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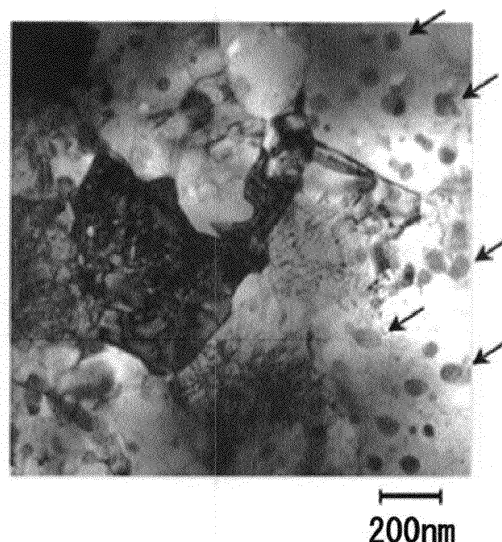
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(54) **NI-GROUP SUPERALLOY STRENGTHENED BY OXIDE-PARTICLE DISPERSION**

(57) An oxide particle dispersion-strengthened Ni-base superalloy includes Ni, 0.1% by weight to 14.0% by weight of Ru, 0.1% by weight to 14.0% by weight of Al, and inevitable impurities and has a crystal structure containing 0.01% by weight to 3.0% by weight of dispersed oxide particles based on the total amount of the superalloy.

FIG.2



## Description

## Citation List

## Technical Field

## Patent Literatures

**[0001]** The present invention relates to an oxide particle dispersion-strengthened Ni-base superalloy.

5 **[0006]**

## Background Art

Patent Literature 1: US 3,926,568  
 Patent Literature 2: JP 49-74616 A  
 Patent Literature 3: US 4,386,976  
 Patent Literature 4: JP 62-99433 A  
 Patent Literature 5: US 4,717,435  
 Patent Literature 6: JP 63-53232 A

**[0002]** Components to be exposed to high-temperature environments, such as aircraft engines and power generation gas turbines, are required to be made of materials having high mechanical properties and high oxidation resistance in a wide temperature range from room temperature to high temperatures. Examples of such materials used include superalloys such as Ni-base superalloys. Even now, there has still been a demand for the development of materials with a higher allowable temperature because the thermal efficiency of gas turbine equipment is required to be further improved.

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## Non Patent Literature

**[0003]** In general, Ni-base superalloys exhibit excellent properties based on solid solution strengthening and  $\gamma'$  phase precipitation strengthening mechanisms. Many excellent single crystal casting alloys have already been developed based on such strengthening mechanisms. However, the allowable temperature improvement based on these strengthening mechanisms gradually becomes difficult with increasing temperature. On the other hand, oxide particle dispersion-strengthened Ni-base superalloys are promising materials because it is considered that their allowable temperature can be improved based on an oxide fine particle dispersion strengthening mechanism in addition to the above strengthening mechanisms.

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**[0007]**

Non Patent Literature 1: G. A. J. Hack, "Oxide Particle Dispersion-Strengthened Superalloy," *Denki-Seiko*, 57 (1986), 341

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Non Patent Literature 2: Yozo Kawasaki, Katsuyuki Kusunoki, Shizuo Nakazawa, Michio Yamazaki, "Development of TMO-2 Alloy," *Tetsu-to-Hagane*, 75 (1989), 529-536

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Non Patent Literature 3: Isao Tomizuka, Yutaka Koizumi, Shizuo Nakazawa, Hideo Numata, Katsumi Ono, Akimitsu Miyazaki, "High-Temperature Corrosion and High-Temperature Oxidation of Yttria Particle Dispersion-Strengthened Alloy," *Zairyo-to-Kanryo*, 42 (1993), 514-520

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## Summary of Invention

**[0004]** Oxide particle dispersion-strengthened Ni-base superalloys have a characteristic structure in which a large number of oxide fine particles typically with sizes of 1  $\mu\text{m}$  or less are dispersed in the matrix phase where elements other than Ni form a solid solution in Ni. Depending on alloy composition, they can also have a structure in which a precipitate such as the  $\gamma'$  phase is also dispersed in addition to the oxide particles.

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## Technical Problem

**[0005]** Oxide particle dispersion-strengthened Ni-base superalloys developed so far include MA6000 alloys (Patent Literatures 1 to 3 and Non Patent Literature 1) and TMO-2 alloys (Patent Literatures 4 to 5 and Non Patent Literature 2). Basically, these alloys are produced by a process that includes preparing an alloy powder by mechanical alloying and then consolidating the alloy powder by hot extrusion or other processes. TMO-2 alloys have a higher level of high-temperature strength because they have a tungsten (W) or tantalum (Ta) content higher than that of MA6000 alloys. Other oxide particle dispersion-strengthened Ni-base superalloys have also been proposed (Patent Literature 6). High-temperature corrosion and high-temperature oxidation of an yttria particle dispersion-strengthened alloy have also been examined and reported (Non Patent Literature 3).

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**[0008]** As mentioned above, many types of oxide particle dispersion-strengthened Ni-base superalloys have been developed so far. However, a sharp rise in energy prices and an increase in energy demand have created a demand for further improvement of the thermal efficiency of gas turbine equipment. Now, the development of materials with a higher allowable temperature is demanded in order to achieve further improvement of thermal efficiency.

