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(54) **RARE EARTH-CONTAINING HEAT-RESISTANT ALLOY STEEL AND SLAB CONTINUOUS CASTING PRODUCTION PROCESS THEREFOR**

SELTENE ERDEN ENTHALTENDER, HITZEBESTÄNDIGER LEGIERUNGSSTAHL UND VERFAHREN ZUR HERSTELLUNG VON BRAMMEN DURCH STRANGGIESSEN

ACIER ALLIÉ RÉSISTANT À LA CHALEUR CONTENANT DES TERRES RARES ET PROCÉDÉ DE PRODUCTION DE COULÉE CONTINUE DE BRAME ASSOCIÉ

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Description

TECHNICAL FIELD

[0001] The present invention relates to a metal material and a manufacturing method thereof, in particular to a rare earth-bearing heat-resistant alloy steel and a continuous casting production process therefor.

BACKGROUND

[0002] In industrial production, heat-resistant alloys have been produced for many years, and many well-known foreign metallurgical enterprises produce heat-resistant alloys. The heat-resistant alloys have the advantages of high aperture ratio, large specific surface area, low heat capacity, high thermal conductivity and high strength. The heat-resistant alloys can be used as main raw materials for metal carriers in an exhaust gas purification device, and are widely used in automobiles, diesel locomotives, motorcycles, small general machinery and other industries.

[0003] A rare earth-bearing heat-resistant alloy is a material with Fe, Cr and Al as the matrix and adding some alloys such as Mo, Cu, Nb, V and mixed rare earths, which can improve high-temperature performance, electrical resistivity and grain refinement. For the smelting process for the rare earth-bearing heat-resistant alloys, die casting and electroslag processes are mainly used at present, and continuous casting process is used in a few cases, followed by hot rolling and cold rolling.

[0004] In the iron and steel metallurgy industry around the world, with the continuous casting technology being gradually applied to the production of special steels, some enterprises have used slab continuous caster to produce special alloy products. However, the rare earth-bearing heat-resistant alloys are prone to precipitation of brittle phases during the cooling process of continuous casting, resulting in the formation of cracks and inclusion defects in the continuous casting slabs. WO 0100896 discloses a Fe-Cr-Al-Y-Hf alloy.

SUMMARY

[0005] One of the objectives of the present invention is to provide a rare earth-bearing heat-resistant alloy steel, which has an electrical resistivity of 1.3-1.5 $\mu\Omega$•m at room temperature, can withstand an applicable temperature of 1000-1300 °C, and has an elongation of 5-25% and an oxidative weight loss of 0.2-8.0 g/(cm^2•h) at the applicable temperature of 1000-1300 °C, thus exhibiting good quality and excellent heat resistance.

[0006] In order to achieve the above-mentioned objective, the present invention provides a rare earth-bearing heat-resistant alloy steel according to claim 1.

[0007] The expression "at least one of rare earth elements Nos. 57 to 71 in Periodic Table of Elements: 0.01-0.1%" means that: when the alloy steel comprises one of the rare earth elements Nos. 57 to 71, the content of the rare earth element is 0.01-0.1%; and when the alloy steel comprises more than one of the rare earth elements Nos. 57 to 71, the total content of these rare earth elements is 0.01-0.1%.

[0008] In the rare earth-bearing heat-resistant alloy steel of the present invention, the design principles of each chemical element are as follows:

C: In the rare earth-bearing heat-resistant alloy steel of the present invention, carbon can increase the electrical resistance of the steel and increase the strength of the steel.

[0009] However, it should be noted that carbon is prone to be austenitized, which tends to form carbide precipitates with Cr, thereby reducing the service life of the steel. Therefore, the less content of carbon in steel, the property will be better. In the rare earth-bearing heat-resistant alloy steel of the present invention, the content of C in mass percentage is controlled to be $0<C\leq0.05\%$.

[0010] In some preferred embodiments, the content of C in mass percentage can be controlled to be $0.01\leq C\leq0.05\%$.

[0011] In some more preferred embodiments, the content of C in mass percentage can be controlled to be $0.01\leq C\leq0.03\%$.

[0012] Si: In the rare earth-bearing heat-resistant alloy steel of the present invention, silicon is generally brought in by the raw materials and alloy materials. A high content of silicon in the steel will increase electrical resistance and room-temperature strength; the anti-oxidation effect of silicon at a medium temperature can reduce the loss of aluminum and rare earth; and silicon can reduce nitrogen absorption at a high temperature. However, it should be noted that silicate inclusions will adversely affect the alloy matrix. Especially in a high-temperature anti-oxidation film composition, if there is silicon oxide, the integrity of an Al_2O_3 oxide film will be affected. Therefore, the silicon content should not be too high. In the rare earth-bearing heat-resistant alloy steel of the present invention, the content of Si in mass percentage is controlled to be $0.02\leq Si\leq1.0\%$.

[0013] In some more preferred embodiments, the content of Si in mass percentage can be controlled to be $0.2\leq Si\leq0.5\%$.

[0014] Mn: In the rare earth-bearing heat-resistant alloy steel of the present invention, manganese can increase the toughness of the steel, and is prone to be austenitized. However, it should be noted that manganese can form oxides with a low melting point in the rare earth-bearing heat-resistant alloy steel, thereby reducing the thermal stability of the alloy. Therefore, in the rare earth-bearing heat-resistant alloy steel of the present invention, the content of Mn in mass percentage is controlled to be 0.05≤Mn≤1.0%

[0015] In some more preferred embodiments, the content of Mn in mass percentage can be controlled to be 0.2≤Mn≤0.4%.

[0016] Cr: In the rare earth-bearing heat-resistant alloy steel of the present invention, chromium and iron have many properties that are not very different, both of which are body-centered cubic lattices, and their lattice constants are similar. The chromium content in ferrite stainless steel is usually not less than 13%. The addition of chromium to iron can greatly increase the electrical resistivity of iron, and the electrical resistivity of iron will increase rapidly with the increasing content of Cr. However, it should be noted that when the content of chromium in the steel exceeds 28%, a σ brittle phase will precipitate and a hardening phase will be dissolved, and the electrical resistivity will gradually decrease. At the same time, the addition of chromium will cause the strength of the steel to improve rapidly and the brittleness of the steel to increase continuously. Therefore, in the rare earth-bearing heat-resistant alloy steel of the present invention, the content of Cr in mass percentage is controlled to be 13.0-28.0%.

