(19) Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

(11) EP 3 719 153 A1

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

(43) Date of publication:
07.10.2020 Bulletin 2020/41

(21) Application number: **18883639.9**

(22) Date of filing: **29.11.2018**

(51) Int Cl.:
C22C 19/05 $^{(2006.01)}$ ***B21J 13/02*** $^{(2006.01)}$
C22F 1/10 $^{(2006.01)}$ ***C22F 1/00*** $^{(2006.01)}$

(86) International application number:
PCT/JP2018/044012

(87) International publication number:
WO 2019/107502 (06.06.2019 Gazette 2019/23)

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

(30) Priority: **29.11.2017 JP 2017228956**

(71) Applicant: **Hitachi Metals, Ltd.**
Tokyo 108-8224 (JP)

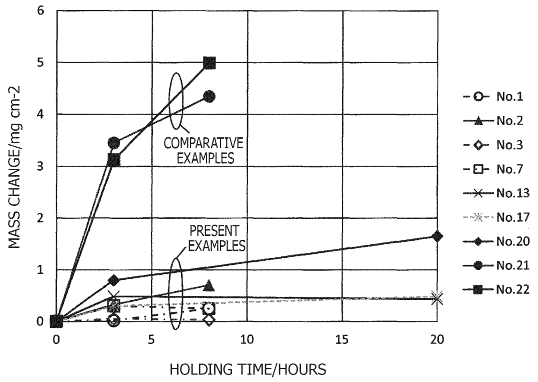
(72) Inventors:
- **SUZUKI Shogo**
  Tokyo 108-8224 (JP)
- **AOKI Chuya**
  Tokyo 108-8224 (JP)
- **UENO Tomonori**
  Tokyo 108-8224 (JP)

(74) Representative: **HGF**
1 City Walk
Leeds LS11 9DX (GB)

(54) HOT-DIE NI-BASED ALLOY, HOT-FORGING DIE EMPLOYING SAME, AND FORGED-PRODUCT MANUFACTURING METHOD

(57) Provided are a Ni-based alloy for hot die having a high high-temperature compressive strength and a good oxidation resistance and being capable of suppressing the deterioration in the working environment and the shape deterioration, a hot forging die using the Ni-based alloy for hot die, and a method for manufacturing a forged product using the hot forging die. The present invention provides a hot forging die comprising a Ni-based alloy for hot die comprising, in mass%, W: 7.0 to 15.0%, Mo: 2.5 to 11.0%, Al: 5.0 to 7.5%, Cr: 0.5 to 7.5%, and the balance of Ni with inevitable impurities, wherein at least 80% of a surface area of the Ni-based alloy for hot die is covered with an aluminum oxide layer. In addition to the composition, the Ni-based alloy for hot die may further comprise 7.0% or less of Ta and may further comprise one or two or more elements selected from Zr: 0.5% or less, Hf: 0.5% or less, rare-earth elements: 0.2% or less, Y: 0.2% or less, and Mg: 0.03% or less.

FIG.1



Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a Ni-based alloy for a hot die, a hot forging die made thereof, and a method for manufacturing a forged product.

BACKGROUND ART

[0002] In the forging of a product made of heat-resistant alloy, a material for forging is heated to a predetermined temperature to reduce the deformation resistance. The heat-resistant alloy has a high strength even at a high temperature and a hot forging die to be used in the forging of the heat-resistant alloy is required to have high mechanical strength at a high temperature. In hot forging, when the temperature of a hot forging die is lower than the temperature of a material for forging, the workability of the material for forging decreases due to heat removal, and thus, products of poor workability materials such as Alloy 718 and Ti alloy are forged by heating the hot forging die with the raw material. Consequently, the hot forging die should have a high mechanical strength at a high temperature equal to or near the temperature to which the material for forging is heated. As a hot forging die that satisfies this requirement, Ni-based heat-resistant super alloys that can be used in hot forging at a die temperature of 1000°C or more in the air are proposed (for example, see Patent Documents 1 to 5).

[0003] As used herein, the term hot forging includes hot die forging in which the temperature of the hot forging die is close to the temperature of the material for forging and isothermal forging in which the hot forging die is heated to the same temperature as the material for forging.

REFERENCE DOCUMENT LIST

PATENT DOCUMENTS

[0004]

Patent Document 1: JP 62-50429 A
Patent Document 2: JP 60-221542 A
Patent Document 3: JP 2016-069702 A
Patent Document 4: JP 2016-069703 A
Patent Document 5: US 4740354 B

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0005] The Ni-based heat-resistant super alloys described above have an advantage of having a high-temperature compressive strength. But in terms of oxidation resistance, fine scales of nickel oxide are scattered from a die surface upon cooling after heating in the air and this may result in the deterioration in the working environment and the shape deterioration. In order to maximize the effect of being capable of using in the air, oxidation of the die surface and scattering of scales associated therewith become large problems.

[0006] It is an object of the present invention to provide a Ni-based alloy for hot die having a high high-temperature compressive strength and a good oxidation resistance and being capable of suppressing the deterioration in the working environment and the shape deterioration, a hot forging die using the Ni-based alloy for hot die, and a method for manufacturing a forged product using the hot forging die.

MEANS FOR SOLVING THE PROBLEM

[0007] The present inventors have studied the deterioration in the working environment and the shape deterioration caused by oxidation of the die surface and scattering of scales associated therewith, and found a composition having a high high-temperature compressive strength and a good oxidation resistance, and thereby achieved the present invention.

[0008] The present invention provides a hot forging die comprising a Ni-based alloy for hot die comprising, in mass%, W: 7.0 to 15.0%, Mo: 2.5 to 11.0%, Al: 5.0 to 7.5%, Cr: 0.5 to 7.5%, and the balance of Ni with inevitable impurities, wherein at least 80% of a surface area of the Ni-based alloy for hot die is covered with an aluminum oxide layer.

[0009] According to the present invention, the Ni-based alloy for hot die may further comprise one or two or more elements selected from Zr: 0.5% or less, Hf: 0.5% or less, rare-earth elements: 0.2% or less, Y: 0.2% or less, and Mg: 0.03% or less, in addition to the composition described above.

[0010] According to the present invention, the Ni-based alloy for hot die may further comprise 7.0% or less of Ta, in addition to the composition described above.

[0011] According to the present invention, the Ni-based alloy for hot die may further comprise one or two elements selected from Ti and Nb in a total amount of 3.5% or less in which a total content of Ta, Ti, and Nb is within a range of 1.0 to 7.0%, in addition to the composition described above.

[0012] According to the present invention, the Ni-based alloy for hot die may further comprise 15.0% or less of Co, in addition to the composition described above.

[0013] Further preferably, the hot forging die using the Ni-based alloy for hot die has a covering layer of an antioxidant on at least one of a die surface or a side surface of the hot forging die.

[0014] The present invention provides a Ni-based alloy for hot die comprising, in mass%, W: 7.0 to 15.0%, Mo: 2.5 to 11.0%, Al: 5.0 to 7.5%, Cr: 0.5 to 7.5%, Ta: 0 to 7.0%, Co: 0 to 15.0%, and the balance of Ni with inevitable impurities.

[0015] According to the present invention, the Ni-based alloy for hot die may further comprise, in mass%, one or two or more elements selected from Zr: 0.5% or less, Hf: 0.5% or less, rare-earth elements: 0.2% or less, Y: 0.2% or less, and Mg: 0.03% or less, in addition to the composition described above.

[0016] According to the present invention, the Ni-based alloy for hot die may further comprise, in mass%, one or two elements selected from Ti and Nb in a total amount of 3.5% or less in which a total content of Ta, Ti, and Nb is within a range of 1.0 to 7.0%, in addition to the composition described above.

[0017] According to the present invention, 0.2% compressive strength at a test temperature of 1000°C and a strain rate of 10^{-3}/sec is preferably 500 MPa or more.

[0018] Further preferably, 0.2% compressive strength at a test temperature of 1100°C and a strain rate of 10^{-3}/sec is 300 MPa or more.

[0019] In addition, the present invention is the hot forging die using the Ni-based alloy for hot die.

[0020] The present invention provides a method for manufacturing a forged product comprising: a first step of heating a material for forging, and a second step of hot forging the material for forging heated in the first step by using the hot forging die.

[0021] Further preferably, the second step is performed by heating the hot forging die to 1000°C or more in the method for manufacturing a forged product.

[0022] In the present invention, the Ni-based alloy for hot die is pre-heated in the air to 1000°C or more to form an aluminum oxide layer on 80% or more of the surface of the Ni-based alloy for hot die, before the step of heating the hot forging die to 1000°C or more.

EFFECTS OF THE INVENTION

[0023] The present invention can provide a Ni-based alloy for hot die having a high high-temperature compressive strength and a good oxidation resistance. This enables to suppress the deterioration in the working environment and the shape deterioration in hot forging.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024]

Fig. 1 is a graph showing oxidation resistance of the present examples and the comparative examples under test conditions simulating prolonged use of a die.