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**[0009]** Although having superior high-temperature strength, the TMO-2 alloys contains 12% by weight or more of W so as to have improved high-temperature strength. Such a high W content is effective in improving mechanical properties but may reduce high-temperature corrosion resistance.

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**[0010]** It is therefore an object of the present invention to provide a novel oxide particle dispersion-strengthened Ni-base superalloy that can have superior high-temperature corrosion resistance and a higher level of mechanical properties such as high-temperature strength.

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## Solution to Problem

**[0011]** To solve the problem, the inventors have investigated the composition of oxide particle dispersion-strengthened Ni-base superalloys. As a result, the inventors have found that when having a ruthenium (Ru) content in the range of 0.1% by weight to 14.0% by weight, oxide particle dispersion-strengthened Ni-base superalloys can have good high-temperature corrosion resistance and a higher level of mechanical properties such as high-temperature strength. The present invention has been accomplished based on such findings.

**[0012]** That is, an oxide particle dispersion-strengthened Ni-base superalloy of the present invention has a composition including Ni, 0.1% by weight to 14.0% by weight of Ru, 0.1% by weight to 14.0% by weight of aluminum (Al), and inevitable impurities, the superalloy also has a crystal structure containing 0.01% by weight to 3.0% by weight of dispersed oxide particles based on the total amount of the superalloy.

## Advantageous Effects of Invention

**[0013]** The oxide particle dispersion-strengthened Ni-base superalloy of the present invention containing 0.1% by weight to 14.0% by weight of Ru can have good high-temperature corrosion resistance and a significantly improved level of high-temperature strength and other mechanical properties, such as a significantly improved level of mechanical properties after heating at a temperature in the range of 1,260°C to 1,300°C as shown in the examples below.

## Brief Description of Drawings

### [0014]

Fig. 1 is a chart showing the result of X-ray diffraction of an extruded material according to an example of the present invention in comparison with that of a mechanical alloying powder.

Fig. 2 is a photograph of the structure of an extruded material according to an example of the present invention, which is observed with a transmission electron microscope.

Fig. 3 is a graph showing plots of micro Vickers hardness versus annealing temperature for a comparison between Examples 1 to 3 of the present invention and Comparative Example after annealing.

## Description of Embodiments

**[0015]** As described above, an oxide particle dispersion-strengthened Ni-base superalloy of the present invention has a composition including Ni, 0.1% by weight to 14.0% by weight of Ru, 0.1% by weight to 14.0% by weight of aluminum (Al) inevitable impurities, the superalloy also has a crystal structure containing 0.01% by

weight to 3.0% by weight of dispersed oxide particles based on the total amount of the superalloy.

**[0016]** Such an oxide particle dispersion-strengthened Ni-base superalloy of the present invention may also preferably include 0.1% by weight to 14.0% by weight of Ru, 0.1% by weight to 14.0% by weight of Al, and at least one of 0.1% by weight to 14.0% by weight of Re, 0.1% by weight to 20.0% by weight of Co, 0.1% by weight to 20.0% by weight of Cr, 0.1% by weight to 15.0% by weight of Mo, 0.1% by weight to 20.0% by weight of W, 0.1% by weight to 10.0% by weight of Ti, 0.1% by weight to 10.0% by weight of Nb, 0.1% by weight to 15.0% by weight of Ta, 0.01% by weight to 10.0% by weight of Hf, 0.01% by weight to 10.0% by weight of Zr, 0.1% by weight to 5.0% by weight of V, 0.1% by weight to 10.0% by weight of Pt, 0.1% by weight to 10.0% by weight of Pd, 0.1% by weight to 10.0% by weight of Ir, 0.001% by weight to 1.0% by weight of B, or 0.001% by weight to 1.0% by weight of C.

**[0017]** Ru, which is one of the elements characteristic of the present invention, can form a solid solution in the  $\gamma$  phase as the matrix phase and increase the high-temperature strength by solid solution strengthening. Ru can suppress the precipitation of the TCP phase, which can form when Re or other elements are added, so that Ru can increase the high-temperature strength. The Ru content is preferably in the range of 0.1 to 14.0% by weight, more preferably in the range of 1.0 to 14.0% by weight. If the Ru content is less than 0.1% by weight, the TCP phase would precipitate at high temperatures, which can make it impossible to ensure a high level of high-temperature strength and thus is not preferred. On the other hand, if the Ru content is more than 14% by weight, the  $\epsilon$  phase would precipitate to reduce the high-temperature strength, which is not preferred. The base metal price of Ru is about 200 to 300 times higher than that of Ni or other metals. Therefore, the Ru content is preferably as low as possible in the range where solid solution strengthening can be produced to increase the high-temperature strength. Economically, the Ru content preferably has an upper limit of 8.0% by weight.

**[0018]** The addition of Al can cause the  $\gamma'$  phase precipitation and thus contribute to the improvement of strength by precipitation strengthening. The Al content is preferably in the range of 0.1 to 14.0% by weight. If the Al content is less than 0.1% by weight, the precipitation strengthening would be insufficient, which can make it impossible to ensure the desired high-temperature strength and thus is not preferred. If the Al content is more than 14.0% by weight, a large amount of a coarse  $\gamma'$  phase would be formed to degrade the mechanical properties.

