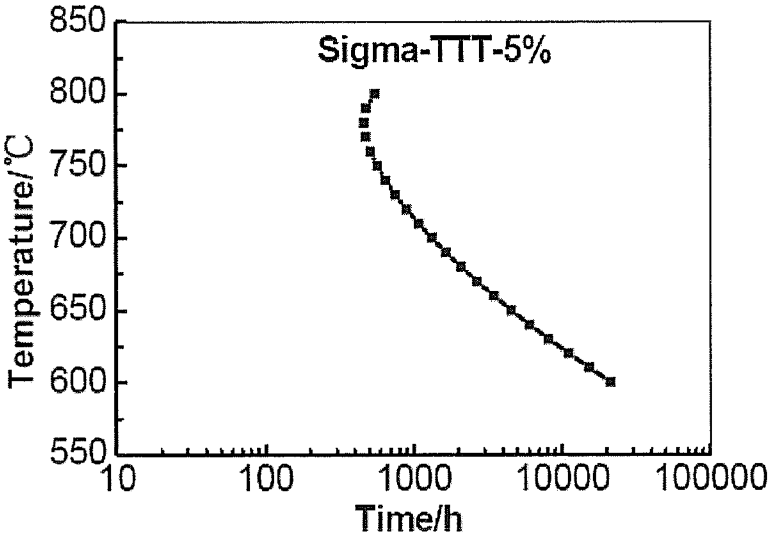
Sigma-TTT-5%
Temperature/°C
850
800
750
700
650
600
550
10
100
1000
10000
100000
Time/h

Fig. 4

INTERNATIONAL SEARCH REPORT	International application No. PCT/CN2014/075474

A. CLASSIFICATION OF SUBJECT MATTER

C22C 19/05 (2006.01) i; C22C 30/00 (2006.01) i; C22C 1/03 (2006.01) i; C22C 1/06 (2006.01) i; C22F 1/10 (2006.01) i
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 19; C22C 1

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, CNKI, WPI, EPODOC: Cr, Chromium, Chrome, Chrom, Co, cobalt, Mo, Molybdenum, W, Tungsten, Wolfram, Nb, Niobium, Niob, Ti, Tianium, Titanic, Al, Aluminium, Aluminum, B, boron, boracium, Zr, Zirconium, Mg, Magnesium, V, Vanadium, RE, REM, rare earth, La, lanthanum,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006157171 A1 (HONDA MOTOR CO LTD et al.) 20 July 2006 (20.07.2006) the whole document	1-9
A	CN 86108748 A (BEIJING IRON AND ST) 10 August 1988 (10.08.1988) the whole document	1-9
A	US 5855699 A (DAIDO STEEL CO LTD et al.) 05 January 1999 (05.01.1999) the whole document	1-9
A	CN 102084014 A (HUNTINGTON ALLOYS CORP.) 01 June 2011 (01.06.2011) the whole document	1-9
A	US 6458318 B1 (SUMITOMO METAL IND) 01 October 2002 (01.10.2002) the whole document	1-9
A	CN 102719683 (SHANXI TAIGANG STAINLESS STEEL CO., LTD.) 10 October 2012 (10.10.2012) the whole document	7-9

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 October 2014	04 December 2014
Name and mailing address of the ISA State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No. (86-10) 62019451	Authorized officer DANG, Xing Telephone No. (86-10) 62084417

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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		JP 3644532 B	27 April 2005
		DE 60004737 E	02 October 2003
CN 102719683	10 October 2012	None	

Form PCT/ISA /210 (patent family annex) (July 2009)