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(71) Applicant: **JFE Steel Corporation**
Tokyo 100-0011 (JP)

(72) Inventors:
- **ICHINO Kenji**
  Tokyo 100-0011 (JP)
- **SUZUKI Takeshi**
  Tokyo 100-0011 (JP)
- **IWATA Naomichi**
  Tokyo 100-0011 (JP)
- **MOCHIDA Tetsuo**
  Tokyo 100-0011 (JP)
- **ISHIDA Kiyohito**
  Sendai-shi
  Miyagi 980-8577 (JP)
- **OHNUMA Ikuo**
  Sendai-shi
  Miyagi 980-8577 (JP)

(74) Representative: **Haseltine Lake LLP**
Bürkleinstrasse 10
80538 München (DE)

(54) ROLL OUTER LAYER MATERIAL FOR ROLLING, AND COMPOSITE ROLL FOR ROLLING

(57) Provided are an outer layer material for rolls and a composite roll for rolling that have significantly improved wear resistance. The outer layer material for rolls has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of a roll toward an inner circumferential side of the roll. A surface of the outer layer material that is located at a position corresponding to a maximum diameter during use for rolling has a W-Co-based alloy composition containing, in mass %, W: 25 to 70% and Co: 5 to 45% and further containing C: 0.6 to 3.5%, Si: 0.05 to 3%, Mn: 0.05 to 3%, and Mo: 1 to 15%, with the balance being unavoidable impurities. Preferably, the outer layer material for rolls is formed by centrifugal casting. This outer layer material has significantly improved wear resistance as compared with high-speed tool steel rolling mill rolls. The composition may further contain, in mass %, one or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3% and/or Ni: 0.05 to 3%. Preferably, the outer layer material having the above-described composition is used for an outer layer used for a roll. Preferably, the outer layer is integrally fused to an inner layer to prepare a composite roll for rolling. Alternatively, preferably, the outer layer is integrally fused to an intermediate layer, and the intermediate layer is integrally fused to the inner layer to prepare a composite roll for rolling. Also provided is an outer layer material for rolls having significantly improved wear resistance and a significantly higher Young's modulus as compared with those of conventional outer layer materials and having a good rolling load reduction effect. Also provided is a composite roll for rolling using this outer layer material. The outer layer material has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of the roll toward an inner circumferential side of the roll. The material of the outer layer material in a surface layer at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %, W: 25 to 70%, Co: 5 to 45%, C: 0.6 to 3.5%, Si: 0.05 to 3%, Mn: 0.05 to 3%, and Mo: 1 to 15%, with the balance being unavoidable impurities. The contents of W, Co, Mo, and Fe satisfy the following

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formula [1]:

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \quad [1]$$ [1*]

where %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements. The Young's modulus of the outer layer material for rolls is from 270 GPa to 500 GPa inclusive.

Description

Technical Field

[0001] A first embodiment of the present invention relates to an outer layer material for rolling mill rolls that is suitable for hot rolling or cold rolling and to a composite roll for rolling that uses the outer layer material. More particularly, the first embodiment relates to an improvement in wear resistance.

[0002] A second embodiment of the present invention relates to an outer layer material for rolling mill rolls that is suitable for hot rolling or cold rolling and to a composite roll for rolling that uses the outer layer material. More particularly, the second embodiment relates to an improvement in wear resistance and a reduction in rolling load.

Background Art

[First embodiment]

[0003] As for the first embodiment, recent significant progress in steel sheet rolling technology has made the use environment of rolling mill rollers more severe. In particular, the amount of production of steel sheets such as high-strength steel sheets and thin-walled products that require a high rolling load and need to have high surface quality is recently increasing.

[0004] Therefore, in work rolls for cold rolling, good wear resistance and thus high hardness are required. Generally, the wear resistance of a roll material is improved by increasing the degree of alloying of the roll material. However, when the degree of alloying is increased, the grindability of the roll material may deteriorate, or the degree of damage to the rolls at the time of an accident may increase (i.e., accident resistance may deteriorate), so that it is necessary to use a material having both high grindability and accident resistance. To produce a steel sheet with good surface quality, it is necessary that rolls that come into direct contact with a steel sheet have uniform and fine surface texture. Specifically, there is a need to use, as roll materials, cast iron and cast steel having high cleanliness and having a fine microstructure.

[0005] In work rolls for hot rolling, the occurrence of wear and surface deterioration of the rolls forces restrictions to be placed on the materials of products and a dimensional rolling schedule. Moreover, it is difficult to reduce the frequency of replacement of the rolls, so that a reduction in durability of the rolls is a bottleneck in improving productivity and reducing cost. Therefore, in the work rolls for hot rolling, there is a need to prevent the occurrence of wear and surface deterioration to thereby improve the durability of the rolls.

[0006] In view of the above, there has been a strong demand for improving the properties of the rolling mill rolls used, particularly for improving their wear resistance. The improvement in wear resistance of the rolling mill rolls is an important issue directly related to an improvement in steel sheet quality and an improvement in productivity in steel sheet production.

[0007] To meet the demand for improving the wear resistance of rolling mill rolls, high-speed tool steel rolls have been developed in which their outer layer has a composition similar to the composition of high-speed tool steel and contains a large amount of hard carbides dispersed therein to thereby improve the wear resistance significantly, as described in, for example, Non Patent Literature 1 and Non Patent Literature 2. For example, Patent Literature 1 describes a composite roll for hot rolling that has an outer layer formed around a steel-made core by a continuous padding method. In the composite roll for hot rolling described in Patent Literature 1, the outer layer material has a composition containing, in weight %, C: 1.0 to 4.0%, Si: 3.0% or less, Mn: 1.5% or less, Cr: 2 to 10%, Mo: 9% or less, W: 20% or less, and V: 2 to 15% and further containing P: 0.08% or less, S: 0.06% or less, B: 0.0500% or less, with the balance being Fe and unavoidable impurities. The outer layer material has a structure including, in area fraction, 5 to 30% of granular carbides and 6% or more of non-granular carbides, and a base phase has a Vickers hardness (Hv) of 550 or more. It is stated that the outer layer material may further contain Ni: 5.0% or less, Co: 5.0% or less, and Nb: 5.0% or less. It is also stated that, since the non-granular carbides are present in a prescribed amount or more, even when a crack is formed, the crack is prevented from propagating deep into the roll, so that heat cracking resistance is improved. Moreover, since VC-based hard carbides are contained, good wear resistance is obtained.

[0008] In the above outer layer material for high-speed tool steel rolls, it is necessary to disperse a large amount of hard carbides in the base phase in order to improve the wear resistance. However, generally, the hard carbides generated in the high-speed tool steel composition have smaller specific gravities than the base phase, so that segregation is likely to occur during casting. In particular, with a centrifugal casting method that is a typical casting method for an outer layer material for rolls because of its high productivity and economic efficiency, a low-specific gravity phase tends to accumulate/segregate on the inner side due to centrifugal force. Therefore, it has been considered difficult to produce an outer layer material for high-speed tool steel rolls by the centrifugal casting method.

[0009] Patent Literature 2 describes a technique for providing an outer layer material for rolling mill rolls in which segregation etc. do not occur even when the centrifugal casting method is used and which is excellent in wear resistance and cracking resistance. Specifically, Patent Literature 2 describes an outer layer material for rolls that contains, in mass

%, C: 1.5 to 3.5%, Si: 1.5% or less, Mn: 1.2% or less, Ni: 5.5% or less, Cr: 5.5 to 12.0%, Mo: 2.0 to 8.0%, V: 3.0 to 10.0%, and Nb: 0.5 to 7.0%. Nb and V are contained such that the contents of Nb, V, and C satisfy a specific relation and that the ratio of Nb to V falls within a specific range.

[0010] Patent Literature 3 describes an outer layer material for rolls that contains, in mass %, C: 1.5 to 3.5%, Si: 1.5% or less, Mn: 1.2% or less, Cr: 5.5 to 12.0%, Mo: 2.0 to 8.0%, V: 3.0 to 10.0%, and Nb: 0.5 to 7.0%. Nb and V are contained such that the contents of Nb, V, and C satisfy a specific relation and that the ratio of Nb to V falls within a specific range. It is stated that, with this composition, segregation is prevented in the outer layer material for rolls even when the centrifugal casting method is used. Moreover, the wear resistance and the cracking resistance are improved, and this significantly contributes to an improvement in hot rolling productivity.

[0011] Patent Literature 4 describes a centrifugal cast composite roll. The centrifugal cast composite roll described in Patent Literature 4 includes an outer layer and an inner layer formed of cast iron or cast steel. The outer layer has a composition containing, in weight %, C: 1.0 to 3.0%, Si: 0.1 to 3.0%, Mn: 0.1 to 2.0%, Cr: 2.0 to 10.0%, Mo: 0.1 to 10.0%, V: 1.0 to 10.0%, and W: 0.1 to 10.0%, with the balance being Fe and unavoidable impurities, and the alloy components Mo and W satisfy Mo + W: 10.0% or less. It is stated that, with the technique described in Patent Literature 4, crystallization of M_6C-type carbides that tend to aggregate and segregate is prevented. Therefore, in the outer layer, only MC-type + M_7C_3-type carbides precipitate, and the outer layer can be produced using the centrifugal casting method.

[0012] For example, Patent Literature 5 describes a centrifugal cast outer layer material for rolling mill rolls. The centrifugal cast outer layer material for rolling mill rolls described in Patent Literature 5 has a composition containing, in mass %, C: 4.5 to 9%, Si: 0.1 to 3.5%, Mn: 0.1 to 3.5%, and V: 18 to 40% and has a structure including, in area fraction, 20 to 60% of MC carbides dispersed in a base phase having a Vickers hardness HV of preferably 550 to 900. It is stated that, with the technique described in Patent Literature 5, a roll outer layer that contains a large amount of MC carbides can be reliably formed at low cost by actively using centrifugal casting segregation in which the low-specific gravity MC carbides are concentrated on the inner surface side. Specifically, after the centrifugal casting, the outer layer is cut such that only the high-MC carbide concentration layer remains.

[0013] Cemented carbides have been known for a long time as materials with very good wear resistance. As described in, for example, Non Patent Literature 3, a cemented carbide is generally prepared by molding and sintering tungsten carbide (WC) together with Co used as a binder.

[0014] Techniques that use such cemented carbides for rolling mill rolls are described in Patent Literature 6, Patent Literature 7, Patent Literature 8, Patent Literature 9, Patent Literature 10, etc.

[0015] Patent Literature 6 describes a tungsten carbide-based cemented carbide for hot rolling mill rolls and hot rolling guide rolls. The technique described in Patent Literature 6 is a tungsten carbide-based alloy in which the ratio of the weight of chromium to the total weight of cobalt and nickel is 1/1 to 1/99, in which the ratio of the weight of cobalt to the weight of nickel is 9/1 to 1/9, in which the amount of the tungsten carbide is 88% by weight or less, and in which the total amount of cobalt, nickel, and chromium is 12 to 65% by weight. Patent Literature 6 describes examples in which the cemented carbide is applied to hot rolling mill rolls for plain steel materials (wire rods).

[0016] Patent Literature 7 describes a roll for hot wire rods that is formed of cemented carbide. In the technique described in Patent Literature 7, the cemented carbide used includes: a hard carbide phase composed of WC having an average particle diameter of 1 μm to 5 μm or a hard carbide phase composed of WC with 10% by mass or less of the WC replaced with at least one of TiC, TaC, and NbC; and a ternary alloy binder phase. In this cemented carbide, the ratio of Cr in the binder phase to the sum of Ni and Co is 0.30 or less, and the ratio of Cr to the total amount of the binding layer is 0.05 or more. The ratio of Ni in the binder phase to the sum of Ni and Co is from 0.33 to 0.90, and the polarization potential of the cemented carbide with respect to general industrial cooling water is 0.3 V or more. It is stated that, with the above cemented carbide, a roll for hot wire rods that has good surface deterioration resistance can be obtained.

[0017] Patent Literature 8 describes a composite roll for rolling that includes an inner layer formed of a steel- or iron-based material and an outer layer formed of cemented carbide and joined to the outer circumference of the inner layer through an intermediate layer. The intermediate layer is made of cemented carbide formed using a WC raw material powder having an average particle diameter of 3 μm or less. It is stated that the content of the WC particles in the intermediate layer is preferably 70% by weight or less. It is also stated that, in this manner, a cemented carbide-made rolling mill roll excellent in wear resistance and having high reliability in terms of strength can be obtained.

[0018] Patent Literature 9 discloses a cemented carbide-made rolling mill roll having high reliability in terms of strength. This rolling mill roll includes an outer layer formed of cemented carbide excellent in wear resistance and an intermediate layer formed of cemented carbide containing WC and Ni.

[0019] Patent Literature 10 describes a cemented carbide-made composite roll for rolling sheets that includes an inner layer formed of a steel- or iron-based material and an outer layer joined to the outer circumference of the inner layer and formed of cemented carbide having a thermal shock coefficient R of 400 or more. The thermal shock coefficient R is represented by $R = \sigma c(1 - \nu)/E\alpha$ (where σc: flexural strength, ν: Poisson's ratio, E: Young's modulus, and α: thermal expansion coefficient). It is stated that, in this manner, the wear resistance and surface deterioration resistance of the roll are improved and that the occurrence and propagation of a crack at the time of an accident during rolling can be prevented.

[Second embodiment]

[0020] As for the second embodiment, recent significant progress in steel sheet rolling technology has made the use environment of rolling mill rollers more severe. In particular, the amount of production of steel sheets such as high-strength steel sheets and thin-walled products that require a high rolling load and need to have high surface quality is recently increasing.

[0021] Therefore, in work rolls for cold rolling, good wear resistance and thus high hardness are required. Generally, the wear resistance of a roll material is improved by increasing the degree of alloying of the roll material. However, when the degree of alloying is increased, the grindability of the roll material may deteriorate, or the degree of damage to the rolls at the time of an accident may increase (i.e., accident resistance may deteriorate), so that it is necessary to use a material having both high grindability and accident resistance. To produce a steel sheet with good surface quality, it is necessary that rolls that come into direct contact with a steel sheet have uniform and fine surface texture. Specifically, there is a need to use, as roll materials, cast iron and cast steel having high cleanliness and having a fine microstructure.

[0022] In work rolls for hot rolling, the occurrence of wear and surface deterioration of the rolls forces restrictions to be placed on the materials of products and a dimensional rolling schedule. Moreover, it is difficult to reduce the frequency of replacement of the rolls, so that a reduction in durability of the rolls is a bottleneck in improving productivity and reducing cost. Therefore, in the work rolls for hot rolling, there is a need to prevent the occurrence of wear and surface deterioration to thereby improve the durability of the rolls.

[0023] In view of the above, there has been a strong demand for improving the properties of the rolling mill rolls used, particularly for improving their wear resistance. The improvement in wear resistance of the rolling mill rolls is an important issue directly related to an improvement in steel sheet quality and an improvement in productivity in steel sheet production.

[0024] In recent years, in the field of automobiles, the weight of vehicle bodies is being reduced by using high-strength materials in order to improve fuel consumption, and the high-strength materials may be increasingly used in the future. When a high-strength material is rolled, surface layers of work rolls for rolling in contact with the rolled material are elastically deformed. The area of contact (or the length of the arc of contact) between the rolled material and the surface layers of the work rolls for rolling increases, and the rolling load (the rolling pressure acting on the work rolls for rolling from the rolled material) increases. When the rolling load is excessively large, problems arise in that the dimensional accuracy of the rolled material is reduced and that a limit is imposed on the minimum rollable sheet thickness. Therefore, there is a need for an outer layer material for rolling mill rolls that has a high Young's modulus and resists elastic deformation.

[0025] To meet the demand for improving the wear resistance of rolling mill rolls, high-speed tool steel rolls have been developed in which their outer layer has a composition similar to the composition of high-speed tool steel and contains a large amount of hard carbides dispersed therein to thereby improve the wear resistance significantly, as described in, for example, Non Patent Literature 1 and Non Patent Literature 2. For example, Patent Literature 1 describes a composite roll for hot rolling that has an outer layer formed around a steel-made core by a continuous padding method. In the composite roll for hot rolling described in Patent Literature 1, the outer layer material has a composition containing, in weight %, C: 1.0 to 4.0%, Si: 3.0% or less, Mn: 1.5% or less, Cr: 2 to 10%, Mo: 9% or less, W: 20% or less, and V: 2 to 15% and further containing P: 0.08% or less, S: 0.06% or less, B: 0.0500% or less, with the balance being Fe and unavoidable impurities. The outer layer material has a structure including, in area fraction, 5 to 30% of granular carbides and 6% or more of non-granular carbides, and a base phase has a Vickers hardness (HV) of 550 or more. It is stated that the outer layer material may further contain Ni: 5.0% or less, Co: 5.0% or less, and Nb: 5.0% or less. It is also stated that, since the non-granular carbides are present in a prescribed amount or more, even when a crack is formed, the crack is prevented from propagating deep into the roll, so that heat cracking resistance is improved. Moreover, since VC-based hard carbides are contained, good wear resistance is obtained.

[0026] In the above outer layer material for high-speed tool steel rolls, it is necessary to disperse a large amount of hard carbides in the base phase in order to improve the wear resistance. However, generally, the hard carbides generated in the high-speed tool steel composition have smaller specific gravities than the base phase, so that segregation is likely to occur during casting. In particular, with a centrifugal casting method that is a typical casting method for an outer layer material for rolls because of its high productivity and economic efficiency, a low-specific gravity phase tends to accumulate/segregate on the inner side due to centrifugal force. Therefore, it has been considered difficult to produce an outer layer material for high-speed tool steel rolls by the centrifugal casting method.

[0027] Patent Literature 2 describes a technique for providing an outer layer material for rolling mill rolls in which segregation etc. do not occur even when the centrifugal casting method is used and which is excellent in wear resistance and cracking resistance. Specifically, Patent Literature 2 describes an outer layer material for rolls that contains, in mass %, C: 1.5 to 3.5%, Si: 1.5% or less, Mn: 1.2% or less, Ni: 5.5% or less, Cr: 5.5 to 12.0%, Mo: 2.0 to 8.0%, V: 3.0 to

10.0%, and Nb: 0.5 to 7.0%. Nb and V are contained such that the contents of Nb, V, and C satisfy a specific relation and that the ratio of Nb to V falls within a specific range.