[0017] In some preferred embodiments, the content of Cr in mass percentage can be controlled to be 17.0-25.0%.

[0018] Al: In the rare earth-bearing heat-resistant alloy steel of the present invention, when the content of aluminum in the Fe-Cr alloy is not less than 2%, the anti-oxidation performance will be improved; especially at a high temperature, an oxide film composition can be transformed from Cr_2O_3 to Al_2O_3, so that an oxide film is more stable and firmer, which greatly increases the applicable temperature and prolongs the service life. However, it should be noted that the addition of aluminum will increase the brittleness of the alloy steel. When the content of Al in the steel exceeds 8%, it is difficult to carry out both cold and hot workability. Therefore, in the rare earth-bearing heat-resistant alloy steel of the present invention, the content of Al in mass percentage is controlled to be 2.0-8.0%.

[0019] In some preferred embodiments, the content of Al in mass percentage can be controlled to be 3.0-6.0%.

[0020] Nb: In the rare earth-bearing heat-resistant alloy steel of the present invention, Nb can improve the high-temperature strength, reduce high-temperature creep, and prolong the service life of the rare earth-bearing heat-resistant alloy steel. However, considering that the cost and the production difficulty will increase as the content of Nb increases, the content of Nb in mass percentage in the rare earth-bearing heat-resistant alloy steel of the present invention is controlled to be 0.02≤Nb≤0.50%.

[0021] In some more preferred embodiments, the content of Nb in mass percentage can be controlled to be 0.02≤Nb≤0.40%.

[0022] In the most preferred embodiment, the content of Nb in mass percentage can be controlled to be 0.05≤Nb≤0.40%.

[0023] Co: In the rare earth-bearing heat-resistant alloy steel of the present invention, Co has similar effect with Nb, and Co can also increase the high-temperature strength, reduce high-temperature creep, and prolong the service life of the rare earth-bearing heat-resistant alloy. Similarly, considering that the production cost and the production difficulty will increase as the content of Co increases, the content of Co in mass percentage in the rare earth-bearing heat-resistant alloy steel of the present invention is controlled to be 0.01≤Co≤0.50%.

[0024] In some more preferred embodiments, the content of Co in mass percentage can be controlled to be 0.01≤Co≤0.20%.

[0025] In the most preferred embodiment, the content of Co in mass percentage can be controlled to be 0.05≤Nb≤0.20%.

[0026] Mo, Y: In the rare earth-bearing heat-resistant alloy steel of the present invention, a small amount of molybdenum (Mo) and yttrium (Y) are added. Molybdenum can effectively reduce the high-temperature creep rate and prolong the service life of the steel. Yttrium can refine alloy grains, thereby improving the room-temperature strength and high-temperature strength of the steel, and reducing the brittleness. The affinity of yttrium to oxygen is between that of lanthanum and that of aluminum, and it can form an enamel-like oxide film, thereby improving the high-temperature oxidation resistance and the nitriding resistance of the alloy steel. Like molybdenum, yttrium can effectively reduce the high-temperature creep rate and prolong the service life of the steel. However, it should be noted that when the content of molybdenum in the steel is too high, it is difficult to perform both hot and cold machining. When pickling the oxide scales, peeling or overwashing is common. Correspondingly, it tends to burn during smelting when the content of yttrium in the steel is too high. Therefore, in the rare earth-bearing heat-resistant alloy steel of the present invention, the content of Mo in mass percentage is controlled to be 0.5-6.0%, and the content of Y in mass percentage is controlled to be 0.01-0.2%.

[0027] In some preferred embodiments, the content of Mo in mass percentage can be controlled to be 1.5-5.0%, and the content of Y in mass percentage can be controlled to be 0.05-0.15%.

[0028] It should be noted that in the rare earth-bearing heat-resistant alloy steel of the present invention, the present inventors use lanthanide rare earth elements Nos. 57 to 71 while using Y, which mainly play the role of significantly prolonging the service life. A larger added content of rare earths indicates a higher service life value. However, in practical production, if more rare earths are added, more rare earths will be burned, and the possibility of increasing impurities and hydrogen absorption will be larger, while the increase in the residual content of rare earths in the alloy after burning is less. When the amount of the lanthanide rare earth added in the alloy is greater than 0.1%, the service life value of the steel shows a downward trend. Furthermore, the cost of the lanthanide rare earth is high, and the content should not be too high. Therefore, in the rare earth-bearing heat-resistant alloy steel of the present invention, the added content of at least one of rare earth elements Nos. 57 to 71 in Periodic Table of Elements in mass percentage is controlled to be 0.01-0.1%.

[0029] Preferably, the content of at least one of rare earth elements Nos. 57 to 71 in Periodic Table of Elements in mass percentage can be controlled to be 0.02-0.05%.

[0030] Preferably, in the rare earth-bearing heat-resistant alloy steel of the present invention, the content of Nb and Co in mass percentage further satisfies: Nb+Co≤0.50%, which can increase the high-temperature strength, reduce the high-temperature creep, and prolong the service life of the rare earth-bearing heat-resistant alloy. In case of Nb+Co>0.5%, the continuous casting production is difficult, the crack sensitivity is high, and the alloy cost is increased. Nb and Co in the formula represent the content of each corresponding element in mass percentage respectively.

[0031] In the rare earth-bearing heat-resistant alloy steel of the present invention, in the inevitable impurities, the content of P, S and N satisfies P≤0.040%, S≤0.020%, and N≤0.020%.

[0032] Preferably, in the rare earth-bearing heat-resistant alloy steel of the present invention, in the inevitable impurities, the content of P, S and N satisfies at least one of P≤0.020%, S≤0.010%, and N≤0.010%.

[0033] In the above technical solution, in the rare earth-bearing heat-resistant alloy steel of the present invention, P, N and S are all inevitable impurity elements in the steel, and the content of these impurity elements in the steel should not be too high. Both P and S can generate brittle substances with a low melting point, which tend to cause hot brittleness. Correspondingly, if the content of N in the rare earth-bearing heat-resistant alloy steel is too high, brittle aluminum nitride will be formed, which tend to cause brittle fracture and hinder the formation of Al_2O_3 oxide film.

