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(71) Applicant: **National University Corporation Hokkaido University**
Sapporo-shi, Hokkaido 060-0808 (JP)

(72) Inventors:
• **Ukai Shigeharu**
Hokkaido 0608628 (JP)
• **OONUKI Soumei**
Hokkaido 0608628 (JP)
• **HAYASHI Shigenari**
Hokkaido 0608628 (JP)
• **HOSHINO Takeshi**
Hokkaido 0608628 (JP)

(74) Representative: **Niizuma, Yo**
Niizuma Wasner GmbH
Patentanwaltskanzlei
Postfach 273
4125 Riehen 1 (CH)

(54) **OXIDE-DISPERSION-STRENGTHENED ALLOY**

(57) [Problem to be Solved]

The present invention provides an oxide dispersion strengthened alloy in which even with aluminum contained, the particle diameter and dispersion spacing of the oxide are decreased, and the strength at high temperature, the high temperature oxidation and the corrosion resistance can be improved.

[Solution]

An oxide dispersion strengthened alloy being a nickel-base alloy containing aluminum, hafnium, and yttrium oxide, wherein a complex oxide of the yttrium oxide and hafnium oxide is dispersed in a matrix of the nickel-base alloy, with the aluminum contained.

Fig. 3

		Ni (wt%)	Y ₂ O ₃ (wt%)	Al (wt%)	Hf (wt%)	OTHERS (wt%)	AVERAGE PARTICLE DIAMETER (nm)	AVERAGE DISPERSION SPACING (nm)	YIELD STRESS (1000°C) (MPa)	VICKERS HARDNESS (HV)
COMPARATIVE EXAMPLE	1 (PM1000)	REMAINDER	0.6	0.3	—	23.5	16	150	93	325
	2		1	—	—	—	13	112	187	377
	3		1	0.5	—	—	14	179	126	366
EXAMPLE	1	REMAINDER	1	0.5	0.8	—	7	47	350	458
	2		1	0.5	0.4	—	8	51	340	439
	3		1	0.5	1.6	—	8	55	319	424
	4		1	4.5	0.8	25.71	17	120	185	611
	5		1	0.5	0.08	—	13	140	154	343
	6		1	0.5	3.2	—	11	89	226	401
	7		1	4.5	5	25.71	12	108	196	577
	8		1	2	0.8	—	10	140	166	390
	9		1	4	0.8	—	12	195	128	472
	10		0.6	0.3	—	23.5	14	210	109	403
			0.6	0.3	0.5	23.5	9	97	229	469

Description

Technical Field

5 **[0001]** The present invention relates to an oxide dispersion strengthened alloy and particularly to an oxide dispersion strengthened alloy that is preferred as a material for the rotor blade or stator blade of a gas turbine, a high temperature heating furnace member, or the like used at high temperature.

Background Art

10 **[0002]** Conventionally, the research and development of materials called oxide dispersion strengthened (hereinafter referred to as "ODS") alloys, as high temperature-resistant materials used for gas turbines and the like, have been performed. For these ODS alloys, an alloy powder and an oxide powder are subjected to mechanical alloying treatment by a ball mill, and then, particles of an oxide, such as yttrium oxide, are finely dispersed in a base material, such as
15 nickel, by annealing treatment so as to improve high temperature strength.

[0003] As such an ODS alloy, for example, an ODS alloy described in Japanese Patent Laid-Open No. 7-90438 is proposed (Patent Literature 1). This ODS alloy comprises 2% or less of one or more elements selected from the group consisting of titanium, zirconium, and hafnium, 15 to 35% of chromium, 0.01 to 0.4% of carbon, and 0.1 to 2.0% of an oxide comprising yttrium, by weight, and the remainder substantially comprising nickel, and is formed by dispersing an
20 oxide comprising yttrium, as particles, in the matrix of a nickel-base alloy containing one or more elements selected from the group consisting of titanium, zirconium, and hafnium, chromium, and carbon.

Citation List

25 Patent Literature

[0004]

Patent Literature 1: Japanese Patent Laid-Open No. 7-90438

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Summary of Invention

Technical Problem

35 **[0005]** However, in the invention described in Patent Literature 1, aluminum is excluded from the alloy composition, focusing on the problem that when a complex oxide of aluminum oxide and yttrium oxide is formed, the oxide particles are coarsened, and the high temperature strength decreases. Therefore, a problem of the above Patent Literature 1 is that a positive effect of the addition of aluminum on an ODS alloy, that is, the effect of improving high temperature oxidation and corrosion resistance, is not obtained.

40 **[0006]** In other words, it is known that in an ODS alloy containing aluminum, the high temperature oxidation and the corrosion resistance are improved by the action of the aluminum. Therefore, there is a high practical demand to add aluminum to an ODS alloy. On the other hand, a problem is that in the presence of aluminum having low oxide formation energy, aluminum oxide forms a complex oxide with yttrium oxide, decreasing the high temperature strength, as pointed out in Patent Literature 1.

45 **[0007]** In addition, in a nickel-based ODS alloy, the so-called gamma prime (γ') phase is precipitated, depending on the content of aluminum. This gamma prime phase has a property that as the temperature increases, the yield strength increases, but a problem of this gamma prime phase is that at a high temperature of 900°C or more, it dissolves, and therefore, the high temperature strength decreases. Conventional ODS alloys are put to practical use for high temperature members, such as gas turbine blades, but a decrease in strength occurs at a high temperature of 900°C or more, as
50 described above, and therefore, the situation is that the limit point is set in the temperature range. This is an important problem to be solved, particularly in industries where more efficient energy conservation has been required in recent years.

[0008] On the other hand, it is known that in a nickel-based ODS alloy, yttrium oxide particles govern high temperature strength at 1000°C or more. However, the yttrium oxide particles have an average particle diameter of about 16 nm and are relatively coarse. In addition,
55 it is known that when yttrium oxide forms a complex oxide with aluminum oxide, the oxide particles are coarsened. Therefore, a problem of conventional ODS alloys is that the effect of improving high temperature strength by the dispersion of oxide particles is not sufficiently obtained.

[0009] In the invention in Patent Literature 1, it is described that by adding 2.0 wt% or less of titanium oxide, zirconium

oxide, or hafnium oxide, a complex oxide with yttrium oxide is formed. But, in addition to containing no aluminum, actually, only experiments in which the amount of zirconium oxide and hafnium oxide added is 0.05 wt% and 0.30 wt% respectively are performed, and moreover, their creep rupture strength at 900°C is considerably lower, compared with other test pieces, and only a lower result is obtained, even compared with nickel-based ODS alloys, such as MA6000 (Special Metals Corporation) and TMO-2 (National Institute for Materials Science), put to practical use.

[0010] The present invention has been made to solve such problems, and it is an object of the present invention to provide an oxide dispersion strengthened alloy in which even with aluminum contained, the particle diameter and dispersion spacing of the oxide are decreased, and the strength at high temperature, the high temperature oxidation and the corrosion resistance can be improved.

Solution to Problem

[0011] An oxide dispersion strengthened alloy according to the present invention is a nickel-base alloy containing aluminum, hafnium, and yttrium oxide, wherein a complex oxide of the yttrium oxide and hafnium oxide is dispersed in a matrix of the nickel-base alloy, with the aluminum contained.

[0012] In addition, in the present invention, the complex oxide may have an average particle diameter of 7 to 11 nm and an average dispersion spacing of 47 to 97 nm.

[0013] In addition, in the present invention, less than 2% of an aluminum element, 0.4 to 3.2% of a hafnium element, and 0.5 to 2.0% of yttrium oxide by weight may be contained.

[0014] Further, in the present invention, the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide may be 1:0.5 to 1:4.

[0015] In addition, in the present invention, 0.5% of an aluminum element, 0.8% of a hafnium element, and 1% of yttrium oxide by weight may be contained.

[0016] Further, in the present invention, the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide may be 1:1.

[0017] In addition, in the present invention, 26% or less by weight of one or two or more elements selected from the group consisting of chromium, titanium, tantalum, tungsten, molybdenum, iron, zirconium, carbon, and boron may be further contained.

Advantageous Effects of Invention

[0018] According to the present invention, even with aluminum contained, the particle diameter and dispersion spacing of the oxide are decreased, and the strength at high temperature, the high temperature oxidation and the corrosion resistance can be improved.