Fig. 2 are micrographs of surfaces of test specimens of the present examples and the comparative example after holding at 1100°C for 8 hours in the air.

Fig. 3 are cross-sectional micrographs showing backscattered electron images and element maps of oxide layers formed on surfaces of test specimens of the present examples and the comparative example after holding at 1100°C for 3 hours or 8 hours in the air.

Fig. 4 is a graph showing the oxidation resistance of the present example and the comparative example under test conditions simulating heating and cooling due to repeated use of a die.

Fig. 5 is a graph showing high-temperature compressive strength of the present examples and the comparative example.

Fig. 6 is a photograph showing an effect of preventing oxidation of a die surface by applying an antioxidant.

MODE FOR CARRYING OUT THE INVENTION

[0025] Hereinafter, the Ni-based alloy for hot die of the present invention will be described in detail. The unit for the chemical composition is mass%. Note that the Ni-based alloy for hot die becomes the base material of the hot forging die of the present invention.

W

[0026] W forms a solid solution in an austenitic matrix, and forms a solid solution also in a gamma prime phase (γ' phase) basically composed of Ni_3Al that is a precipitation strengthening phase to enhance the high-temperature strength of the alloy. Meanwhile, W has an effect of reducing the oxidation resistance and an effect of facilitating the precipitation of harmful phases such as the TCP (Topologically Close Packed) phase. From the viewpoint of enhancing the high-temperature strength and suppressing the reduction of the oxidation resistance and the precipitation of harmful phases, the content of W in the Ni-based alloy of the present invention is 7.0 to 15.0%. In order to more reliably achieve the effect of W, the lower limit is preferably 10.0%, the upper limit is preferably 12.0%, and the upper limit is further preferably 11.0%.

Mo

[0027] Mo forms a solid solution in an austenitic matrix and forms a solid solution also in a gamma prime phase basically composed of Ni_3Al that is a precipitation strengthening phase to enhance the high-temperature strength of the alloy. Meanwhile, Mo has an effect of reducing the oxidation resistance. From the viewpoint of enhancing the high-temperature strength and suppressing the reduction of the oxidation resistance, the content of Mo in the Ni-based heat-resistant super alloy of the present invention is 2.5 to 11.0%. In order to suppress the precipitation of harmful phases such as the TCP phase associated with the addition of W and Ta, Ti, and Nb described below, the preferred lower limit of Mo is preferably set by taking into consideration the content of W, Ta, Ti, and Nb. In order to reliably achieve the effect of Mo, the lower limit is preferably 4.0%, and the lower limit is further preferably 4.5%. The upper limit of Mo is preferably 10.5%, further preferably 9.0%, and more preferably 6.0%.

Al

[0028] Al has effects of binding to Ni to precipitate a gamma prime phase composed of Ni_3Al, enhancing the high-temperature strength of the alloy, producing an alumina film on the surface of the alloy, and imparting the oxidation resistance to the alloy. Meanwhile, an excess content of Al also has an effect of excessively producing eutectic gamma prime phases to reduce the high-temperature strength of the alloy. From the viewpoint of enhancing the oxidation resistance and the high-temperature strength, the content of Al in the Ni-based alloy of the present invention is 5.0 to 7.5%. In order to more reliably achieve the effect of Al, the lower limit is preferably 5.2%, and further preferably 5.4%. The upper limit of Al is preferably 6.7%, further preferably 6.5%, and more preferably 6.0%.

Cr

[0029] Cr has effects of promoting the formation of a continuous layer of alumina on the surface of or inside the alloy and increasing the oxidation resistance of the alloy. Thus, 0.5% or more of Cr is required to be contained. When Cr is added in addition to Al, W, and the like, 3.0 to 7.5% of Cr can achieve a high compressive strength at 1000°C as shown in Table 4, Fig. 5, and the like described below. Furthermore, with the content of Cr of 3.0% or less, a high compressive strength can be obtained not only at 1000°C, but also at a temperature of 1000°C to 1100°C. However, the addition of Cr in a range more than 7.5% reduces the compressive strength at 1000°C or more and thus should be avoided. The addition of Cr is not necessarily disadvantageous for the high-temperature strength. It was revealed by the present invention that the addition of Cr of 0.5 to 7.5% in addition to Al, W, and the like rather increases the high-temperature strength and increases the oxidation resistance while maintaining a high high-temperature strength. In order to reliably achieve the effect of Cr, the lower limit is preferably 1.0%, and more preferably 1.3%. Meanwhile, an excess content of Cr also has an effect of facilitating the precipitation of harmful phases such as the TCP (Topologically Close Packed) phase. Particularly when numerous elements such as W, Mo, Ta, Ti, and Nb that increase the high-temperature strength of the alloy, harmful phases are likely to be precipitated. From the viewpoint of increasing the oxidation resistance and suppressing the precipitation of harmful phases while maintaining the content of elements that increase the high-temperature strength at a high level, the upper limit of the content of Cr in the present invention is preferably 3.0%. The upper limit is further preferably 2.0%.

Ta

[0030] The Ni-based heat-resistant super alloy according to the present invention may contain Ta. Ta forms a solid solution by substituting into the Al site in a gamma prime phase composed of Ni_3Al, thereby enhancing the high-temperature strength of the alloy. Ta increases the adhesiveness and the oxidation resistance of an oxide film formed on the surface of the alloy, and has an effect of further increasing the oxidation resistance of the alloy particularly under heat cycle conditions of short heating and cooling cycles of a die. Meanwhile, an excess content of Ta also has an effect of facilitating precipitation of harmful phases such as the TCP phase. From the viewpoint of enhancing the oxidation resistance and the high-temperature strength and suppressing the precipitation of harmful phases, the upper limit of Ta according to the present invention in the case of containing Ta is 7.0%. In order to more reliably achieve the effect in the case of containing Ta, the lower limit is preferably 0.5%, and the lower limit is further preferably 2.5%, and more preferably 5.0%. The upper limit of Ta is preferably 6.7%, and further preferably 6.5%.

Zr, Hf, rare-earth elements, Y, and Mg

[0031] The Ni-based heat-resistant super alloy according to the present invention may contain one or two or more elements selected from Zr, Hf, rare-earth elements, Y, and Mg. Zr, Hf, rare-earth elements, and Y suppress the diffusion of metal ions and oxygen at the grain boundary by segregation of the oxide film into the grain boundary. This suppression of grain boundary diffusion reduces the growth rate of the oxide film and changes the growth mechanism of promoting the spallation of the oxide film, which increases the adhesion between the film and the alloy. That is, these elements have an effect of increasing the oxidation resistance of the alloy due to the reduction of the growth rate and the increase of the film adhesion described above, particularly under heat cycle conditions of short heating and cooling cycles of a die. Rare-earth elements, Y, and Mg form sulfide with S (sulfur) that reduces the adhesion of the film through the segregation to the interface between the oxide film and the alloy and the inhibition of the chemical bonding between them, and they increase the adhesion by preventing segregation of S, and have an effect of increasing the oxidation resistance of the alloy particularly under heat cycle conditions of short heating and cooling cycles of a die. Note that S is an element that may be contained as impurities.

[0032] Among the rare-earth elements, La is preferably used. That is because La has a large effect of increasing the oxidation resistance. La also has an effect of preventing segregation of S in addition to the effect of suppressing the diffusion described above and is excellent in these effects, and thus La may be selected among rare-earth elements. The addition of Y is also preferred since Y has a similar effect of La. Two or more elements including La and Y are particularly preferably used.

[0033] When toughness is required in addition to oxidation resistance to suppress the cracks of the die associated with excess thermal stress generated particularly under heat cycle conditions of short heating and cooling cycles of a die, Hf or Zr having a lower effect of reducing the toughness than rare-earth elements and Y is preferably used. Of Zr and Hf, Hf is particularly preferably used, since Hf has a much lower effect of reducing the toughness and an effect of preventing cracks during casting can also be expected. When no rare-earth element and Y are contained and one or two elements of Zr and Hf are contained, Zr and Hf have a lower effect of preventing segregation of S than rare-earth elements and Y, and thus the simultaneous addition of Mg further increases the oxidation resistance. Consequently, in order to enhance the oxidation resistance and the toughness in a balanced manner, Hf and Mg are particularly preferably simultaneously used.

[0034] Excess addition of Zr, Hf, rare-earth elements, Y, and Mg causes the excess production of intermetallic compounds between them and Ni and the like, and reduces the toughness of the alloy. Thus, when these elements to be optionally added are contained, the following contents are preferred.

[0035] From the viewpoint of enhancing the oxidation resistance and suppressing the reduction of the toughness, the upper limit of each content of Zr and Hf in the present invention in the case of containing Zr and Hf is 0.5%. The upper limit of each content of Zr and Hf is preferably 0.3%, and further preferably 0.2%. The lower limit in the case of containing Zr and Hf may be 0.001%. The lower limit at which the effect of containing Zr and Hf can be sufficiently exerted may be preferably 0.01%, further preferably 0.05%, and more preferably 0.1% or more.