[0034] Preferably, in the rare earth-bearing heat-resistant alloy steel of the present invention, the content of chemical elements in mass percentage satisfies at least one of: 0.01≤C≤0.03%, 0.2≤Si≤0.5%, 0.2≤Mn≤0.4%, Cr: 17.0-25.0%, Al: 3.0-6.0%, 0.02≤Nb≤0.40%, 0.01≤Co≤0.20%, Mo: 1.5-5.0%, Y: 0.05-0.15%, and at least one of rare earth elements Nos. 57 to 71 in Periodic Table of Elements: 0.02-0.05%.

[0035] Preferably, in the rare earth-bearing heat-resistant alloy steel of the present invention, the main microstructure is ferrite.

[0036] Preferably, the properties of the rare earth-bearing heat-resistant alloy steel of the present invention satisfy at least one of: being able to withstand an applicable temperature of 1000-1300 °C; having an elongation of 5-25% and an oxidative weight loss of 0.2-8.0 g/(cm^2•h) at the applicable temperature of 1000-1300 °C; and having an electrical resistivity of 1.3-1.5 μΩ•m at room temperature.

[0037] Correspondingly, another objective of the present invention is to provide a slab continuous casting production process for rare earth-bearing heat-resistant alloy steel. The slab continuous casting production process can effectively improve the quality of the continuous casting slab, and the produced continuous casting slab has excellent characteristics of good quality on a surface and center of the continuous casting slab. It can fully exert the advantages of continuous casting production, can effectively suppress recesses and cracks of the casting slab, significantly improve the surface and center quality of the casting slab and achieve sequence casting. The slab continuous casting production process of the present invention is a key technology for achieving continuous casting production and quality assurance of rare earth-bearing heat-resistant alloy slabs, and has extremely high promotion and application value for the development of rare-earth-bearing varieties and optimization of the process for enterprises that use a continuous casting process to achieve production and testing. It can not only increase production capacity, and but also effectively reduce production cost, so that the comprehensive competitiveness of an enterprise is greatly enhanced.

[0038] In order to achieve the above objectives, the present invention provides the above-mentioned slab continuous casting production process for the rare earth-bearing heat-resistant alloy steel. In the continuous casting process, the specific water ratio of secondary cooling is controlled to be 1.02±0.10 L/kg.

[0039] In the slab continuous casting production process of the present invention, a structure of rare earth-bearing heat-resistant alloy after solidification is mainly ferrite, and the columnar crystals are developed. Through a large number of experiments, the inventors have found that if weak cooling is used, the solidification time will be long, the columnar crystals will fully grow, and transgranular structure will appear in the casting slab at a low magnification, resulting in crack defects after rolling. In the slab continuous casting production process of the present invention, the present inventors have designed that: a strong cooling process is performed on the rare earth-bearing heat-resistant alloy steel in the secondary cooling zone, wherein when the specific water ratio of secondary cooling is controlled to be 1.02±0.10 L/kg, the lengths of primary columnar crystal and the spacing of secondary columnar crystals are the shortest, which are the prerequisites for improving the internal quality of the casting slab; and the electromagnetic stirring and soft reduction process of the present invention is further used to further ensure the internal quality of the casting slab. In some preferred embodiments, in the continuous casting process, the specific water ratio of secondary cooling can be controlled to be 1.02±0.06 L/kg, and the Mannesmann rating of the casting slab at low magnification is M1.7-2.0.

[0040] Preferably, in the slab continuous casting production process of the present invention, in the continuous casting step, a temperature for hot grinding the casting slab is controlled to be 100-600 °C.

[0041] In the slab continuous casting production process of the present invention, the surface of the continuous casting slab of the rare earth-bearing heat-resistant alloy steel will have defects such as local recesses, slag pits and deep vibration marks in different degrees. These defects will affect the surface quality of subsequent hot-rolled and cold-rolled products. At the same time, considering that the brittle phase is precipitated in the cooling process for the rare earth-bearing heat-resistant alloy steel, a hot grinding process can be used for the casting slab to effectively alleviate the above defects.

[0042] However, it should be noted that if the temperature in the hot grinding process is lower than 100 °C, the precipitated brittle phase tends to cause grinding cracks; and if the temperature is higher than 600 °C, it will exceed the capacity of the grinding equipment. Therefore, in the slab continuous casting production process of the present invention, the temperature for hot grinding the casting slab is controlled to be 100-600 °C. In some preferred embodiments, in the slab continuous casting production process of the present invention, the temperature for hot grinding the casting slab can be controlled to be 300-500 °C.

[0043] Preferably, in the slab continuous casting production process of the present invention, process parameters of the continuous casting process are controlled to satisfy at least one of

- the specific water ratio of secondary cooling is controlled to be 1.02±0.06 L/kg;
- the temperature for hot grinding the casting slab is 300-500 °C;
- the electromagnetic stirring current is 1000-2000 A;
- the soft reduction amount is 3-10 mm;
- the solid fraction *f*s of the casting slab center corresponding to a reduction zone is 0.10-0.90;
- the grinding amount on one casting slab side is 3-10 mm;
- the superheat degree of molten steel in a tundish is controlled to be 10-50 °C;
- the average casting speed of continuous casting is controlled to be 0.40-1.50 m/min; and
- the submerged depth of a continuous casting crystallizer nozzle is controlled to be 90-130 mm.

[0044] In the slab continuous casting production process of the present invention, in order to improve the segregation problem that may be possibly caused by the ferrite in the rare earth-bearing heat-resistant alloy during the continuous casting process, an electromagnetic stirring in the secondary cooling zone and dynamic soft reduction process can be added in the slab continuous casting production process of the present invention.