**[0019]** The content of oxide particles added for dispersion strengthening should be 0.01% by weight to 3.0% by weight. The oxide particles may be of any type. In particular, the oxide particles are preferably of yttrium oxide, which has high chemical stability at high temperatures. When high-purity yttrium oxide is added, howev-

er, some elements in the alloy may react with yttrium oxide to form a complex oxide during manufacture or high-temperature use. Therefore, a complex oxide of yttrium oxide and aluminum oxide, such as  $Y_4Al_2O_9$ , is also preferably used instead of yttrium oxide.

**[0020]** The type and content of elements other than Ru and Al are not restricted and may be controlled depending on the intended use or desired properties. Depending on the intended use, other alloying elements may preferably include 0.1 % by weight to 14.0% by weight of Re, 0.1 % by weight to 20.0% by weight of Co, 0.1 % by weight to 20.0% by weight of Cr, 0.1 % by weight to 15.0% by weight of Mo, 0.1 % by weight to 20.0% by weight of W, 0.1 % by weight to 10.0% by weight of Ti, 0.1 % by weight to 10.0% by weight of Nb, 0.1 % by weight to 15.0% by weight of Ta, 0.01 % by weight to 10.0% by weight of Hf, 0.01 % by weight to 10.0% by weight of Zr, 0.1 % by weight to 5.0% by weight of V, 0.1 % by weight to 10.0% by weight of Pt, 0.1 % by weight to 10.0% by weight of Pd, 0.1 % by weight to 10.0% by weight of Ir, 0.001 % by weight to 1.0% by weight of B, or 0.001 % by weight to 1.0% by weight of C.

**[0021]** A more preferred composition (% by weight) may be as follows.

**[0022]**

Ru: 1.0-8.0  
Al: 1.0-10.0  
Cr: 1.0-10.0  
Co: 1.0-10.0  
Mo: 0.1-4.0  
W: 1.0-8.0  
Ta: 1.0-10.0  
Hf: 0.05-5.0  
Zr: 0.05-5.0  
Ti: 0.1-5.0  
Nb: 0.1-5.0  
Re: 0.1-8.0  
V: 0.1-2.0  
Pt: 0.1-6.0  
Pd: 0.1-6.0  
Ir: 0.1-6.0  
B: 0.005-0.05  
C: 0.005-0.05  
Oxide particles: 0.1-3.0

**[0023]** Re can form a solid solution in the  $\gamma$  phase as the matrix phase and increase the high-temperature strength by solid solution strengthening. Re can also be effective in improving corrosion resistance. However, the addition of a large amount of Re may cause the TCP phase to precipitate as a harmful phase at high temperatures and thus reduce the high-temperature strength. For such addition of Re, the Re content is more preferably in the range of 0.1 to 14.0% by weight.

**[0024]** If the Re content is less than 0.1 % by weight, the solid solution strengthening of the  $\gamma$  phase may be insufficient, which can make it impossible to ensure the

desired high-temperature strength and thus is not preferred. If the Re content is more than 14.0% by weight, the TCP phase may precipitate at high temperatures, which can make it impossible to ensure a high level of high-temperature strength and thus is not preferred.

**[0025]** Cr is an element highly resistant to oxidation and can increase the high-temperature corrosion resistance. If the Cr content is less than 0.1 % by weight, the high-temperature corrosion resistance can fail to be achieved. A Cr content of more than 20.0% by weight can suppress the  $\gamma'$  phase precipitation and cause the production of a harmful phase such as the  $\sigma$  or  $\mu$  phase, which can reduce the high-temperature strength and thus is not preferred.

**[0026]** Co can increase the solid solution limit of Al, Ta or other elements in the matrix phase at high temperatures and can cause the  $\gamma'$  phase precipitation and thus increase the high-temperature strength. If the Co content is less than 0.1% by weight, the  $\gamma'$  phase precipitation can be insufficient, which can make it impossible to increase the high-temperature strength. If the Co content is more than 20.0% by weight, the balance between Co and any of other elements such as Al, Ta, Mo, W, Hf, and Cr can be broken, which can cause the precipitation of a harmful phase and the reduction of the high-temperature strength and thus is not preferred.

**[0027]** Mo can form a solid solution in the  $\gamma$  phase as the matrix phase when coexisting with W and Ta so that Mo can increase the high-temperature strength and contribute to the high-temperature strength by precipitation hardening. If the Mo content is less than 0.1 % by weight, these effects can be insufficient, which can make it impossible to increase the high-temperature strength. A Mo content of more than 15.0% by weight can reduce the high-temperature corrosion resistance and thus is not preferred.

**[0028]** W can increase the high-temperature strength by the action of solid solution strengthening and precipitation hardening when coexisting with Mo and Ta. If the W content is less than 0.1 % by weight, the formation of the solid solution in the  $\gamma$  and  $\gamma'$  phases can be insufficient, which can make it impossible to increase the high-temperature strength. The W content is preferably 20.0% by weight or less. This is because a W content of more than 20.0% by weight may reduce the high-temperature corrosion resistance.

**[0029]** Pt, Pd, and Ir can also form a solid solution in the  $\gamma$  phase as the matrix phase and thus increase the high-temperature strength by solid solution strengthening. In order to obtain this effect, the content of each of these elements should be at least 0.1 % by weight. However, since the price of these elements, which belong to the platinum group metals, is about 500 to 3,000 times higher than that of Ni, the content of each of these elements is preferably 10.0% by weight or less, more preferably 6.0% by weight or less.