[0028] Patent Literature 3 describes an outer layer material for rolls that contains, in mass %, C: 1.5 to 3.5%, Si: 1.5% or less, Mn: 1.2% or less, Cr: 5.5 to 12.0%, Mo: 2.0 to 8.0%, V: 3.0 to 10.0%, and Nb: 0.5 to 7.0%. Nb and V are contained such that the contents of Nb, V, and C satisfy a specific relation and that the ratio of Nb to V falls within a specific range. It is stated that, with this composition, segregation is prevented in the outer layer material for rolls even when the centrifugal casting method is used. Moreover, the wear resistance and the cracking resistance are improved, and this significantly contributes to an improvement in hot rolling productivity.

[0029] Patent Literature 4 describes a centrifugal cast composite roll. The centrifugal cast composite roll described in Patent Literature 4 includes an outer layer and an inner layer formed of cast iron or cast steel. The outer layer has a composition containing, in weight %, C: 1.0 to 3.0%, Si: 0.1 to 3.0%, Mn: 0.1 to 2.0%, Cr: 2.0 to 10.0%, Mo: 0.1 to 10.0%, V: 1.0 to 10.0%, and W: 0.1 to 10.0%, with the balance being Fe and unavoidable impurities, and the alloy components Mo and W satisfy Mo + W: 10.0% or less. It is stated that, with the technique described in Patent Literature 4, crystallization of M_6C-type carbides that tend to aggregate and segregate is prevented. Therefore, in the outer layer, only MC-type + M_7C_3-type carbides precipitate, and the outer layer can be produced using the centrifugal casting method.

[0030] For example, Patent Literature 5 describes a centrifugal cast outer layer material for rolling mill rolls. The centrifugal cast outer layer material for rolling mill rolls described in Patent Literature 5 has a composition containing, in mass %, C: 4.5 to 9%, Si: 0.1 to 3.5%, Mn: 0.1 to 3.5%, and V: 18 to 40% and has a structure including, in area fraction, 20 to 60% of MC carbides dispersed in a base phase having a Vickers hardness HV of preferably 550 to 900. It is stated that, with the technique described in Patent Literature 5, a roll outer layer that contains a large amount of MC carbides can be reliably formed at low cost by actively using centrifugal casting segregation in which the low-specific gravity MC carbides are concentrated on the inner surface side. Specifically, after the centrifugal casting, the outer layer is cut such that only the high-MC carbide concentration layer remains.

[0031] Cemented carbides have been known for a long time as materials with very good wear resistance and high Young's modulus. As described in, for example, Non Patent Literature 3, a cemented carbide is generally prepared by molding and sintering tungsten carbide (WC) together with Co used as a binder.

[0032] Techniques that use such cemented carbides for rolling mill rolls are described in Patent Literature 6, Patent Literature 7, Patent Literature 8, Patent Literature 9, Patent Literature 10, etc.

[0033] Patent Literature 6 describes a tungsten carbide-based cemented carbide for hot rolling mill rolls and hot rolling guide rolls. The technique described in Patent Literature 6 is a tungsten carbide-based alloy in which the ratio of the weight of chromium to the total weight of cobalt and nickel is 1/1 to 1/99, in which the ratio of the weight of cobalt to the weight of nickel is 9/1 to 1/9, in which the amount of the tungsten carbide is 88% by weight or less, and in which the total amount of cobalt, nickel, and chromium is 12 to 65% by weight. Patent Literature 6 describes examples in which the cemented carbide is applied to hot rolling mill rolls for plain steel materials (wire rods).

[0034] Patent Literature 7 describes a rolling mill roll for hot wire rods that is formed of cemented carbide. In the technique described in Patent Literature 7, the cemented carbide used includes: a hard carbide phase composed of WC having an average particle diameter of 1 μm to 5 μm or a hard carbide phase composed of WC with 10% by mass or less of the WC replaced with at least one of TiC, TaC, and NbC; and a ternary alloy binder phase. In this cemented carbide, the ratio of Cr in the binder phase to the sum of Ni and Co is 0.30 or less, and the ratio of Cr to the total amount of the binding layer is 0.05 or more. The ratio of Ni in the binder phase to the sum of Ni and Co is from 0.33 to 0.90, and the polarization potential of the cemented carbide with respect to general industrial cooling water is 0.3 V or more. It is stated that, with the above cemented carbide, a roll for hot wire rods that has good surface deterioration resistance can be obtained.

[0035] Patent Literature 8 describes a composite roll for rolling that includes an inner layer formed of a steel- or iron-based material and an outer layer formed of cemented carbide and joined to the outer circumference of the inner layer through an intermediate layer. The intermediate layer is made of cemented carbide formed using a WC raw material powder having an average particle diameter of 3 μm or less. It is stated that the content of the WC particles in the intermediate layer is preferably 70% by weight or less. It is also stated that, in this manner, a cemented carbide-made rolling mill roll excellent in wear resistance and having high reliability in terms of strength can be obtained.

[0036] Patent Literature 9 discloses a cemented carbide-made rolling mill roll having high reliability in terms of strength. This rolling mill roll includes an outer layer formed of cemented carbide excellent in wear resistance and an intermediate layer formed of cemented carbide containing WC and Ni.

[0037] Patent Literature 10 describes a cemented carbide-made composite roll for rolling sheets that includes an inner layer formed of a steel- or iron-based material and an outer layer joined to the outer circumference of the inner layer and formed of cemented carbide having a thermal shock coefficient R of 400 or more. The thermal shock coefficient R is represented by $R = \sigma c(1 - \nu)/E\alpha$ (where σc: flexural strength, ν: Poisson's ratio, E: Young's modulus, and α: thermal expansion coefficient). It is stated that, in this manner, the wear resistance and surface deterioration resistance of the roll are improved and that the occurrence and propagation of a crack at the time of an accident during rolling can be prevented.

Citation List

Patent Literature

[0038]

PTL 1: Japanese Unexamined Patent Application Publication No. 4-141553
PTL 2: Japanese Unexamined Patent Application Publication No. 4-365836
PTL 3: Japanese Unexamined Patent Application Publication No. 5-1350
PTL 4: Japanese Unexamined Patent Application Publication No. 8-60289
PTL 5: International Publication No. WO2006/030795
PTL 6: Japanese Examined Patent Application Publication No. 57-6502
PTL 7: Japanese Examined Patent Application Publication No. 58-39906
PTL 8:Japanese Unexamined Patent Application Publication No. 2004-243341
PTL 9: Japanese Unexamined Patent Application Publication No. 2006-175456
PTL 10: Japanese Unexamined Patent Application Publication No. 2004-268140

Non Patent Literature

[0039]

NPL 1: Kamata et al., Hitachi Hyoron (Hitachi Review) Vol. 72, No. 5 (1990), p. 69
NPL 2: Hashimoto et.Al., Seitetsu Kenkyu (Iron-Making research) Vol. 338 (1990), p. 62
NPL 3: Kaizo Monma, "Iron and steel materials, Revised edition" Jikkyo Shuppan, (1981), p. 368
NPL 4: Matsunaga et al., Analytical technique for increasing service life of rolls (1999), p. 11
NPL 5: Hashimoto et al., Shinnittetsu Giho (Nippon Steel Technical Report) Vol. 355 (1995), p. 76

Summary of Invention

Technical Problem

[First embodiment]

[0040] In the first embodiment, problems with the technique described in Patent Literature 1 are low productivity and high cost. This is because the outer layer is formed around the steel-made core using the continuous padding method. In the techniques described in Patent Literature 2 and Patent Literature 3, the wear resistance and the cracking resistance are improved mainly by the MC-type carbides uniformly dispersed while the contents of Nb, V, and C are limited within specific ranges. However, in practice, considerable amounts of M_7C_3-type carbides and M_6C-type carbides that contain a large amount of Cr or Mo are present. Therefore, a further improvement in the properties is not sufficiently achieved only by uniformly dispersing the MC-type carbides. In the technique described in Patent Literature 4, to prevent crystallization of the M_6C-type carbides that tend to aggregate or segregate, the amount of Mo + W is limited to 10.0% or less. This allows the outer layer material for rolls to be produced by the centrifugal casting method. However, the limitation imposed on the contents of Mo and W poses difficulty in meeting the recent demand for further improving the wear resistance.

[0041] In the production of a rolling mill roll using the centrifugal casting method, when the amounts of carbide-forming elements such as Mo, V, and W are increased, lightweight carbides are formed. In this case, the carbides formed may accumulate on the inner surface side and aggregate at the interface with the inner layer, and this may cause a reduction in the bonding strength at the interface.

[0042] With the technique described in Patent Literature 5, the wear resistance of the roll is improved. However, it is necessary to perform an operation for removing an outer surface region containing a reduced amount of the MC-type carbides. Another problem is that the yield is very low, so that the advantages of the centrifugal casting method, i.e., high productivity and low cost, are lost.

[0043] The techniques described in Patent Literature 6 and Patent Literature 7 and using cemented carbide are provided for small rolls for rolling wire rods, and it is difficult to apply these techniques to production of large rolls such as rolls for cold rolling and rolls for hot rolling without any modification. Moreover, it is necessary to use HIP treatment, which is a more expensive process than the process for centrifugal cast products. A problem with these techniques is that the production cost is high although the products are small.

[0044] The techniques described in Patent Literature 8, Patent Literature 9, and Patent Literature 10 use cemented carbide as the outer layer material for rolling sheets. In these techniques, it is assumed that the outer layer material is formed by a sintering-HIP process, and a problem is that the production cost is very high. These techniques use soft Co and Ni as the binder, and a problem is that dents (hollows) are easily formed during rolling, so that these techniques are not often used practically.

[0045] It is an object of the first embodiment of the present invention to solve the problems in the conventional techniques and to provide, at low cost, an outer layer material for rolls that has wear resistance significantly improved as compared with that of conventional products and is excellent in wear resistance. It is also an object to provide, at low cost, a composite roll for rolling that uses the outer layer material.

[Second embodiment]

[0046] In the second embodiment, problems with the technique described in Patent Literature 1 are low productivity and high cost. This is because the outer layer is formed around the steel-made core using the continuous padding method. In the techniques described in Patent Literature 2 and Patent Literature 3, the wear resistance and the cracking resistance are improved mainly by the MC-type carbides uniformly dispersed while the contents of Nb, V, and C are limited within specific ranges. However, in practice, considerable amounts of M_7C_3-type carbides and M_6C-type carbides that contain a large amount of Cr or Mo are present. Therefore, a further improvement in the properties is not sufficiently achieved only by uniformly dispersing the MC-type carbides. In the technique described in Patent Literature 4, to prevent crystallization of the M_6C-type carbides that tend to aggregate or segregate, the amount of Mo + W is limited to 10.0% or less. This allows the outer layer material for rolls to be produced by the centrifugal casting method. However, the limitation imposed on the contents of Mo and W poses difficulty in meeting the recent demand for further improving the wear resistance.

[0047] In the production of a rolling mill roll using the centrifugal casting method, when the amounts of carbide-forming elements such as Mo, V, and W are increased, VC-based hard carbides having specific gravities less than the specific gravity of a molten metal forming the base phase are generated. In this case, the VC-based hard carbides generated may accumulate on the inner surface side and aggregate at the interface with the inner layer, and this may cause a reduction in the bonding strength at the interface.

[0048] With the technique described in Patent Literature 5, the wear resistance of the roll is improved. However, it is necessary to perform an operation for removing an outer surface region containing a reduced amount of the MC-type carbides. Another problem is that the yield is very low, so that the advantages of the centrifugal casting method, i.e., high productivity and low cost, are lost.

[0049] The techniques described in Patent Literature 6 and Patent Literature 7 and using cemented carbide are provided for small rolls for rolling wire rods, and it is difficult to apply these techniques to production of large rolls such as rolls for cold rolling and rolls for hot rolling without any modification. Moreover, it is necessary to use HIP treatment, which is a more expensive process than the process for centrifugal cast products. A problem with these techniques is that the production cost is high although the products are small.

[0050] The techniques described in Patent Literature 8, Patent Literature 9, and Patent Literature 10 use cemented carbide as the outer layer material for rolling sheets. In these techniques, it is assumed that the outer layer material is formed by a sintering-HIP process, and a problem is that the production cost is very high. These techniques use soft Co and Ni as the binder, and a problem is that dents (hollows) are easily formed during rolling, so that these techniques are not often used practically.

[0051] It is an object of the second embodiment of the present invention to solve the problems in the conventional techniques and to provide, at low cost, an outer layer material for rolls that has wear resistance and a Young's modulus significantly improved as compared with those of conventional products, is excellent in wear resistance, and has a high rolling load reduction effect. It is also an object to provide, at low cost, a composite roll for rolling that uses the outer layer material.

Solution to Problem

[First embodiment]

[0052] First, in the first embodiment, to achieve the above objects, the inventors have conducted extensive studies on the conditions that allow a rolling mill roll having very high wear resistance comparable to that of cemented carbide to be produced using the centrifugal casting method excellent in productivity and economic efficiency. The inventors have found that, if hard carbides can be aggregated and concentrated on the outer surface side of the roll by utilizing the centrifugal force acting on the molten metal and crystalized phases during centrifugal casting, the wear resistance of the centrifugal cast rolling mill roll can be improved significantly. The inventors have conducted further studies and found that, to aggregate and concentrate the hard carbides on the outer surface side of the roll during centrifugal casting, it is necessary to find conditions under which the carbides having larger specific gravities than the liquid phase can be crystalized as primary phases from the liquid phase on which centrifugal force acts.

[0053] Specifically, when a carbide having a larger specific gravity than the liquid phase is crystallized in the liquid phase on which centrifugal force acts, the centrifugal force toward an outer circumference acts on the carbide. In this case, if it is possible to allow the carbide to crystallize as a primary phase directly from the liquid phase while the carbide and a γ phase around the carbide do not undergo eutectic solidification, the carbide can easily move toward the outer circumferential side and be accumulated because the carbide is still surrounded by the liquid phase.

[0054] The inventors have focused attention on W having a large specific gravity as a carbide-forming element that fulfills the above conditions. The inventors have contemplated that a large amount of W is added. The inventors have repeated various casting experiments, used phase diagram calculations, and found the following.

(1) When the molten metal used is a W-Co-based alloy containing a large amount of W having a large specific gravity and further containing 0.6% by mass or more of C, M_6C-type carbides in which W is concentrated appear as primary phases.

(2) When this molten W-Co-based alloy is subjected to centrifugal casting, a morphology in which the M_6C-type carbides crystallized as the primary phases are segregated at high concentration on the outer surface side of the outer layer material is obtained.

[0055] The inventors have also found that, when the alloy used is an Fe-based alloy, the formation of W-based eutectic carbides is facilitated and the appearance of the M_6C-type carbides as the primary phases is inhibited. The inventors have also found the following. When the alloy used is the W-Co-based alloy that increases the activity of carbon, the formation of W-based eutectic carbides is suppressed, and a large amount of M_6C-type carbides in which W is concentrated appear as primary phases in the molten metal. When the amount of C is less than 0.6% by mass, no primary phase M_6C-type carbides appear. When the amount of C is higher than 3% by mass, the liquidus temperature is excessively high. In this case, the alloy does not easily melt and is not easily cast. Moreover, very brittle MC-type carbides and M_2C-type carbides grow and coarsen, so that breakage of rolls occurs easily.

[0056] The present invention has been completed by conducting further studies on the basis of the above findings. The present invention is summarized as follows.

(1) An outer layer material for rolling mill rolls, the outer layer material being made of a W-Co-based alloy, wherein the outer layer material has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of a roll toward an inner circumferential side of the roll, and wherein a surface of the outer layer material that is located at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %, W: 25 to 70%, Co: 5 to 45%, C: 0.6 to 3.5%, Si: 0.05 to 3%, Mn: 0.05 to 3%, and Mo: 1 to 15%, with the balance being unavoidable impurities.

(2) The outer layer material for rolling mill rolls according to (1), wherein the composition further contains, in mass %, one or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3%.

(3) The outer layer material for rolling mill rolls according to (1) or (2), wherein the composition further contains, in mass %, Ni: 0.05 to 3%.

(4) The outer layer material for rolling mill rolls according to any of (1) to (3), wherein the outer layer material for rolling mill rolls is formed by centrifugal casting.

(5) A composite roll for rolling, including an outer layer and an inner layer integrally fused to the outer layer, wherein the outer layer is the outer layer material for rolling mill rolls according to any of (1) to (3).

(6) A composite roll for rolling, including an outer layer, an intermediate layer integrally fused to the outer layer, and an inner layer integrally fused to the intermediate layer, wherein the outer layer is the outer layer material for rolling mill rolls according to any of (1) to (3).

(7) The composite roll for rolling according to (5) or (6), wherein the outer layer is formed by centrifugal casting.

[Second embodiment]

[0057] In the second embodiment, to achieve the above-described objects, the inventors have conducted extensive studies on the conditions that allow a rolling mill roll having very high wear resistance and a high Young's modulus comparable to those of cemented carbide to be produced using the centrifugal casting method excellent in productivity and economic efficiency. The inventors have found that, if hard carbides can be aggregated and concentrated on the outer surface side of the roll by utilizing the centrifugal force acting on the molten metal and crystalized phases during centrifugal casting, the wear resistance of the centrifugal cast rolling mill roll can be improved significantly. The inventors have conducted further studies and found that, to aggregate and concentrate the hard carbides on the outer surface side of the roll during centrifugal casting, it is necessary to find conditions under which the carbides having larger specific gravities than the liquid phase can be crystalized as primary phases from the liquid phase on which centrifugal force acts. The inventors have also found that, to improve the Young's modulus, it is necessary not only to aggregate and concentrate the hard carbides on the outer surface side of the roll but also to increase the amounts of W and Mo dissolved in a base phase.

[0058] Specifically, when a carbide having a larger specific gravity than the liquid phase is crystallized in the liquid phase on which centrifugal force acts, the centrifugal force toward an outer circumference acts on the carbide. In this case, if it is possible to allow the carbide to crystallize as a primary phase directly from the liquid phase while the carbide and a γ phase around the carbide do not undergo eutectic solidification, the carbide can easily move toward the outer circumferential side and be accumulated because the carbide is still surrounded by the liquid phase.

[0059] The inventors have focused attention on W having a large specific gravity as a carbide-forming element that fulfills the above conditions. The inventors have contemplated that a large amount of W is added. The inventors have repeated various casting experiments, used phase diagram calculations, and found the following.