[0045] When the electromagnetic stirring in the secondary cooling zone and dynamic soft reduction process are used, if the current of electromagnetic stirring is less than 1000 A, and the soft reduction amount is less than 3 mm, it will not be effective in improving the quality of the center of a ferrite slab. If the current of electromagnetic stirring is higher than 2000 A, a liquid level of the crystallizer fluctuates greatly, and the slab is prone to negative segregation. If the soft reduction amount is greater than 10 mm, the narrow side of the casting slab is prone to bulge, and intermediate cracks are prone to be generated in the casting slab. In the ferrite structure of the rare earth-bearing heat-resistant alloy, the columnar crystals are developed; and through a lot of experiments, the results have shown that dynamic soft reduction is suitable for the whole solidification process of the two-phase region. Therefore, in the slab continuous casting production process of the present invention, the current of electromagnetic stirring is controlled to be 1000-2000 A, the soft reduction amount is controlled to be 3-10 mm, and the solid fraction *f*s of the casting slab center corresponding to a reduction zone is controlled to be 0.10-0.90. If *f*s corresponding to the reduction zone is less than 0.10, which is equivalent to complete liquid phase reduction, the columnar crystals have not been completely formed, and the effect of improving segregation is not obvious. If *f*s corresponding to the reduction zone is more than 0.90, the casting slab being nearly completely solidified, the columnar crystals cannot be completely crushed by reduction, and there is risk of internal cracks. Thus, the solid fraction *f*s in the center of the casting slab corresponding to the reduction zone being 0.10-0.90 is an important condition to control the Mannesmann rating of the casting slab at low magnification to be M1.7-2.0. In some preferred embodiments, the electromagnetic stirring current can be controlled to be 1400-2000 A, the soft reduction amount can be controlled to be 6-9 mm, and the solid fraction *f*s of the casting slab center corresponding to the reduction zone can be controlled to be 0.20-0.90.

[0046] In addition, it should be noted that when grinding the casting slab, if the grinding amount on one casting slab side is less than 3 mm, the defects may not be completely removed. If the grinding amount on one side is greater than 10 mm, the yield of the casting slab will be affected. Therefore, in the slab continuous casting production process of the present invention, the grinding amount on one casting slab side can be controlled to be 3-10 mm. In some preferred embodiments, the grinding amount on one casting slab side can be controlled to be 5-8 mm.

[0047] In the continuous casting process, if the superheat degree of molten steel is lower than 10 °C, the fluidity of the molten steel is poor, which will easily lead to the freezing of steel at the crystallizer nozzle to force pouring to be interrupted, and the melting effect of covering slag is not good. If the superheat degree of molten steel is higher than 50

°C, the rare earth-bearing heat-resistant alloy steel is prone to segregation, resulting in long solidification time and sufficient selective crystallization, which will exacerbate the quality issues of the casting slab. Therefore, in the slab continuous casting production process of the present invention, the superheat degree of molten steel in the tundish is controlled to be 10-50 °C. In some preferred embodiments, the superheat degree of molten steel in the tundish can be controlled to be 15-30 °C.

[0048] In addition, in the continuous casting process, if the average casting speed of continuous casting is faster than 1.50 m/min, the initial slab shell is thin, and the slab cooling is uneven, which tend to cause longitudinal cracks and even bleed-out. If the average casting speed of continuous casting is slower than 0.40 m/min, the cooling time of the slab in the crystallizer is too long, the molten steel at the meniscus is in a low-temperature state and the melting effect of the covering slag is not good, which tend to cause cracks and affect the overall production capacity of the continuous caster. Therefore, in the slab continuous casting production process of the present invention, the average casting speed of continuous casting is controlled to be 0.40-1.50 m/min. In some preferred embodiments, the average casting speed of continuous casting can be controlled to be 0.80-1.2 m/min.

[0049] Correspondingly, in the continuous casting process, if the submerged depth of the crystallizer nozzle is too shallow, the impact of the nozzle stream on the steel slag interface will be too strong, which will increase the probability of reaction between the molten steel and covering slag in the crystallizer, and increase the probability of slag entrapment on the meniscus. If the submerged depth of the crystallizer nozzle is too deep, the casting slab is prone to cracks. Therefore, in the slab continuous casting production process of the present invention, the submerged depth of the continuous casting crystallizer nozzle is controlled to be 90-130 mm. In some preferred embodiments, the submerged depth of the continuous casting crystallizer nozzle can be controlled to be 100-125 mm.

[0050] Preferably, in the slab continuous casting production process of the present invention, the process parameters of the continuous casting process are controlled to satisfy at least one of:

- the electromagnetic stirring current is 1400-2000 A;
- the soft reduction amount is 6-9 mm;
- the solid fraction *f*s of casting slab center corresponding to a reduction zone is 0.20-0.90;
- the grinding amount on one casting slab side is 5-8 mm;
- the superheat degree of molten steel in the tundish is controlled to be 15-30 °C;
- the average casting speed of continuous casting is controlled to be 0.80-1.2 m/min; and
- the submerged depth of the continuous casting crystallizer nozzle is controlled to be 100-125 mm.

[0051] Compared with the prior art, the rare earth-bearing heat-resistant alloy steel and the slab continuous casting production process therefor according to the present invention have the following advantages and beneficial effects:

[0052] The rare earth-bearing heat-resistant alloy steel of the present invention has an electrical resistivity of 1.3-1.5 μΩ•m at room temperature, can withstand an applicable temperature of 1000-1300 °C, and has an elongation of 5-25% and an oxidative weight loss of 0.2-8.0 g/(cm^2•h) at the applicable temperature of 1000-1300 °C, exhibiting good quality and excellent properties.

[0053] In addition, the slab continuous casting production process for the rare earth-bearing heat-resistant alloy steel of the present invention can effectively improve the quality of a continuous casting slab. The produced continuous casting slab has excellent characteristics such as good quality on the surface and center of the continuous casting slab. It can fully exert the advantages of continuous casting production, can effectively suppress the occurrence of recesses and cracks of the casting slab, significantly improve the surface and center quality of the casting slab and achieve sequence casting. The slab continuous casting production process of the present invention is a key technology for realizing continuous casting production and quality assurance of rare earth-bearing heat-resistant alloy slabs, and has extremely high promotion and application value for the development of rare-earth-bearing varieties and optimization of the process for enterprises that use a continuous casting process to achieve production and testing. It not only increases production capacity, and but also effectively reduces production cost, so that the comprehensive competitiveness of an enterprise can be greatly enhanced.