[0036] Rare-earth elements and Y have a higher effect of reducing the toughness than Zr and Hf as described above, the upper limit of each content of these elements according to the present invention in the case of containing rare-earth elements and Y is 0.2%, and the upper limit is preferably 0.02%, and further preferably 0.005%. The lower limit in the case of containing rare-earth elements and Y may be 0.001%. The lower limit at which the effect of containing rare-earth elements and Y can be sufficiently exerted may be preferably 0.002%, and further preferably 0.003% or more.

[0037] Mg should be contained only in an amount required to form sulfide with S that is contained in the alloy as impurities. Thus, the upper limit of the content in the case of containing Mg is 0.03%. The lower limit in the case of containing Mg may be 0.001%. The upper limit of Mg is preferably 0.025%, and more preferably 0.02%. Meanwhile, the lower limit may be 0.005% so that the effect of adding Mg can be more reliably exerted.

Ti and Nb

[0038] The Ni-based alloy for hot die of the present invention may contain one or two selected from Ti and Nb in a total amount within a range of 3.5% or less. Ti and Nb form a solid solution like Ta by substituting into the Al site in a gamma prime phase composed of Ni_3Al, thereby enhancing the high-temperature strength of the alloy. Ti and Nb are low-cost elements as compared with Ta and advantageous in terms of die cost. Meanwhile, an excess content of Ti and Nb has, like Ta, an effect of facilitating the precipitation of harmful phases such as the TCP phase and has also an effect of excessively producing a eutectic gamma prime phase to reduce the high-temperature strength of the alloy. In addition, Ti and Nb have a lower effect of increasing the high-temperature strength as compared with Ta and have no effect of increasing the oxidation resistance, unlike Ta.

[0039] From the above, from the viewpoint of suppressing the reduction in high-temperature strength associated with the precipitation of harmful phases and the excess production of the eutectic gamma prime phase, while limiting the total content of Ta, Ti, and Nb, Ta is desired to be substituted by Ti or Nb that are advantageous in terms of die cost within a range in which the high-temperature strength property and the oxidation resistance are maintained at the same level as the case containing only Ta. According to the present invention, it is preferred that the upper limit of the total content of Ta, Ti, and Nb is 7.0% and the upper limit of the content of one or two elements selected from Ti and Nb is 3.5%, when Ti and/or Nb are/is contained. The upper limit of the total content of Ta, Ti, and Nb is preferably 6.5%, and the upper limit of the content of one or two elements selected from Ti and Nb is preferably 2.7%. From the viewpoint of reliably achieve an effect of enhancing the high-temperature strength, the lower limit of the total content of Ta, Ti, and Nb may be 1.0%, and from the viewpoint of reliably achieve an effect of reducing the die cost, the lower limit of the content of one or two elements selected from Ti and Nb may be 0.5%. The lower limit of the total content of Ta, Ti, and Nb is preferably 3.0%, and the lower limit is further preferably 4.0%. The lower limit of the content of one or two elements selected from Ti and Nb is preferably 1.0%.

[0040] When either Ti or Nb is selected, Ti is preferably used from an economical viewpoint. When the high-temperature strength is particularly important, Nb is preferably used. When both die cost and high-temperature strength are important, Ti and Nb are particularly preferably simultaneously used.

Co

[0041] The Ni-based alloy for hot die according to the present invention may contain Co. Co forms a solid solution in an austenitic matrix to enhance the high-temperature strength of the alloy. Meanwhile, an excess content of Co increases the die cost since Co is an expensive element as compared with Ni, and Co has an effect of facilitating the precipitation of harmful phases such as the TCP phase. From the viewpoint of enhancing the high-temperature strength and suppressing the increase in die cost and the precipitation of harmful phases, Co may be contained within a range of 15.0% or less. In order to reliably achieve the effect of Co in the case of containing Co, the lower limit is preferably 0.5%, further preferably 2.5%. The upper limit is preferably 13.0%, and further preferably 6.0%.

C and B

[0042] The Ni-based alloy for hot die of the present invention may contain one or two elements selected from 0.25% or less of C (carbon) and 0.05% or less of B (boron). C and B increase the strength of grain boundaries of the alloy and enhance the high-temperature strength and the ductility. Meanwhile, an excess content of C and B causes the formation of a coarse carbide or boride and has an effect of reducing the strength of the alloy. From the viewpoint of enhancing the strength of grain boundaries of the alloy and suppressing the formation of the coarse carbide or boride, the range of the content of C is preferably 0.005 to 0.25% and the range of the content of B is 0.005 to 0.05%, when C is contained in the present invention. In order to reliably achieve the effect of C, the lower limit is preferably 0.01% and the upper limit is preferably 0.15%. In order to reliably achieve the effect of B, the lower limit is preferably 0.01% and the upper limit is preferably 0.03%, and the upper limit is more preferably 0.02%.

[0043] When the cost-efficiency or the high-temperature strength is important, only C is particularly preferably used, and when the ductility is particularly important, only B is particularly preferably used. When both high-temperature strength and ductility are important, C and B are particularly preferably simultaneously used.

[0044] The elements other than the elements to be added described above are Ni and inevitable impurities. In the Ni-based heat-resistant super alloy according to the present invention, Ni is the main element for constituting a gamma phase and constitutes also a gamma prime phase together with Al, Ta, Mo, W, and the like. Among the inevitable impurity elements, S is particularly preferably 0.0030% or less. More preferably, S is limited to a range of 0.0010% or less to prevent the reduction of the adhesion of the film through the segregation to the interface between the oxide film and the alloy and the inhibition of the chemical bonding between them.

[0045] As revealed in Examples described below, the composition according to the present invention preferably contains W, Mo, Al, Cr, Ta, Hf, and Mg. Especially, the following range is preferred.

[0046] The Ni-based alloy for hot die has a composition comprising, in mass%, W: 10.0 to 12.0%, Mo: 4.0 to 6.0%, Al: 5.0 to 6.5%, Cr: 1.0 to 3.0%, Ta: 2.5 to 6.7%, Hf: 0.01 to 0.3%, Mg: 0.001 to 0.025%, and the balance of Ni with inevitable impurities.

Oxide film

[0047] According to the present invention, it is important that 80% or more of the surface be covered with an oxide layer of aluminum, when the die is heated to 1000 to 1100°C in the air. The Ni-based alloy for hot die of the present invention can be used in hot die forging and isothermal forging in the air. The temperature of 1000°C is a temperature at which the hot die forging is assumed. The temperature of 1100°C is a temperature at which the isothermal forging is assumed. As used herein, the surface refers to a die surface that is most important in the die. The die surface and the side surface of the die are preferably covered with an oxide layer of aluminum, and the whole surface of the die is more preferably covered therewith.

[0048] In order to form an aluminum oxide layer on 80% or more of the surface of the Ni-based alloy for hot die in this temperature range, for example, blast processing such as shot blasting can be applied to promote the formation of an oxide layer (oxide film). However, if the Ni-based alloy for hot die has excess segregation of components, the oxide film is likely to be non-uniform. Thus, non-uniform formation of aluminum oxide is preferably prevented in advance by applying a treatment that enables to mitigate segregation of components, for example, a homogenization heat treatment at 1100 to 1300°C for about 10 to 100 hours that is performed after an antioxidant is applied to the whole surface of a casting raw material in the air or under an inert atmosphere. If coverage by aluminum oxide layer is lower than 80% of the surface, this causes a problem of an increase of the scattering amount of scales. Thus, the area fraction of aluminum oxide formed on the surface of the Ni-based alloy for hot die surface is 80% or more in the present invention. The area fraction is preferably 90% or more, and most preferably 100%. For the verification of the coverage (area fraction) of the aluminum oxide layer of the present invention, a range of at least 25 mm^2 may be observed with an optical microscope.

[0049] By pre-heating a die that is machined and thereafter degreased and cleaned at a temperature of 1000°C or more in the air and covering 80% or more of the surface with an oxide layer of aluminum, the inhibition of the formation of the oxide layer of aluminum by dirt of fats and oils and the like that are attached to the surface during the assembling operation of the die and the like, or seizing of the die and the member can be suppressed. The oxide layer of aluminum formed on the die surface has an effect of increasing the wettability of a glass lubricant that is used as the lubricant. The upper limit of the pre-heating temperature may be 1150°C. Although the pre-heating time depends on the size of the hot forging die, about 10 minutes to 3 hours are sufficient.

Hot forging die

[0050] According to the present invention, a hot forging die using the Ni-based alloy for hot die that has the alloy composition described above and is covered with an aluminum oxide layer within a range defined by the present invention can be constituted. The hot forging die of the present invention can be obtained by the sintering of alloy powder or casting. Casting having inexpensive manufacturing costs is preferred to sintering of alloy powder. Furthermore, in order to suppress the generation of cracks in the raw material due to the stress during solidification, a sand mold or a ceramic mold is preferably used as the casting mold.