(1) When the molten metal used is a W-Co-based alloy containing a large amount of W having a large specific gravity and further containing 0.6% by mass or more of C, M_6C-type carbides in which W is concentrated appear as primary phases.
(2) When this molten W-Co-based alloy is subjected to centrifugal casting, a morphology in which the M_6C-type carbides crystallized as the primary phases are segregated at high concentration on the outer surface side of the outer layer material is obtained.

[0060] The inventors have also found that, when the alloy used is an Fe-based alloy, the formation of W-based eutectic carbides is facilitated and the appearance of the M_6C-type carbides as the primary phases is inhibited. The inventors have also found the following. When the alloy used is the W-Co-based alloy that increases the activity of carbon, the formation of W-based eutectic carbides is suppressed, and a large amount of M_6C-type carbides in which W is concentrated appear as primary phases in the molten metal. When the amount of C is less than 0.6% by mass, no primary phase M_6C-type carbides appear. When the amount of C is higher than 3% by mass, the liquidus temperature is excessively high. In this case, the alloy does not easily melt and is not easily cast. Moreover, very brittle MC-type carbides and M_2C-type carbides grow and coarsen, so that breakage of rolls occurs easily.

[0061] The present invention has been completed by conducting further studies on the basis of the above findings. The present invention is summarized as follows.

(1) An outer layer material for rolling mill rolls, the outer layer material being made of a W-Co-based alloy, wherein the outer layer material has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of a roll toward an inner circumferential side of the roll, wherein the outer layer material in a surface layer at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %, W: 25 to 70%, Co: 5 to 45%, C: 0.6 to 3.5%, Si: 0.05 to 3%, Mn: 0.05 to 3%, and Mo: 1 to 15%, with the balance being unavoidable impurities, and wherein the contents of W, Co, Mo, and Fe satisfy the following formula [1] :

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \qquad [1]$$

where %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements.
(2) The outer layer material for rolling mill rolls according to (1), wherein the Young's modulus of the outer layer material in the surface layer at the position corresponding to the maximum diameter during use for rolling is from 270 GPa to 500 GPa inclusive.
(3) The outer layer material for rolling mill rolls according to (1) or (2), wherein the composition further contains, in mass %, one or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3%.
(4) The outer layer material for rolling mill rolls according to any of (1) to (3), wherein the composition further contains, in mass %, Ni: 0.05 to 3%.
(5) The outer layer material for rolling mill rolls according to any of (1) to (4), wherein the outer layer material for rolling mill rolls is formed by centrifugal casting.
(6) A composite roll for rolling, including an outer layer and an inner layer integrally fused to the outer layer, wherein the outer layer is made of a W-Co-based alloy and has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of the roll toward an inner circumferential side of the roll,

wherein a material of the outer layer in a surface layer at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %, W: 25 to 70%, Co: 5 to 45%, C: 0.6 to 3.5%, Si: 0.05 to 3%, Mn: 0.05 to 3%, and Mo: 1 to 15%, with the balance being unavoidable impurities, and wherein the contents of W, Co, Mo, and Fe satisfy the following formula [1]:

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \quad [1]$$

where %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements.

(7) The composite roll for rolling according to (6), wherein the Young's modulus of the material of the outer layer in the surface layer at the position corresponding to the maximum diameter during use for rolling is from 270 GPa to 500 GPa inclusive.

(8) The composite roll for rolling according to (6) or (7), wherein the composition further contains, in mass %, one or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3%.

(9) The composite roll for rolling according to any of (6) to (8), wherein the composition further contains, in mass %, Ni: 0.05 to 3%.

(10) A composite roll for rolling, including an outer layer, an intermediate layer integrally fused to the outer layer, and an inner layer integrally fused to the intermediate layer, wherein the outer layer is made of a W-Co-based alloy and has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of the roll toward an inner circumferential side of the roll, wherein a material of the outer layer in a surface layer at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %, W: 25 to 70%, Co: 5 to 45%, C: 0.6 to 3.5%, Si: 0.05 to 3%, Mn: 0.05 to 3%, Mo: 1 to 15%, and Fe: 5 to 40%, with the balance being unavoidable impurities, and wherein the contents of W, Co, Mo, and Fe satisfy the following formula [1]:

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \quad [1]$$

where %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements.

(11) The composite roll for rolling according to (10), wherein the Young's modulus of the material of the outer layer in the surface layer at the position corresponding to the maximum diameter during use for rolling is from 270 GPa to 500 GPa inclusive.

(12) The composite roll for rolling according to (10) or (11), wherein the composition further contains, in mass %, one or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3%.

(13) The composite roll for rolling according to any of (10) to (12), wherein the composition further contains, in mass %, Ni: 0.05 to 3%.

(14) The composite roll for rolling according to any of (6) to (13), wherein the outer layer is formed by centrifugal casting.

Advantageous Effects of Invention

[0062] According to the present invention, in the first embodiment, a rolling mill roll, particularly a centrifugal cast rolling mill roll, suitable for a hot rolling or cold rolling mill roll and having significantly high wear resistance can be produced easily at low cost, so that industrially significant effects can be obtained.

[0063] According to the present invention, in the second embodiment, a rolling mill roll, particularly a centrifugal cast rolling mill roll, suitable for a hot rolling or cold rolling mill roll and having significantly high wear resistance and a significantly high rolling load reduction effect can be produced easily at low cost, so that industrially significant effects can be obtained.

Brief Description of Drawings

[0064]

Fig. 1(a) is a photograph of the structure of sleeve No. 13 (test material No. 13) in Example 1 under a scanning electron microscope, and Fig. 1(b) is a photograph of the structure of sleeve No. 5 (test material No. 5) in Example 1 under the scanning electron microscope.

Fig. 2 is a schematic illustration showing the outline of a wear test in Example 1.

Fig. 3 is a schematic illustration showing an exemplary composite roll in the present invention.

Fig. 4 is a schematic illustration showing a cross section of an exemplary composite roll for rolling in the invention, the composite roll including an outer layer and an inner layer integrally fused to the outer layer.

Fig. 5 is a schematic illustration showing a cross section of an exemplary composite roll for rolling in the invention, the composite roll including an outer layer, an intermediate layer integrally fused to the outer later, and an inner layer integrally fused to the intermediate layer.

Fig. 6(a) is a photograph showing the structure of sleeve No. 13 in Example 2 under a scanning electron microscope, and Fig. 13(b) is a photograph of the structure of sleeve No. 5 in Example 2 under the scanning electron microscope.

Fig. 7 is a schematic illustration showing the outline of a wear test in Example 2.

Fig. 8 is a schematic illustration of a composite roll for rolling load evaluation in Example 2. Description of Embodiments

[0065] The first embodiment and the second embodiment in the present invention will be described with reference to the drawings.

[First embodiment]

[0066] The outer layer material for rolling mill rolls of the present invention is produced by centrifugal casting. The "centrifugal cast outer layer material for rolling mill rolls" means an outer layer material for rolling mill rolls that is produced by a centrifugal casting method conventionally used as a method for producing rolling mill rollers. The outer layer material for rolling mill rolls produced using the centrifugal casting method (the "centrifugal cast" outer layer material for rolling mill rolls) can be clearly distinguished from rolling mill rolls produced by other conventional production methods in the sense of "products." It is unrealistic to identify the "centrifugal cast" outer layer material for rolling mill rolls from its structure and properties because it requires enormous efforts.

[0067] The outer layer material for rolling mill rolls of the invention is made of a W-Co-based alloy and has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of a roll toward an inner circumferential side of the roll. A surface of the outer layer material that is located at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %, W: 25 to 70% and Co: 5 to 45% and further containing C: 0.6 to 3.5%, Si: 0.05 to 3%, Mn: 0.05 to 3%, and Mo: 1 to 15%, with the balance being unavoidable impurities. It is preferable that the above-described composition is satisfied in a radial location located on the outer surface side and having a volume corresponding to at least 20% of the total volume of the outer layer material. For example, in a sleeve with an outer diameter of 250 mm and an inner diameter of 140 mm, it is preferable that the above-described composition is satisfied also in a position at least 9 mm in the radial direction from the position corresponding to the maximum diameter during use for rolling toward the inner circumference side.

[0068] The "surface of the outer layer material that is located at the position corresponding to the maximum diameter during use for rolling" is a surface of the outer layer material at a position corresponding to the maximum diameter of a roll product that is prepared by polishing and removing a layer formed on the outer surface of an as-cast outer layer material (e.g., a portion formed when the molten metal in contact with a mold is rapidly cooled and solidified) and is used for rolling for the first time. Specifically, the above surface is a surface of the outer layer material at a position corresponding to the maximum usable diameter of the product (the outer layer material for rolls). More specifically, the "surface of the outer layer material that is located at the position corresponding to the maximum diameter during use for rolling" is a location corresponding to a region located on the outer surface side, having a volume corresponding to at least 20% of the total volume of the outer layer material, and extending in the radial direction toward the inner circumferential side from the surface of the outer layer material located at the position corresponding to the maximum diameter of the roll product that is prepared by polishing and removing the layer formed on the outer surface of the as-cast outer layer material and is used for rolling for the first time.

[0069] The composition of the surface of the outer layer material may be analyzed by instrumental analysis such as X-ray fluorescence analysis or emission spectroscopic analysis or may be analyzed by destructive inspection. Specifically, a block-shaped sample having a thickness in the roll diameter direction of less than 10 mm is cut from a location including the surface of the outer layer material and is subjected to chemical analysis.

[0070] First, a description will be given of the reasons for the limitations on the composition of the outer layer material for rolling mill rolls of the invention. In the following description, "mass %" in the composition is simply denoted by %.

C: 0.6 to 3.5%

[0071] C is an element that bonds to carbide-forming elements such as W, Mo, Cr, V, and Nb to form hard carbides and has the function of increasing wear resistance. The form of the carbides, the amount of crystallized carbides, and the temperature of crystallization vary depending on the amount of C. When the content of C is 0.6% or more, M_6C-type carbides are crystallized as primary phases. In a morphology obtained in this case, the M_6C-type carbides segregate on the outer surface side during centrifugal casting, and the wear resistance is thereby improved. If the content of C is less than 0.6%, the amount of M_6C-type carbides crystallized as the primary phases is insufficient, and the wear resistance deteriorates. If the content of C is large, i.e., more than 3.5%, the outer layer material is difficult to produce. Moreover, very brittle M_2C carbides and MC carbides are formed and coarsen, and breakage of rolls tends to occur during rolling. Therefore, C is limited within the range of 0.6 to 3.5%. The range of C is preferably 1.0 to 3.0%. The range of C is more preferably 1.2 to 2.8%.

Si: 0.05 to 3%

[0072] Si is an element that functions as a deoxidizer and has the function of strengthening the base phase. To obtain these effects, the content of Si must be 0.05% or more. If the content of Si exceeds 3%, its effects are saturated. Moreover, graphite flakes appear, and this causes a reduction in toughness. Therefore, Si is limited within the range of 0.05 to 3%. The range of Si is preferably 0.1 to 2%. The range of Si is more preferably 0.2 to 1.8%.

Mn: 0.05 to 3%

[0073] Mn is an element that fixes S having an adverse effect on material quality in the form of MnS and therefore has the function of rendering S harmless. Mn dissolves in the base phase and contributes to an improvement in hardenability. To obtain these effects, the content of Mn must be 0.05% or more. Even when the content of Mn is more than 3%, the above effects are saturated, and a reduction in material quality occurs. Therefore, Mn is limited within the range of 0.05 to 3. The range of Mn is preferably 0.1 to 1%. The range of Mn is more preferably 0.2 to 0.8%.

Mo: 1 to 15%

[0074] Mo is a carbide-forming element that bonds to C to form a carbide. In particular, in the present invention, Mo dissolves in hard M_6C-type carbides, which are primary phase carbides in which W is concentrated, to thereby strengthen the carbides and therefore has the function of improving the fracture resistance of the outer layer material for rolls. Mo improves the hardenability during heat treatment and contributes to an increase in the hardness of the outer layer material for rolls. Mo is an element heavier than Co and dose not impede centrifugation of the primary phase carbides toward the outer surface or has the function of facilitating the centrifugation. To obtain these effects, the content of Mo must be 1% or more. If the content of Mo is large, i.e., more than 15%, hard and brittle carbides composed mainly of Mo appear, and this causes a reduction in wear resistance. Therefore, Mo is limited within the range of 1 to 15%. The range of Mo is preferably 2 to 10%. The range of Mo is more preferably 4 to 10%.

W: 25 to 70%

[0075] W is the most important element in the present invention, and a large amount, i.e., 25% or more, of W is contained in the alloy composition. This allows a large amount of hard M_6C-type carbides in which W is concentrated to appear as primary phases, so that the outer layer material for rolling mill rolls can have significantly improved wear resistance. If the content of W is less than 25%, the outer layer material for rolling mill rolls excellent in wear resistance, which is the object of the invention, is difficult to obtain. If the content of W exceeds 70%, the M_6C-type carbides coarsen and become brittle. Moreover, the melting point of the molten metal increases, so that it is difficult to perform melting, casting, etc. Therefore, W is limited within the range of 25 to 70%. The range of W is preferably 30 to 65%. The range of W is more preferably 35 to 55%.

Co: 5 to 45%

[0076] Co, as well as W, is an important element in the present invention. When a large amount of Co and a large amount of W are contained, the activity of C increases. In this case, the formation of a large amount of hard carbides (e.g., M_6C-type, M_2C-type, and MC-type) in which W is concentrated as the primary phases is facilitated, and this contributes to an improvement in the wear resistance of the outer layer material for rolling mill rolls. To obtain this effect, the content of Co must be 5% or more. If the content of Co is large, i.e., more than 45%, a γ phase is stabilized, and the base phase is softened. When this outer layer material is used for a rolling mill roll, a large number of dents (hollows) are formed, causing a significant reduction in the wear resistance. Therefore, Co is limited within the range of 5 to 45%. The range of Co is preferably 10 to 40%. The range of Co is more preferably 15 to 35%.

[0077] The components described above are basic components. In addition to the basic composition, one or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3% and/or Ni: 0.05 to 3% may be optionally contained.

One or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3%

[0078] Fe, Cr, V, and Nb are carbide-forming elements, dissolve in carbides, and have the function of strengthening the carbides. One or two or more of them may be optionally contained.

[0079] Fe dissolves in carbides, dissolves also in the base phase, contributes to strengthening of the base phase, and has the function of preventing the formation of dents (hollows) when the outer layer material is used for rolling mill rolls. To obtain these effect, the content of Fe is preferably 5% or more. When the content of Fe exceeds 40%, the amount of the hard M_6C-type carbides appearing as the primary phases decreases, and the amount of brittle M_3C-type carbides increases, so that the wear resistance deteriorates. When Fe is contained, it is preferable that Fe is limited within the range of 5 to 40%. The range of Fe is more preferably 10 to 35%. The range of Fe is still more preferably 12 to 30%.

[0080] When the base phase of the W-Co-based alloy contains Fe, the base phase is strengthened, but the mechanism of strengthening is unclear at present. This may be because of any of the following base phase strengthening phenomena. First, the γ phase stabilization effect of Co and the α phase stabilization effect of Fe offset each other, and this results in an increase in the strength of the base phase. Second, the α phase stabilization effect of Fe is high, and the base phase has a hard martensite or bainite structure. In this case, a structure including fine carbides precipitated in the base phase may appear.

[0081] Cr is a strong carbide-forming element, forms mainly eutectic carbides, and has the function of improving the strength of the carbides formed. The eutectic carbides are crystallized in regions between the primary phase M_6C-type carbides and therefore function to strengthen the regions between the M_6C-type carbides. Cr also has the function of suppressing the appearance of graphite. In the W-Co-based alloy, the activity coefficient of C is high, so that graphite appears easily. The appearance of graphite causes a reduction in toughness. Preferably, in the present invention, to prevent the appearance of graphite to allow the W-Co-based alloy to be stably used for rolling mill rolls, the W-Co-based alloy may contain Cr optionally. To obtain these effects, it is preferable that the content of Cr is 0.1% or more. If the content of Cr exceeds 10%, a large amount of Cr-based eutectic carbides appear, and this causes a reduction in toughness. Therefore, when Cr is contained, it is preferable that Cr is limited within the range of 0.1 to 10%. The range of Cr is more preferably 1 to 8%. The range of Cr is still more preferably 1.5 to 7%.

[0082] V is an element that bonds to C to form hard VC (MC-type carbides containing Mo, Nb, Cr, W, etc.). The MC-type carbides formed are crystallized as primary phases and serve as crystallization nuclei for M_6C-type carbides in which W is concentrated, so that the formation of the M_6C-type carbides is facilitated. Therefore, V has the function of dispersing fine M_6C-type carbides at high density. To obtain this effect, it is preferable that the content of V is 0.1% or more. If the content of V is large, i.e., more than 6%, the amount of low-specific gravity V-based MC-type carbides increases even when a large amount of W is contained, and these carbides coarsen and are centrifuged toward the inner surface of the outer layer material for rolls during centrifugal casting. In this case, the amount of the hard M_6C-type carbides on the outer surface side is insufficient, and the wear resistance of the outer layer material for rolls during use deteriorates. When the amount of the V-based MC-type carbides centrifuged toward the inner surface side is large, the strength of the interface with the inner or intermediate layer of the roll decreases. Therefore, when V is contained, it is preferable that V is limited within the range of 0.1 to 6%. The range of V is more preferably 1 to 5%. The range of V is still more preferably 1.5 to 4%.

[0083] Nb bonds to C with very high bonding strength, is a strong carbide-forming element, and easily forms complex carbides with V and W. The complex carbides of Nb, V, and W are crystallized as primary phases and serve as crystallization nuclei for the M_6C-type carbides in which W is concentrated. The complex carbides facilitate the formation of the M_6C-type carbides and therefore have the function of dispersing fine M_6C-type carbides at high density. To obtain this effect, the content of Nb must be 0.1% or more. If the content of Nb is high, i.e., more than 3%, low-density Nb-based MC-type carbides are formed and coarsen. During centrifugal casting, these carbides tend to be centrifuged toward the inner surface of the outer layer material for rolls, and the amount of the MC-type carbides on the inner surface side of the outer layer material increases. Moreover, when the amount of the MC-type carbides centrifuged toward the inner surface side of the outer layer material increases, the quality on the inner surface side deteriorates. Specifically, for example, the strength of the interface with the inner or intermediate layer of the roll decreases. Therefore, when Nb is contained, it is preferable that Nb is limited within the range of 0.1 to 3%. The range of Nb is more preferably 0.5 to 2%. The range of Nb is still more preferably 0.6 to 1.8%.