DETAILED DESCRIPTION

[0054] The rare earth-bearing heat-resistant alloy steel and the slab continuous casting production process therefor according to the present invention will be further explained and illustrated below in combination with specific embodiments. However, the technical solution of the present disclosure is not limited to the explanation and illustration.

Inventive Examples 1-6 and Comparative Examples 1-4

[0055] Table 1 shows the content of chemical elements in mass percentage in rare earth-bearing heat-resistant alloy steels in Inventive Examples 1-6 and Comparative Examples 1-4.

Table 1 (wt%, the balance being Fe and inevitable impurities other than P, S and N)

No.	Chemical elements													
	C	Si	Mn	Cr	Al	Nb	Co	Mo	Y	P	S	N	Re	Nb+Co
Inventive Example 1	0.01	0.38	0.27	22.3	4.7	0.19	0.01	3.5	0.1	0.017	0.001	0.008	0.03	0.20
Inventive Example 2	0.012	0.53	0.05	28.0	2.0	0.23	0.15	3.0	0.13	0.011	0.001	0.010	0.10	0.38
Inventive Example 3	0.015	0.35	0.3	17.2	5.4	0.02	0.10	2.0	0.2	0.016	0.002	0.013	0.01	0.12
Inventive Example 4	0.02	1.0	1.0	13.0	8.0	0.50	0.02	3.5	0.09	0.014	0.002	0.002	0.025	0.52
Inventive Example 5	0.03	0.02	0.65	21.2	3.2	0.03	0.50	6.0	0.01	0.020	0.001	0.005	0.072	0.53
Inventive Example 6	0.05	0.25	0.12	19.6	2.8	0.02	0.06	0.5	0.017	0.007	0.001	0.007	0.015	0.08
Comparative Example 1	0.01	0.40	0.27	***12***	***1.0***	0.10	0.10	***0.1***	0.16	0.010	0.001	0.008	***0***	0.20
Comparative Example 2	0.02	0.8	0.50	***8***	***1.8***	0.05	0.05	***0.4***	0.12	0.008	0.002	0.003	***0.008***	0.10
Comparative Example 3	0.03	0.2	0.72	20	***8.2***	***0.55***	***0.8***	3.3	0.08	0.020	0.001	0.004	***0.21***	1.35
Comparative Example 4	0.04	0.35	0.8	15.6	***9.8***	***0.61***	***0.63***	2.3	0.03	0.007	0.001	0.009	***0.25***	1.24

[0056] It should be noted that Re in Inventive Examples 1-6 and Comparative Examples 1-4 in Table 1 represents the content of any one element or the total content of several elements among elements Nos. 57 to 71 in Periodic Table of Elements in mass percentage.

[0057] The rare earth-bearing heat-resistant alloy steels of Inventive Examples 1-6 of the present invention and Comparative Examples 1-4 were prepared by the following continuous casting production process:

In the continuous casting process, firstly, the superheat degree of molten steel in the continuous casting tundish was controlled to be 10-50 °C and the submerged depth of the continuous casting crystallizer nozzle was controlled to be 90-130 mm. Then continuous casting pouring was started, wherein the average casting speed was controlled to be 0.40-1.50 m/min and the specific water ratio of secondary cooling was controlled to be 1.02±0.10 L/kg. After the casting slab entered the secondary cooling zone, electromagnetic stirring was started. The electromagnetic stirring current was 1000-2000 A, the soft reduction amount was controlled to be 3-10 mm, and the solid fraction *f*s of the casting slab center corresponding to the reduction zone was controlled to be 0.10-0.90. Finally, after the casting slab was released from the caster, the temperature for hot grinding the casting slab was controlled to be 100-600 °C, and the grinding amount on one casting slab side was controlled to be 3-10 mm.

[0058] Table 2 shows specific process parameters of manufacturing methods of the rare earth-bearing heat-resistant alloy steels of Inventive Examples 1-6 and Comparative Examples 1-4.

Table 2

No.	Sectional dimension of slab (mm)	Specific water ratio of secondary cooling (L/kg)	Temperature for hot grinding (°C)	Electromagnetic stirring current (A)	Soft reduction amount (mm)	Solid fraction *f*s of casting slab center corresponding to reduction zone	Grinding amount on one casting slab side (mm)	Average superheat degree of molten steel in tundish (°C)	Average casting speed of continuous casting (m/min)	Submerged depth of continuous casting crystallizer nozzle (mm)
Inventive Example 1	250×1200	0.96	450	1600	8.0	0.1-0.9	8	26	0.76	120
Inventive Example 2	200×1140	0.98	330	1400	6.5	0.1-0.9	7	32	0.92	105
Inventive Example 3	150×1300	1.08	200	1200	4.5	0.1-0.9	3	12	1.2	120
Inventive Example 4	200×1250	1.02	350	2000	7.0	0.1-0.9	5	39	1.0	125
Inventive Example 5	150×1450	1.12	280	1000	3.5	0.1-0.9	4	33	1.5	115
Inventive Example 6	230×1080	0.92	570	1800	9.0	0.1-0.9	10	47	0.4	90
Comparative Example 1	150×1000	1.10	550	1200	5.0	0.1-0.9	3	18	1.4	120
Comparative Example 2	200×1200	1.00	450	1600	6.0	0.1-0.9	5	26	1.2	125
Comparative Example 3	250×1350	0.94	250	2000	8.5	0.1-0.9	7	40	0.8	105
Comparative Example 4	230×1100	0.96	300	1800	7.5	0.1-0.9	6	30	1.0	95

[0059] Various performance tests were performed on the rare earth-bearing heat-resistant alloy steels of Inventive Examples 1-6 and Comparative Examples 1-4, and the test results were listed in Table 3. Performance test methods: GB/T 4338-2006 "Metallic materials - Tensile Testing at elevated temperature"; GB/T 13303-1991 "Steels - Determination method of oxidation resistance"; GB/T 351-2019 "Metallic materials - Resistivity measurement method"; and "Mannesmann Demark Steel Corporation - Standard and method for inspection of defects of continuous casting slab".