[0051] At least one of the die surface or the side surface of the hot forging die of the present invention can be a surface having a covering layer of an antioxidant. This more reliably prevents the oxidation of the die surface caused by the contact of oxygen in the air and the base material of the die at a high temperature and scattering of the scale associated therewith, allowing the deterioration in the working environment and the shape deterioration to be prevented. The antioxidant described above is preferably an inorganic material formed by any one or more of nitride, oxide, carbide. This is for forming dense oxygen blocking films by the coating layer formed by nitride, oxide, or carbide and for preventing the oxidation of a die base material. The coating layer may be a single layer of nitride, oxide, and carbide, or may be a lamination structure formed by combining any two or more of nitride, oxide, and carbide. Furthermore, a coating layer may be a mixture of any two or more of nitride, oxide, and carbide. In the present invention, ordinary methods such as applying and spraying can be applied to form a covering layer, but the formation of the coating layer is preferred from the economic viewpoint. The formation of oxygen blocking films by the application allows to easily increase the film thickness, thereby more reliably preventing contact of oxygen in the air and the base material of the die. Even if the thickness of the application layer is made too thick, the effect is saturated, and thus, the thickness of the application layer is preferably 100 to 200 μm. The antioxidant before the application is preferably a slurry that can be easily applied, and furthermore, the application method is preferably a simple application method using a brush.

[0052] The hot forging die using the Ni-based alloy for hot die of the present invention described above has a high high-temperature compressive strength and a good oxidation resistance and is capable of preventing oxidation of the die surface caused by the contact of oxygen in the air and base material of the die at a high temperature and scattering of scales associated therewith, and thereby more reliably suppressing the deterioration in the working environment and the shape deterioration.

Method for manufacturing forged product

[0053] Representative steps in the case of manufacturing a forged product by using the hot forging die using the Ni-based alloy for hot die will be described.

[0054] First, a material for forging is heated to a predetermined forging temperature as a first step. Since the forging temperature differs depending on materials, the temperature is appropriately adjusted. The hot forging die using the Ni-based alloy for hot die has a property of being capable of being used in isothermal forging and hot die forging even at a high temperature in the air atmosphere, and thus, it is suitable for the hot forging of Ni-based heat-resistant super alloy, Ti alloy, or the like that are known as poor workability materials. Representative forging temperature is within a range of 1000 to 1150°C.

[0055] Then, the material for forging heated in the first step is subjected to hot forging by using the hot forging die (second step). The second step can be performed by heating the hot forging die to 1000°C or more before hot forging. In the case of the hot die forging or the isothermal forging described above, the hot forging in the second step is preferably closed die forging. As described above, by particularly adjusting the Cr content, the Ni-based alloy for hot die of the present invention can be used in hot forging at a high temperature of 1000°C or more in the air.

EXAMPLES

[0056] The present invention will be described in more detail by way of the following Examples. Ingots of the Ni-based alloy for hot die shown in Table 1 were produced by vacuum melting using a ceramic mold. The unit is mass%. Each of P, N, and O contained in the ingots described below is 0.003% or less. Each of Si, Mn, and Fe is 0.03% or less. In Table 1, No. 1 to 20 are Ni-based alloys for hot die having the composition of "the present example" and No. 21 and 22 are Ni-based alloys for hot die having the composition of "the comparative example".

Table 1

(mass%)

No.	Mo	W	Al	Cr	Ta	Ti	Nb	Co	Hf	Zr	La	Y	B	C	Mg	S	Balance
1	10.0	10.6	6.2	1.5	-	-	-	-	-	-	-	-	-	-	-	0.0002	Ni and inevitable impurities
2	10.0	10.6	6.2	1.5	-	-	-	-	-	0.08	-	0.03	-	-	-	0.0002	Same as above
3	9.8	10.6	6.2	7.1	-	-	-	-	-	0.03	-	0.04	-	-	-	0.0003	Same as above
4	4.9	10.4	5.5	1.6	6.5	-	-	-	-	-	-	-	-	-	-	0.0002	Same as above
5	4.9	10.3	5.5	1.6	6.5	-	-	-	0.12	-	-	-	-	-	-	0.0003	Same as above
6	4.9	11.0	5.5	1.6	6.3	-	-	-	-	-	-	-	-	-	0.017	0.0002	Same as above
7	4.9	10.6	5.5	1.6	6.4	-	-	-	0.17	-	-	-	-	-	0.017	0.0002	Same as above
8	8.6	7.6	6.8	1.5	3.1	-	-	-	-	-	-	-	-	-	-	0.0003	Same as above
9	8.6	7.6	6.8	1.5	3.1	-	-	-	-	0.07	-	-	-	-	-	0.0003	Same as above
10	8.6	7.6	6.7	1.5	3.1	-	-	-	-	-	0.07	-	-	-	-	0.0003	Same as above
11	4.9	10.4	5.7	1.6	3.3	1.5	-	-	0.14	-	-	-	-	-	0.007	0.0002	Same as above
12	4.9	10.4	5.6	1.6	3.3	-	2.6	-	0.15	-	-	-	-	-	0.006	0.0003	Same as above
13	4.9	10.4	5.5	1.6	3.3	0.8	1.4	-	0.15	-	-	-	-	-	0.002	0.0002	Same as above
14	2.7	13.3	5.5	1.6	3.2	1.5	-	-	0.15	-	-	-	-	-	0.006	0.0002	Same as above
15	2.6	13.4	5.4	2.2	3.2	1.5	-	-	0.15	-	-	-	-	-	0.006	0.0002	Same as above
16	2.7	13.5	5.7	1.5	3.2	1.5	-	5.0	0.15	-	-	-	-	-	0.006	0.0002	Same as above
17	2.6	13.4	5.8	1.6	3.2	1.5	-	12.5	0.16	-	-	-	-	-	0.006	0.0002	Same as above
18	2.6	13.4	5.8	1.6	3.2	1.5	-	12.5	0.16	-	-	-	0.017	-	0.006	0.0002	Same as above
19	2.6	13.5	5.8	1.6	3.2	1.5	-	12.5	0.15	-	-	-	-	0.1	0.006	0.0003	Same as above
20	2.6	13.5	5.8	1.6	3.2	1.5	-	12.5	0.15	-	-	-	0.018	0.1	0.005	0.0003	Same as above
21	10.4	10.7	6.3	-	-	-	-	-	-	-	-	-	-	-	-	0.0002	Same as above
22	10.0	10.6	6.2	-	-	-	-	-	-	0.08	-	0.03	-	-	-	0.0004	Same as above

* The symbol "-" means no addition.

[0057] Cubes having a side of 10 mm were cut out from each of the ingots and their surfaces were polished by the one equivalent to #1000 to produce oxidation resistance test specimens and then the oxidation resistance was evaluated. In the oxidation resistance test, two tests, that is, a test simulating prolonged use and a test simulating repeated use of the die for hot forging in the air were performed.

[0058] By using test specimens of No. 1 to 20 of the present examples and No. 21 and 22 of the comparative examples, a heating test was performed as an oxidation resistance test simulating prolonged use as follows. The test specimens were loaded into a furnace heated to 1100°C in a state being placed in a ceramic crucible made of SiO_2 and Al_2O_3, held at 1100°C for a predetermined time, then taken out the crucible in which test specimens are placed from the furnace. Immediately after taking out, the crucible was covered with a lid made of identical materials to prevent spallation of scales outside the crucible and then air-cooled. In order to evaluate the oxidation resistance to prolonged use, the heating test was performed for each of the test specimens under the conditions of holding times of 3 hours, 8 hours, or 20 hours. When pre-heating is assumed, the first heating (3 hours) corresponds to pre-heating and it is assumed that the second heating (8 hours and 20 hours) is the accumulation of the holding time at a high temperature when hot forging is repeatedly performed.

[0059] For each of the test specimens, the surface area and the mass of the crucible in which test specimens were placed were measured before the heating test, and the mass of the crucible in which test specimens were placed was measured after the crucible was cooled to room temperature after the heating test. The mass change per unit surface area of the test specimens after each test was calculated by subtracting the mass measured before the test from the mass measured after each test, and then dividing the value by the surface area measured before the test. The higher the value of mass change is, the higher the amount of scales formed per unit area is. The mass change was determined as follows.

$$\text{Mass change} = (\text{mass after the test - mass before the test})/\ \text{surface area before the test}$$

[0060] The mass change per unit surface area of the test specimens calculated in the heating test of each holding time is shown in Table 2. The unit of the mass change is mg/cm^2. The relationship between the holding time at 1100°C in the air and the mass change in No. 1 to 3, 7, 13, 17, and 20 of the present examples and No. 21 and 22 of the comparative examples is shown in Fig. 1.

[0061] As shown in Table 2 and Fig. 1, the amount of scales generated is suppressed and the weight change after 8 hours is less than half in No. 1 to 20 of the present examples in which Cr was added, as compared with that in No. 21 and 22 of the comparative examples in which no Cr was added. No. 1 to 20 are found to have a good oxidation resistance against prolonged use by the addition of Cr.