Ni: 0.05 to 3%

[0084] Ni is an element having the function of improving the hardenability and may be optionally contained in order to, for example, compensate for insufficient hardenability of large rolls. To obtain this effect, it is preferable that the content of Ni is 0.05% or more. When the content of Ni is less than 0.05%, which corresponds to the level of impurities, the effect is not obtained. When the content of Ni is more than 3%, the γ phase is stabilized, and the desired hardenability cannot be obtained. Therefore, when Ni is contained, it is preferable that Ni is limited within the range of 0.05 to 3%. The range of Ni is more preferably 0.1 to 2.5%.

[0085] The balance other than the above components is unavoidable impurities. Examples of the unavoidable impurities include P, S, N, and B. P segregates at grain boundaries and has adverse effects such as embrittlement of the material. It is therefore desirable to reduce the amount of P present as an impurity as much as possible, and a permissible level of P is 0.05% or less. S, as well as P, segregates at grain boundaries and has adverse effects such as embrittlement of the material. It is therefore desirable to reduce the amount of S present as an impurity as much as possible, and a permissible level of S is 0.05% or less because part of S is combined with Mn and is present as harmless sulfide-based inclusions. In an ordinary melting process, N is mixed as an impurity in an amount of about 0.01 to about 0.1%. When the amount of N is as described above, N has no influence on the effects of the present invention. However, since N may cause the formation of gas defects at the boundary between the outer and intermediate layers of the composite roll or the boundary between the outer and inner layers, it is preferable that N is limited to less than 0.07%. B may be mixed from raw material scraps to be melted and a casting flux and may be contained as an unavoidable impurity. B may dissolve in carbides and the base phase and change the properties of the carbides. B may dissolve in the base phase, affect the hardenability of the base phase, and cause variations in quality. It is therefore preferable to reduce the amount of B as much as possible. However, when B is 0.1% or less, the effects of the invention are not adversely affected. Preferably, the total amount of the above unavoidable impurities is adjusted to less than 1%.

[0086] Next, a preferred method for producing the outer layer material for rolling mill rolls of the invention will be described.

[0087] In the present invention, in terms of productivity and production cost, the outer layer material for rolling mill rolls is produced by a centrifugal casting method in which a casting mold is rotated. In this manner, the outer layer material for rolling mill rolls excellent in wear resistance can be produced at low cost.

[0088] First, a molten metal having the composition of the above outer layer material for rolls is poured into the rotating mold such that a prescribed wall thickness is obtained and then subjected to centrifugal casting to obtain the outer layer material for rolling mill rolls. Generally, to protect the mold, the inner surface of the mold is coated with a refractory composed mainly of zircon. In the present invention, it is preferable to perform the centrifugal casting while the number of revolutions is controlled such that a centrifugal force of 120 to 250 G is obtained. By applying a high centrifugal force, the dispersion density of the high-density hard carbides on the outer surface side can be increased.

[0089] In the present invention, the obtained outer layer material for rolling mill rolls may be used as a single sleeve, and a rolling mill roll may be prepared by fitting a shaft member into the sleeve. For example, as shown in Fig. 3, the outer layer material for rolling mill rolls may be shrink-fitted onto a shaft member (roll shaft) made of forged carbon steel to form a composite roll. The obtained outer layer material for rolling mill rolls may include an intermediate layer integrally fused to the inner side of the outer layer material. In this case, the outer layer material is used as a sleeve with the intermediate layer, and a shaft member may be fitted into the sleeve to form a rolling mill roll. Preferably, the intermediate layer is formed as follows. During or after completion of solidification of the outer layer material for rolls, a molten metal having the composition of the intermediate layer is poured into a mold while the mold is rotated and then subjected to centrifugal casting. Examples of the material of the intermediate layer include graphitic steel, high carbon steel containing 1 to 2% by mass of C, and hypoeutectic cast iron. No particular limitation is imposed on the shaft member of the rolling mill roll. However, the shaft member is preferably a steel forging (a forged steel shaft) produced separately, a cast steel product (shaft) produced separately, or a cast iron product (shaft) produced separately.

[0090] In the present invention, the composite roll may include an outer layer formed from the above outer layer material for rolling mill rolls and an inner layer integrally fused to the outer layer (see, for example, a schematic cross section of the composite roll in Fig. 4). Alternatively, the composite roll may include an outer layer formed from the above outer layer material for rolling mill rolls, an intermediate layer integrally fused to the outer layer, and an inner layer integrally fused to the intermediate layer (see, for example, a schematic cross section of the composite roll in Fig. 5).

[0091] Preferably, the intermediate layer is formed by centrifugal casting as follows. During or after completion of solidification of the outer layer material for rolls, a molten metal having the composition of the intermediate layer is poured into a mold while the mold is rotated. Preferably, the material of the intermediate layer used is graphite steel, high-carbon steel containing 1 to 2% by mass of C, hypoeutectic cast iron, etc. The intermediate layer and the outer layer are integrally fused together, and about 10 to about 90% of the components of the outer layer are mixed into the intermediate layer. To reduce the amount of the components of the outer later mixed into the inner layer, it is desirable to reduce the amount of the components of the outer layer mixed into the intermediate layer as much as possible.

[0092] Generally, the inner layer is formed by static casting. Specifically, after complete solidification of the outer layer or the intermediate layer, the rotation of the mold is stopped, and the mold is erected. Then the material of the inner layer is subjected to static casting. Preferably, the material of the inner layer that is subjected to static casting is nodular graphite cast iron, vermicular graphite cast iron (CV cast iron), etc. that are excellent in casting performance and mechanical properties. In the composite roll including no intermediate layer and including the outer layer and the inner layer integrally fused together, about 1 to about 10% of the components of the outer layer material are often mixed into the inner layer. W, Cr, V, etc. contained in the outer layer material are strong carbide-forming elements. When these elements are mixed into the inner layer, the inner layer is embrittled. Therefore, in the present invention, it is preferable that the amount of the components of the outer layer mixed into the inner layer is reduced to less than 5%.

[0093] Preferably, the above outer layer material for rolling mill rolls and the composite roll for rolling are subjected to heat treatment after casting. Preferably, in the heat treatment, the step of heating the outer layer material or the composite roll to 1,000 to 1,200°C, holding it at this temperature for 5 to 40 h, and cooling it in the furnace or subjecting it to air cooling or air blast cooling is performed, and then the step of heating the outer layer material or the composite roll to 400 to 600°C, holding it at this temperature, and then cooling it is performed. These steps are performed at least once. Preferably, the hardness of the outer layer material for rolling mill rolls of the invention and the hardness of the composite roll for rolling of the invention are adjusted within the range of 79 to 100HS according to their intended applications. It is recommended that the heat treatment after casting be controlled so that the above hardness is stably achieved.

[Second embodiment]

[0094] The outer layer material for rolling mill rolls of the present invention is produced by centrifugal casting. The "centrifugal cast outer layer material for rolling mill rolls" means an outer layer material for rolling mill rolls that is produced by a centrifugal casting method conventionally used as a method for producing rolling mill rollers. The outer layer material for rolling mill rolls produced using the centrifugal casting method (the "centrifugal cast" outer layer material for rolling mill rolls) can be clearly distinguished from rolling mill rolls produced by other conventional production methods in the sense of "products." It is unrealistic to identify the "centrifugal cast" outer layer material for rolling mill rolls from its structure and properties because it requires enormous efforts.

[0095] The outer layer material for rolling mill rolls of the invention is made of a W-Co-based alloy and has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of a roll toward an inner circumferential side of the roll. The outer layer material in a surface layer at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %, W: 25 to 70% and Co: 5 to 45% and further containing C: 0.6 to 3.5%, Si: 0.05 to 3%, Mn: 0.05 to 3%, and Mo: 1 to 15%, with the balance being unavoidable impurities. Moreover, the contents of W, Co, Mo, and Fe satisfy formula [1] below. It is preferable that the above-described composition is satisfied in a radial location located on the outer surface side and having a volume corresponding to at least 20% of the total volume of the outer layer material. For example, in a sleeve with an outer diameter of 250 mm and an inner diameter of 140 mm, it is preferable that the above-described composition is satisfied also in a position at least 9 mm in the radial direction from the position corresponding to the maximum diameter during use for rolling toward the inner circumference side.

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \qquad [1]$$

[0096] Here, %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements and are 0 when not contained.

[0097] The "outer layer material in the surface layer at the position corresponding to the maximum diameter during use for rolling" is the outer layer material in a surface layer at a position corresponding to the maximum diameter of a roll product that is prepared by polishing and removing a layer formed on the outer surface of an as-cast outer layer material (e.g., a portion formed when the molten metal in contact with a mold is rapidly cooled and solidified) and is used for rolling for the first time. Specifically, the above outer layer material is the outer layer material in a surface layer that is located at the position corresponding to the maximum usable diameter of the product (the outer layer material for rolls) and has a thickness of at least 9 mm in the radial direction.

[0098] The composition of the outer layer material in the surface layer may be analyzed by instrumental analysis such as X-ray fluorescence analysis or emission spectroscopic analysis or may be analyzed by destructive inspection. Specifically, a block-shaped sample having a thickness in the roll diameter direction of less than 10 mm is cut from a location including the outer layer material in the surface layer and is subjected to chemical analysis.

[0099] First, a description will be given of the reasons for the limitations on the composition of the outer layer material for rolling mill rolls of the invention. In the following description, "mass %" in the composition is simply denoted by %.

C: 0.6 to 3.5%

[0100] C is an element that bonds to carbide-forming elements such as W, Mo, Cr, V, and Nb to form hard carbides and has the function of increasing wear resistance. The form of the carbides, the amount of crystallized carbides, and the temperature of crystallization vary depending on the amount of C. When C is 0.6% or more, M_6C-type carbides are crystallized as primary phases. In a morphology obtained in this case, the M_6C-type carbides segregate on the outer surface side during centrifugal casting, and the wear resistance is thereby improved. If C is less than 0.6%, the amount of M_6C-type carbides crystallized as the primary phases is insufficient, and the wear resistance deteriorates. If the content of C is large, i.e., more than 3.5%, the outer layer material is difficult to produce. Moreover, very brittle M_2C carbides and MC carbides are formed and coarsen, and breakage of rolls tends to occur during rolling. Therefore, C is limited within the range of 0.6 to 3.5%. The range of C is preferably 1.0 to 3.0%. The range of C is more preferably 1.2 to 2.8%.

Si: 0.05 to 3%

[0101] Si is an element that functions as a deoxidizer and has the function of strengthening the base phase. To obtain these effects, the content of Si must be 0.05% or more. If the content of Si exceeds 3%, its effects are saturated. Moreover, graphite flakes appear, and this causes a reduction in toughness. Therefore, Si is limited within the range of 0.05 to 3%. The range of Si is preferably 0.05 to 2%. The range of Si is more preferably 0.2 to 1.8%.

Mn: 0.05 to 3%

[0102] Mn is an element that fixes S having an adverse effect on material quality in the form of MnS and therefore has the function of rendering S harmless. Mn dissolves in the base phase and contributes to an improvement in hardenability. To obtain these effects, the content of Mn must be 0.05% or more. Even when the content of Mn is more than 3%, the above effects are saturated, and a reduction in material quality occurs. Therefore, Mn is limited within the range of 0.05 to 3. The range of Mn is preferably 0.1 to 1%. The range of Mn is more preferably 0.2 to 0.8%.

Mo: 1 to 15%

[0103] Mo is a carbide-forming element that bonds to C to form carbides. In particular, in the present invention, Mo dissolves in hard M_6C-type carbides, which are primary phase carbides in which W is concentrated, to thereby strengthen the carbides and therefore has the function of improving the fracture resistance of the outer layer material for rolls. Mo improves the hardenability during heat treatment and contributes to an increase in the hardness of the outer layer material for rolls. Mo is an element heavier than Co and dose not impede centrifugation of the primary phase carbides toward the outer surface or has the function of facilitating the centrifugation. To obtain these effects, the content of Mo must be 1% or more. If the content of Mo is large, i.e., more than 15%, hard and brittle carbides composed mainly of Mo appear, and this causes a reduction in wear resistance. Therefore, Mo is limited within the range of 1 to 15%. The range of Mo is preferably 2 to 10%. The range of Mo is more preferably 4 to 10%.

W: 25 to 70%

[0104] W is the most important element in the present invention, and a large amount, i.e., 25% or more, of W is contained in the alloy composition. This allows a large amount of hard M_6C-type carbides in which W is concentrated to appear as primary phases, so that the outer layer material for rolling mill rolls can have significantly improved wear resistance. If the content of W exceeds 70%, the M_6C-type carbides coarsen and become brittle. Moreover, the melting point of the molten metal increases, so that it is difficult to perform melting, casting, etc. Therefore, W is limited within the range of 25 to 70%. The range of W is preferably 30 to 65%. The range of W is more preferably 35 to 55%.

Co: 5 to 45%

[0105] Co, as well as W, is an important element in the present invention. When a large amount of Co and a large amount of W are contained, the activity of C increases. In this case, the formation of a large amount of hard carbides (e.g., M_6C-type, M_2C-type, and MC-type) in which W is concentrated as the primary phases is facilitated, and this contributes to an improvement in the wear resistance of the outer layer material for rolling mill rolls. To obtain this effect, the content of Co must be 5% or more. If the content of Co is large, i.e., more than 45%, a γ phase is stabilized, and the base phase is softened. When this outer layer material is used for a rolling mill roll, a large number of dents (hollows) are formed, causing a significant reduction in the wear resistance. Therefore, Co is limited within the range of 5 to 45%. The range of Co is preferably 10 to 40%. The range of Co is more preferably 12 to 35%.

[0106] The components described above are basic components. In addition to the basic composition, one or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3% and/or Ni: 0.05 to 3% may be optionally contained.

One or two or more selected from Fe: 5 to 40%, Cr: 0.1 to 10%, V: 0.1 to 6%, and Nb: 0.1 to 3%

[0107] Fe, Cr, V, and Nb are carbide-forming elements, dissolve in carbides, and have the function of strengthening the carbides. One or two or more of them may be optionally contained.

[0108] Fe dissolves in carbides, dissolves also in the base phase, contributes to strengthening of the base phase, and has the function of preventing the formation of dents (hollows) when the outer layer material is used for rolling mill rolls. To obtain these effect, the content of Fe is preferably 5% or more. When the content of Fe exceeds 40%, the amount of the hard M_6C-type carbides appearing as the primary phases decreases, and the amount of brittle M_3C-type carbides increases, so that the wear resistance deteriorates. When Fe is contained, it is preferable that Fe is limited within the range of 5 to 40%. The range of Fe is more preferably 10 to 35%. The range of Fe is still more preferably 12 to 30%.

[0109] When the base phase of the W-Co-based alloy contains Fe, the base phase is strengthened, but the mechanism of strengthening is unclear at present. This may be because of any of the following base phase strengthening phenomena. First, the γ phase stabilization effect of Co and the α phase stabilization effect of Fe offset each other, and this results in an increase in the strength of the base phase. Second, the α phase stabilization effect of Fe is high, and the base phase has a hard martensite or bainite structure. In this case, a structure including fine carbides precipitated in the base phase may appear.

[0110] Cr is a strong carbide-forming element, forms mainly eutectic carbides, and has the function of improving the strength of the carbides formed. The eutectic carbides are crystallized in regions between the primary phase M_6C-type carbides and therefore function to strengthen the regions between the M_6C-type carbides. Cr also has the function of suppressing the appearance of graphite. In the W-Co-based alloy, the activity coefficient of C is high, so that graphite appears easily. The appearance of graphite causes a reduction in toughness. Preferably, in the present invention, to prevent the appearance of graphite to allow the W-Co-based alloy to be stably used for rolling mill rolls, the W-Co-based alloy may contain Cr optionally. To obtain these effects, it is preferable that the content of Cr is 0.1% or more. If the content of Cr exceeds 10%, a large amount of Cr-based eutectic carbides appear, and this causes a reduction in toughness. Therefore, when Cr is contained, it is preferable that Cr is limited within the range of 0.1 to 10%. The range of Cr is more preferably 1 to 8%. The range of Cr is still more preferably 1.5 to 7%.

[0111] V is an element that bonds to C to form hard VC (MC-type carbides containing Mo, Nb, Cr, W, etc.). The MC-type carbides formed are crystallized as primary phases and serve as crystallization nuclei for M_6C-type carbides in which W is concentrated, so that the formation of the M_6C-type carbides is facilitated. Therefore, V has the function of dispersing fine M_6C-type carbides at high density. To obtain this effect, it is preferable that the content of V is 0.1% or more. If the content of V is large, i.e., more than 6%, the amount of low-specific gravity V-based MC-type carbides increases even when a large amount of W is contained, and these carbides coarsen and are centrifuged toward the inner surface of the outer layer material for rolls during centrifugal casting. In this case, the amount of the hard M_6C-type carbides on the outer surface side is insufficient, and the wear resistance of the outer layer material for rolls during use deteriorates. When the amount of the V-based MC-type carbides centrifuged toward the inner surface side is large, the strength of the interface with the inner or intermediate layer of the roll decreases. Therefore, when V is contained, it is preferable that V is limited within the range of 0.1 to 6%. The range of V is more preferably 1 to 5%. The range of V is still more preferably 1.5 to 4%.

[0112] Nb bonds to C with very high bonding strength, is a strong carbide-forming element, and easily forms complex carbides with V and W. The complex carbides of Nb, V, and W are crystallized as primary phases and serve as crystallization nuclei for the M_6C-type carbides in which W is concentrated. The complex carbides facilitate the formation of the M_6C-type carbides and therefore have the function of dispersing fine M_6C-type carbides at high density. To obtain this effect, the content of Nb must be 0.1% or more. If the content of Nb is high, i.e., more than 3%, low-specific gravity Nb-based MC-type carbides are formed and coarsen. During centrifugal casting, these carbides tend to be centrifuged toward the inner surface of the outer layer material for rolls, and the amount of the MC-type carbides on the inner surface side of the outer layer material increases. Moreover, when the amount of the MC-type carbides centrifuged toward the inner surface side of the outer layer material increases, the quality on the inner surface side deteriorates. Specifically, for example, the strength of the interface with the inner or intermediate layer of the roll decreases. Therefore, when Nb is contained, it is preferable that Nb is limited within the range of 0.1 to 3%. The range of Nb is more preferably 0.5 to 2%. The range of Nb is still more preferably 0.6 to 1.8%.