[0060] Table 3 shows the performance test results of the rare earth-bearing heat-resistant alloy steels of Inventive Examples 1-6 and Comparative Examples 1-4.

Table 3

No.	Elongation at applicable temperature of 1000-1300 °C (%)	Oxidative weight loss at applicable temperature of 1000-1300 °C g/ (cm^2·h)	Electrical resistivity at room temperature (μΩ·m)	Quality of casting slab
Inventive Example 1	17.3	0.46	1.303	No cracks, casting slab rating at low magnification of M1.8
Inventive Example 2	24.7	7.98	1.446	No cracks, casting slab rating at low magnification of M2.0
Inventive Example 3	13.5	0.37	1.444	No cracks, casting slab rating at low magnification of M1.7
Inventive Example 4	5.1	0.22	1.499	No cracks, casting slab rating at low magnification of M2.0
Inventive Example 5	20.1	2.33	1.496	No cracks, casting slab rating at low magnification of M2.0
Inventive Example 6	22.7	6.55	1.461	No cracks, casting slab rating at low magnification of M2.0
Comparative Example 1	8.2	***9.7***	***1.232***	No cracks, casting slab rating at low magnification of M1.8
Comparative Example 2	11.6	***10.1***	***1.195***	No cracks, casting slab rating at low magnification of M1.9
Comparative Example 3	***3.4***	0.9	1.356	***Cracks, casting slab rating at low magnification of M2.4***
Comparative Example 4	***2.8***	2.9	1.421	***Cracks, casting slab rating at low magnification of M2.2***

[0061] It can be seen from Table 3 that the rare earth-bearing heat-resistant alloy steel of each Inventive Example of the present invention had an electrical resistivity of 1.3-1.5 μΩ•m at room temperature, was able to withstand an applicable temperature of 1000-1300 °C, and had an elongation of 5-25% at the applicable temperature of 1000-1300 °C. Test results on oxidization resistance of alloys showed that the oxidative weight loss in each Inventive Example at the applicable temperature of 1000-1300 °C was 0.2-8.0 g/(cm^2•h). Thus, the rare earth-bearing heat-resistant alloy steels in Inventive Examples exhibited excellent heat resistance. Furthermore, the casting slab in each Inventive Example of the present invention exhibited good quality, had no cracks, and had a Mannesmann rating at low magnification of M1.7-2.0.

[0062] In Comparative Examples 1 and 2, the contents of Al, Cr, Mo and Re were lower than the claimed ranges of the present invention, and the "Oxidative weight loss at applicable temperature of 1000-1300 °C" and the "Electrical resistivity at room temperature" in the heat resistance properties did not satisfy the requirements. In Comparative Examples 3 and 4, the contents of Al, Co, Nb and Re were higher than the claimed ranges of the present invention, the "Elongation at applicable temperature of 1000-1300 °C" was less than 5%, and the rating of casting slab at low magnification exceeded M2.0. In Comparative Examples 3 and 4, the contents of Al and Re were high, such that the casting slabs were prone to subcutaneous inclusions, which would become the source of cracks in the continuous casting slab; and the contents of Co and Nb were high, such that the casting slabs fell into the third brittle zone in the high-temperature range, which would increase the crack susceptibility of the casting slab. Therefore, when the contents of Al, Co, Nb and Re were higher than the claimed ranges of the present invention, the casting slab exhibited low quality.

[0063] It should be noted that the above-listed examples are only specific embodiments of the present disclosure. Apparently, the present disclosure is not limited to the above embodiments but by the appended claims.

Claims

1. A rare earth-bearing heat-resistant alloy steel, comprising the following chemical elements in mass percentage:

   $0<C\leq 0.05\%$, $0.02\leq Si\leq 1.0\%$, $0.05\leq Mn\leq 1.0\%$, Cr: 13.0-28.0%, Al: 2.0-8.0%, $0.02<Nb<0.50\%$, $0.01\leq Co\leq 0.50\%$, Mo: 0.5-6.0%, Y: 0.01-0.2%, and at least one of rare earth elements Nos. 57 to 71 in Periodic Table of Elements: 0.01-0.1%, and the balance being Fe and inevitable impurities;
   wherein in the inevitable impurities, the content of P, S and N satisfies: $P\leq 0.040\%$, $S\leq 0.020\%$, and $N\leq 0.020\%$.

2. The rare earth-bearing heat-resistant alloy steel according to claim 1, wherein the content of Nb and Co in mass percentage further satisfies: $Nb+Co\leq 0.50\%$.

3. The rare earth-bearing heat-resistant alloy steel according to claim 1, wherein in the inevitable impurities, the content of P, S and N satisfies at least one of: $P\leq 0.020\%$, $S\leq 0.010\%$, and $N\leq 0.010\%$.

4. The rare earth-bearing heat-resistant alloy steel according to claim 1, wherein the content of chemical elements in mass percentage satisfies at least one of:
   $0.01\leq C\leq 0.03\%$, $0.2\leq Si\leq 0.5\%$, $0.2\leq Mn\leq 0.4\%$, Cr: 17.0-25.0%, Al: 3.0-6.0%, $0.02\leq Nb\leq 0.40\%$, $0.01<Co\leq 0.20\%$, Mo: 1.5-5.0%, Y: 0.05-0.15%, and at least one of rare earth elements Nos. 57 to 71 in Periodic Table of Elements: 0.02-0.05%.

5. The rare earth-bearing heat-resistant alloy steel according to claim 1, wherein a microstructure of the rare earth-bearing heat-resistant alloy steel comprises ferrite.

6. The rare earth-bearing heat-resistant alloy steel according to claim 1, wherein the properties of the rare earth-bearing heat-resistant alloy steel satisfy at least one of: being able to withstand an applicable temperature of 1000-1300 °C; having an elongation of 5-25% and an oxidative weight loss of 0.2-8.0 $g/(cm^2\cdot h)$ at the applicable temperature of 1000-1300 °C; and having an electrical resistivity of 1.3-1.5 $\mu\Omega\cdot m$ at room temperature.

7. A slab continuous casting production process for the rare earth-bearing heat-resistant alloy steel according to any of claims 1 to 6, wherein in a continuous casting step, a specific water ratio of secondary cooling is controlled to be 1.02 ± 0.10 L/kg.