Brief Description of Drawings

[0019]

[Figure 1] Figure 1 is a graph showing the relationship between the free energy of oxide formation and a diffusion coefficient for various alloy elements.

[Figure 2] Figure 2 is a graph showing the relationship between temperature and the standard free energy of formation for various oxides.

[Figure 3] Figure 3 is a table showing formulation components and properties for each Example of an oxide dispersion strengthened alloy according to the present invention.

[Figure 4] Figure 4 is (a) an image of oxide particles by a transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Comparative Example 1.

[Figure 5] Figure 5 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Comparative Example 2.

[Figure 6] Figure 6 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Comparative Example 3.

[Figure 7] Figure 7 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Example 1.

[Figure 8] Figure 8 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Example 2.

[Figure 9] Figure 9 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Example 3.

[Figure 10] Figure 10 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of

the distribution of oxide particles based on the particle diameter for the sample of Example 4.

[Figure 11] Figure 11 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Example 5.

[Figure 12] Figure 12 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Example 6.

[Figure 13] Figure 13 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Example 7.

[Figure 14] Figure 14 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Example 8.

[Figure 15] Figure 15 is (a) an image of oxide particles by the transmission electron microscope and (b) a graph of the distribution of oxide particles based on the particle diameter for the sample of Example 9.

[Figure 16] Figure 16 is a graph showing the relationship of an average particle diameter to hafnium concentration in these Examples.

[Figure 17] Figure 17 is a graph showing the relationship of a dispersion spacing to hafnium concentration in these Examples.

[Figure 18] Figure 18 is a graph showing the relationship of yield stress to hafnium concentration in these Examples.

[Figure 19] Figure 19 is a graph showing the relationship of Vickers hardness to hafnium concentration in these Examples.

[Figure 20] Figure 20 is a graph showing the relationship of yield stress to aluminum concentration in these Examples.

[Figure 21] Figure 21 is images of oxide particles by the transmission electron microscope (a) when no hafnium is added and (b) when hafnium is added, for the sample of Example 10.

[Figure 22] Figure 22 is the result of the X-ray diffraction test of a nickel-base alloy manufactured in Example 1.

Description of Embodiments

[0020] The present inventors have repeated trial and error and studied diligently in order to solve the above-described problems, and, as a result, found that the above-described problems can be solved by an oxide dispersion strengthened alloy being a nickel-base alloy containing aluminum, hafnium, and yttrium oxide, wherein a complex oxide of the above yttrium oxide and hafnium oxide is formed and dispersed in the matrix of this nickel-base alloy, with the aluminum contained.

[0021] First, the basic principle of the present invention will be described. It is found that in an ODS alloy, in a case where the volume fraction f of the oxide particles is fixed, as the radius r of the oxide particles is decreased, the dispersion spacing l_s of the oxide particles decreases proportionally, as shown in the following formula (1).

$$l_s = \beta (r/\sqrt{f}) \dots \text{formula (1)}$$

wherein β is a constant.

[0022] In addition, the yield stress σ of the ODS alloy increases in inverse proportion to the dispersion spacing l_s of the oxide particles, as shown in the following formula (2).

$$\sigma \propto 1/l_s \dots \text{formula (2)}$$

Therefore, it is found that as the size of the oxide particles decreases, the yield stress σ of the ODS alloy is improved inversely proportionally, as shown in the following formula (3) obtained from the above formulas (1) and (2).

$$\sigma \propto (\sqrt{f}/r) \dots \text{formula (3)}$$

[0023] From the above, it is found that when a nickel-based ODS alloy containing oxide particles smaller than oxide particles that conventional nickel-based ODS alloys put to practical use contain can be manufactured, an ODS alloy having higher yield stress is obtained. Specifically, adding an element that has a lower free energy of oxide formation (forms an oxide more easily) and a smaller diffusion coefficient than aluminum has been conceived as a method for suppressing the growth and coarsening of yttrium oxide.

[0024] In the present invention, hafnium (Hf) has been selected as an element that satisfies the above conditions, based on the relationship between the free energy of oxide formation and diffusion ability of alloy elements shown in Figure 1, and a diagram of the standard free energy of formation of oxides shown in Figure 2.

[0025] The function of each element contained in an oxide dispersion strengthened alloy according to the present invention will be described below.

[0026] Aluminum (Al) is an element that is effective for improving high temperature oxidation and corrosion resistance. In addition, aluminum is an element that causes a gamma prime (γ') phase to be precipitated in the matrix of a nickel-base alloy, depending on the amount of aluminum added. In this embodiment, by adding aluminum in a range in which this gamma prime phase is not precipitated, dispersion strengthening by oxide particles is intended, while the high temperature oxidation and the corrosion resistance are maintained.

[0027] Yttrium oxide (Y_2O_3) is dispersed in the matrix of a nickel-base alloy and improves strength particularly in a high temperature environment at more than about 900°C.

If the content of yttrium oxide is less than 0.5 wt%, sufficient high temperature strength may not be obtained. On the other hand, if the content of yttrium oxide is more than 2.0 wt%, the ductility and the working and forming properties may degrade significantly. Therefore, the content of yttrium oxide is preferably selected in the range of 0.5 to 2.0 wt%. In this embodiment, 1 wt% is selected, but the content of yttrium oxide is not limited to this, and may be appropriately changed and selected in a range in which a preferred effect of yttrium oxide is obtained, and in a range in which the demerit is acceptable.

[0028] Hafnium (Hf) serves the function of suppressing the growth and coarsening of yttrium oxide particles. In this embodiment, hafnium forms a complex oxide with yttrium oxide in the form of hafnium oxide (HfO_2). Therefore, yttrium oxide is prevented from forming a complex oxide with aluminum oxide (Al_2O_3), and the particle diameter and dispersion spacing of the oxide particles are small.

[0029] In this embodiment, the amount of hafnium added is selected so that the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide is 1:0.5 to 1:4 in order to effectively form a complex oxide of yttrium oxide and hafnium oxide. More preferably, the amount of hafnium added is preferably such that the ratio of the number of molecules is 1:1. However, the amount of hafnium added is not limited to this, and the amount of hafnium formulated may be appropriately changed and selected as long as the dispersion spacing of the above complex oxide can be decreased to maintain high temperature strength.

[0030] Next, a method for manufacturing the oxide dispersion strengthened alloy in this embodiment will be described.

[0031] First, in addition to a nickel powder that is a matrix, predetermined amounts of aluminum, hafnium, and yttrium oxide powders that are basic components are formulated. At this time, when aluminum is added at an added weight at which the gamma prime phase is not precipitated, the gamma prime phase is not precipitated, and dispersion strengthening by the oxide phase alone is intended.

[0032] Next, the formulated mixed powders are introduced into a planetary ball mill, and mechanical alloying treatment is performed. This mechanical alloying treatment is treatment in which the collision energy of balls provided in the planetary ball mill is used to repeatedly cause the folding and rolling of the powders for alloying. By this mechanical alloying treatment, the mixed powders are alloyed on the atomic order even under room temperature conditions.

[0033] Then, the alloyed mixed powders are sintered by hot pressing. At this time, aluminum and hafnium are each oxidized, and aluminum oxide and hafnium oxide are each formed, and the above hafnium oxide forms a complex oxide with yttrium oxide. Thus, the complex oxide is finely dispersed in the matrix of the nickel-base alloy, and the growth and coarsening of the oxide particles are suppressed. Therefore, the size and dispersion spacing of the oxide particles decrease, and the yield stress of the oxide dispersion strengthened alloy itself is improved.

[0034] When the stator blade of a gas turbine is manufactured using the oxide dispersion strengthened alloy in this embodiment, it is possible to form a blade shape from an ingot after final heat treatment by machining. In addition, when a combustor liner and a transition piece are manufactured, it is possible to repeat hot rolling to make a thin plate, then hot-work the thin plate into a cylindrical shape, and then perform heat treatment. In addition, when a cylinder without a joining portion is manufactured, it is possible to hollow the central portion of a cylindrical ingot to make a thick cylinder, and perform hot ring rolling.

[0035] According to this embodiment as described above, such effects are achieved that even with aluminum contained, the particle diameter and dispersion spacing of the oxide are decreased, and the strength at high temperature, the high temperature oxidation and the corrosion resistance can be improved, and the like.