**[0030]** Ta, Ti, and Nb can contribute to precipitation strengthening by substituting for Al sites in the  $\gamma'$  phase.

Ta, Ti, and Nb can also increase the high-temperature strength by the action of solid solution strengthening and precipitation strengthening when coexisting with Mo and W. If the Ta content is less than 0.1% by weight, these effects can fail to be achieved. The Ta content is preferably 15.0% by weight or less. This is because a Ta content of more than 15.0% by weight can cause the formation of the  $\sigma$  or  $\mu$  phase and thus reduce the high-temperature strength. If the content of each of Ti and Nb is less than 0.1 % by weight, it can be impossible to achieve precipitation strengthening or solid solution strengthening in the co-presence of Mo and W. The content of each of Ti and Nb is preferably 10.0% by weight or less. This is because if the Ti or Nb content is more than 10.0% by weight, a harmful phase may form to reduce the high-temperature strength.

**[0031]** V is an element that can form a solid solution in the  $\gamma'$  phase and strengthen the  $\gamma'$  phase. If the V content is less than 0.1 % by weight, these effects can fail to be achieved. The V content is preferably 5.0% by weight or more. This is because if the V content is more than 5.0% by weight, the creep strength may decrease.

**[0032]** Hf is a grain boundary segregating element which can segregate at the grain boundary between the  $\gamma$  and  $\gamma'$  phases to strengthen the grain boundary, so that it can increase the high-temperature strength. To achieve these effects, the Hf content should be at least 0.01 % by weight. If the Hf content is more than 10.0% by weight, local melting can occur, which may reduce the high-temperature strength and thus is not preferred.

**[0033]** In addition to Hf, the same may apply to the addition of Zr.

**[0034]** B is a grain boundary strengthening element which can increase the high-temperature strength. To achieve these effects, the B content should be at least 0.001 % by weight. If the B content is more than 1.0% by weight, a harmful carbide can precipitate at grain boundaries, which is not preferred.

**[0035]** In addition to B, the same may apply to the addition of C.

**[0036]** More specifically, examples of the elemental composition of the oxide particle dispersion-strengthened Ni-base superalloy of the present invention include the following as well as those of the examples shown below.

Ni-Ru-Al-Re-Co-Cr-Mo-W-Ta-Hf-oxide particles  
 Ni-Ru-Al-Re-Co-Cr-Mo-W-Ta-Hf-(B,C)-oxide particles  
 Ni-Ru-Al-Re-Co-Cr-Mo-W-Ta-(Ti,Nb)-(Hf,Zr)-(B,C)-oxide particles  
 Ni-Ru-Al-Re-Co-Cr-Mo-(W,V)-Ta-(Pt,Pd,Ir)-(B,C)-oxide  
 Ni-Ru-Al-Re-Cr-(Mo,W,Co,V)-(Ta,Ti)-(B,C)-oxide particles  
 Ni-Ru-Al-Cr-(W,Co,V)-(Ta,Ti)-(B,C)-oxide particles  
 Ni-Ru-Al-Cr-(Ta,Ti)-oxide particles

**[0037]** There is no restriction on the method for producing the oxide particle dispersion-strengthened Ni-base superalloy of the present invention. In general, a powder metallurgy technique may be used to uniformly disperse the oxide particles. For example, the oxide particle dispersion-strengthened Ni-base superalloy of the present invention can be produced by a process that includes producing an alloy powder by mechanical alloying, then sealing the alloy powder in a case, and then consolidating the alloy powder by hot extrusion or other techniques. Alternatively, the alloy powder may be solidified by hot isostatic pressing (HIP), hot pressing, or other techniques. Alternatively, the oxide particle dispersion-strengthened Ni-base superalloy of the present invention may be produced by solidifying the alloy powder by any of these techniques and then subjecting the solidified product to hot extrusion or hot rolling.

**[0038]** In general, the combination of base and additive elements for constituting a heat-resistant alloy is determined depending on the intended use of the alloy and cost effectiveness. For example, alloys for gas turbines are required to have high-temperature strength in the temperature range of 400 to 500°C, when they are for use in turbine disks, or required to have high strength and high-temperature corrosion resistance in the temperature range of about 800 to about 1,000°C, when they are for use in combustors, nozzles, turbine blades, shrouds, and other components.

**[0039]** In addition, finer oxide particles with a shorter particle-particle distance can increase the strengthening effect of the dispersed particles, in other words, can increase the effect of preventing dislocation motion, which would otherwise allow the oxide particles to cause deformation. However, excessive addition of the dispersed particles can make it difficult to perform deformation. In order for the dispersion-strengthened alloy to be workable and have an appropriate level of toughness, the dispersed particle size distribution is preferably in the range of 0.001  $\mu\text{m}$  to 5  $\mu\text{m}$ , and thus the oxide particles to be used preferably has a primary particle size distribution of 1  $\mu\text{m}$  or less, taking into account particle aggregation during the production. The content of the oxide particles, for example, in the Ni-base alloy for gas turbines is, in particular, preferably 0.5 to 3.0% based on the total amount of the alloy in order to obtain high-temperature strength at 800°C or higher. The particle size distribution of the alloy or metal powder to be used may have an upper limit of, for example, 250  $\mu\text{m}$ , so that mechanical alloying and sintering for consolidation can be performed with improved efficiency.