8. The slab continuous casting production process according to claim 7, wherein in the continuous casting step, a temperature for hot grinding a casting slab is controlled to be 100-600 °C.

9. The slab continuous casting production process according to claim 7 or 8, wherein process parameters of the continuous casting step are controlled to satisfy at least one of:

   the specific water ratio of secondary cooling is controlled to be 1.02 ± 0.06 L/kg;
   a temperature for hot grinding a casting slab is 300-500 °C;
   an electromagnetic stirring current is 1000-2000 A;
   a soft reduction amount is 3-10 mm;
   a solid fraction *fs* of casting slab center corresponding to a reduction zone is 0.10-0.90;
   a grinding amount on one casting slab side is 3-10 mm;

a superheat degree of molten steel in a tundish is controlled to be 10-50 °C;
an average casting speed of continuous casting is controlled to be 0.40-1.50 m/min; and
a submerged depth of a continuous casting crystallizer nozzle is controlled to be 90-130 mm.

10. The slab continuous casting production process according to claim 9, wherein the process parameters of the continuous casting step are controlled to satisfy at least one of:

the electromagnetic stirring current is 1400-2000 A;
the soft reduction amount is 6-9 mm;
the solid fraction *f*s of casting slab center corresponding to the reduction zone is 0.20-0.90;
the grinding amount on one casting slab side is 5-8 mm;
the superheat degree of molten steel in the tundish is controlled to be 15-30 °C;
the average casting speed of continuous casting is controlled to be 0.80-1.2 m/min; and
the submerged depth insertion depth of the continuous casting crystallizer nozzle is controlled to be 100-125 mm.

Patentansprüche

1. Seltenerdhaltiger hitzebeständiger Legierungsstahl, der die folgenden chemischen Elemente in Massenprozent umfasst:

0<C≤0,05 %, 0,02≤Si≤1,0 %, 0,05≤Mn≤1,0 %, Cr: 13,0-28,0 %, Al: 2,0-8,0 %, 0,02≤Nb≤0,50 %, 0,01≤Co≤0,50 %, Mo: 0,5-6,0 %, Y: 0,01-0,2 % und mindestens eines der Seltenerdelemente Nr. 57 bis 71 im Periodensystem der Elemente: 0,01-0,1 %, und wobei der Rest aus Fe und unvermeidlichen Verunreinigungen besteht;
wobei bei den unvermeidlichen Verunreinigungen der Gehalt an P, S und N Folgendes erfüllt: P≤0,040 %, S≤0,020 % und N≤0,020 %.

2. Seltenerdhaltiger hitzebeständiger Legierungsstahl nach Anspruch 1, wobei der Gehalt an Nb und Co in Massenprozent ferner Folgendes erfüllt: Nb+Co≤0,50 %.

3. Seltenerdhaltiger hitzebeständiger Legierungsstahl nach Anspruch 1, wobei bei den unvermeidlichen Verunreinigungen der Gehalt an P, S und N mindestens eines von Folgendem erfüllt: P≤0,020 %, S≤0,010 % und/oder N≤0,010 %.

4. Seltenerdhaltiger hitzebeständiger Legierungsstahl nach Anspruch 1, wobei der Gehalt an chemischen Elementen in Massenprozent mindestens eines von Folgendem erfüllt:
0,01≤C≤0,03 %, 0,2≤Si≤0,5 %, 0,2≤Mn≤0,4 %, Cr: 17,0-25,0 %, Al: 3,0-6,0 %, 0,02≤Nb≤0,40 %, 0,01<Co≤0,20 %, Mo: 1,5-5,0 %, Y: 0,05-0,15 % und mindestens eines der Seltenerdelemente Nr. 57 bis 71 im Periodensystem der Elemente: 0,02-0,05 %.

5. Seltenerdhaltiger hitzebeständiger Legierungsstahl nach Anspruch 1, wobei eine Mikrostruktur des seltenerdhaltigen hitzebeständigen Legierungsstahls Ferrit umfasst.

6. Seltenerdhaltiger hitzebeständiger Legierungsstahl nach Anspruch 1, wobei die Eigenschaften des seltenerdhaltigen hitzebeständigen Legierungsstahls mindestens eines von Folgendem erfüllen: in der Lage sein, einer anwendbaren Temperatur von 1000-1300 °C standhalten zu können; Aufweisen einer Dehnung von 5-25 % und eines oxidativen Gewichtsverlusts von 0,2-8,0 g/(cm^2•h) bei der anwendbaren Temperatur von 1000-1300 °C; Aufweisen einer elektrischen Widerstandsfähigkeit von 1,3-1,5 μΩ•m bei Raumtemperatur.

7. Brammen-Strangguss-Verfahren für den seltenerdhaltigen hitzebeständigen Legierungsstahl nach einem der Ansprüche 1 bis 6, wobei in einem Stranggussschritt ein spezifisches Wasserverhältnis der Sekundärkühlung auf 1,02±0,10 L/kg geregelt wird.

8. Brammen-Strangguss-Verfahren nach Anspruch 7, wobei in dem Stranggussschritt eine Temperatur für das Warmschleifen einer Gussbramme auf 100-600 °C geregelt wird.

9. Brammen-Strangguss-Verfahren nach Anspruch 7 oder 8, wobei die Verfahrensparameter des Stranggussschritts so gesteuert werden, dass sie mindestens eines von Folgendem erfüllen:

das spezifische Wasserverhältnis der Sekundärkühlung wird auf 1,02±0,06 L/kg geregelt;
eine Temperatur für das Warmschleifen einer Gussbramme beträgt 300-500 °C;
ein elektromagnetischer Rührstrom beträgt 1000-2000 A;
ein weicher Reduzierungsbetrag beträgt 3-10 mm;
eine feste Fraktion *f*s der Gussbrammenmitte, die einer Reduktionszone entspricht, beträgt 0,10-0,90;
ein Schleifbetrag auf einer Gussbrammenseite beträgt 3-10 mm;
ein Überhitzungsgrad von geschmolzenem Stahl in einer Gießwanne wird auf 10-50 °C geregelt;
eine durchschnittliche Strangguss-Gießgeschwindigkeit wird auf 0,40-1,50 m/min geregelt; und
eine Eintauchtiefe einer Strangguss-Kristaiiisatordüse wird auf 90-130 mm geregelt.