[0036] Next, Examples of the oxide dispersion strengthened alloy according to the present invention will be described. Specifically, in order to confirm a preferred content of the oxide dispersion strengthened alloy according to the present invention and its effect, oxide dispersion strengthened alloys having various formulation components shown in Figure 3 were each manufactured, and the average particle diameter, the average dispersion spacing, the yield stress, and the Vickers hardness were measured.

[0037] In these Examples, in the manufacture of the oxide dispersion strengthened alloys with formulation amounts allocated, mechanical alloying treatment was performed using a planetary ball mill (manufactured by Fritsch). For the

treatment conditions, the number of revolutions of the ball mill was 400 rpm, and the treatment time was 24 hours, at room temperature in an Ar gas atmosphere. Then, at a temperature of 1200°C, hot pressing under a load of 1 ton for 3 hours was performed for sintering.

[0038] In the measurement of the average particle diameter and the average dispersion spacing, the sintered sample was cut, then a thin film sample was fabricated by electropolishing, and the oxide particles were observed using a transmission electron microscope (JEL-2000EX/T: manufactured by JEOL Ltd.). The complex oxide particles in these Examples are present in a polygonal shape or an elliptical shape, to be exact, but they are in a range in which they can be approximated by a circular shape. Therefore, in these Examples, each particle in images obtained by the transmission electron microscope was approximated by a circular shape, and the average particle diameter and the average dispersion spacing were calculated by statistical processing and analysis. Specifically, from four TEM (Transmission Electron Microscope) photographs having a field-of-view size of about 300 μm $\times$ 300 μm , statistical processing and analysis with circle approximation were performed using image processing software (Mac-view: manufactured by Mountech Co., Ltd.).

[0039] In addition, for the yield stress, the yield stress at 1000°C was tentatively calculated according to a void strengthening theory based on the above formula (3). For the measurement of the Vickers hardness, the Vickers hardness was measured under a load of 1 kg at room temperature, using a Vickers hardness tester (Micro Vickers: manufactured by SHIMADZU CORPORATION). «Comparative Example 1»

[0040] First, various properties were measured for a nickel-based ODS alloy put to practical use (PM1000: manufactured by PLANSEE) as Comparative Example 1. This PM1000 is a nickel-base alloy and contains 0.6 wt% of yttrium oxide, 0.3 wt% of aluminum, and, in addition, 23.5 wt% of chromium and the like.

[0041] As shown in Figure 3 and Figure 4, in the ODS alloy of Comparative Example 1, the oxide particles had an average particle diameter of 16 nm and an average dispersion spacing of 150 nm. In addition, this ODS alloy had a yield stress of 93 MPa at 1000°C and a Vickers hardness of 325 HV. The low yield stress is caused also by a small amount of yttrium oxide added, and it cannot be said that the high temperature strength is so high.

«Comparative Example 2»

[0042] Next, as Comparative Example 2, the present inventors manufactured a nickel-based oxide dispersion strengthened alloy containing no hafnium and aluminum. Specifically, 1 wt% of yttrium oxide was contained in a nickel-base alloy.

[0043] As shown in Figure 3 and Figure 5, in the ODS alloy of Comparative Example 2, the oxide particles had an average particle diameter of 13 nm and an average dispersion spacing of 112 nm. In addition, this ODS alloy had a yield stress of 187 MPa at 1000°C and a Vickers hardness of 377 HV.

«Comparative Example 3»

[0044] As Comparative Example 3, the present inventors manufactured a nickel-based oxide dispersion strengthened alloy containing no hafnium. Specifically, 1 wt% of yttrium oxide and 0.5 wt% of aluminum were contained in a nickel-base alloy.

[0045] As shown in Figure 3 and Figure 6, in the ODS alloy of Comparative Example 3, the oxide particles had an average particle diameter of 14 nm and an average dispersion spacing of 179 nm. In addition, this ODS alloy had a yield stress of 126 MPa at 1000°C and a Vickers hardness of 366 HV.

[0046] As described above, in the ODS alloys of Comparative Example 2 and Comparative Example 3 containing only the basic components, the diameter of the oxide particles is almost equal to that of Comparative Example 1 put to practical use. According to the results of the Comparative Examples described above, it was confirmed that in the simple basic components, the formation of oxide particles in a nickel-based ODS alloy was appropriately reproduced.

Example 1

[0047] Next, as Example 1, one obtained by further adding hafnium to the formulation of Comparative Example 3, that is, a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 0.5 wt% of aluminum, and 0.8 wt% of hafnium were contained in a nickel-base alloy.

[0048] The amount of hafnium added was determined so that the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide was 1:1 in order to effectively form a complex oxide of yttrium oxide (Y_2O_3) and hafnium oxide (HfO_2).

[0049] As shown in Figure 3 and Figure 7, in the ODS alloy of this Example 1, the oxide particles had an average particle diameter of 7 nm and an average dispersion spacing of 47 nm. In addition, this ODS alloy had a yield stress of 350 MPa at 1000°C and a Vickers hardness of 458 HV. Therefore, it was confirmed that by the addition of hafnium, the average particle diameter decreased to half, and the average dispersion spacing decreased to as small as about 1/4,

compared with Comparative Example 3. With this, it was considered that the yield stress of the ODS alloy was improved by about 2.8 times, and it was confirmed that actually, the hardness was improved by as much as about 1.2 times or more.

[0050] In addition, in the sample of this Example 1, the electron beam diffraction spots obtained from the oxide particles match the diffraction spots of $Y_2Hf_2O_7$ that is a complex oxide of yttrium oxide and hafnium oxide, and the oxide particles

in the ODS alloy of this Example 1 are of a complex oxide of yttrium oxide and hafnium oxide.

[0051] According to this Example 1 as described above, it was shown that by the addition of hafnium, even with aluminum oxide contained, yttrium oxide forms a complex oxide with hafnium oxide and is dispersed in the matrix of a nickel-base alloy. In addition, it was shown that by the addition of hafnium, the average particle diameter and average dispersion spacing of the oxide particles are minimized, and the yield stress and Vickers hardness of the ODS alloy are improved.

Example 2

[0052] In Example 2, the amount of hafnium added was reduced with respect to the formulation of Example 1, and a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 0.5 wt% of aluminum, and 0.4 wt% of hafnium were contained in a nickel-base alloy. The amount of hafnium added was determined so that the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide was 1:0.5.

[0053] As shown in Figure 3 and Figure 8, in the ODS alloy of this Example 2, the oxide particles had an average particle diameter of 8 nm and an average dispersion spacing of 51 nm. In addition, this ODS alloy had a yield stress of 340 MPa at 1000°C and a Vickers hardness of 439 HV. Therefore, also in this Example 2, as in Example 1, it was confirmed that by the addition of hafnium, the average particle diameter decreased to almost half, and the average dispersion spacing was reduced to as small as about 1/4, compared with Comparative Example 3. With this, it was considered that the yield stress at 1000°C of the ODS alloy was improved by about 2.7 times, and it was confirmed that

the hardness was improved by about 1.2 times.

[0054] According to this Example 2 as described above, it was shown that even if the amount of hafnium added, with respect to 1 wt% of yttrium oxide, is 0.4 wt%, the average particle diameter and average dispersion spacing of the oxide particles are reduced, and the yield stress and Vickers hardness of the ODS alloy are improved.

Example 3

[0055] In Example 3, the amount of hafnium added was increased with respect to the formulation of Example 1, and a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 0.5 wt% of aluminum, and 1.6 wt% of hafnium were contained in a nickel-base alloy. The amount of hafnium added was determined so that the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide was 1:2.

[0056] As shown in Figure 3 and Figure 9, in the ODS alloy of this Example 3, the oxide particles had an average particle diameter of 8 nm and an average dispersion spacing of 55 nm. This ODS alloy had a yield stress of 319 MPa at 1000°C and a Vickers hardness of 424 HV. Therefore, it was confirmed that in the ODS alloy of this Example 3, by the addition of hafnium, the average particle diameter decreased to almost half, and the average dispersion spacing was minimized to as small as about 30%, compared with Comparative Example 3. It was confirmed that with this, the yield stress of the ODS alloy was improved by about 2.5 times or more, and the hardness was improved by about 1.2 times. Therefore, also in Example 3, the same level of improvement in yield stress and hardness as in Example 1 was confirmed.

[0057] According to this Example 3 as described above, it was shown that even if the amount of hafnium added, with respect to 1 wt% of yttrium oxide, is 1.6 wt%, the average particle diameter and average dispersion spacing of the oxide particles are reduced, and the yield stress and Vickers hardness of the ODS alloy are improved.