Ni: 0.05 to 3%

[0113] Ni is an element having the function of improving the hardenability and may be optionally contained in order to, for example, compensate for insufficient hardenability of large rolls. To obtain this effect, it is preferable that the content of Ni is 0.05% or more. When the content of Ni is less than 0.05%, which corresponds to the level of impurities, the effect is not obtained. When the content of Ni is more than 3%, the γ phase is stabilized, and the desired hardenability cannot be obtained. Therefore, when Ni is contained, it is preferable that Ni is limited within the range of 0.05 to 3%.

The range of Ni is more preferably 0.1 to 2.5%.

[0114] The balance other than the above components is unavoidable impurities. Examples of the unavoidable impurities include P, S, N, and B. P segregates at grain boundaries and has adverse effects such as embrittlement of the material. It is therefore desirable to reduce the amount of P present as an impurity as much as possible, and a permissible level of P is 0.05% or less. S, as well as P, segregates at grain boundaries and has adverse effects such as embrittlement of the material. It is therefore desirable to reduce the amount of S present as an impurity as much as possible, and a permissible level of S is 0.05% or less because part of S is combined with Mn and is present as harmless sulfide-based inclusions. In an ordinary melting process, N is mixed as an impurity in an amount of about 0.01 to about 0.1%. When the amount of N is as described above, N has no influence on the effects of the present invention. However, since N may cause the formation of gas defects at the boundary between the outer and intermediate layers of the composite roll or the boundary between the outer and inner layers, it is preferable that N is limited to less than 0.07%. B may be mixed from raw material scraps to be melted and a casting flux and may be contained as an unavoidable impurity. B may dissolve in carbides and the base phase and change the properties of the carbides. B may dissolve in the base phase, affect the hardenability of the base phase, and cause variations in quality. It is therefore preferable to reduce the amount of B as much as possible. However, when B is 0.1% or less, the effects of the invention are not adversely affected. Preferably, the total amount of the above unavoidable impurities is adjusted to less than 1%.

[0115] The outer layer material in the surface layer at the position corresponding to the maximum diameter during use for rolling has the above composition, and the contents of W, Co, Mo, and Fe satisfy the following formula [1].

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \qquad [1]$$

[0116] Here, %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements and are 0 when not contained.

[0117] When (%W + %Mo)/(%Co + %Fe) is 1.2 or more, a large amount of hard carbides are accumulated, and the amounts of W and Mo dissolved in the base phase increase. Because of the synergistic effect of them, a Young's modulus of 270 GPa or more is obtained. In conventional high-speed tool steel-based rolls, the Young's modulus of their surface layers to be in contact with a rolled material is about 220 to about 235 GPa (see, for example, Non Patent Literature 4 and Non Patent Literature 5). When the Young's modulus is 270 GPa or more, the elastic deformation of the surface layers of the rolls is reduced, and the effect of reducing the rolling load is obtained. Even when (%W + %Mo)/(%Co + %Fe) is less than 1.2, the outer layer material for rolling mill rolls can have good wear resistance when the above-described composition ranges are satisfied. However, since the Young's modulus is less than 270GPa, no significant rolling load reduction effect is obtained. To increase (%W + %Mo)/(%Co + %Fe) to 9.0 or more, it is necessary to add large amounts of expensive W and Mo, and this is economically disadvantageous. Therefore, the upper limit of (%W + %Mo)/(%Co + %Fe) is set to 9.0. The inventors have conducted extensive studies and found that, when (%W + %Mo)/(%Co + %Fe) satisfies formula [1] above, the total amount of W and Mo dissolved in the base phase is 3.5% or more and the Young's modulus is 270 GPa or more. To control (%W + %Mo)/(%Co + %Fe), the composition of the molten metal, the casting temperature during the centrifugal casting, and the centrifugal force may be adjusted. Preferably, (%W + %Mo)/(%Co + %Fe) is from 4.8 to 7.8 inclusive.

[0118] In the outer layer material for rolling mill rolls of the present invention, it is preferable that the Young's modulus of the outer layer material in the surface layer at the position corresponding to the maximum diameter during use for rolling is from 270 GPa to 500 GPa inclusive in order to obtain a good rolling load reduction effect. As described above, in the conventional high-speed tool steel-based rolls, the Young's modulus of their surface layers to be in contact with the rolled material is about 220 to about 235 GPa (see, for example, Non Patent Literature 4 and Non Patent Literature 5). When the Young's modulus is 270 GPa or more, the elastic deformation of the surface layers of the rolls is reduced, and the effect of reducing the rolling load is obtained. However, to increase the Young's modulus to more than 500 GPa, large amounts of alloy elements must be added, and this is economically disadvantageous. Therefore, the Young's modulus is preferably from 270 GPa to 500 GPa inclusive.

[0119] To measure the Young's modulus, a compression test piece or a tensile test piece is cut from the outer layer material at the position corresponding to the maximum diameter during use for rolling, and the Young's modulus is computed from the gradient during elastic deformation in the compression test or the tensile test. The Young's modulus may be measured by a nondestructive measurement method such as an ultrasonic method.

[0120] Next, a preferred method for producing the outer layer material for rolling mill rolls of the invention will be described.

[0121] In the present invention, in terms of productivity and production cost, the outer layer material for rolling mill rolls is produced by a centrifugal casting method in which a casting mold is rotated. In this manner, the outer layer material for rolling mill rolls excellent in wear resistance can be produced at low cost.

[0122] First, a molten metal having the composition of the above outer layer material for rolls is poured into the rotating mold such that a prescribed wall thickness is obtained and then subjected to centrifugal casting to obtain the outer layer material for rolling mill rolls. Generally, to protect the mold, the inner surface of the mold is coated with a refractory composed mainly of zircon. In the present invention, it is preferable to perform the centrifugal casting while the number of revolutions is controlled such that the centrifugal force at the position corresponding to the maximum diameter during use for rolling is 120 to 250 G. By applying a high centrifugal force, the dispersion density of the high-specific gravity hard carbides on the outer surface side can be increased.

[0123] In the present invention, the obtained outer layer material for rolling mill rolls may be used as a single sleeve, and a rolling mill roll may be prepared by fitting a shaft member into the sleeve (see, for example, Fig. 8). The obtained outer layer material for rolling mill rolls may include an intermediate layer integrally fused to the inner side of the outer layer material. In this case, the outer layer material is used as a sleeve with the intermediate layer, and a shaft member may be fitted into the sleeve to form a rolling mill roll. Preferably, the intermediate layer is formed as follows. During or after completion of solidification of the outer layer material for rolls, a molten metal having the composition of the intermediate layer is poured into a mold while the mold is rotated and then subjected to centrifugal casting. Examples of the material of the intermediate layer include graphitic steel, high carbon steel containing 1 to 2% by mass of C, and hypoeutectic cast iron. No particular limitation is imposed on the shaft member of the rolling mill roll. However, the shaft member is preferably a steel forging (a forged steel shaft) produced separately, a cast steel product (shaft) produced separately, or a cast iron product (shaft) produced separately.

[0124] In the present invention, the composite roll may include an outer layer formed from the above outer layer material for rolling mill rolls and an inner layer integrally fused to the outer layer. Alternatively, the composite roll may include an outer layer formed from the above outer layer material for rolling mill rolls, an intermediate layer integrally fused to the outer layer, and an inner layer integrally fused to the intermediate layer.

[0125] Preferably, the intermediate layer is formed by centrifugal casting as follows. During or after completion of solidification of the outer layer material for rolls, a molten metal having the composition of the intermediate layer is poured into a mold while the mold is rotated. Preferably, the material of the intermediate layer used is graphite steel, high-carbon steel containing 1 to 2% by mass of C, hypoeutectic cast iron, etc. The intermediate layer and the outer layer are integrally fused together, and about 10 to about 90% of the components of the outer layer are mixed into the intermediate layer. To reduce the amount of the components of the outer later mixed into the inner layer, it is desirable to reduce the amount of the components of the outer layer mixed into the intermediate layer as much as possible.

[0126] Generally, the inner layer is formed by static casting. Specifically, after complete solidification of the outer layer or the intermediate layer, the rotation of the mold is stopped, and the mold is erected. Then the material of the inner layer is subjected to static casting. Preferably, the material of the inner layer that is subjected to static casting is nodular graphite cast iron, vermicular graphite cast iron (CV cast iron), etc. that are excellent in casting performance and mechanical properties. In the composite roll including no intermediate layer and including the outer layer and the inner layer integrally fused together, about 1 to about 10% of the components of the outer layer material are often mixed into the inner layer. W, Cr, V, etc. contained in the outer layer material are strong carbide-forming elements. When these elements are mixed into the inner layer, the inner layer is embrittled. Therefore, in the present invention, it is preferable that the amount of the components of the outer layer mixed into the inner layer is reduced to less than 5%.

[0127] Preferably, the above outer layer material for rolling mill rolls and the composite roll for rolling are subjected to heat treatment after casting. Preferably, in the heat treatment, the step of heating the outer layer material or the composite roll to 1,000 to 1,200°C, holding it at this temperature for 5 to 40 h, and cooling it in the furnace or subjecting it to air cooling or air blast cooling is performed, and then the step of heating the outer layer material or the composite roll to 400 to 600°C, holding it at this temperature, and then cooling it is performed. These steps are performed at least once. Preferably, the hardness of the outer layer material for rolling mill rolls of the invention and the hardness of the composite roll for rolling of the invention are adjusted within the range of 79 to 100HS according to their intended applications. It is recommended that the heat treatment after casting be controlled so that the above hardness is stably achieved.

Examples

[Example 1]

[0128] Examples for the first embodiment described above will be described.

[0129] A molten metal having one of compositions shown in Table 1 was melted using a high-frequency induction furnace and cast to produce a sleeve-shaped outer layer material for rolls (outer diameter: 250 mmϕ, radial wall thickness: 55 mm) used as a test material by the centrifugal casting method. The casting temperature was 1,450 to 1,550°C, and the centrifugal force in multiples of gravity was 140 to 220 G. In one test material (molten metal No. S), significant segregation of carbides on the inner surface was found, and therefore the centrifugal force was reduced to 60 G in order to reduce the segregation. After the casting, each test material was subjected to quenching treatment in which the test material was reheated to 1,050 to 1,200°C, held for 10 h, and cooled to 100°C or lower and then subjected to tempering treatment in which the test material was heated to 400 to 560°C, held at this temperature, and then cooled. The quenching treatment and the tempering treatment were repeated once or twice. In this manner, the hardness at a position 5 mm from the outer surface of the test material in the thickness direction was adjusted to about 85 to 100HS. A molten metal (molten metal No. V) having the composition of a commercial centrifugal cast outer layer material (high-speed tool roll-based composition: 2.2% C-0.4% Si-0.4% Mn-5.3% Cr-5.2% Mo-5.6% V-1.1% Nb) used for hot finishing rolling mill rolls for steel was melted. Then the molten metal was cast to produce a sleeve-shaped outer layer material for rolls in the same manner as described above, and the cast sleeve-shaped outer layer material was subjected to heat treatment to obtain a test material (hardness: 85HS) in Conventional Example (test material No. 22) .

[0130] Test pieces for composition analysis and test pieces for a wear test were cut from each of the heat-treated test materials. The test material No. 19 was very brittle, and it was very difficult to cut the test material.

[0131] Each test piece for composition analysis was cut from a corresponding heat-treated test material as follows. The outer surface of the test material was ground to a depth of 5 mm in the radial direction, and a test piece having a thickness of 5 mm measured in the radial direction from the ground outer surface and having a size of 10 mm × 10 mm in a plane parallel to the outer surface was cut. Analysis of elemental components was performed using the test pieces obtained. The analysis methods used were chemical analysis. A combustion method was used for C, and a gravimetric method was used for Si and W. An atomic absorption method was used for Mn, Cr, and Mo, and a volumetric method was used for Co. The volumetric method or the atomic absorption method was used for Fe.

[0132] The results obtained are shown in Table 2.

[0133] Each wear test piece (outer diameter: 60 mmϕ × width 10 mm) was cut from a corresponding heat-treated test piece such that the widthwise center of the wear test piece was located at a position 10 mm from the outer surface of the test material in the radial direction. As shown in Fig. 2, the wear test was performed using the test piece (wear test piece) and a counterpart (material: S45C, outer diameter 190 mmϕ × width 15mm) by a two-disc slip rolling method.

[0134] In the wear test, while the test piece was water-cooled, the counterpart heated to 850°C was pressed against the test piece rotated at revolutions per minute of 700 rpm (peripheral speed: 2.1 m/s) under a load of 980 N and rotated at a slip ratio of 14.2%. The counterpart was changed every 21,000 revolutions of the test piece, and the test piece was rotated until the number of total revolutions reached 168,000. After completion of the test, the wear loss of the wear test piece was examined. The wear loss in the Comparative Example (test material No. 22) was used as a reference (1.0). The wear loss obtained for each test material was used to compute the ratio of the wear loss with respect to the reference (wear resistance ratio = (wear loss in Comparative Example)/(wear loss of test material)), and the wear resistance was evaluated. When the wear resistance ratio was 3 or more, the symbol "⊙" was assigned. When the wear resistance ratio was 2 or more and less than 3, the symbol "○" was assigned. When the wear resistance ratio was less than 2, the symbol "×" was assigned. The evaluation symbol ⊙ represents very good, and the evaluation symbol ○ represents good. The evaluation symbol × represents poor.

[0135] The results obtained are shown in Table 3.

[Table 1]

Molten metal No.	Chemical composition (% by mass)								
	W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance
A	55.7	31.2	4.3	2.3	0.4	0.6	Cr:4.9	-	Unavoidable impurities
B	29.9	50.4	8.7	1.6	0.1	0.5	Cr:8.2, V:0.3	-	Unavoidable impurities
C	52.6	22.4	4.1	0.7	1.2	0.6	Fe:8.7, Cr:3.6, V: 5.5	-	Unavoidable impurities
D	38.6	24.5	5.5	1.6	0.4	1.2	Fe:15.8, Cr:9.2, Nb:3.2	-	Unavoidable impurities
E	26.5	28.8	9.0	1.9	2.1	0.4	Fe:24.3, Cr:6.0, V:0.8, Nb:0.4	-	Unavoidable impurities
F	34.9	29.1	4.8	2.1	0.5	0.6	Fe:20.5, Cr:5.4, V:0.5, Nb:1.6	0.2	Unavoidable impurities
G	31.4	33.5	7.2	1.9	0.7	0.3	Fe:23.6, Cr:1.4	-	Unavoidable impurities
H	38.6	28.2	1.9	1.6	0.3	0.4	Fe:21.8, Cr:6.6	-	Unavoidable impurities
I	22.1	29.1	12.2	0.9	0.4	0.4	Fe:28.7, Cr:5.6	0.8	Unavoidable impurities
J	38.6	31.2	7.4	1.9	0.4	0.4	Fe:10.9, Cr:8.6	0.5	Unavoidable impurities
K	33.2	30.0	6.7	1.6	0.4	0.5	Fe:21.2, Cr:6.5	-	Unavoidable impurities

(continued)

Molten metal No.	Chemical composition (% by mass)								
	W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance
L	34.3	37.6	3.9	1.7	0.3	0.3	Fe:17.3, Cr:4.5	-	Unavoidable impurities
M	34.2	21.8	4.7	1.9	0.5	2.6	Fe:24.4, Cr:9.8	-	Unavoidable impurities
N	35.3	31.1	4.1	1.8	0.4	0.4	Fe:21.6, Cr:4.8	-	Unavoidable impurities
O	29.6	27.6	6.1	2.6	0.2	0.3	Fe:25.7, Cr:5.2, V:1.8, Nb:0.6	-	Unavoidable impurities
P	52.3	18.3	9.6	1.4	0.4	0.4	Fe:17.4	-	Unavoidable impurities
Q	32.4	12.4	5.8	1.6	0.6	1.4	Fe:38.4, Cr:7.2	-	Unavoidable impurities
R	12.3	37.8	5.2	1.1	0.6	0.6	Fe:34.4, Cr:7.8	-	Unavoidable impurities
S	27.4	5.1	4.2	5.9	0.4	0.4	Fe:31.1, Cr:6.3, V:18.8	0.2	Unavoidable impurities
T	29.6	44.7	3.7	0.5	0.5	0.6	Fe:8.3, Cr:7.5, Cr:3.8	0.5	Unavoidable impurities
U	26.3	3.4	4.5	1.3	0.4	0.4	Fe:57.1, Cr:6.2	-	Unavoidable impurities
V	-	-	5.2	2.2	0.4	0.4	Cr:5.3, V:5.6, Nb: 1.1	-	Fe and unavoidable impurities
W	57.1	18.6	19.8	3.0	0.4	1.0	-	-	Unavoidable impurities

[Table 2]

Test material No.	Molten metal No.	Chemical composition (% by mass)									Remarks
		W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance***	
1	A	64.6	21.9	4.9	2.4	0.3	0.5	Cr:4.4	-	Unavoidable impurities	Inventive Example
2	B	40.1	38.6	9.3	1.7	0.1	0.4	Cr: 8.0, V: 0.3	-	Unavoidable impurities	Inventive Example
3	C	61.8	16.3	4.7	0.8	1.1	0.3	Fe: 7.1, Cr: 2.7, V: 4.3	-	Unavoidable impurities	Inventive Example
4	D	48.6	17.3	6.4	1.6	0.4	1.0	Fe: 13.9, Cr: 7.9, Nb:2.8	-	Unavoidable impurities	Inventive Example
5	E	37.2	20.4	11.4	1.9	2.1	0.4	Fe: 20.1, Cr: 5.4, V: 0.7, Nb:0.4	-	Unavoidable impurities	Inventive Example

(continued)