10. Brammen-Strangguss-Verfahren nach Anspruch 9, wobei die Verfahrensparameter des Stranggussschritts so gesteuert werden, dass sie mindestens eines von Folgendem erfüllen:

der elektromagnetische Rührstrom beträgt 1400-2000 A;
der weiche Reduzierungsbetrag beträgt 6-9 mm;
die feste Fraktion *f*s der Gussbrammenmitte, die der Reduktionszone entspricht, beträgt 0,20-0,90;
der Schleifbetrag auf einer Gussbrammenseite beträgt 5-8 mm;
der Überhitzungsgrad des geschmolzenen Stahls in der Gießwanne wird auf 15-30 °C geregelt;
die durchschnittliche Strangguss-Gießgeschwindigkeit wird auf 0,80-1,2 m/min geregelt; und
die Eintauchtiefe der Strangguss-Kristallisatordüse wird auf 100-125 mm geregelt.

Revendications

1. Acier allié résistant à la chaleur contenant des terres rares, comprenant les éléments chimiques suivants en pourcentage de masse :

0<C≤0,05 %, 0,02≤Si≤1,0 %, 0,05≤Mn≤1,0 %, Cr : 13,0-28,0 %, Al : 2,0-8,0 %, 0,02≤Nb≤0,50 %, 0,01≤Co≤0,50 %, Mo: 0,5-6,0 %, Y: 0,01-0,2 %, et au moins un parmi des éléments de terres rares n° 57 à 71 du tableau périodique des éléments : 0,01-0,1%, et le reste étant du Fe et des impuretés inévitables ;
où dans les impuretés inévitables, la teneur en P, S et N satisfait : P≤0,040 %, S≤0,020 %, et N≤0,020 %.

2. Acier allié résistant à la chaleur contenant des terres rares selon la revendication 1, où la teneur en Nb et Co en pourcentage de masse satisfait en outre : Nb+Co≤0,50 %.

3. Acier allié résistant à la chaleur contenant des terres rares selon la revendication 1, où dans les impuretés inévitables, la teneur en P, S et N satisfait au moins une parmi P≤0,020 %, S≤0,010 %, et N≤0,010 %.

4. Acier allié résistant à la chaleur contenant des terres rares selon la revendication 1, où la teneur en éléments chimiques en pourcentage de masse satisfait au moins une parmi :
0,01≤C≤0,03 %, 0,2≤Si≤0,5 %, 0,2≤Mn≤0,4 %, Cr: 17,0-25,0 %, Al: 3,0-6,0 %, 0,02≤Nb≤0,40 %, 0,01<Co≤0,20 %, Mo: 1,5-5,0 %, Y: 0,05-0,15 %, et au moins un parmi des éléments de terres rares n° 57 à 71 du tableau périodique des éléments : 0,02-0,05 %.

5. Acier allié résistant à la chaleur contenant des terres rares selon la revendication 1, où une microstructure de l'acier allié résistant à la chaleur contenant des terres rares comprend de la ferrite.

6. Acier allié résistant à la chaleur contenant des terres rares selon la revendication 1, où les propriétés de l'acier allié résistant à la chaleur contenant des terres rares satisfont au moins à une parmi : être capable de résister à une température applicable de 1000 à 1300 °C ; avoir un allongement de 5 à 25 % et une perte de poids par oxydation de 0,2 à 8,0 g/(cm^2•h) à la température applicable de 1000 à 1300 °C ; et avoir une résistivité électrique de 1,3 à 1,5 μΩ•m à température ambiante.

7. Procédé de production de coulée continue de brames pour l'acier allié résistant à la chaleur contenant des terres rares selon l'une quelconque des revendications 1 à 6, où, dans une étape de coulée continue, un rapport d'eau spécifique de refroidissement secondaire est contrôlé pour être de 1,02±0,10 L/kg.

8. Procédé de production de coulée continue de brames selon la revendication 7, où, dans l'étape de coulée continue, une température pour meuler à chaud une brame de coulée est contrôlée pour être de 100 à 600 °C.

9. Procédé de production de coulée continue de brames selon la revendication 7 ou 8, où les paramètres de procédé de l'étape de coulée continue sont contrôlés pour satisfaire au moins un parmi :

le rapport d'eau spécifique de refroidissement secondaire est contrôlé pour être de 1,02±0,06 L/kg ;
une température pour meuler à chaud une brame de coulée est de 300 à 500 °C ;
un courant d'agitation électromagnétique est de 1000 à 2000 A ;
une quantité de réduction tendre est de 3 à 10 mm ;
une fraction solide *f*s de centre de brame de coulée correspondant à une zone de réduction est de 0,10 à 0,90 ;
une quantité de meulage sur un côté de brame de coulée est de 3 à 10 mm ;
un degré de surchauffe d'acier fondu dans un répartiteur est contrôlé pour être de 10 à 50 °C ;
une vitesse de coulée moyenne de coulée continue est contrôlée pour être de 0,40 à 1,50 m/min ; et
une profondeur submergée d'une buse de cristalliseur de coulée continue est contrôlée pour être de 90 à 130 mm.

10. Procédé de production de coulée continue de brames selon la revendication 9, où les paramètres de procédé de l'étape de coulée continue sont contrôlés pour satisfaire au moins un parmi :

le courant d'agitation électromagnétique est de 1400 à 2000 A ;
la quantité de réduction tendre est de 6 à 9 mm ;
la fraction solide *f*s de centre de brame de coulée correspondant à la zone de réduction est de 0,20 à 0,90 ;
la quantité de meulage sur un côté de brame de coulée est de 5 à 8 mm ;
le degré de surchauffe d'acier fondu dans le répartiteur est contrôlé pour être de 15 à 30 °C ;
la vitesse de coulée moyenne de coulée continue est contrôlée pour être de 0,80 à 1,2 m/min ; et
la profondeur submergée de la buse de cristalliseur de coulée continue est contrôlée pour être de 100 à 125 mm.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 0100896 A **[0004]**