Example 4

[0058] Next, in Example 4, the amount of aluminum added was increased with respect to the formulation of Example 1, and a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 4.5 wt% of aluminum, and 0.8 wt% of hafnium were contained in a nickel-base alloy. The amount of aluminum added was determined, based on the aluminum content of MA6000 (Special Metals Corporation) that was a gamma prime precipitation strengthened alloy, among ODS alloys put to practical use.

[0059] In addition, in this Example 4, 25.71 wt% of one or two or more elements selected from the group consisting of chromium, titanium, tantalum, tungsten, molybdenum, iron, zirconium, carbon, and boron were contained. Chromium is effective for the improvement of oxidation resistance and corrosion resistance. Titanium and tantalum are effective

for the stabilization of the gamma prime phase. Tungsten, iron, and molybdenum are effective as a solid solution strengthening element. Carbon, boron, and zirconium are effective in strengthening grain boundaries.

[0060] As shown in Figure 3 and Figure 10, in the ODS alloy of this Example 4, the oxide particles had an average particle diameter of 17 nm and an average dispersion spacing of 120 nm. In addition, this ODS alloy had a yield stress of 185 MPa at 1000°C and a Vickers hardness of 611 HV. Therefore, when compared with Comparative Examples 1 to 3 in which no hafnium was added, the ODS alloy of this Example 4 was improved to some degree, compared with Comparative Examples 1 and 3, but the average particle diameter and the average dispersion spacing were almost equal to those of Comparative Example 2. In addition, the Vickers hardness was improved, but no improvement in the yield stress at 1000°C was seen.

[0061] According to this Example 4 as described above, it was shown that in a case where aluminum is contained at an added weight at which the gamma prime phase is precipitated, even if 0.8 wt% of hafnium is added, the growth and coarsening of the oxide particles are not sufficiently suppressed, and the average particle diameter and the average dispersion spacing cannot be minimized, and therefore, the yield stress of the ODS alloy also cannot be improved.

Example 5

[0062] Next, in Example 5, the amount of hafnium added was further reduced with respect to the formulation of Example 2, and a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 0.5 wt% of aluminum, and 0.08 wt% of hafnium were contained in a nickel-base alloy. The amount of hafnium added was determined so that the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide was 1:0.1.

[0063] As shown in Figure 3 and Figure 11, in the ODS alloy of this Example 5, the oxide particles had an average particle diameter of 13 nm and an average dispersion spacing of 140 nm. In addition, this ODS alloy had a yield stress of 154 MPa at 1000°C and a Vickers hardness of 343 HV. Therefore, when compared with Comparative Examples 1 to 3 in which no hafnium was added, the ODS alloy of this Example 5 was improved, compared with Comparative Examples 1 and 3, but the average particle diameter and the average dispersion spacing were larger than those of Comparative Example 2. In addition, no improvement was seen in both a yield stress at 1000°C and Vickers hardness.

[0064] According to this Example 5 as described above, it was shown that although 0.08 wt% of hafnium is added with respect to 1 wt% of yttrium oxide, the average particle diameter and average dispersion spacing of the oxide particles are not so small, and the yield stress and Vickers hardness of the ODS alloy are not improved.

Example 6

[0065] In Example 6, the amount of hafnium added was further increased with respect to the formulation of Example 3, and a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 0.5 wt% of aluminum, and 3.2 wt% of hafnium were contained in a nickel-base alloy. The amount of hafnium added was determined so that the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide was 1:4.

[0066] As shown in Figure 3 and Figure 12, in the ODS alloy of this Example 6, the oxide particles had an average particle diameter of 11 nm and an average dispersion spacing of 89 nm. In addition, this ODS alloy had a yield stress of 226 MPa at 1000°C and a Vickers hardness of 401 HV. Therefore, it was confirmed that in the ODS alloy of this Example 6, by the addition of hafnium, the average particle diameter decreased by 20 percent or more, and the average dispersion spacing decreased to half or less, compared with Comparative Example 3. It was confirmed that with this, the yield stress at 1000°C of the ODS alloy was improved by about 1.8 times, and the hardness was improved by about 1.1 times.

[0067] According to this Example 6 as described above, it was shown that although the amount of hafnium added, with respect to 1 wt% of yttrium oxide, is 3.2 wt%, the average particle diameter and average dispersion spacing of the oxide particles are minimized, and the yield stress and Vickers hardness of the ODS alloy are improved.

Example 7

[0068] In Example 7, the amount of hafnium added was increased with respect to the formulation of Example 4, and a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 4.5 wt% of aluminum, and 5 wt% of hafnium were contained in a nickel-base alloy. This is to check whether there is an improvement in average dispersion spacing and yield stress at 1000°C by increasing the amount of hafnium even if the content of aluminum is increased. In addition, as in Example 4, 25.71 wt% of one or two or more elements selected from the group consisting of chromium, titanium, tantalum, tungsten, molybdenum, iron, zirconium, carbon, and boron were contained.

[0069] As shown in Figure 3 and Figure 13, in the ODS alloy of this Example 7, the oxide particles had an average particle diameter of 12 nm and an average dispersion spacing of 108 nm. In addition, this ODS alloy had a yield stress of 196 MPa at 1000°C and a Vickers hardness of 577 HV. Therefore, in the ODS alloy of this Example 7, the average particle diameter and the average dispersion spacing were improved to be smaller, compared with Comparative Examples 1 to 3 in which no hafnium was added, though not a significant improvement, and with this, the yield stress at 1000°C and the Vickers hardness were improved.

[0070] According to this Example 7 as described above, in a case where aluminum was contained at an added weight at which the gamma prime phase was precipitated, by adding 5 wt% of hafnium, the average particle diameter and average dispersion spacing of the oxide particles decreased slightly, and an improvement was also seen in the yield stress at 1000°C of the ODS alloy.

Example 8

[0071] In Example 8, in order to clarify the effect of the aluminum content, the amount of aluminum added was made larger than that of Example 1 and smaller than that of Example 4, and a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 2 wt% of aluminum, and 0.8 wt% of hafnium were contained in a nickel-base alloy. For the amount of hafnium and yttrium oxide formulated, Example 1 with the best effect was referred to. The amount of aluminum added was determined so that the weight ratio of hafnium to aluminum was 0.8:2.

[0072] As shown in Figure 3 and Figure 14, in the ODS alloy of this Example 8, the oxide particles had an average particle diameter of 10 nm and an average dispersion spacing of 140 nm. In addition, this ODS alloy had a yield stress of 166 MPa at 1000°C and a Vickers hardness of 390 HV. Therefore, when the ODS alloy of this Example 8 was compared with Comparative Examples 1 to 3 in which no hafnium was added, the average particle diameter and the average dispersion spacing decreased somewhat, and the yield stress at 1000°C was also improved to some degree, compared with Comparative Examples 1 and 3, but no improvement effect was seen, compared with Comparative Example 2.

[0073] According to this Example 8 as described above, it is found that when 2 wt% of aluminum is contained in 1 wt% of yttrium oxide and 0.8 wt% of hafnium, some improvement effect is seen, in view of the balance between aluminum and hafnium, but cannot be said to be sufficient.

Example 9

[0074] In Example 9, in order to clarify the effect of the aluminum content as in Example 8, the amount of aluminum added was made larger than that of Example 8, and a nickel-based ODS alloy containing aluminum, hafnium, and yttrium oxide was manufactured. Specifically, 1 wt% of yttrium oxide, 4 wt% of aluminum, and 0.8 wt% of hafnium were contained in a nickel-base alloy. The amount of aluminum added was determined so that the weight ratio of hafnium to aluminum was 0.8:4.

[0075] As shown in Figure 3 and Figure 15, in the ODS alloy of this Example 9, the oxide particles had an average particle diameter of 12 nm and an average dispersion spacing of 195 nm. In addition, this ODS alloy had a yield stress of 128 MPa at 1000°C and a Vickers hardness of 472 HV. Therefore, in the ODS alloy of this Example 9, both the average particle diameter and the average dispersion spacing increased, compared with Comparative Examples 1 to 3 in which no hafnium was added. In addition, the Vickers hardness was somewhat improved, but no improvement in yield stress was seen. The improvement in Vickers hardness is considered to be caused by the fact that the gamma prime phase was precipitated.