**[0040]** Mechanical alloying becomes possible when in a high-energy ball mill, the impact energy between moving steel balls and between the vessel and moving steel balls (that is mechanical energy) accumulates in the powder between them through the compression crushing and shear milling processes. In this case, the mixture particles are subjected to forge welding and repeated folding, so that atomic-level alloying can occur even at a low tem-

perature such as around room temperature due to diffusion. Successful alloying requires high impact energy, and alloying efficiency should also be improved. For these purposes, the ratio of the mixture power weight to the steel ball weight is preferably 1/10 to 1/20 in an attritor and 1/5 to 1/10 in a planet ball mill, and the rotational speed of the ball mill is preferably 50 to 400 rpm although it depends on the ball mill size. The alloying is preferably performed for 20 hours or more. In case of oxygen contamination during the alloying, purging the inside of the ball mill tank with an inert atmosphere such as argon (Ar) is preferably performed as a pre-alloying treatment.

**[0041]** The consolidation of the dispersed alloy-forming powder by sintering can be performed by a powder metallurgy process that includes charging the powder into a mild steel vessel and then subjecting the powder to hot extrusion or HIP. The sintering of the powder to form the Ni-base alloy is preferably performed in the temperature range of 1,000 to 1,300°C taking into account diffusion, fusion, and densification between the particles, the formation of more solid solution of alloy atoms, and the high-temperature stability limit of the oxide particles. In this process, the inside of the vessel is subjected to a vacuum treatment as a pretreatment for the purpose of removing water, oxygen, and other contaminants, which exist in or adsorb on the space in the vessel, the inner surface of the vessel, and the surface of the powder. The vacuum treatment is preferably a heat treatment under a vacuum of  $10^{-1}$  to  $10^{-3}$  torr at a temperature of 100°C to 600°C for 10 minutes to 10 hours depending on the size of the facility so that oxygen can be prevented as much as possible from being added to the dispersion alloy and a strong oxide can be prevented from forming on the surface of the powder.

[Example 1]

**[0042]** An extruded material with a composition of Ni-6.4Co-4.5Cr-1.1Mo-4.0W-5.8Al-7.5Ta-0.1 Hf-6.3Re-4.9Ru-1.1Y<sub>2</sub>O<sub>3</sub> (each numerical value is in units of % by weight) was prepared as described below. Raw material powders were mixed to reach the target composition as a whole and then subjected to a mechanical alloying process using an attritor. After the process, the alloy powder was charged into a case and subjected to a vacuum treatment, and the case was sealed. The alloy powder was then consolidated by hot isostatic pressing (HIP) at a heating temperature of 1,180°C and a pressure of 118 MPa. The resulting HIP product was subjected to hot extrusion under the conditions of a heating temperature of 1,200°C and an extrusion ratio of 5 to form a round bar-shaped extruded material.

**[0043]** Fig. 1 is a chart showing the result of X-ray diffraction of the extruded material in comparison with that of the mechanical alloying powder. The X-ray diffraction chart (chart A) of the mechanical alloying powder mainly had the (111) and (200) diffraction peaks of the Ni solid solution. In the case of the extruded material (chart B),

the (110) diffraction peak of the  $\gamma'$  phase was observed in addition to the diffraction peaks of the Ni solid solution. This indicates that the extruded material is composed mainly of the Ni solid solution ( $\gamma$ ) phase in which the  $\gamma'$  phase is precipitated.

**[0044]** Fig. 2 shows the structure of the extruded material observed with a transmission electron microscope. In the drawing, the arrows indicate oxide particles. The structure was found to contain a large number of fine oxide particles of several tens of nanometers dispersed in crystal grains.

**[0045]** Small pieces were cut from the extruded material and then each subjected to an isothermal heat treatment at a temperature of 1,260°C to 1,300°C for 1 hour. This heat treatment was performed taking into account the fact that in general, oxide particle dispersion-strengthened Ni-base superalloys are produced as hot extruded materials or hot rolled materials and then further subjected to hot forging or the like at such temperatures so that they can be worked into members with desired size and shape. After the heat treatment, the micro Vickers hardness of each sample was 598 in the case of 1,260°C and 585 in the case of 1,290°C.

**[0046]** The high-temperature corrosion resistance of the resulting alloy was evaluated by a molten salt corrosion test. A cylindrical piece with a diameter of 6 mm and a height of 4.5 mm was cut from the extruded material in such a way that the axis direction coincided with the extrusion direction. The cut piece was immersed in a molten salt and heated at a temperature of 800°C for 4 hours. The molten salt used as a corrosive medium was a 3 : 1 mixture of sodium sulfate and sodium chloride. A crucible was charged with the mixed salt in such an amount that the cylindrical sample could be completely immersed in the salt. The mixed salt was preheated at 800°C in a heating furnace. After the temperature was stabilized sufficiently, the cylindrical sample was immersed in the molten salt. The rate of reduction in the sample diameter between before and after the test was calculated to be 0.17%.