[0062] Optical micrographs of No. 2 and 3 of the present examples and No. 21 of the comparative example that were held at 1100°C for 8 hours in the air are shown in Fig. 2. In addition, the quantitative analysis results of the oxide formed on the surface measured by an energy dispersive X-ray analyzer are shown in Fig. 2 in combination with the area fraction of aluminum oxide analyzed by distinguishing between a black oxide layer of aluminum and green oxides made of nickel and the like from optical micrograph taken at a magnification of × 100. The area measured is $100\ mm^2$.

[0063] It is seen in Fig. 2 that the addition of Cr promotes the formation of aluminum oxide in No. 2 and 3 of the present invention and 80% or more of their surfaces are covered with an oxide layer of aluminum. The surfaces of the present examples other than No. 2 and 3 after the heating test at 1100°C in the air are also covered with an oxide layer of aluminum. In contrast, No. 22 of the comparative example is not covered with aluminum oxide like No. 21. The good oxidation resistance of No. 1 to 20 of the present examples shown in Table 2 and Fig. 1 is caused by this aluminum oxide.

[0064] FE-EPMA backscattered electron images obtained by embedding specimens after the heating test at 1100°C in the air in a resin, then they were mirror polished, and then observing near the surface from the cross-sectional direction, and element maps of Al, Mo, W, and O of No. 1 and 7 of the present examples and No. 21 of the comparative example are shown in Fig. 3. The density in element map images corresponds to the concentration of the element to be measured and a whiter color indicates a higher concentration. No. 1 of the present example and No. 21 of the comparative example are specimens after holding for 8 hours, and No. 7 of the present example is a specimen after holding for 3 hours. It is found that a composite oxide composed of Al, Mo, and W is formed and no continuous layer of aluminum oxide is formed on the surface of No. 21 of the comparative example, but a continuous layer of aluminum oxide is formed on the surface of No. 1 and 7 of the present examples. From the above, it is found that the aluminum oxide on the surface of the present examples is formed in layers and these layers are formed by the addition of Cr.

Table 2

No.	Mass change after 3 hours	Mass change after 8 hours	Mass change after 20 hours
1	<0.1	0.2	-
2	0.3	0.7	-
3	<0.1	<0.1	-
4	0.2	0.2	-
5	0.3	0.2	-
6	0.3	0.2	-
7	0.3	0.2	-
8	0.2	0.2	-
9	0.2	0.2	-
10	0.5	0.5	-
11	0.4	-	0.4
12	0.6	-	0.7
13	0.5	-	0.4
14	0.7	-	0.9
15	0.2	-	0.3
16	0.6	-	1.0
17	0.3	-	0.5
18	0.5	-	1.2
19	0.3	-	0.3
20	0.8	-	1.6
21	3.5	4.3	-
22	3.1	5.0	-

[0065] By using test specimens of the alloys of No. 1 to 8 and 10 of the present examples and the alloy of No. 21 of the comparative example, a heating test was performed as an oxidation resistance test simulating repeated use, as follows. The test specimens were loaded into a furnace heated to 1100°C in a state disposed on a ceramic container made of SiO_2 and Al_2O_3, held at 1100°C for 3 hours, then taken out from the furnace, and air-cooled. In order to evaluate the oxidation resistance to repeated use, the heating test was repeated 5 times by cooling and then reloading.

[0066] For each of the test specimens, the surface area and the mass of the test specimens were measured before the first heating test, and each mass of the test specimens that were cooled to room temperature after the first to fifth heating tests and then scales on their surfaces that were removed by a blower were measured. The mass change per unit surface area of the test specimens after each test was calculated by subtracting the mass measured before the first test from the mass measured after each test, and then dividing the value by the surface area measured before the first test. The higher the absolute value of the value of mass change is, the higher the scattering amount of scales per unit area is. Each mass change after the number of repetitions was determined as follows.

Mass change = (mass after the test - mass before the first test)/surface area before the first test

[0067] The mass change per unit surface area of the test specimens calculated after each heating test is shown in Table 3. The unit of the mass change is mg/cm^2. The relationship between the number of heating tests and the mass change is shown in Fig. 4.

[0068] As shown in Table 3 and Fig. 4, the generation of scales (scattering) is suppressed and the absolute value of the value of mass change is low in the alloys of No. 1 to 8 and 10 of the present examples, as compared with that in the alloy of No. 21 of the comparative example, and the alloys of No. 1 to 8 and 10 are found to have a good oxidation resistance against repeated use. Scattering of scales is suppressed in No. 4 and 8 of the present examples in which Ta was added in addition to Cr and No. 2 and 3 of the present examples in which La and Zr were added in addition to Cr, as compared with No. 1 in which only Cr was added.

[0069] Scattering of scales is more suppressed in No. 5 of the present example in which Hf was added in addition to Cr and Ta and No. 6 of the present example in which Mg was added, as compared with No. 4 of the present example in which only Cr and Ta were added. Furthermore, it is found that scattering of scales is more suppressed in No. 7 of the present example in which Hf and Mg were simultaneously added, as compared with No. 5 and 6 of the present examples. This is because Hf and Mg caused an increase of the adhesion of scales by different mechanisms to each other and it is found that good results with extremely less mass change can be obtained. Scattering of scales is more suppressed in No. 10 of the present example in which La was added in addition to Cr and Ta, as compared with No. 8 of the present example in which only Cr and Ta were added, and it is found that No. 10 has an oxidation resistance substantially equal to that of No. 7 of the present example described above. This is because La has both two mechanisms of Hf and Mg of increasing the adhesion of scales.

Table 3

No.	Mass changeafter 1 time	Mass change after 2 times	Mass change after 3 times	Mass change after 4 times	Mass change after 5 times
1	0.0	-2.7	-9.2	-19.5	-27.6
2	-0.8	-2.0	-2.7	-3.0	-3.5
3	-0.1	-0.6	-0.8	-0.8	-1.0
4	0.1	-0.8	-6.0	-8.2	-9.4
5	0.1	1.2	-3.0	-4.3	-4.6
6	0.2	0.5	-0.1	-0.2	-0.2
7	0.3	0.3	0.2	0.2	0.2
8	-0.1	-4.0	-5.6	-6.2	-9.1
10	0.0	0.3	0.4	0.4	0.5
21	-2.3	-8.6	-18.0	-29.5	-39.0

[0070] Then, raw materials for collecting test specimens having a diameter of 8 mm and a height of 12 mm were cut out from each of the ingots of No. 1 to 20 of the present examples and No. 21 and 22 of the comparative examples in Table 1, and their surfaces were polished by the one equivalent to #1000 to produce compression test specimens. By using these compression test specimens, the compression test was performed at each temperature of 900°C, 1000°C, and 1100°C under the test conditions of the strain rate of 10^{-3}/sec and the compression rate of 10%. The 0.2% compressive strength was derived from stress-strain curves obtained by the compression test and the high-temperature compressive strength were evaluated. This compression test is to test whether the die has enough compressive strength even under high temperature as the die for hot forging. The test temperature of 900°C and 1000°C is mainly used to verify application to "hot die forging" and the test temperature of 1100°C is mainly used to verify application to "isothermal forging". When the compressive strength is 300 MPa or more at the test temperature of 1100°C at which the isothermal forging is assumed, it can be said that the die has sufficient strength. The compressive strength is preferably 350 MPa or more, and further preferably 380 MPa or more. When the compressive strength is 500 MPa or more at the test temperature of 900°C and 1000°C at which the hot die forging is assumed, it can be said that the die has sufficient strength. The compressive strength is preferably 550 MPa or more, and further preferably 600 MPa or more.

[0071] The 0.2% compressive strength of the test specimens of No. 1 to 20 of the present examples and No. 21 and 22 of the comparative examples at each test temperature is shown in Table 4. The relationship between each test temperature and 0.2% compressive strength of No. 1 to 3 of the present examples and No. 21 of the comparative example is shown in Fig. 5.

[0072] It is found from Table 4 that the compressive strength of No. 1 to 3 at 1000°C and at a strain rate of 10^{-3}/sec is 500 MPa or more. No. 1 and 2 have achieved 600 MPa or more of compressive strength. It is found that the compressive strength of No. 1 and 2, 4 to 20 having a preferred amount of Cr at 1100°C and at a strain rate of 10^{-3}/sec is 300 MPa or more. Among these are ones that have achieved 350 MPa or more of compressive strength, or ones that have achieved 400 MPa or more of compressive strength. In addition, it is revealed from Fig. 5 that the compressive strength of No. 1 to 3 to which amounts of Cr added are less than the upper limit of 7.5% at 1000°C is greater than or equal to the compressive strength of No. 21 of the comparative example that contains no Cr, and the compressive strength of No. 1 and 2 of the present examples whose amounts of Cr added are 3.0% or less at 1000 to 1100°C is greater than or equal to the compressive strength of No. 21 of the comparative example. From the above, it is found that any of the alloys of the present invention have a high high-temperature compressive strength.