[0076] According to this Example 9 as described above, it was shown that in a case where 4 wt% of aluminum is contained in 1 wt% of yttrium oxide, even if 0.8 wt% of hafnium is added, the average particle diameter and average dispersion spacing of the oxide particles are not minimized, and the yield stress of the ODS alloy is not improved.

[0077] Here, the dependence of various properties on hafnium concentration is considered for Comparative Example 3 and Examples 1 to 3, 5, and 6 containing 0.5 wt% of aluminum and 1 wt% of yttrium oxide, among the above Examples. Figure 16 to Figure 19 are graphs respectively showing the relationships of the average particle diameter, the average dispersion spacing, the yield stress, and the Vickers hardness to the hafnium concentration.

[0078] As shown in Figure 16 to Figure 19, it is found that by adding hafnium, the effect of making the oxide particles finer and reducing the average dispersion spacing is obtained, leading to an improvement in yield stress at 1000°C. Particularly, a clear improvement is seen in the samples of Examples 1 to 3 and 6. Therefore, it was shown that in the nickel-base alloys containing 0.5 wt% of aluminum and 1 wt% of yttrium oxide, the hafnium concentration at which the oxide particles can be made finer, and the average dispersion spacing can be reduced is 0.4 wt% to 3.2 wt%, and when the hafnium concentration is 0.8 wt% (Example 1), the effect is the highest. When this is expressed in terms of the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide, 1:0.5 to 1:4 is preferred and 1.1 is more preferred.

[0079] Next, in order to consider the dependence on aluminum concentration, the data of Examples 8 and 9 in which the aluminum concentration is increased with respect to the formulation of Example 1 are shown in Figure 16 to Figure 19. In addition, the relationship of the yield stress to the aluminum concentration is shown in Figure 20.

[0080] As shown in Figure 16 and Figure 17, it was confirmed that as the aluminum concentration increased, the average particle diameter and the average dispersion spacing were coarsened. As shown in Figure 18 and Figure 20, it was confirmed that as the aluminum concentration increased, the yield stress decreased. On the other hand, as shown in Figure 19, in Example 8 with an aluminum concentration of 2 wt%, the Vickers hardness decreased, whereas, in Example 9 with an aluminum concentration of 4 wt%, the Vickers hardness was improved in reverse. This is considered to be caused by the fact that the gamma prime phase was precipitated due to the increase of the aluminum concentration.

[0081] From the above, it was shown that the high temperature strength, the high temperature oxidation and the corrosion resistance can be improved by an oxide dispersion strengthened alloy containing less than 2 wt%, an added weight at which the gamma prime phase is not precipitated, of an aluminum element, 0.4 to 3.2 wt% of a hafnium element, and 1 wt% of yttrium oxide. In addition, in this oxide dispersion strengthened alloy, the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide is 1:0.5 to 1:4.

[0082] Further, it was shown that the high temperature strength, the high temperature oxidation and the corrosion resistance can be most improved by an oxide dispersion strengthened alloy containing 0.5 wt% of an aluminum element, 0.8 wt% of a hafnium element, and 1 wt% of yttrium oxide. In addition, in this oxide dispersion strengthened alloy, the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide is 1:1.

[0083] In addition, 26 wt% or less of one or two or more elements selected from the group consisting of chromium, titanium, tantalum, tungsten, molybdenum, iron, zirconium, carbon, and boron may be contained, as in the above Examples 4 and 7. It is considered that this secondarily improves the high temperature strength, the high temperature oxidation and the corrosion resistance, and the like.

[0084] Further, from the results of the above Examples, it was shown that the high temperature strength, the high temperature oxidation and the corrosion resistance can be improved by an oxide dispersion strengthened alloy in which a complex oxide of yttrium oxide and hafnium oxide has an average particle diameter of 7 to 11 nm and an average dispersion spacing of 47 to 89 nm.

[0085] In addition, as shown in Figure 4 to Figure 6, in Comparative Examples 1 to 3, there are large variations in the particle diameter of the oxide particles, and it can be confirmed that the oxide particles are coarsened. On the other hand, as shown in Figure 7 to Figure 15, in these Examples, the variations in the particle diameter of the oxide particles are smaller, compared with the Comparative Examples, and it can be confirmed that particularly when the amount of hafnium added is 0.4 to 1.6 wt% (Examples 1 to 3), the coarsening of the oxide particles is effectively suppressed.

Example 10

[0086] In Example 10, a nickel-based ODS alloy having a composition similar to that of the alloy put to practical use (PM1000: manufactured by PLANSEE) used in the above Comparative Example 1 was fabricated, and the effect of the addition of hafnium was verified together. Specifically, as the nickel-based ODS alloy corresponding to the alloy put to practical use, 0.6 wt% of yttrium oxide and 0.3 wt% of aluminum were contained in a nickel-base alloy. In addition, 0.5 wt% of hafnium was further contained in this alloy.

[0087] For the fabrication method, the element powders were mixed, and then, mechanical alloying (MA) treatment was performed in an Ar gas atmosphere, using the planetary ball mill, for 24 hours. Then, the MA powder was consolidated and formed by hot pressing (1200°C, 10 kN, 3 hours), also for the precipitation treatment of the oxide particles. The consolidated and formed sample was cut, then a thin film sample was fabricated by electropolishing, and the oxide particles were observed using the transmission electron microscope (TEM).

[0088] As shown in Figure 3 and Figure 21, it was confirmed that when no hafnium was added, the average particle diameter of the oxide particles was 14 nm, whereas when hafnium was added, the average particle diameter was made ultrafine to as small as 9 nm. In addition, also for the average dispersion spacing, it was confirmed that when no hafnium was added, the average dispersion spacing was 210 nm, whereas when hafnium was added, the average dispersion spacing decreased to as small as 97 nm. Further, for the yield stress, by adding hafnium, the yield stress increased from 109 MPa to 229 MPa by 2 times or more, and the Vickers hardness was also improved from 403 HV to 469 HV.

[0089] In this Example 10, the content of yttrium oxide is 0.6 wt%, and the content of hafnium is 0.5 wt%, and therefore, the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide is equal to 1:1. In addition, it is considered that the average dispersion spacing is larger, compared with the above-described other Examples because the content of yttrium oxide in other Examples is 1 wt%, whereas in this Example 10, the content of yttrium oxide is as low as 0.6 wt%, and the volume fraction of yttrium oxide is small.

[0090] According to this Example 10 as described above, it was confirmed that also for an alloy corresponding to a nickel-based ODS alloy put to practical use, the addition of hafnium is effective in making the oxide particles finer and narrowing the average dispersion spacing. In addition, it was shown that the yield stress and Vickers hardness of the

ODS alloy are improved.

[0091] Further, from the results of the above Examples 1 to 3, 6, and 10, it was shown that the high temperature strength, the high temperature oxidation and the corrosion resistance can be improved by an oxide dispersion strengthened alloy in which a complex oxide of yttrium oxide and hafnium oxide has an average particle diameter of 7 to 11 nm and an average dispersion spacing of 47 to 97 nm.

Example 11

[0092] In this Example 11, for the nickel-base alloy (Ni-0.5Al-0.8Hf-1Y₂O₃) manufactured in the above Example 1, an experiment for identifying the oxide particles that were made finer was performed. Specifically, an X-ray diffraction test was performed on the sample obtained by solidifying the mechanically alloyed powder of the nickel-base alloy by hot pressing, manufactured in the above Example 1. The result is shown in Figure 22.

[0093] As shown in Figure 22, diffraction peaks corresponding to Y₂Hf₂O₇ that was a complex oxide of yttrium oxide and hafnium oxide were detected from the oxide particles that were made finer. Therefore, according to this Example 11, it was confirmed that the yttrium oxide added in Example 1 formed a compound with hafnium, was made finer, and dispersed as a complex oxide of yttrium oxide and hafnium oxide.

[0094] The oxide dispersion strengthened alloy according to the present invention is not limited to the above-described embodiment and Examples, and can be appropriately changed.