Test material No.	Molten metal No.	Chemical composition (% by mass)									Remarks
		W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance***	
6	F	46.4	21.7	5.3	2.2	0.4	0.4	Fe: 17.7, Cr: 4.8, V: 0.2, Nb:0.8	0.1	Unavoidable impurities	Inventive Example
7	G	40.0	26.1	8.4	2.0	0.6	0.1	Fe: 21.9, Cr:0.9	-	Unavoidable impurities	Inventive Example
8	H	49.7	19.8	2.5	1.6	0.3	0.3	Fe: 19.0, Cr:5.9	-	Unavoidable impurities	Inventive Example
9	I	27.6	23.0	14.5	1.0	0.3	0.2	Fe: 27.5, Cr:5.1	0.6	Unavoidable impurities	Inventive Example
10	J	47.0	24.5	8.6	1.9	0.4	0.3	Fe: 9.2, Cr:7.8	0.3	Unavoidable impurities	Inventive Example
11	K	45.0	22.8	7.8	1.9	0.4	0.3	Fe: 16.0, Cr:5.8	-	Unavoidable impurities	Inventive Example
11a*		24.1	36.1	6.6	1.4	0.6	0.4	Fe: 23.9, Cr:6.9	-	Unavoidable impurities	Reference
11b**		19.6	41.1	5.6	1.2	0.5	0.4	Fe: 24.1, Cr:7.5	-	Unavoidable impurities	Reference
12	L	42.5	33.4	4.2	1.8	0.2	0.4	Fe: 13.8, Cr:3.7	-	Unavoidable impurities	Inventive Example
13	M	44.4	15.4	4.9	2.0	0.5	2.4	Fe: 21.5, Cr:8.9	-	Unavoidable impurities	Inventive Example
14	N	46.2	25.0	4.5	1.9	0.4	0.2	Fe: 17.8, Cr:4.0	-	Unavoidable impurities	Inventive Example
15	O	44.7	18.7	7.0	3.0	0.1	0.2	Fe: 20.5, Cr: 4.6, V: 1.0, Nb:0.2	-	Unavoidable impurities	Inventive Example
16	P	69.4	7.2	11.2	1.6	0.3	0.3	Fe: 10.0	-	Unavoidable impurities	Inventive Example

(continued)

Test material No.	Molten metal No.	Chemical composition (% by mass)									Remarks
		W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance***	
17	Q	39.2	8.3	6.6	1.4	0.6	1.4	Fe: 35.0, Cr:7.4	-	Unavoidable impurities	Inventive Example
18	R	12.5	37.2	5.3	1.2	0.6	0.6	Fe: 34.6, Cr:8.0	-	Unavoidable impurities	Comparative Example
19	S	27.3	5.5	5.8	5.7	0.4	0.4	Fe: 31.4, Cr: 6.5, V: 16.7	0.3	Unavoidable impurities	Comparative Example
20	T	30.0	44.6	3.7	0.4	0.5	0.6	Fe: 8.2, Cr: 7.5, V: 4.0	0.5	Unavoidable impurities	Comparative Example
21	U	29.0	2.7	4.5	1.2	0.4	0.4	Fe: 55.6, Cr:6.2	-	Unavoidable impurities	Comparative Example
22	V	-	-	5.2	2.2	0.4	0.4	Cr: 5.3, V: 5.6, Nb:1.1	-	Fe and unavoidable impurities	Conventional Example
23	W	69.5	10.7	14.6	3.5	0.4	1.0	-	-	Unavoidable impurities	Inventive Example

*) At position 18 mm from outer surface of heat-treated test material (roll outer layer material)
**) At position 38 mm from outer surface of heat-treated test material (roll outer layer material)
***) Balance: S, P, N, B, Ti, Al, etc. (not analyzed)

[Table 3]

Test material No.	Molten metal No.	Wear resistance		Remarks
		Wear resistance ratio Reference = 1.0	Evaluation	
1	A	4.4	⊙	Inventive Example
2	B	3.3	⊙	Inventive Example
3	C	4.2	⊙	Inventive Example
4	D	4.1	⊙	Inventive Example
5	E	3.0	⊙	Inventive Example
6	F	4.3	⊙	Inventive Example
7	G	3.3	⊙	Inventive Example
8	H	4.2	⊙	Inventive Example
9	I	2.5	○	Inventive Example
10	J	4.3	⊙	Inventive Example

(continued)

Test material No.	Molten metal No.	Wear resistance		Remarks
		Wear resistance ratio Reference = 1.0	Evaluation	
11	K	4.3	⊙	Inventive Example
11a*		1.9	-	Reference
11b**		0.8	-	Reference
12	L	3.5	⊙	Inventive Example
13	M	3.9	⊙	Inventive Example
14	N	4.0	⊙	Inventive Example
15	O	4.7	⊙	Inventive Example
16	P	5.2	⊙	Inventive Example
17	Q	2.3	○	Inventive Example
18	R	1.2	×	Comparative Example
19	S	Cracked	×	Comparative Example
20	T	1.3	×	Comparative Example
21	U	1.5	×	Comparative Example
22	V	1.0 (reference)	-	Conventional Example
23	W	2.1	○	Inventive Example

*) At position 18 mm from outer surface of heat-treated test material (roll outer layer material)
**) At position 38 mm from outer surface of heat-treated test material (roll outer layer material)

[0136] In all the Inventive Examples in Example 1, the wear resistance ratio was 2.1 or more, and the wear resistance was significantly improved as compared with that in the Conventional Example (high-speed tool steel rolls). In the Comparative Examples outside the scope of the present invention, cracking occurred during the test, or the wear resistance ratio was less than 2. The degree of improvement in wear resistance relative to the Conventional Example was low.

[0137] The structures in Inventive Examples (No. 13 and No. 5) were observed and shown in Fig. 1. A test piece for structure observation was cut from each of the heat-treated test materials such that an observation surface is located at a position 5 mm from the outer surface of the test material in the radial direction, and the observation surface was observed under a scanning electron microscope (magnification: 250X) to obtain a backscattered electron image. White regions were found to be primary phase carbides (M_6C-type carbides in which W is concentrated). As can be seen, in each of these Inventive Examples, the primary phase carbides are dispersed on the outer surface side of the test material (the sleeve-shaped outer layer material for rolls) at high density.

[0138] For reference purposes, test pieces for composition analysis were cut from test material No. 11 (Inventive Example). Specifically, the test pieces were cut from positions 18 mm and 38 mm (18 mm and 38 mm positions) from the outer surface of the heat-treated test material (sleeve-shaped outer layer material for rolls) in the radial direction. Each test piece was cut so as to have a thickness of 5 mm measured from the 18 mm or 38 mm position in the radial direction and have a size of 10 mm × 10 mm in a plane parallel to the outer surface. The composition at each of these positions was analyzed by chemical analysis. The results obtained are also shown in Table 2.

[0139] Wear test pieces were cut from test material No. 11 (Inventive Example). Specifically, a wear test piece was cut such that its test surface was located at a position 18 mm (18 mm position) from the outer surface of the heat-treated test material in the radial direction, and another wear test piece was cut such that its test surface was located at a position (38 mm position) within the range of 38 to 48mm from the outer surface in the radial direction. The wear test was performed under the same conditions as described above to measure the wear loss. The results obtained are also shown in Table 3.

[0140] As can be seen from Table 2, mainly W is concentrated on the outer surface of the test material (the sleeve-shaped outer layer material for rolls). The ratio of W is smaller at the position (18 mm position) 18 mm from the outer surface in the radial direction and the position (38 mm position) 38 mm from the outer surface in the radial direction, and the ratios of Co, Fe, etc. are larger at these positions, so that the test material clearly has a graded composition. Therefore, as can be seen from Table 3, the wear resistance is lower at the position (18 mm position) 18 mm from the outer surface in the radial direction and the position (38 mm position) 38 mm from the outer surface in the radial direction than in a region within 10 mm from the outer surface in the radial direction.

[Example 2]

[0141] Examples for the second embodiment described above will be described.

[0142] A molten metal having one of compositions shown in Table 4 was melted using a high-frequency induction furnace and cast to produce a sleeve-shaped outer layer material for rolls (outer diameter: 250 mmϕ, radial wall thickness: 55 mm) used as a test material by the centrifugal casting method. The casting temperature was 1,450 to 1,550°C, and the centrifugal force in multiples of gravity was 140 to 220 G. In one test material (molten metal No. S), significant segregation of carbides on the inner surface was found, and therefore the centrifugal force was reduced to 60 G in order to reduce the segregation. After the casting, each test material was subjected to quenching treatment in which the test material was reheated to 1,050 to 1,200°C, held for 10 h, and cooled to 100°C or lower and then subjected to tempering treatment in which the test material was heated to 400 to 560°C, held at this temperature, and then cooled. The quenching treatment and the tempering treatment were repeated once or twice. In this manner, the hardness at a position 5 mm from the outer surface of the test material in the thickness direction was adjusted to about 85 to 100HS. A molten metal (molten metal No. V) having the composition of a commercial centrifugal cast outer layer material (high-speed tool roll-based composition: 2.2% C-0.4% Si-0.4% Mn-5.3% Cr-5.2% Mo-5.6% V-1.1% Nb) used for hot finishing rolling mill rolls for steel was melted. Then the molten metal was cast to produce a sleeve-shaped outer layer material for rolls in the same manner as described above, and the cast sleeve-shaped outer layer material was subjected to heat treatment to obtain a test material (hardness: 85HS) in Conventional Example (test material No. 22) .

[0143] Test pieces for composition analysis, test pieces for a wear test, test pieces for Young's modulus measurement, and roll test pieces for rolling load evaluation were cut from each of the heat-treated test materials. The test material No. 19 was very brittle, and it was very difficult to cut the test material.

[0144] Each test piece for composition analysis was cut from a corresponding heat-treated test material as follows. The outer surface of the test material was ground to a depth of 5 mm in the radial direction, and a test piece having a thickness of 5 mm measured in the radial direction from the ground outer surface and having a size of 10 mm × 10 mm in a plane parallel to the outer surface was cut. Analysis of elemental components was performed using the test pieces obtained. The analysis methods used were chemical analysis. A combustion method was used for C, and a gravimetric method was used for Si and W. An atomic absorption method was used for Mn, Cr, and Mo, and a volumetric method was used for Co. The volumetric method or the atomic absorption method was used for Fe.

[0145] The results obtained are shown in Table 5.

[0146] Each wear test piece (outer diameter: 60 mmϕ × width 10 mm) was cut from a corresponding heat-treated test piece such that the widthwise center of the wear test piece was located at a position 10 mm from the outer surface of the test material in the radial direction. As shown in Fig. 7, the wear test was performed using the test piece (wear test piece) and a counterpart (material: S45C, outer diameter 190 mmϕ × width 15mm) by a two-disc slip rolling method.

[0147] In the wear test, while the test piece was water-cooled, the counterpart heated to 850°C was pressed against the test piece rotated at revolutions per minute of 700 rpm (peripheral speed: 2.1 m/s) under a load of 980 N and rotated at a slip ratio of 14.2%. The counterpart was changed every 21,000 revolutions of the test piece, and the test piece was rotated until the number of total revolutions reached 168,000. After completion of the test, the wear loss of the wear test piece was examined. The wear loss in the Comparative Example (test material No. 22) was used as a reference (1.0). The wear loss obtained for each test material was used to compute the ratio of the wear loss with respect to the reference (wear resistance ratio = (wear loss in Comparative Example)/(wear loss of test material)), and the wear resistance was evaluated. When the wear resistance ratio was 3 or more, the wear resistance was rated "⊙." When the wear resistance ratio was 2 or more and less than 3, the wear resistance was rated "○." When the wear resistance ratio was less than 2, the wear resistance was rated "×." The symbol ⊙ represents very good, and the symbol ○ represents good. The symbol × represents poor.

[0148] Each test piece for Young's modulus measurement (ϕ16 × 5 mm thickness) was cut from a corresponding heat-treated test material as follows. The outer surface of the test material was ground to a depth of 5 mm in the radial direction, and a test piece having a thickness of 5 mm measured in the radial direction from the ground outer surface and having a diameter of ϕ16 mm in a plane parallel to the outer surface was cut. The Young's modulus was measured by an ultrasonic method using the test piece obtained.

[0149] The outer surface of each heat-treated test material was ground to a depth of 10 mm in the radial direction, and a roll test piece (outer diameter 230 mmϕ × width 40 mm) with the ground surface serving as its outer surface was cut. The roll test piece was shrink-fitted to a forged carbon steel-made shaft member to prepare a composite roll for rolling load evaluation, as shown in Fig. 8. The composite roll was placed in a 4Hi sheet cold rolling mill (backup rolls: outer diameter 500 mmϕ × barrel length 40 mm). A steel sheet (sheet width 20 mm, sheet thickness 1.5 mm × length 20 m) with a tensile strength of 590 MPa was used as a rolled material, and a rolling load during cold rolling at a thickness reduction ratio of 20% was measured. Using the measurement results, a percentage reduction in rolling load of each roll test piece with respect to the rolling load of test material No. 22, i.e., the Conventional Example, (= 100 - rolling load of roll test piece/rolling load of Conventional Example × 100) was computed. When the reduction in rolling load was 10% or more, the roll test piece was judged as having the effect of reducing the rolling load.

[0150] The results obtained are shown in Table 6.

[Table 4]

Molten metal No.	Chemical composition (% by mass)								
	W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance
A	55.7	31.2	4.3	2.3	0.4	0.6	Cr:4.9	-	Unavoidable impurities
B	29.9	50.4	8.7	1.6	0.1	0.5	Cr:8.2, V:0.3	-	Unavoidable impurities
C	52.6	22.4	4.1	0.7	1.2	0.6	Fe:8.7, Cr:3.6, V: 5.5	-	Unavoidable impurities
D	38.6	24.5	5.5	1.6	0.4	1.2	Fe:15.8, Cr:9.2, Nb:3.2	-	Unavoidable impurities
E	26.5	28.8	9.0	1.9	2.1	0.4	Fe:24.3, Cr:6.0, V:0.8, Nb:0.4	-	Unavoidable impurities
F	34.9	29.1	4.8	2.1	0.5	0.6	Fe:20.5, Cr:5.4, V:0.5, Nb:1.6	0.2	Unavoidable impurities
G	31.4	33.5	7.2	1.9	0.7	0.3	Fe:23.6, Cr:1.4	-	Unavoidable impurities
H	38.6	28.2	1.9	1.6	0.3	0.4	Fe:21.8, Cr:6.6	-	Unavoidable impurities
I	22.1	29.1	12.2	0.9	0.4	0.4	Fe:28.7, Cr:5.6	0.8	Unavoidable impurities
J	38.6	31.2	7.4	1.9	0.4	0.4	Fe:10.9, Cr:8.6	0.5	Unavoidable impurities
K	33.2	30.0	6.7	1.6	0.4	0.5	Fe:21.2, Cr:6.5	-	Unavoidable impurities
L	34.3	37.6	3.9	1.7	0.3	0.3	Fe:17.3, Cr:4.5	-	Unavoidable impurities
M	34.2	21.8	4.7	1.9	0.5	2.6	Fe:24.4, Cr:9.8	-	Unavoidable impurities
N	35.3	31.1	4.1	1.8	0.4	0.4	Fe:21.6, Cr:4.8	-	Unavoidable impurities
O	29.6	27.6	6.1	2.6	0.2	0.3	Fe:25.7, Cr:5.2, V:1.8, Nb:0.6	--	Unavoidable impurities
P	52.3	18.3	9.6	1.4	0.4	0.4	Fe:17.4	-	Unavoidable impurities
Q	32.4	12.4	5.8	1.6	0.6	1.4	Fe:38.4, Cr:7.2	-	Unavoidable impurities
R	12.3	37.8	5.2	1.1	0.6	0.6	Fe:34.4, Cr:7.8	-	Unavoidable impurities
S	27.4	5.1	4.2	5.9	0.4	0.4	Fe:31.1, Cr:6.3, V:18.8	0.2	Unavoidable impurities
T	29.6	44.7	3.7	0.5	0.5	0.6	Fe:8.3, Cr:7.5, Cr:3.8	0.5	Unavoidable impurities
U	26.3	3.4	4.5	1.3	0.4	0.4	Fe:57.1, Cr:6.2	-	Unavoidable impurities
V	-	-	5.2	2.2	0.4	0.4	Cr:5.3, V:5.6, Nb: 1.1	-	Fe and unavoidable impurities
W	57.1	18.6	19.8	3.0	0.4	1.0	-	-	Unavoidable impurities
X	53.1	20.4	10.3	2.7	0.6	0.7	Fe:11.3, Cr:0.8	-	Unavoidable impurities
Y	54.6	16.7	11.9	2.7	0.3	0.5	Fe:13.2	-	Unavoidable impurities
Z	56.3	12.0	14.2	3.1	0.6	0.4	Fe:13.3	-	Unavoidable impurities
α	56.9	12.2	16.5	2.6	0.5	0.4	Fe:10.8	-	Unavoidable impurities

(continued)

Molten metal No.	Chemical composition (% by mass)								
	W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance
β	57.6	9.9	19.3	3.1	0.3	0.4	Fe:9.3	-	Unavoidable impurities
γ	56.6	24.4	13.8	3.3	0.8	1.0	-	-	Unavoidable impurities
δ	54.1	26.6	12.7	1.7	2.1	2.7	-	-	Unavoidable impurities

[Table 5]

Test material No.	Molten metal No.	Chemical composition (% by mass)									(%W+%Mo)/(%Co+%Fe)	Remarks
		W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance***		
1	A	64.6	21.9	4.9	2.4	0.3	0.5	Cr:4.4	-	Unavoidable impurities	3.2	Inventive Example
2	B	40.1	38.6	9.3	1.7	0.1	0.4	Cr:8.0, V:0.3	-	Unavoidable impurities	1.3	Inventive Example
3	C	61.8	16.3	4.7	0.8	1.1	0.3	Fe:7.1, Cr:2.7, V:4.3	-	Unavoidable impurities	2.8	Inventive Example
4	D	48.6	17.3	6.4	1.6	0.4	1.0	Fe:13.9, Cr:7.9, Nb:2.8	-	Unavoidable impurities	1.8	Inventive Example
5	E	37.2	20.4	11.4	1.9	2.1	0.4	Fe:20.1, Cr:5.4, V:0.7, Nb:0.4	-	Unavoidable impurities	1.2	Inventive Example
6	F	46.4	21.7	5.3	2.2	0.4	0.4	Fe:17.7, Cr:4.8, V:0.2, Nb:0.8	0.1	Unavoidable impurities	1.3	Inventive Example
7	G	40.0	26.1	8.4	2.0	0.6	0.1	Fe:21.9, Cr:0.9	-	Unavoidable impurities	1.0	Comparative Example
8	H	49.7	19.8	2.5	1.6	0.3	0.3	Fe:19.0, Cr:5.9	-	Unavoidable impurities	1.3	Inventive Example
9	I	27.6	23.0	14.5	1.0	0.3	0.2	Fe:27.5, Cr:5.1	0.6	Unavoidable impurities	0.8	Comparative Example
10	J	47.0	24.5	8.6	1.9	0.4	0.3	Fe:9.2, Cr:7.8	0.3	Unavoidable impurities	1.6	Inventive Example
11	K	45.0	22.8	7.8	1.9	0.4	0.3	Fe:16.0, Cr:5.8	-	Unavoidable impurities	1.4	Inventive Example
11a*		24.1	36.1	6.6	1.4	0.6	0.4	Fe:23.9, Cr:6.9	-	Unavoidable impurities	-	Reference
11b**		19.6	41.1	5.6	1.2	0.5	0.4	Fe:24.1, Cr:7.5	-	Unavoidable impurities	-	Reference
12	L	42.5	33.4	4.2	1.8	0.2	0.4	Fe:13.8, Cr:3.7	-	Unavoidable impurities	1.0	Comparative Example