Table 4

No.	Compression test value (MPa)		
	900°C	1000°C	1100°C
1	-	684	376
2	740	614	378
3	686	503	256
4	-	-	406
5	-	-	332
6	-	-	396
7	-	-	400
8	-	-	390
9	-	-	406
10	-	-	332
11	-	-	436
12	-	-	375
13	-	-	374
14	-	-	418
15	-	-	404
16	-	-	423
17	-	-	449
18	-	-	456
19	-	-	424
20	-	-	374
21	-	504	390
22	752	648	303
* The symbol "-" means not performed.			

[0073] Then, an effect of preventing oxidation and scale scattering of a hot forging die by an antioxidant was evaluated by using a hot forging die that satisfies the composition of the Ni-based alloy for hot die of the present invention as shown in Table 5, and to which surface was applied an antioxidant made of oxides shown in Table 6 in a thickness of about 150 μm.

[0074] A photograph showing the appearance of the surface of the hot forging die that was applied with an antioxidant and thereafter heated at 1000°C or more is shown in Fig. 6. It is found from Fig. 6 that there is no exfoliation of the antioxidant applied to the surface of the hot forging die. Scattering of scales was also not seen. From this, it is found that the antioxidant prevents oxidation and scattering of scales of a die.

Table 5

				(mass%)
Mo	W	Al	Cr	Balance
9.9	10.7	6.2	1.5	Ni and inevitable impurities*
* inevitable impurities (P, S: <0.003%, C, Si, Mn, Co, Ti, Nb, Fe: <0.03%)				

Table 6

				(mass%)
SiO_2	B_2O_3	Al_2O_3	CaO	Balance
53.0	5.6	12.7	18.0	Trace amount of oxide added*
* Trace amount of oxide added (Na_2O: 0.6%, K_2O: 0.1%, Fe_2O_3: 0.2%, MgO: 0.5%, TiO_2: 0.6%, SrO: 0.2%)				

[0075] From the results described above, it is found that the Ni-based alloy for hot die of the present invention has sufficient oxidation resistance and a high compressive strength at a high temperature at the same time when used in hot forging in the air. It is found from this that the hot forging die using the Ni-based alloy for hot die of the present invention is useful in the forging (for example, hot die forging or isothermal forging) of products made of heat-resistant alloys. Since generation of scales was able to be particularly significantly suppressed, the deterioration in the working environment and the shape deterioration can be suppressed.

[0076] When a hot forging die is produced by using the Ni-based alloy for hot die of the present invention and an application layer of an antioxidant is formed on at least one of the die surface or the side surface of the hot forging die, the deterioration in working environment can further be prevented and the shape deterioration can also be prevented. Therefore, it is found that the hot forging die made of the Ni-based alloy for hot die of the present invention is suitable for hot die forging and isothermal forging in the air.

Claims

1. A hot forging die comprising a Ni-based alloy for hot die comprising, in mass%, W: 7.0 to 15.0%, Mo: 2.5 to 11.0%, Al: 5.0 to 7.5%, Cr: 0.5 to 7.5%, and the balance of Ni with inevitable impurities, wherein at least 80% of a surface area of the Ni-based alloy for hot die is covered with an aluminum oxide layer.

2. The hot forging die according to claim 1, wherein the Ni-based alloy for hot die further comprises, in mass%, one or two or more elements selected from Zr: 0.5% or less, Hf: 0.5% or less, rare-earth elements: 0.2% or less, Y: 0.2% or less, and Mg: 0.03% or less.

3. The hot forging die according to claim 1 or 2, wherein the Ni-based alloy for hot die further comprises, in mass%, Ta: 7.0% or less.

4. The hot forging die according to claim 2 or 3, wherein the Ni-based alloy for hot die further comprises, in mass%, one or two elements selected from Ti and Nb in a total amount of 3.5% or less, and a total content of Ta, Ti, and Nb is 1.0 to 7.0%.

5. The hot forging die according to any one of claims 1 to 4, wherein the Ni-based alloy for hot die further comprises, in mass%, Co: 15.0% or less.

6. The hot forging die according to any one of claims 1 to 5, wherein the Ni-based alloy for hot die further comprises, in mass%, one or two elements selected from C: 0.25% or less and B: 0.05% or less.

7. The hot forging die according to any one of claims 1 to 6, wherein the hot forging die has a covering layer of an antioxidant on at least one of a die surface or a side surface of the hot forging die.

8. A Ni-based alloy for hot die comprising, in mass%, W: 7.0 to 15.0%, Mo: 2.5 to 11.0%, Al: 5.0 to 7.5%, Cr: 0.5 to 7.5%, Ta: 0 to 7.0%, Co: 0 to 15.0%, and the balance of Ni with inevitable impurities.

9. A Ni-based alloy for hot die, wherein the Ni-based alloy for hot die according to claim 8 further comprises, in mass%, one or two or more elements selected from Zr: 0.5% or less, Hf: 0.5% or less, rare-earth elements: 0.2% or less, Y: 0.2% or less, and Mg: 0.03% or less.

10. A Ni-based alloy for hot die, wherein the Ni-based alloy for hot die according to claim 8 or 9 further comprises, in mass%, one or two elements selected from Ti and Nb in a total amount of 3.5% or less, and a total content of Ta, Ti, and Nb is 1.0 to 7.0%.

11. The Ni-based alloy for hot die according to any one of claims 8 to 10, wherein 0.2% compressive strength at a test temperature of 1000°C and a strain rate of 10^{-3}/sec is 500 MPa or more.

12. The Ni-based alloy for hot die according to any one of claims 8 to 10, wherein 0.2% compressive strength at a test temperature of 1100°C and a strain rate of 10^{-3}/sec is 300 MPa or more.

13. A method for manufacturing a forged product, comprising:

a first step of heating a material for forging, and
a second step of hot forging the material for forging heated in the first step by using the hot forging die according to any one of claims 1 to 7.

14. The method for manufacturing a forged product according to claim 13, wherein the second step is performed by heating the hot forging die to 1000°C or more.

15. The method for manufacturing a forged product according to claim 14, wherein a Ni-based alloy for hot die is preheated in the air to 1000°C or more to form an aluminum oxide layer on 80% or more of a surface area of the Ni-based alloy for hot die, before the step of heating the hot forging die to 1000°C or more.

FIG.1

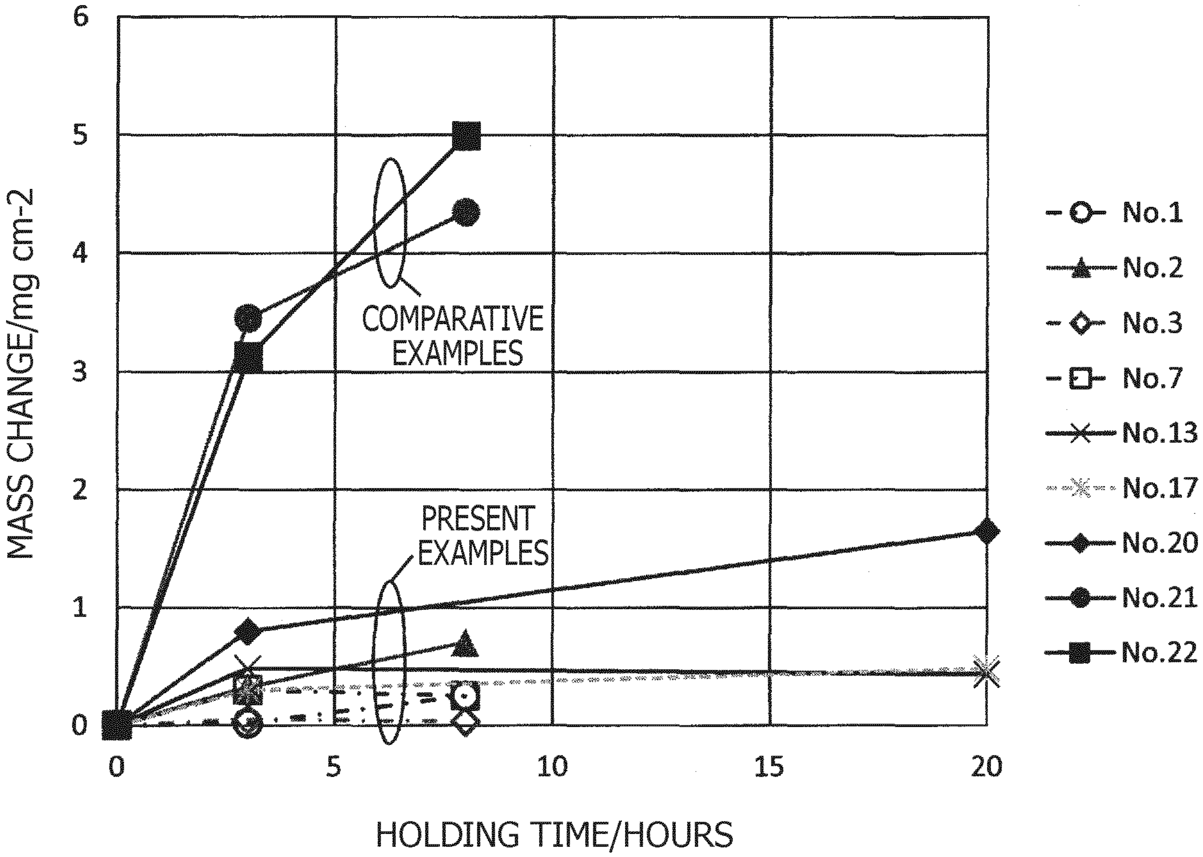
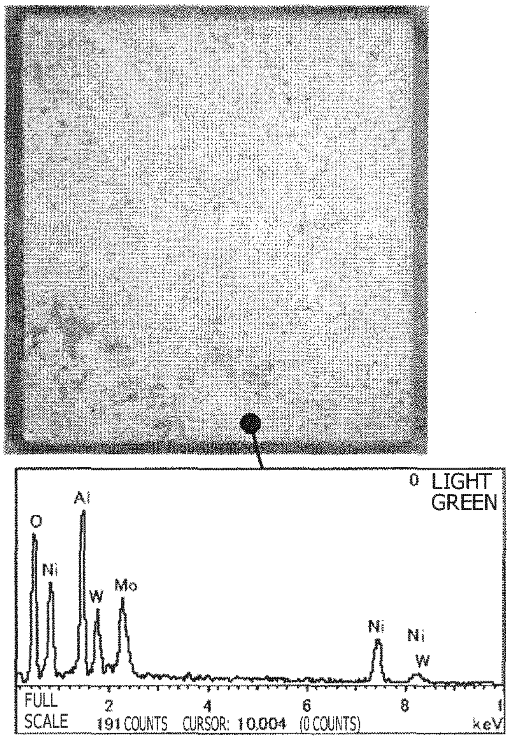