Claims

1. An oxide dispersion strengthened alloy being a nickel-base alloy comprising aluminum, hafnium, and yttrium oxide, wherein a complex oxide of the yttrium oxide and hafnium oxide is dispersed in a matrix of the nickel-base alloy, with the aluminum contained.
2. The oxide dispersion strengthened alloy according to claim 1, wherein the complex oxide has an average particle diameter of 7 to 11 nm and an average dispersion spacing of 47 to 97 nm.
3. The oxide dispersion strengthened alloy according to claim 1 or claim 2, containing less than 2% of an aluminum element, 0.4 to 3.2% of a hafnium element, and 0.5 to 2.0% of yttrium oxide by weight.
4. The oxide dispersion strengthened alloy according to claim 1 or claim 2, wherein a ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide is 1:0.5 to 1:4.
5. The oxide dispersion strengthened alloy according to claim 3, comprising 0.5% of an aluminum element, 0.8% of a hafnium element, and 1% of yttrium oxide by weight.
6. The oxide dispersion strengthened alloy according to claim 4, wherein the ratio of the number of molecules of yttrium oxide to the number of molecules of hafnium oxide is 1:1.
7. The oxide dispersion strengthened alloy according to any of claim 1 to claim 6, further comprising 26% or less by weight of one or two or more elements selected from the group consisting of chromium, titanium, tantalum, tungsten, molybdenum, iron, zirconium, carbon, and boron.

Fig. 1

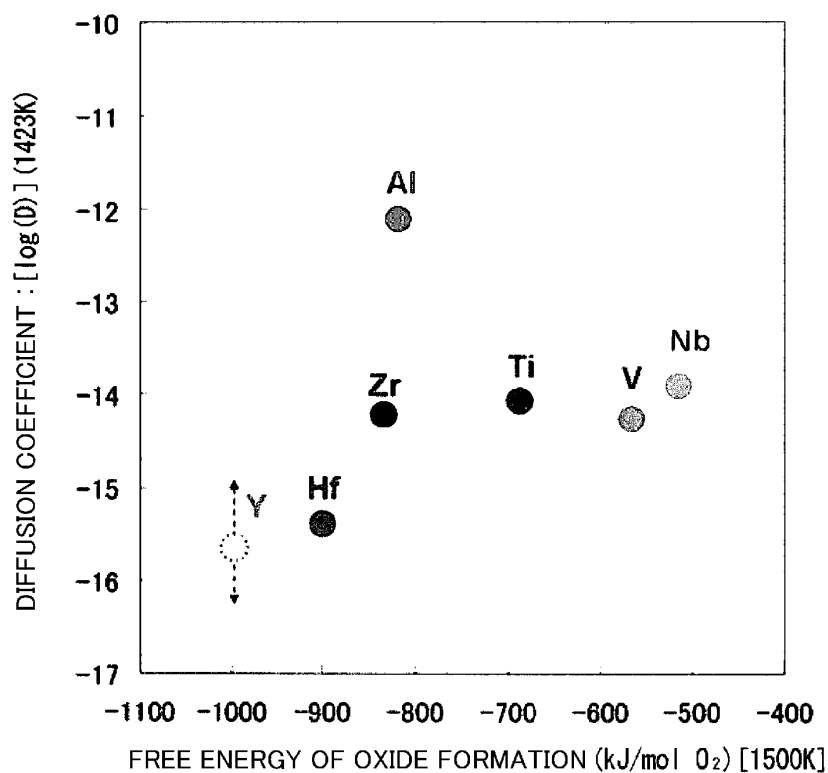


Fig. 2

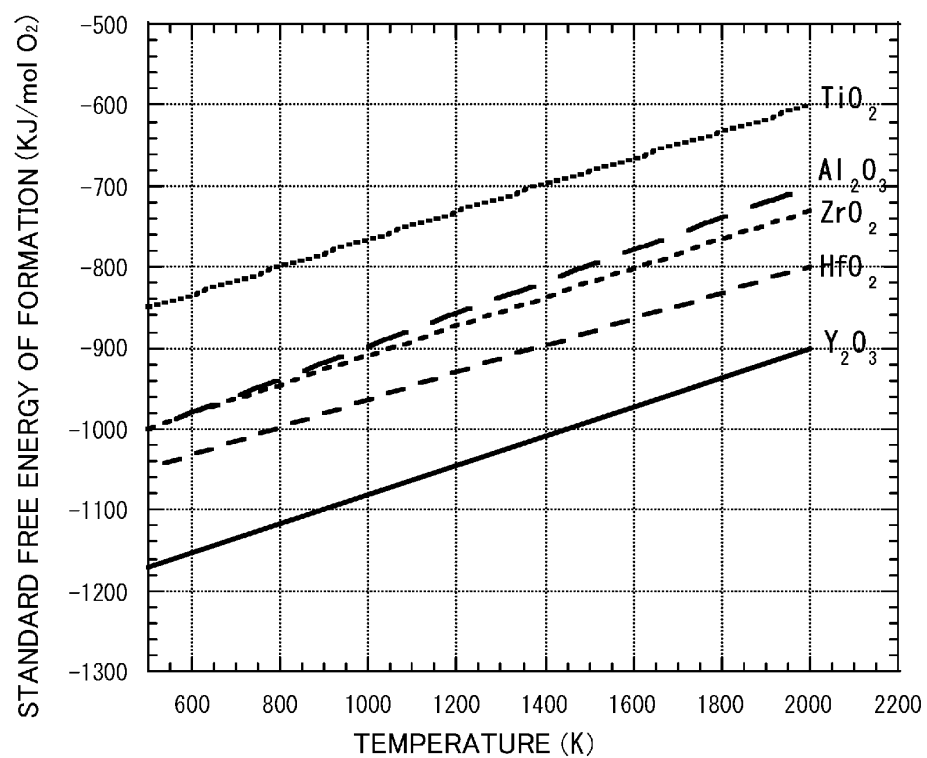
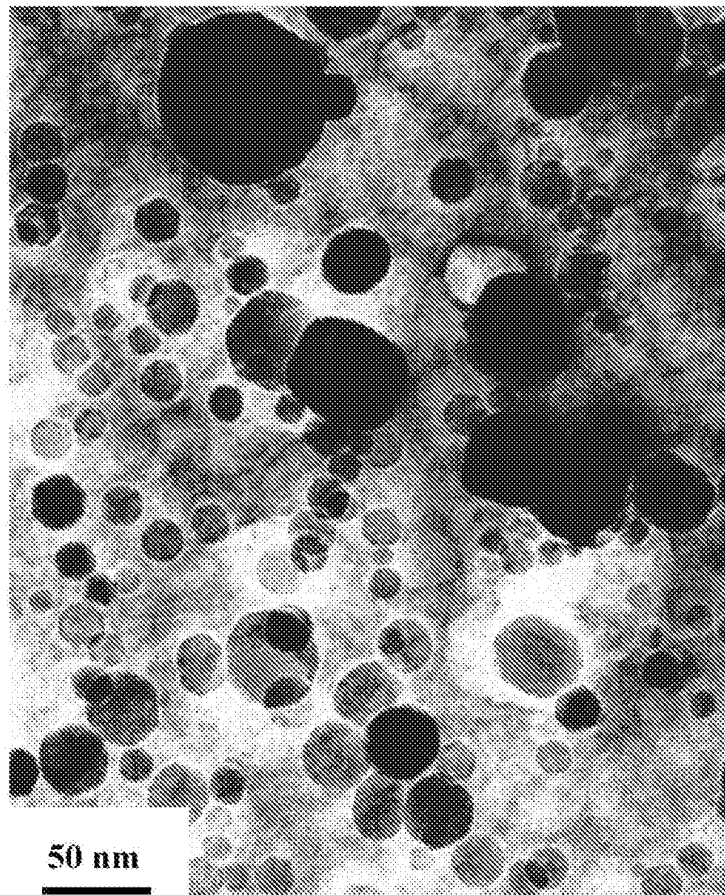


Fig. 3

		Ni (wt%)	Y ₂ O ₃ (wt%)	Al (wt%)	Hf (wt%)	OTHERS (wt%)	AVERAGE PARTICLE DIAMETER (nm)	AVERAGE DISPERSION SPACING (nm)	YIELD STRESS (1000°C) (MPa)	VICKERS HARDNESS (HV)
COMPARATIVE EXAMPLE	1 (PM1000)	REMAINDER	0.6	0.3	—	23.5	16	150	93	325
	2		1	—	—	—	13	112	187	377
	3		1	0.5	—	—	14	179	126	366
EXAMPLE	1	REMAINDER	1	0.5	0.8	—	7	47	350	458
	2		1	0.5	0.4	—	8	51	340	439
	3		1	0.5	1.6	—	8	55	319	424
	4		1	4.5	0.8	25.71	17	120	185	611
	5		1	0.5	0.08	—	13	140	154	343
	6		1	0.5	3.2	—	11	89	226	401
	7		1	4.5	5	25.71	12	108	196	577
	8		1	2	0.8	—	10	140	166	390
	9		1	4	0.8	—	12	195	128	472
	10		0.6	0.3	—	23.5	14	210	109	403
			0.6	0.3	0.5	23.5	9	97	229	469