[Example 2]

**[0047]** An extruded material with a composition of Ni-5.9Co-3.8Cr-0.9Mo-3.9W-6.1Al-8.6Ta-0.2Hf-5.3Re-4.6Ru-1.2Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub> (each numerical value is in units of % by weight) was prepared as described below. Raw material powders were mixed to reach the target composition as a whole and then subjected to a mechanical alloying process using an attritor. After the process, the alloy powder was charged into a case and subjected to a vacuum treatment, and the case was sealed. The alloy powder was then subjected to hot extrusion under the conditions of a heating temperature of 1,050°C and an extrusion ratio of 15 to form a round bar-shaped, extruded material.

**[0048]** Small pieces were cut from the extruded material and then each subjected to an isothermal heat treat-

ment at a temperature of 1,260°C to 1,300°C for 1 hour. After the heat treatment, the micro Vickers hardness of each sample was 626 in the case of 1,260°C and 585 in the case of 1,290°C.

**[0049]** The high-temperature corrosion resistance of the resulting alloy was evaluated by the molten salt corrosion test under the same conditions as in Example 1. The sample was immersed in the molten salt and heated at a temperature of 800°C for 4 hours. The rate of reduction in the sample diameter between before and after the test was calculated to be 0.17%.

[Example 3]

**[0050]** An extruded material with a composition of Ni-6.1Co-3.8Cr-0.9Mo-4.2W-6.3Al-9.2Ta-0.2Hf-5.0Re-4.7Ru-1.2Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub> (each numerical value is in units of % by weight) was prepared as described below. Raw material powders were mixed to reach the target composition as a whole and then subjected to a mechanical alloying process using an attritor. After the process, the alloy powder was charged into a case and subjected to a vacuum treatment, and the case was sealed. The alloy powder was then subjected to hot extrusion under the conditions of a heating temperature of 1,050°C and an extrusion ratio of 15 to form a round bar-shaped, extruded material.

**[0051]** Small pieces were cut from the extruded material and then each subjected to an isothermal heat treatment at a temperature of 1,260°C to 1,300°C for 1 hour. After the heat treatment, the micro Vickers hardness of each sample was 664 in the case of 1,260°C and 596 in the case of 1,290°C.

**[0052]** The high-temperature corrosion resistance of the resulting alloy was evaluated by the molten salt corrosion test under the same conditions as in Examples 1 and 2. The sample was immersed in the molten salt and heated at a temperature of 800°C for 4 hours. The rate of reduction in the sample diameter between before and after the test was calculated to be 0.17%.

[Comparative Example]

**[0053]** Non Patent Literature 2 shows the results of the micro Vickers hardness test of an extruded TMO-2 alloy material after an isothermal heat treatment. In this test, the extruded material has an alloy composition of Ni-9.8Co-5.9Cr-2.0Mo-12.4W-4.2Al-4.7Ta-0.8Ti-0.05Zr-0.05C-0.01B-1.1Y<sub>2</sub>O<sub>3</sub> (each numerical value is in units of % by weight). It should be noted that this alloy has a W content about three times higher than that of the alloy composition of the examples.

**[0054]** Non Patent Literature 3 shows the results of the molten salt corrosion test of this alloy under the same conditions as in Examples 1 to 3. This extruded material shows a diameter reduction rate of 29.0%.

**[0055]** Fig. 3 is a graph showing plots of micro Vickers hardness versus annealing temperature for a compari-

son between the materials of Examples 1 to 3 and Comparative Example after the isothermal annealing (1 hour). Open circles represent the results of Example 1, triangles those of Example 2, squares those of Example 3, and solid circles those of Comparative Example. The graph shows that although having a significantly reduced W content, the oxide particle dispersion-strengthened Ni-base superalloy of the present invention has improved mechanical properties after heating at a temperature in the range of 1,260°C to 1,300°C because it contains Ru.

**[0056]** As a result of the molten salt corrosion test, Examples 1 to 3 all show a diameter reduction rate of 0.17% whereas Example shows a diameter reduction rate of 29.0%, which indicates that Examples 1 to 3 have a significantly improved level of high-temperature corrosion resistance. This would be because the alloys of Examples 1 to 3 have a W content significantly lower than that of the alloy of Example.

## Claims

1. An oxide particle dispersion-strengthened Ni-base superalloy having a composition comprising Ni, 0.1 % by weight to 14.0% by weight of Ru, 0.1 % by weight to 14.0% by weight of Al, and inevitable impurities, the superalloy also having a crystal structure containing 0.01% by weight to 3.0% by weight of dispersed oxide particles based on the total amount of the superalloy.
2. The oxide particle dispersion-strengthened Ni-base superalloy according to claim 1, which comprises 0.1 % by weight to 14.0% by weight of Ru, 0.1 % by weight to 14.0% by weight of Al, and at least one of 0.1% by weight to 14.0% by weight of Re, 0.1 % by weight to 20.0% by weight of Co, 0.1 % by weight to 20.0% by weight of Cr, 0.1 % by weight to 15.0% by weight of Mo, 0.1 % by weight to 20.0% by weight of W, 0.1 % by weight to 10.0% by weight of Ti, 0.1 % by weight to 10.0% by weight of Nb, 0.1 % by weight to 15.0% by weight of Ta, 0.1 % by weight to 10.0% by weight of Hf, 0.01 % by weight to 10.0% by weight of Zr, 0.1 % by weight to 5.0% by weight of V, 0.1 % by weight to 10.0% by weight of Pt, 0.1 % by weight to 10.0% by weight of Pd, 0.1 % by weight to 10.0% by weight of Ir, 0.001 % by weight to 1.0% by weight of B, or 0.001 % by weight to 1.0% by weight of C.