6
5
4
3
2
1
0
MASS CHANGE/mg cm-2
0
5
10
15
20
HOLDING TIME/HOURS
COMPARATIVE EXAMPLES
PRESENT EXAMPLES
No.1
No.2
No.3
No.7
No.13
No.17
No.20
No.21
No.22

FIG.2

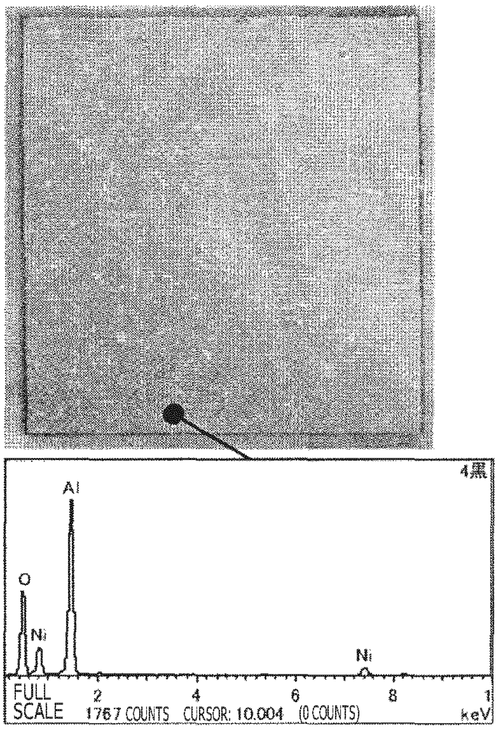
○No.21

AREA FRACTION OF ALUMINUM OXIDE LAYER OF 0%



○No.2

AREA FRACTION OF ALUMINUM OXIDE LAYER OF 84%



○No.3

AREA FRACTION OF ALUMINUM OXIDE LAYER OF 90%

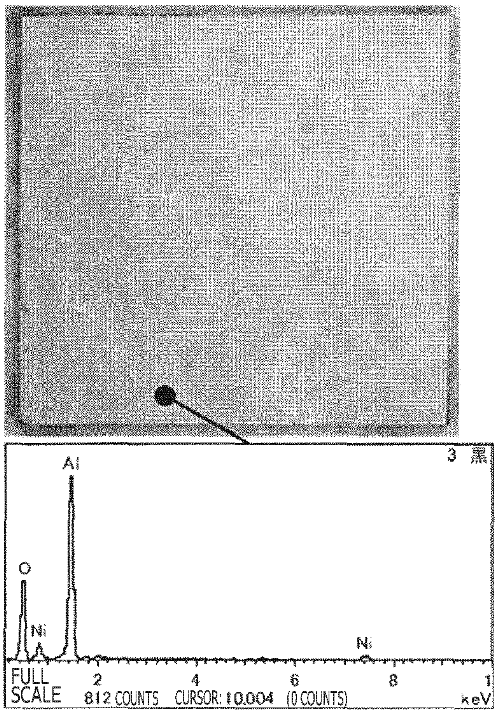


FIG.3

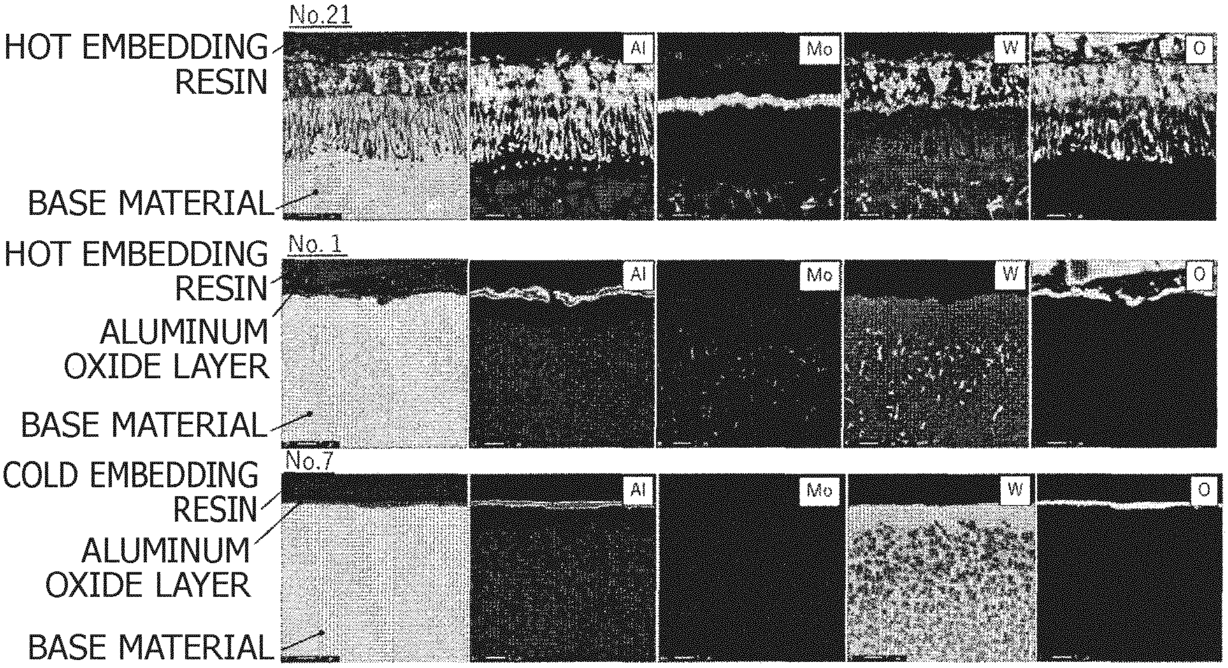

No.21
HOT EMBEDDING RESIN
BASE MATERIAL
Al
Mo
W
O
No. 1
HOT EMBEDDING RESIN
ALUMINUM OXIDE LAYER
BASE MATERIAL
No.7
COLD EMBEDDING RESIN
ALUMINUM OXIDE LAYER
BASE MATERIAL