Fig. 4

(a)



(b)

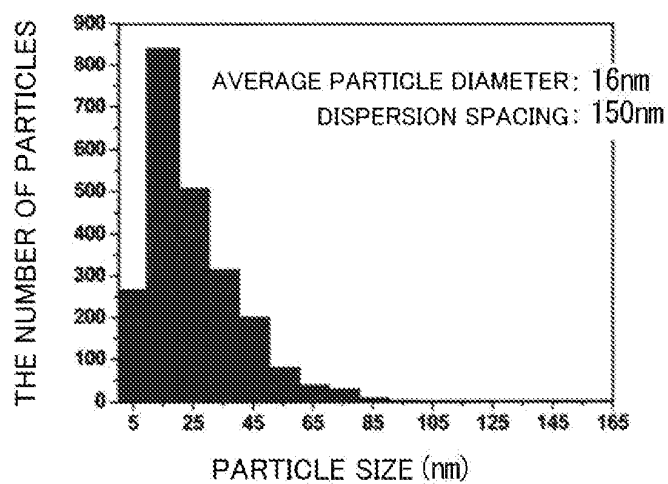


Fig. 5

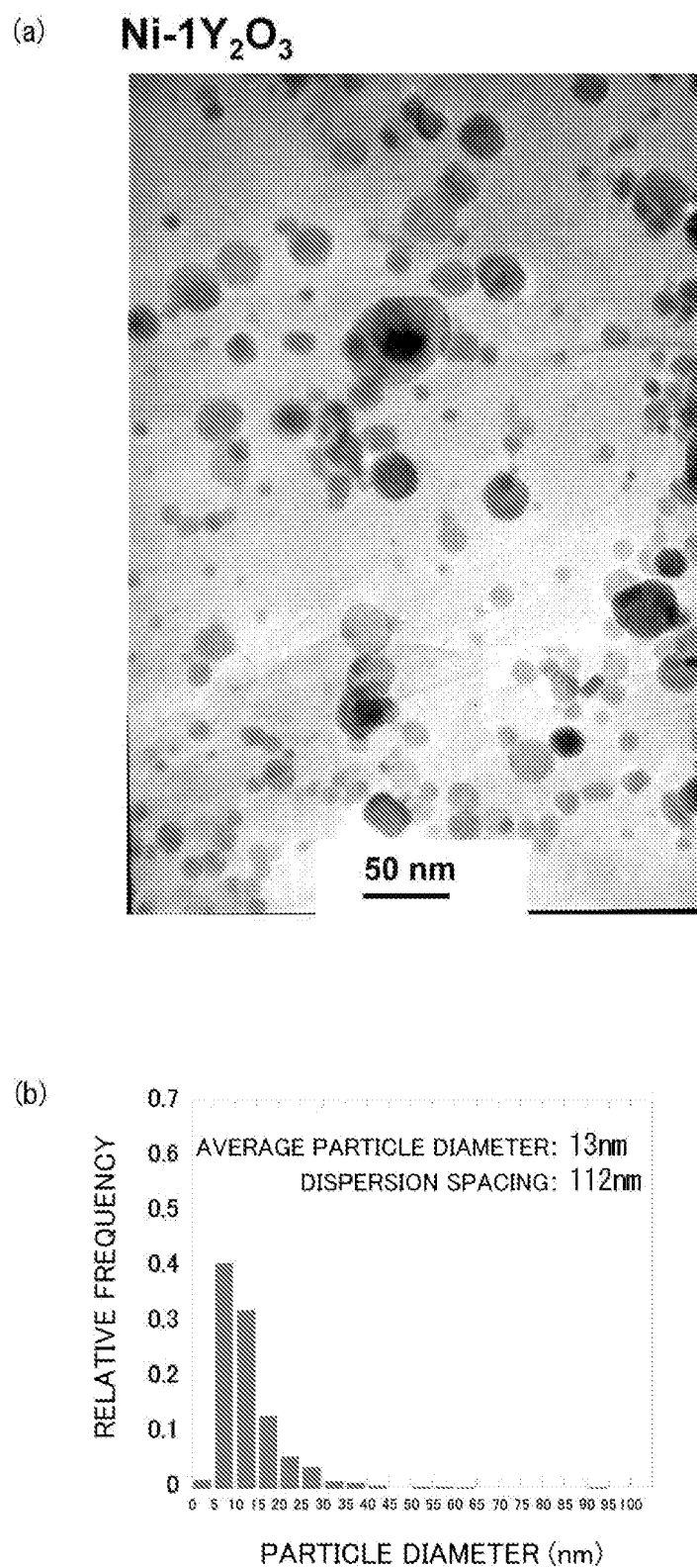


Fig. 6

(a) **Ni-0.5Al-1Y₂O₃**

(b)