(continued)

Test material No.	Molten metal No.	Chemical composition (% by mass)									(%W+%Mo)/ (%Co+%Fe)	Remarks
		W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance***		
13	M	44.4	15.4	4.9	2.0	0.5	2.4	Fe:21.5, Cr:8.9	-	Unavoidable impurities	1.3	Inventive Example
14	N	46.2	25.0	4.5	1.9	0.4	0.2	Fe:17.8, Cr:4.0	-	Unavoidable impurities	1.2	Inventive Example
15	O	44.7	18.7	7.0	3.0	0.1	0.2	Fe:20.5, Cr:4.6, V:1.0, Nb:0.2	-	Unavoidable impurities	1.3	Inventive Example
16	P	69.4	7.2	11.2	1.6	0.3	0.3	Fe:10.0	-	Unavoidable impurities	4.7	Inventive Example
17	Q	39.2	8.3	6.6	1.4	0.6	1.4	Fe:35.0, Cr:7.4	-	Unavoidable impurities	1.1	Comparative Example
18	R	12.5	37.2	5.3	1.2	0.6	0.6	Fe:34.6, Cr:8.0	-	Unavoidable impurities	0.2	Comparative Example
19	S	27.3	5.5	5.8	5.7	0.4	0.4	Fe:31.4, Cr:6.5, V:16.7	0.3	Unavoidable impurities	0.9	Comparative Example
20	T	30.0	44.6	3.7	0.4	0.5	0.6	Fe:8.2, Cr:7.5, V:4.0	0.5	Unavoidable impurities	0.6	Comparative Example
21	U	29.0	2.7	4.5	1.2	0.4	0.4	Fe:55.6, Cr:6.2	-	Unavoidable impurities	0.6	Comparative Example
22	V	-	-	5.2	2.2	0.4	0.4	Cr:5.3, V:5.6, Nb:1.1	-	Fe and unavoidable impurities	-	Conventional Example
23	W	69.5	10.7	14.6	3.5	0.4	1.0	-	-	Unavoidable impurities	7.9	Inventive Example
24	X	69.0	11.3	10.3	2.8	0.4	0.3	Fe:5.3, Cr:0.5	-	Unavoidable impurities	4.8	Inventive Example
25	Y	69.2	8.1	12.5	2.9	0.3	0.5	Fe:6.4	-	Unavoidable impurities	5.6	Inventive Example
26	Z	69.4	6.4	13.1	3.3	0.6	0.4	Fe:6.7	-	Unavoidable impurities	6.3	Inventive Example

(continued)

Test material No.	Molten metal No.	Chemical composition (% by mass)									(%W+%Mo)/(%Co+%Fe)	Remarks
		W	Co	Mo	C	Si	Mn	Fe, Cr, V, Nb	Ni	Balance***		
27	α	69.7	6.2	14.3	2.9	0.5	0.4	Fe:5.9	-	Unavoidable impurities	6.9	Inventive Example
28	β	70.0	5.8	14.5	3.4	0.5	0.6	Fe:5.1	-	Unavoidable impurities	7.8	Inventive Example
29	γ	68.2	12.9	13.2	3.5	0.9	1.2	-	-	Unavoidable impurities	6.3	Inventive Example
30	δ	64.2	15.8	12.9	1.9	2.3	2.8	-	-	Unavoidable impurities	4.9	Inventive Example

*) At position 18 mm from outer surface of heat-treated test material (roll outer layer material)
**) At position 38 mm from outer surface of heat-treated test material (roll outer layer material)
***) Balance: S, P, N, B, Ti, Al, etc. (not analyzed)

[Table 6]

Test material No.	Molten metal No.	Wear resistance		Evaluation of Young's modulus		Percentage reduction in rolling load with respect to Conventional Example (%)	Remarks
		Wear resistance ratio Reference = 1.0	Evaluation	Young's modulus (GPa)	Evaluation		
1	A	4.4	⊙	443	○	40	Inventive Example
2	B	3.3	⊙	278	○	12	Inventive Example
3	C	4.2	⊙	418	○	30	Inventive Example
4	D	4.1	⊙	318	○	19	Inventive Example
5	E	3.0	⊙	271	○	11	Inventive Example
6	F	4.3	⊙	304	○	17	Inventive Example
7	G	3.3	⊙	266	×	9	Comparative Example
8	H	4.2	⊙	325	○	20	Inventive Example
9	I	2.5	○	206	×	0	Comparative Example
10	J	4.3	⊙	308	○	18	Inventive Example
11	K	4.3	⊙	295	○	15	Inventive Example
11a*		1.9	-	-	-	-	Reference
11b**		0.8	-	-	-	-	Reference
12	L	3.5	⊙	261	×	8	Comparative Example
13	M	3.9	⊙	292	○	14	Inventive Example
14	N	4.0	⊙	303	○	18	Inventive Example
15	O	4.7	⊙	293	○	14	Inventive Example
16	P	5.2	⊙	489	○	41	Inventive Example
17	Q	2.3	○	262	×	7	Comparative Example
18	R	1.2	×	213	×	0	Comparative Example

(continued)

Test material No.	Molten metal No.	Wear resistance		Evaluation of Young's modulus		Percentage reduction in rolling load with respect to Conventional Example (%)	Remarks
		Wear resistance ratio Reference = 1.0	Evaluation	Young's modulus (GPa)	Evaluation		
19	S	Cracked	×	205	×	0	Comparative Example
20	T	1.3	×	216	×	0	Comparative Example
21	U	1.5	×	212	×	0	Comparative Example
22	V	1.0 (reference)	-	221	×	0 (reference)	Conventional Example
23	W	2.1	○	490	○	43	Inventive Example
24	X	4.3	⊙	481	○	40	Inventive Example
25	Y	4.9	⊙	491	○	44	Inventive Example
26	Z	5.1	⊙	495	○	48	Inventive Example
27	α	5.5	⊙	497	○	53	Inventive Example
28	β	5.8	⊙	500	○	57	Inventive Example
29	γ	2.2	○	489	○	42	Inventive Example
30	δ	2.9	○	440	○	36	Inventive Example

*) At position 18 mm from outer surface of heat-treated test material (roll outer layer material)
**) At position 38 mm from outer surface of heat-treated test material (roll outer layer material)

[0151] In all the Inventive Examples in Example 2, the wear resistance ratio was 2.1 or more, and the wear resistance was significantly improved as compared with that in the Conventional Example (high-speed tool steel rolls). Moreover, the rolling load was lower by at least 10% than that of the Conventional Example, so that a good rolling load reduction effect was obtained. In the Comparative Examples outside the scope of the present invention, cracking occurred during the test, or the wear resistance ratio was less than 2. Therefore, the degree of improvement in wear resistance relative to the Conventional Example was low. Moreover, the Young's modulus was less than 270 GPa, and therefore the rolling load reduction effect was low.

[0152] The structures in Inventive Examples (No. 13 and No. 5) were observed and shown in Fig. 6. A test piece for structure observation was cut from each of the heat-treated test materials such that an observation surface was located at a position 5 mm from the outer surface of the test material in the radial direction, and the observation surface was observed under a scanning electron microscope (magnification: 250X) to obtain a backscattered electron image. White regions were found to be primary phase carbides (M_6C-type carbides in which W is concentrated). As can be seen, in each of these Inventive Examples, the primary phase carbides are dispersed on the outer surface side of the test material (the sleeve-shaped outer layer material for rolls) at high density.

[0153] For reference purposes, test pieces for composition analysis were cut from test material No. 11 (Inventive

Example). Specifically, the test pieces were cut from positions 18 mm and 38 mm (18 mm and 38 mm positions) from the outer surface of the heat-treated test material (sleeve-shaped outer layer material for rolls) in the radial direction. Each test piece was cut so as to have a thickness of 5 mm measured from the 18 mm or 38 mm position in the radial direction and have a size of 10 mm × 10 mm in a plane parallel to the outer surface. The composition at each of these positions was analyzed by chemical analysis. The results obtained are also shown in Table 5.

[0154] Wear test pieces were cut from test material No. 11 (Inventive Example). Specifically, a wear test piece was cut such that its test surface was located at a position 18 mm (18 mm position) from the outer surface of the heat-treated test material in the radial direction, and another wear test piece was cut such that its test surface was located at a position (38 mm position) within the range of 38 to 48mm from the outer surface in the radial direction. The wear test was performed under the same conditions as described above to measure the wear loss. The results obtained are also shown in Table 6.

[0155] As can be seen from Table 5, mainly W is concentrated on the outer surface of the test material (the sleeve-shaped outer layer material for rolls). The ratio of W is smaller at the position (18 mm position) 18 mm from the outer surface in the radial direction and the position (38 mm position) 38 mm from the outer surface in the radial direction, and the ratios of Co, Fe, etc. are larger at these positions, so that the test material clearly has a graded composition. Therefore, as can be seen from Table 6, the wear resistance is lower at the position (18 mm position) 18 mm from the outer surface in the radial direction and the position (38 mm position) 38 mm from the outer surface in the radial direction than in a region within 10 mm from the outer surface in the radial direction.

Claims

1. An outer layer material for rolling mill rolls, the outer layer material being made of a W-Co-based alloy,
wherein the outer layer material has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of a roll toward an inner circumferential side of the roll, and wherein a surface of the outer layer material that is located at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %,

W: 25 to 70%,
Co: 5 to 45%,
C: 0.6 to 3.5%,
Si: 0.05 to 3%,
Mn: 0.05 to 3%, and
Mo: 1 to 15%,

with the balance being unavoidable impurities.

2. The outer layer material for rolling mill rolls according to claim 1,
wherein the composition further contains, in mass %, one or two or more selected from

Fe: 5 to 40%,
Cr: 0.1 to 10%,
V: 0.1 to 6%, and
Nb: 0.1 to 3%.

3. The outer layer material for rolling mill rolls according to claim 1 or 2,
wherein the composition further contains, in mass %,
Ni: 0.05 to 3%.

4. The outer layer material for rolling mill rolls according to any of claims 1 to 3,
wherein the outer layer material for rolling mill rolls is formed by centrifugal casting.

5. A composite roll for rolling, comprising: an outer layer; and an inner layer integrally fused to the outer layer,
wherein the outer layer is the outer layer material for rolling mill rolls according to any of claims 1 to 3.

6. A composite roll for rolling, comprising: an outer layer; an intermediate layer integrally fused to the outer layer; and an inner layer integrally fused to the intermediate layer,
wherein the outer layer is the outer layer material for rolling mill rolls according to any of claims 1 to 3.

7. The composite roll for rolling according to claim 5 or 6,
wherein the outer layer is formed by centrifugal casting.

8. An outer layer material for rolling mill rolls, the outer layer material being made of a W-Co-based alloy, wherein the outer layer material has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of a roll toward an inner circumferential side of the roll, wherein the outer layer material in a surface layer at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %,

W: 25 to 70%,
Co: 5 to 45%,
C: 0.6 to 3.5%,
Si: 0.05 to 3%,
Mn: 0.05 to 3%, and
Mo: 1 to 15%,

with the balance being unavoidable impurities, and wherein the contents of W, Co, Mo, and Fe satisfy the following formula [1]:

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \qquad [1]$$

where %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements.

9. The outer layer material for rolling mill rolls according to claim 8,
wherein the Young's modulus of the outer layer material in the surface layer at the position corresponding to the maximum diameter during use for rolling is from 270 GPa to 500 GPa inclusive.

10. The outer layer material for rolling mill rolls according to claim 8 or 9,
wherein the composition further contains, in mass %,
one or two or more selected from

Fe: 5 to 40%,
Cr: 0.1 to 10%,
V: 0.1 to 6%, and
Nb: 0.1 to 3%.

11. The outer layer material for rolling mill rolls according to any of claims 8 to 10,
wherein the composition further contains, in mass %,
Ni: 0.05 to 3%.

12. The outer layer material for rolling mill rolls according to any of claims 8 to 11,
wherein the outer layer material for rolling mill rolls is formed by centrifugal casting.

13. A composite roll for rolling, comprising: an outer layer; and an inner layer integrally fused to the outer layer,
wherein the outer layer is made of a W-Co-based alloy and has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of the roll toward an inner circumferential side of the roll, wherein a material of the outer layer in a surface layer at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %,

W: 25 to 70%,
Co: 5 to 45%,
C: 0.6 to 3.5%,
Si: 0.05 to 3%,
Mn: 0.05 to 3%, and
Mo: 1 to 15%,

with the balance being unavoidable impurities, and wherein the contents of W, Co, Mo, and Fe satisfy the following formula [1]:

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \qquad [1]$$

where %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements.

14. The composite roll for rolling according to claim 13,
wherein the Young's modulus of the material of the outer layer in the surface layer at the position corresponding to the maximum diameter during use for rolling is from 270 GPa to 500 GPa inclusive.

15. The composite roll for rolling according to claim 13 or 14,
wherein the composition further contains, in mass %, one or two or more selected from

Fe: 5 to 40%,
Cr: 0.1 to 10%,
V: 0.1 to 6%, and
Nb: 0.1 to 3%.

16. The composite roll for rolling according to any of claims 13 to 15,
the composition further contains, in mass %,
Ni: 0.05 to 3%.

17. A composite roll for rolling, comprising: an outer layer; an intermediate layer integrally fused to the outer layer; and an inner layer integrally fused to the intermediate layer,
wherein the outer layer is made of a W-Co-based alloy and has a graded composition in which the content of W decreases in a radial direction from an outer circumferential side of the roll toward an inner circumferential side of the roll, wherein a material of the outer layer in a surface layer at a position corresponding to a maximum diameter during use for rolling has a composition containing, in mass %,

W: 25 to 70%,
Co: 5 to 45%,
C: 0.6 to 3.5%,
Si: 0.05 to 3%,
Mn: 0.05 to 3%,
Mo: 1 to 15%, and
Fe: 5 to 40%,

with the balance being unavoidable impurities, and wherein the contents of W, Co, Mo, and Fe satisfy the following formula [1]:

$$1.2 \leq (\%W + \%Mo)/(\%Co + \%Fe) \leq 9.0 \qquad [1]$$

where %W, %Mo, %Co, and %Fe are the contents (% by mass) of respective elements.

18. The composite roll for rolling according to claim 17,
wherein the Young's modulus of the material of the outer layer in the surface layer at the position corresponding to the maximum diameter during use for rolling is from 270 GPa to 500 GPa inclusive.

19. The composite roll for rolling according to claim 17 or 18,
wherein the composition further contains, in mass %,
one or two or more selected from

Fe: 5 to 40%,
Cr: 0.1 to 10%,
V: 0.1 to 6%, and
Nb: 0.1 to 3%.

20. The composite roll for rolling according to any of claims 17 to 19, wherein the composition further contains, in mass %,
Ni: 0.05 to 3%.

21. The composite roll for rolling according to any of claims 13 to 20, wherein the outer layer is formed by centrifugal casting.