FIG.4

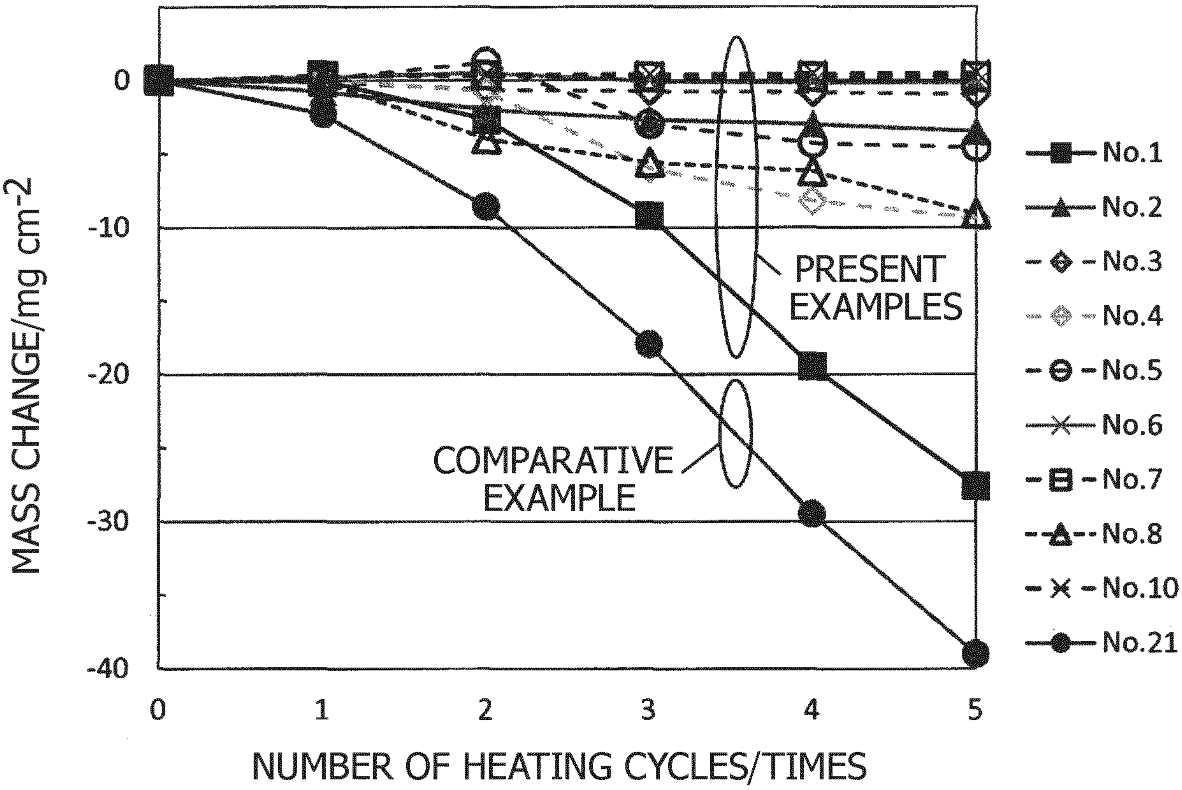

MASS CHANGE/mg cm-2
0
-10
-20
-30
-40
0
1
2
3
4
5
NUMBER OF HEATING CYCLES/TIMES
PRESENT EXAMPLES
COMPARATIVE EXAMPLE
No.1
No.2
No.3
No.4
No.5
No.6
No.7
No.8
No.10
No.21

FIG.5

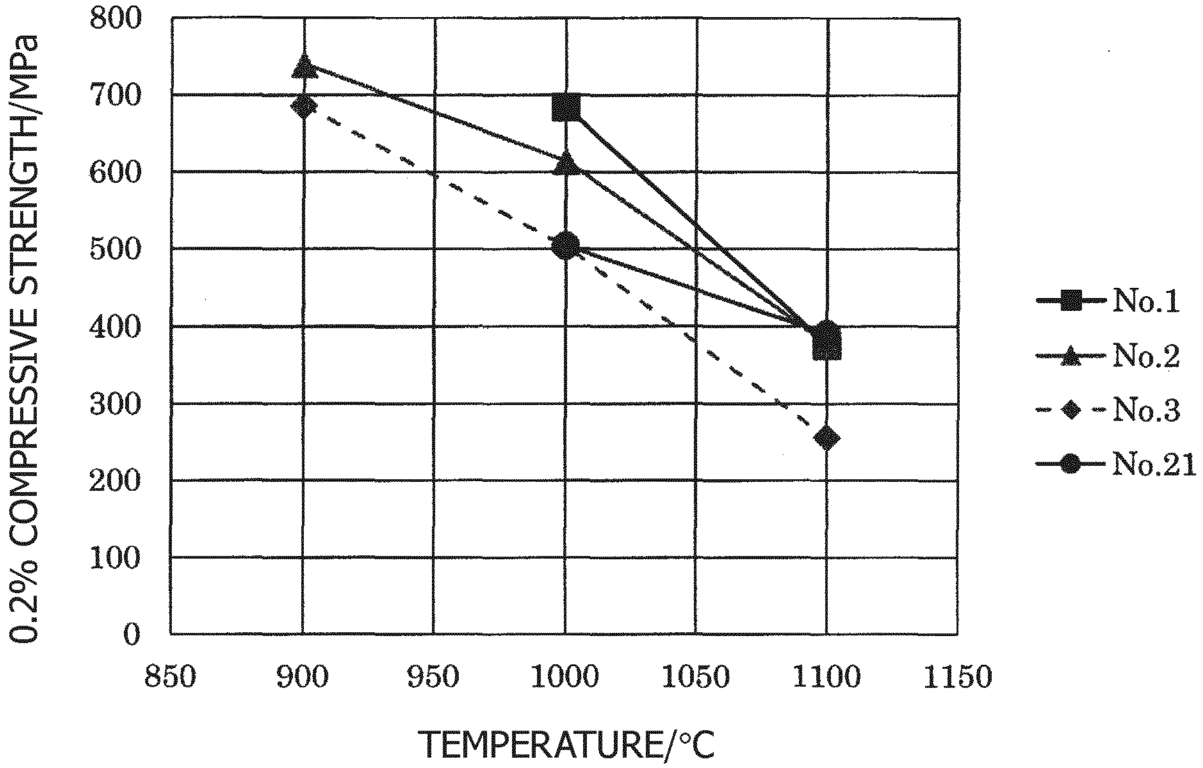
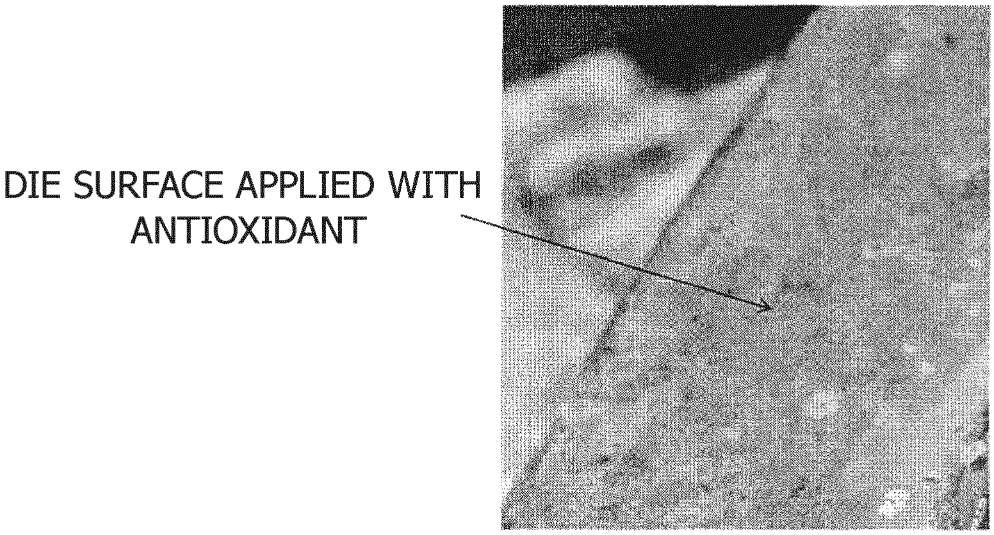

0.2% COMPRESSIVE STRENGTH/MPa
800
700
600
500
400
300
200
100
0
850
900
950
1000
1050
1100
1150
TEMPERATURE/°C
No.1
No.2
No.3
No.21

FIG.6


DIE SURFACE APPLIED WITH ANTIOXIDANT

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/044012

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C22C19/05(2006.01)i, B21J13/02(2006.01)i, C22F1/10(2006.01)i, C22F1/00(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)
Int.Cl. C22C19/05, B21J13/02, C22F1/10, C22F1/00

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

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 2016-69703 A (HITACHI METALS, LTD.) 09 May 2016 (Family: none)	1-15
A	JP 2016-69702 A (HITACHI METALS, LTD.) 09 May 2016 (Family: none)	1-15
A	CN 1718803 A (BEIJING INST. OF AVIATION MATERIAL, CHINA AVIATION INDUSTRY NO. 1 GROUP CORP.) 11 January 2006 (Family: none)	1-15

☒ 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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 21 February 2019 (21.02.2019)	Date of mailing of the international search report 05 March 2019 (05.03.2019)
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/JP2018/044012

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 50-16613 A (THE INTERNATIONAL NICKEL COMPANY, INC.) 21 February 1975 & US 3973952 A & GB 1409040 A & DE 2427704 A1 & FR 2232607 A1 & CH 582751 A5 & SE 7407607 A & AU 6997574 A & IT 1018688 B & SE 395914 B	1-15
P, X	WO 2017/204286 A1 (HITACHI METALS, LTD.) 30 November 2017, claims 1-9, paragraphs [0008]-[0014], [0024]-[0025], [0027], [0030], tables 1-4 (Family: none)	1-4, 6-15
P, X	WO 2018/117226 A1 (HITACHI METALS, LTD.) 28 June 2018, paragraphs [0010]-[0018] (Family: none)	1-15

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 62050429 A **[0004]**
- JP 60221542 A **[0004]**
- JP 2016069702 A **[0004]**
- JP 2016069703 A **[0004]**
- US 4740354 B **[0004]**