FIG. 1

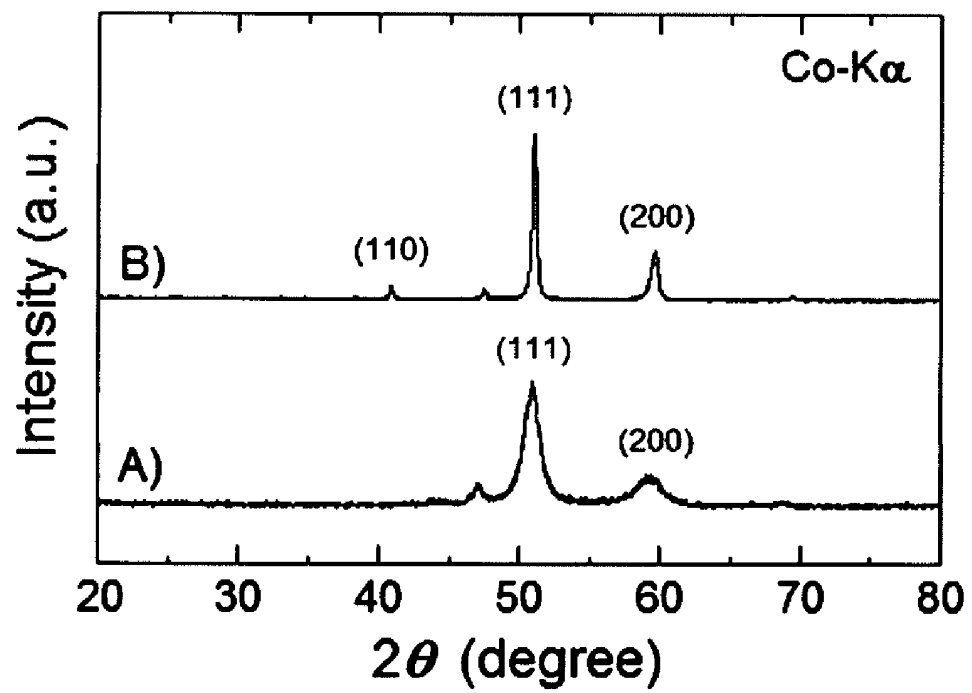


FIG.2

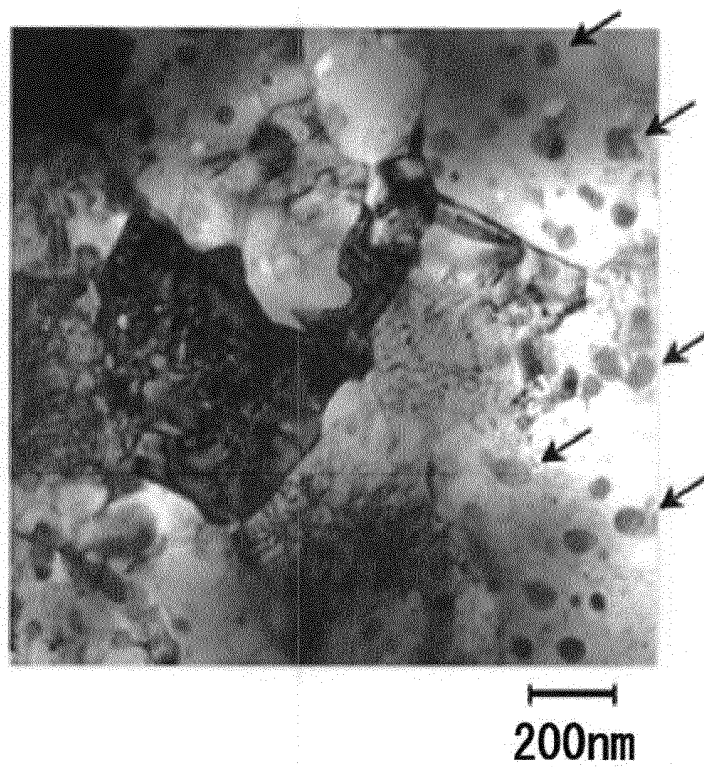
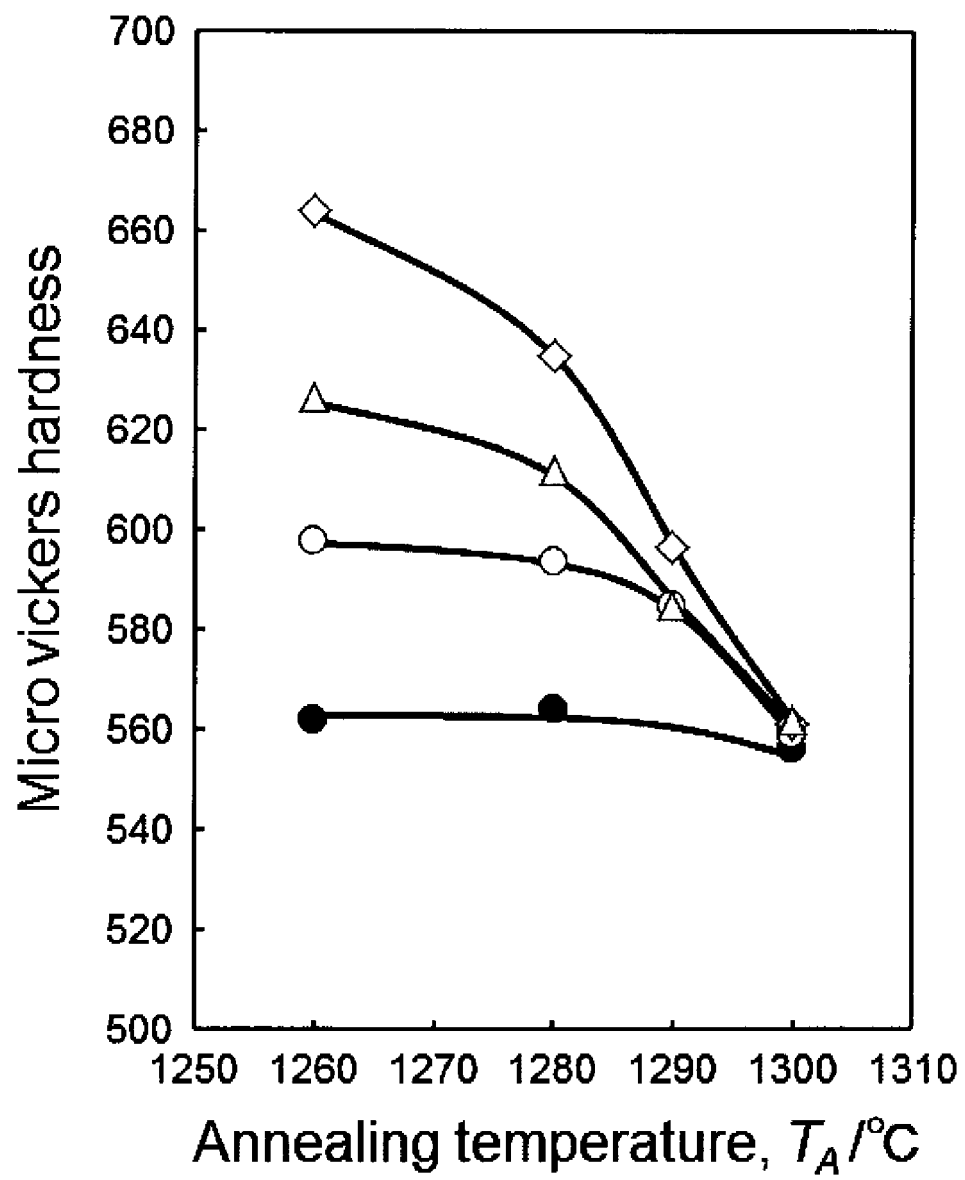