FIG. 1

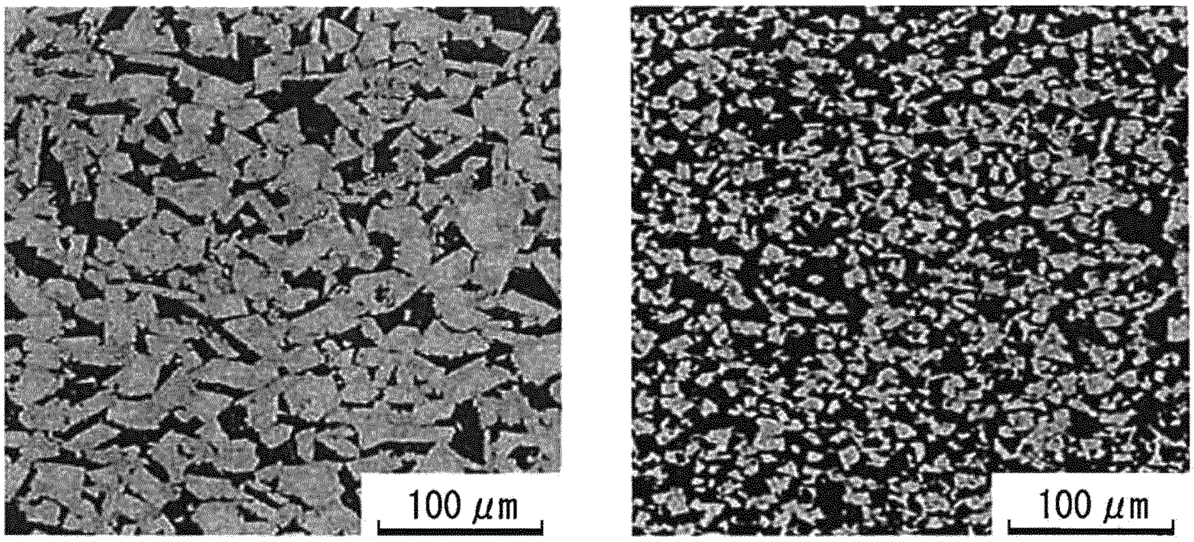

(a)
(b)
100 μm
100 μm

FIG. 2

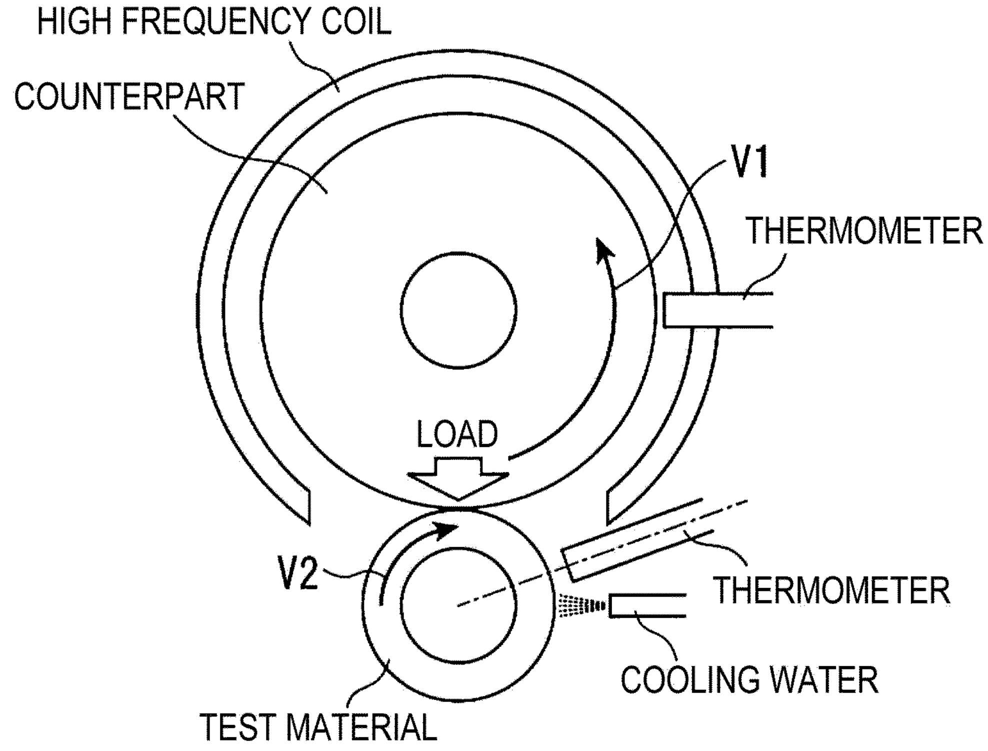

HIGH FREQUENCY COIL
COUNTERPART
V1
THERMOMETER
LOAD
V2
THERMOMETER
COOLING WATER
TEST MATERIAL

FIG. 3

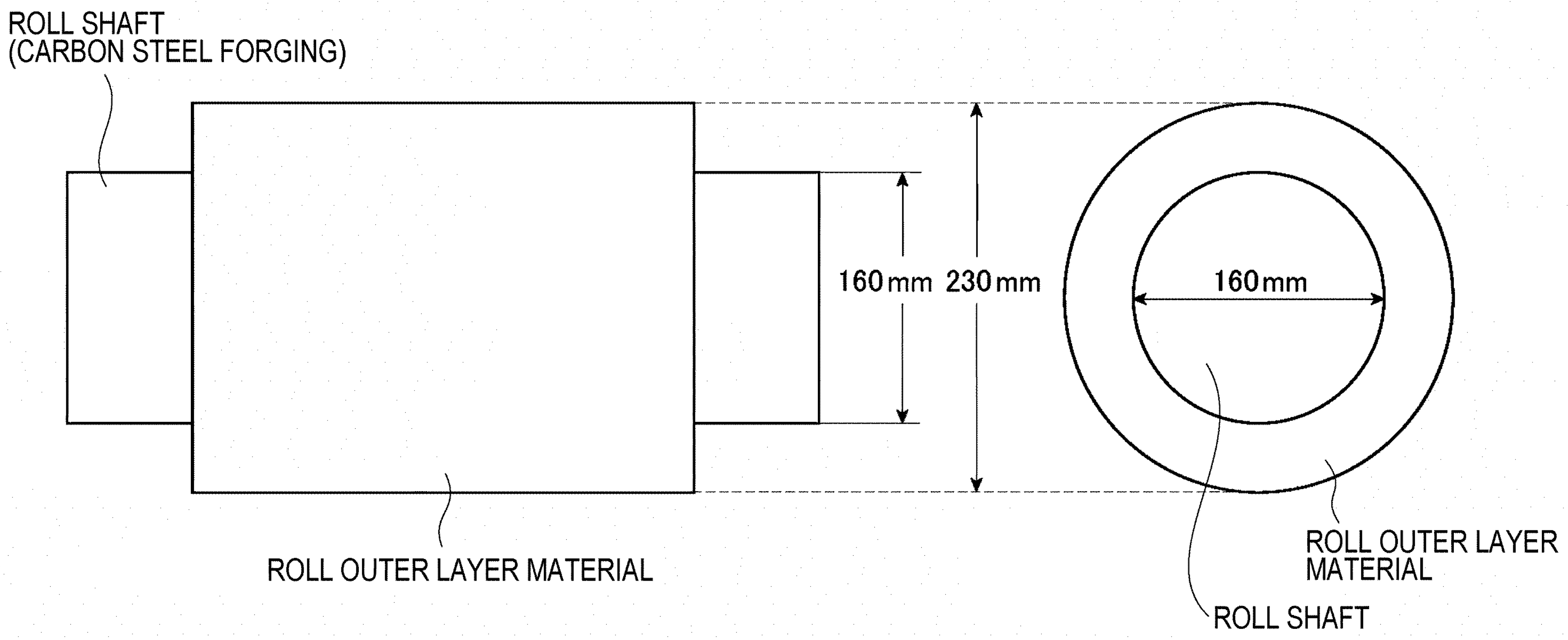

ROLL SHAFT
(CARBON STEEL FORGING)
ROLL OUTER LAYER MATERIAL
160 mm
230 mm
160 mm
ROLL OUTER LAYER MATERIAL
ROLL SHAFT

FIG. 4

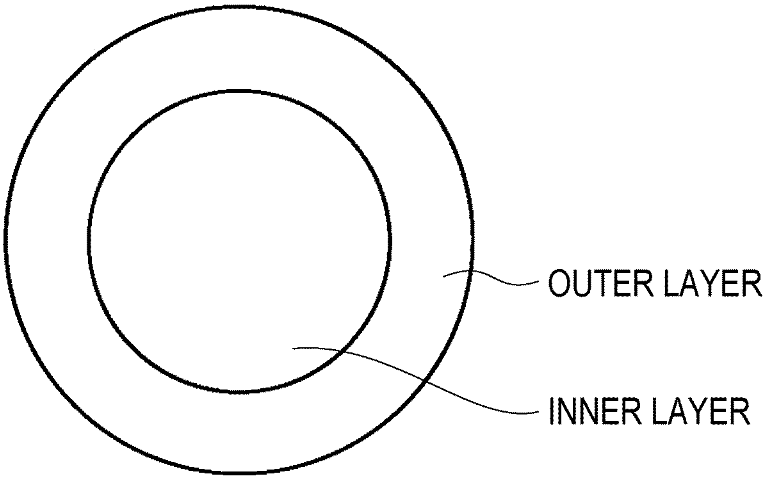

OUTER LAYER
INNER LAYER

FIG. 5

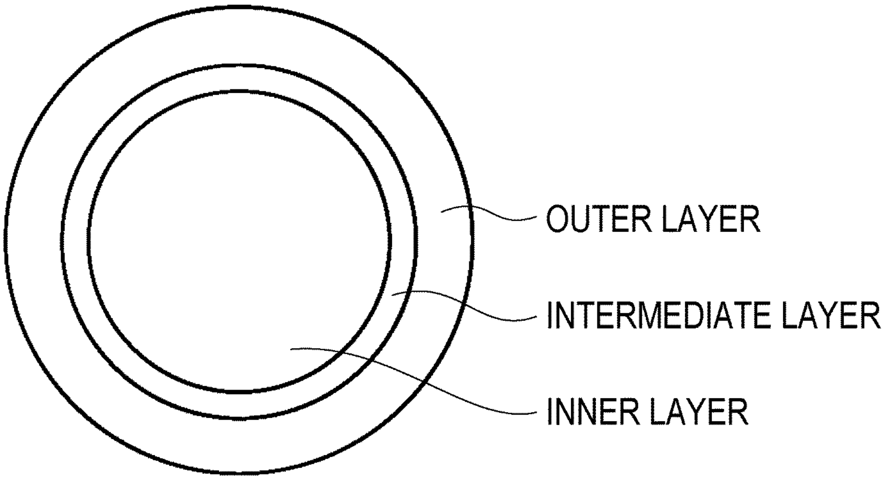

OUTER LAYER
INTERMEDIATE LAYER
INNER LAYER

FIG. 6

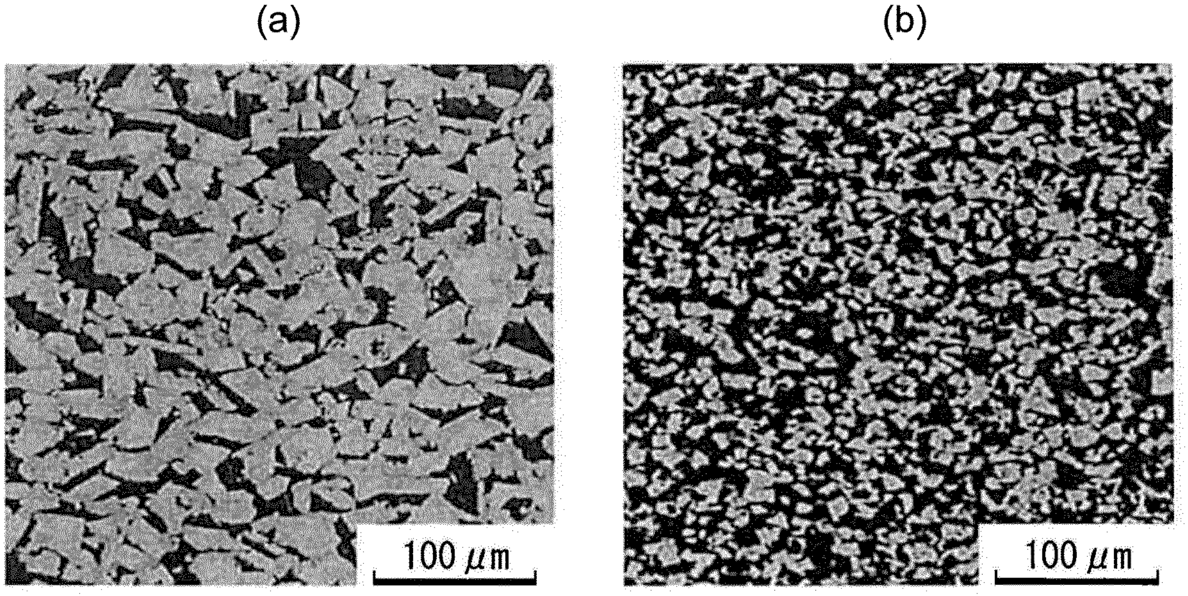
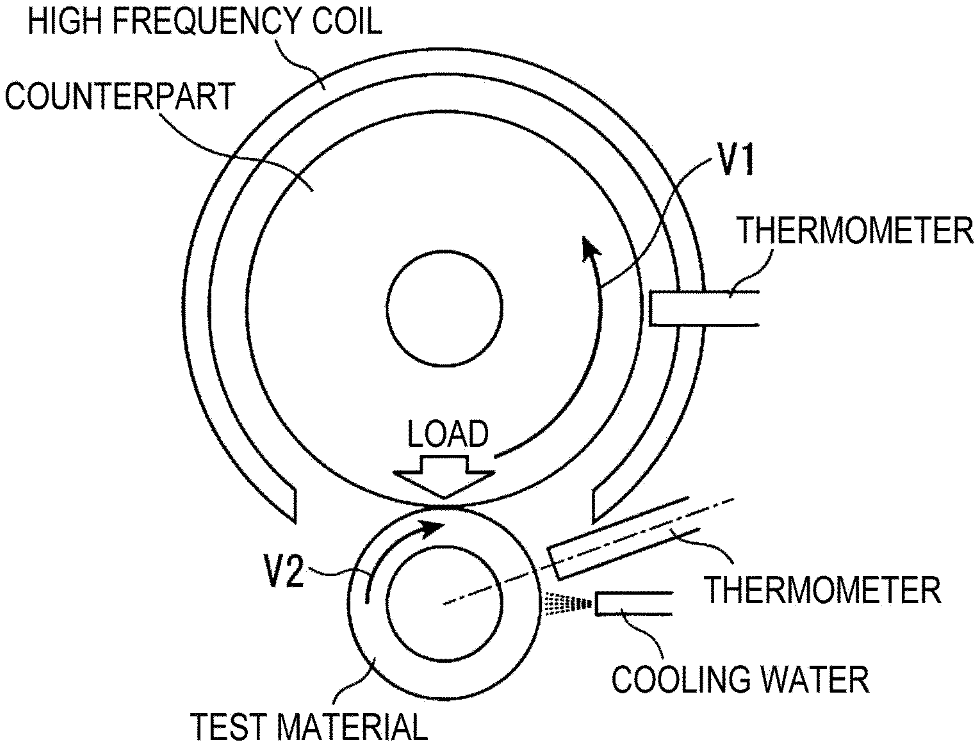

(a)
(b)
100 μm
100 μm

FIG. 7


HIGH FREQUENCY COIL
COUNTERPART
V1
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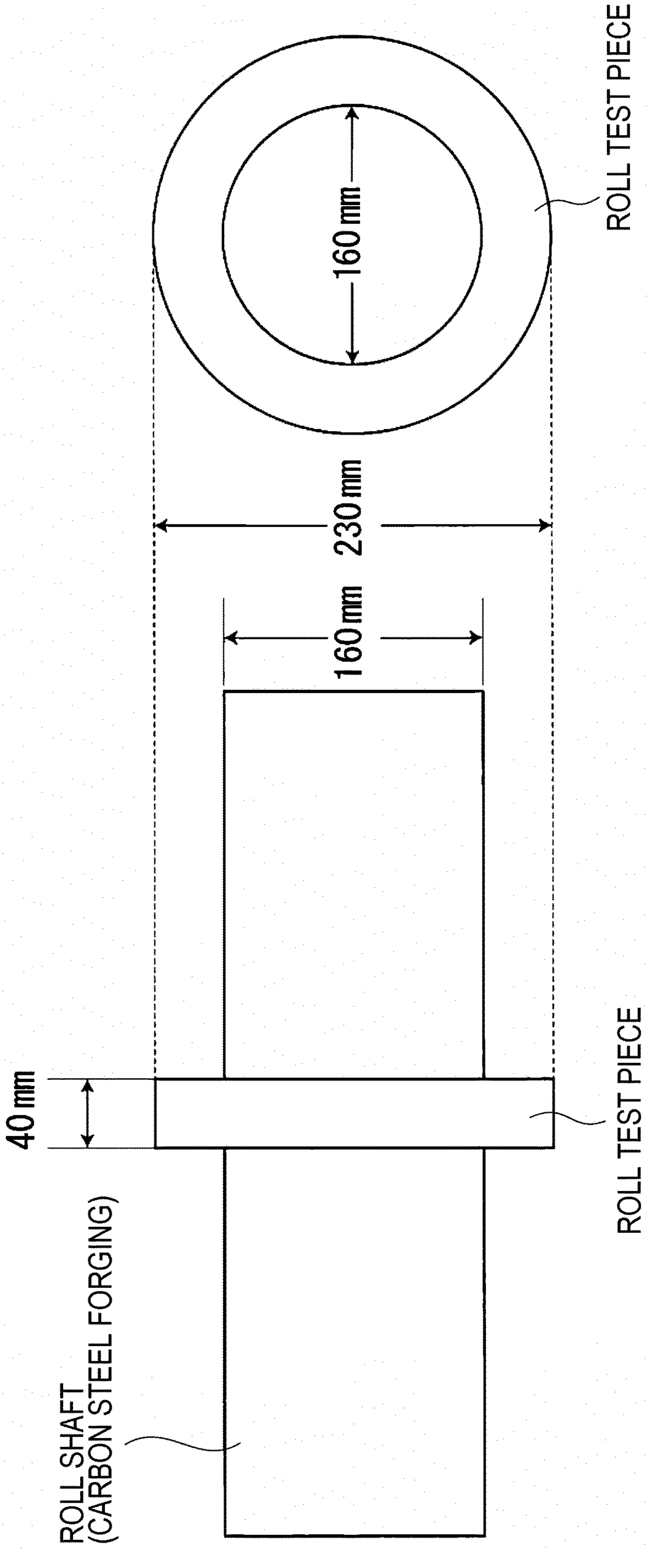
LOAD
V2
THERMOMETER
COOLING WATER
TEST MATERIAL

FIG. 8


ROLL TEST PIECE
160 mm
230 mm
160 mm
40 mm
ROLL TEST PIECE
ROLL SHAFT
(CARBON STEEL FORGING)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/031081

A. CLASSIFICATION OF SUBJECT MATTER
B21B27/00(2006.01)i, *B22D13/02*(2006.01)i, *C22C27/04*(2006.01)n, *C22C30/00*(2006.01)n, *C22F1/00*(2006.01)n, *C22F1/18*(2006.01)n

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)
B21B27/00, B22D13/02, C22C27/04, C22C29/08, C22C30/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 60-177945 A (Kubota Tekko Kabushiki Kaisha), 11 September 1985 (11.09.1985), entire text; fig. 1 (Family: none)	1-21
A	JP 61-60858 A (Kubota Tekko Kabushiki Kaisha), 28 March 1986 (28.03.1986), entire text; fig. 1 to 4 (Family: none)	1-21
A	JP 61-182862 A (Kubota Tekko Kabushiki Kaisha), 15 August 1986 (15.08.1986), entire text; fig. 1 to 3 (Family: none)	1-21

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"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 16 October 2017 (16.10.17)	Date of mailing of the international search report 31 October 2017 (31.10.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/031081

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 48-69719 A (Nippon Tungsten Co., Ltd.), 21 September 1973 (21.09.1973), entire text; drawings (Family: none)	1-21

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

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- JP 4365836 A **[0038]**
- JP 5001350 A **[0038]**
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- WO 2006030795 A **[0038]**
- JP 57006502 A **[0038]**
- JP 58039906 A **[0038]**
- JP 2004243341 A **[0038]**
- JP 2006175456 A **[0038]**
- JP 2004268140 A **[0038]**

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- **HASHIMOTO.** *Seitetsu Kenkyu (Iron-Making research),* 1990, vol. 338, 62 **[0039]**
- **KAIZO MONMA.** Iron and steel materials, Revised edition. *Jikkyo Shuppan,* 1981, 368 **[0039]**
- **MATSUNAGA et al.** *Analytical technique for increasing service life of rolls,* 1999, 11 **[0039]**
- **HASHIMOTO et al.** *Shinnittetsu Giho (Nippon Steel Technical Report),* 1995, vol. 355, 76 **[0039]**