FIG. 3



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/070501

## A. CLASSIFICATION OF SUBJECT MATTER

C22C19/03(2006.01)i, C22C19/05(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C19/03, C22C19/05

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 1996-2014

Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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.
Y	JP 2010-031299 A (Independent Administrative Institution National Institute for Materials Science), 12 February 2010 (12.02.2010), paragraphs [0017] to [0030], [0039] & US 2011/0142714 A1 & EP 2305846 A1 & WO 2009/157556 A1	1, 2
Y	JP 2012-193453 A (Korea Institute of Machinery & Materials), 11 October 2012 (11.10.2012), paragraphs [0004], [0008], [0016] to [0025], [0029] & US 2012/0237391 A1 & KR 10-2012-0105693 A	1, 2

☒ Further documents are listed in the continuation of Box C.
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"&amp;"

document member of the same patent family

Date of the actual completion of the international search

23 October, 2014 (23.10.14)

Date of mailing of the international search report

04 November, 2014 (04.11.14)

Name and mailing address of the ISA/  
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/070501

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 11-050178 A (Hitachi, Ltd.), 23 February 1999 (23.02.1999), claim 1; paragraphs [0004], [0028] (Family: none)	1, 2
Y	JP 10-193174 A (Daido Steel Co., Ltd.), 28 July 1998 (28.07.1998), paragraphs [0003], [0011] (Family: none)	1, 2

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## REFERENCES CITED IN THE DESCRIPTION

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### Patent documents cited in the description

- US 3926568 A [0006]
- JP 49074616 A [0006]
- US 4386976 A [0006]
- JP 62099433 A [0006]
- US 4717435 A [0006]
- JP 63053232 A [0006]

### Non-patent literature cited in the description

- **G. A. J. HACK.** Oxide Particle Dispersion-Strengthened Superalloy. *Denki-Seiko*, 1986, vol. 57, 341 [0007]
- **YOZO KAWASAKI ; KATSUYUKI KUSUNOKI ; SHIZUO NAKAZAWA ; MICHIO YAMAZAKI.** Development of TMO-2 Alloy. *Tetsu-to-Hagane*, 1989, vol. 75, 529-536 [0007]
- **ISAO TOMIZUKA ; YUTAKA KOIZUMI ; SHIZUO NAKAZAWA ; HIDEO NUMATA ; KATSUMI ONO ; AKIMITSU MIYAZAKI.** High-Temperature Corrosion and High-Temperature Oxidation of Yttria Particle Dispersion-Strengthened Alloy. *Zairyo-to-Kankyo*, 1993, vol. 42, 514-520 [0007]