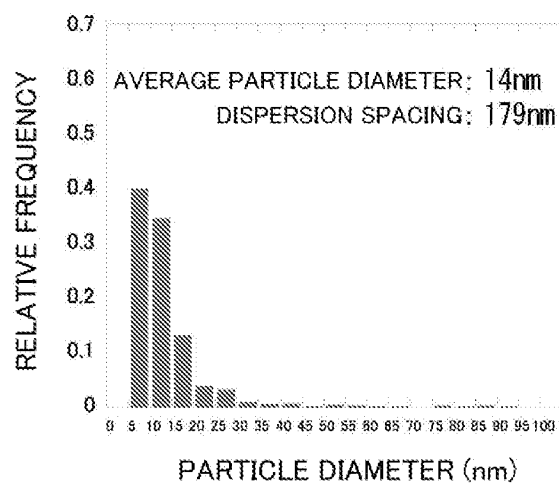


Fig. 7

(a) **Ni-0.5Al-0.8Hf-1Y₂O₃**

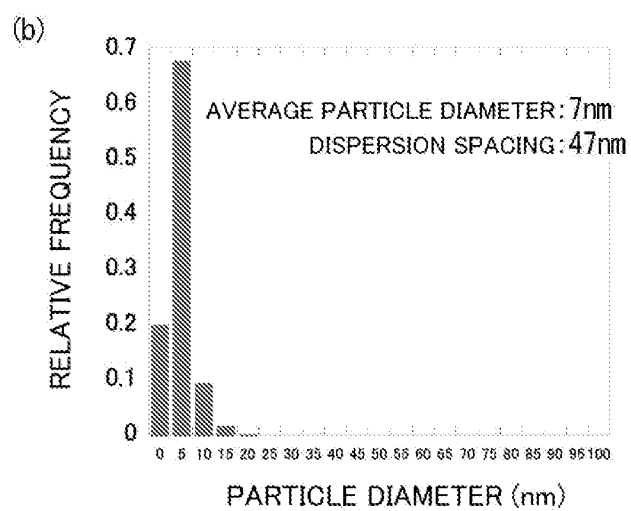


Fig. 8

(a) **Ni-0.5Al-0.4Hf-1Y₂O₃**

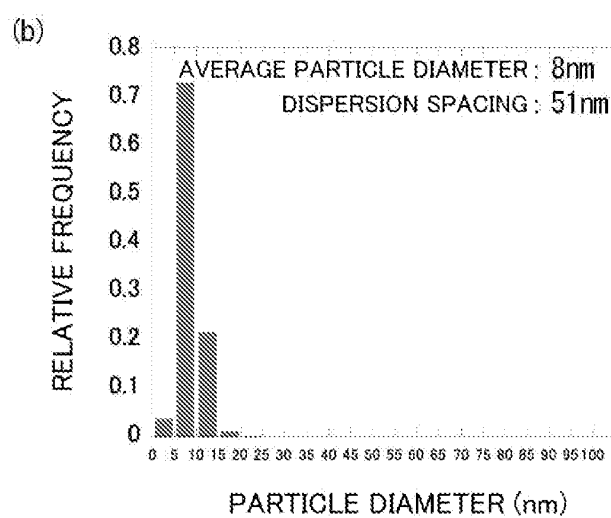
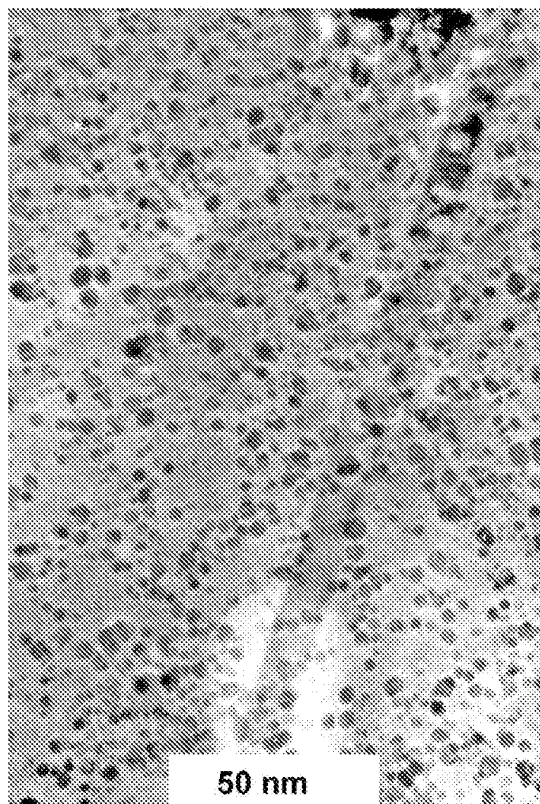


Fig. 9

(a) **Ni-0.5Al-1.6Hf-1Y₂O₃**



(b)

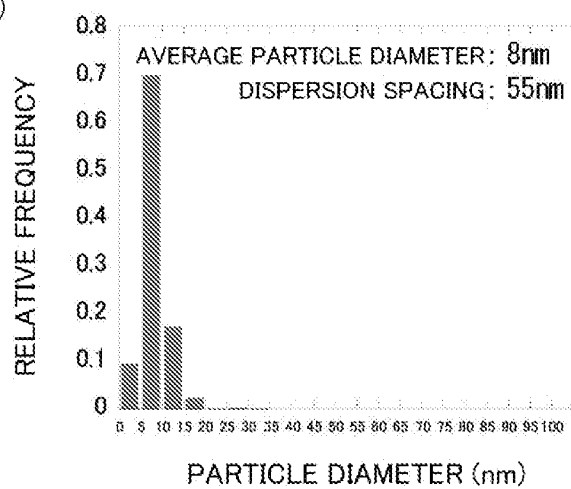


Fig. 10

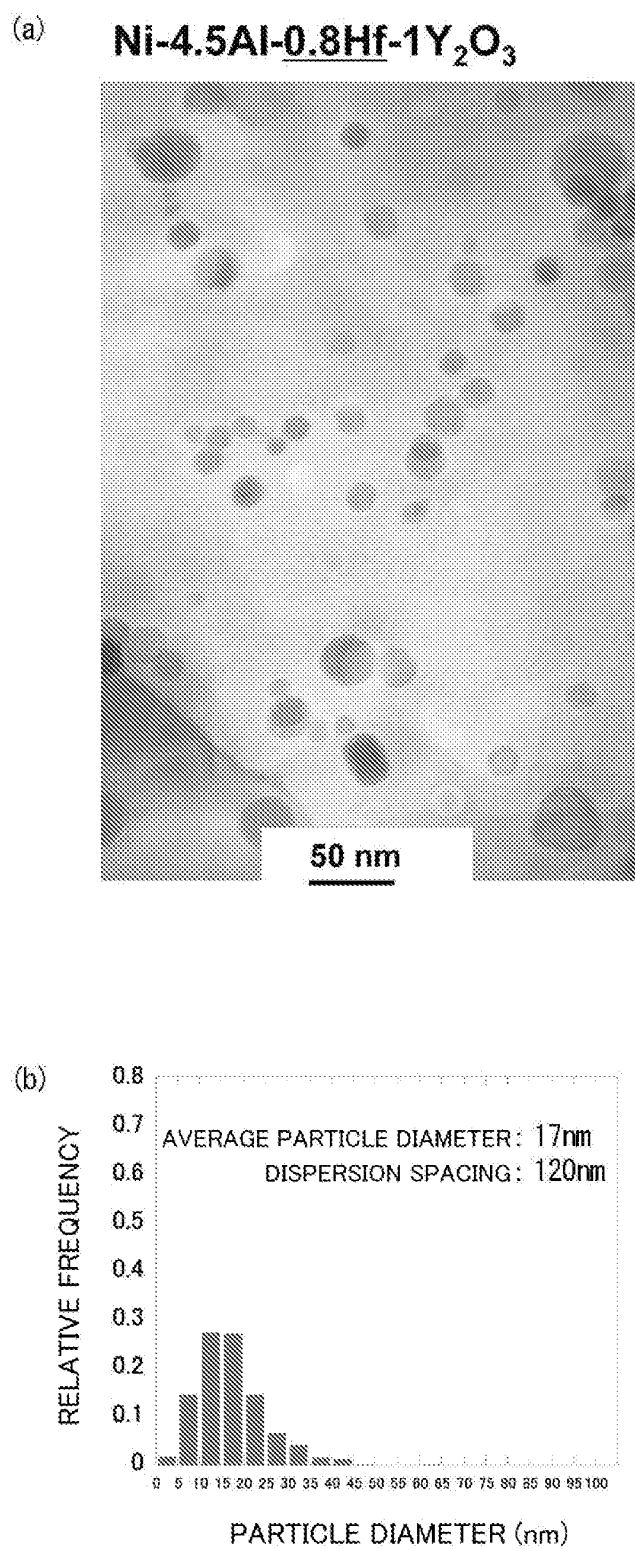
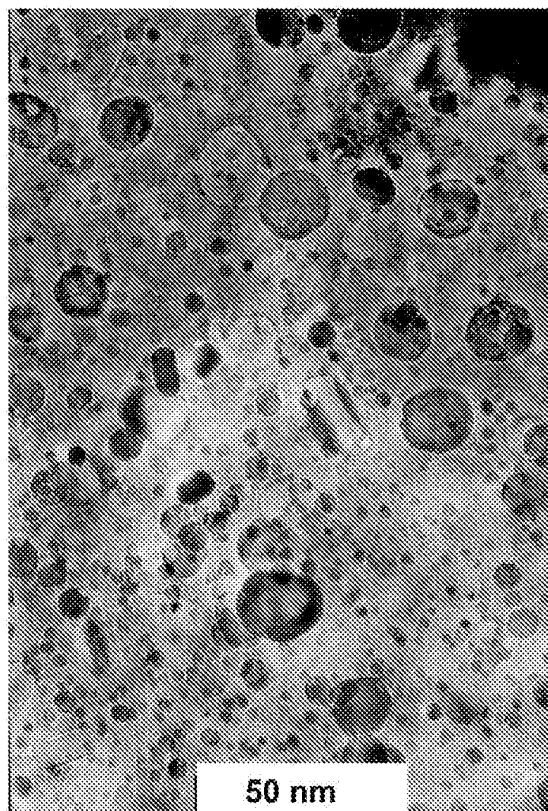


Fig. 11

(a)

Ni-0.5Al-0.08Hf-1Y₂O₃

(b)

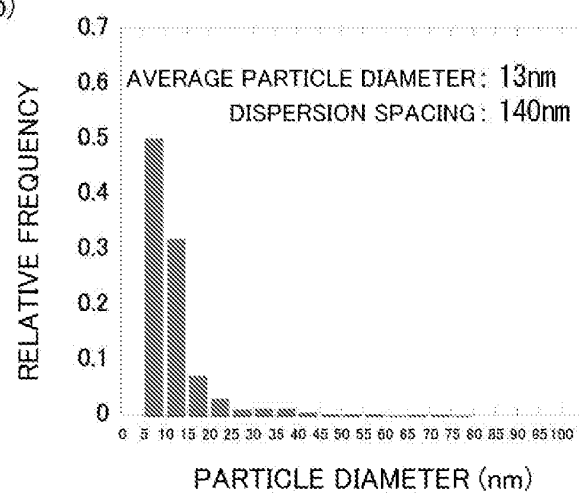


Fig. 12

(a) **Ni-0.5Al-3.2Hf-1Y₂O₃**

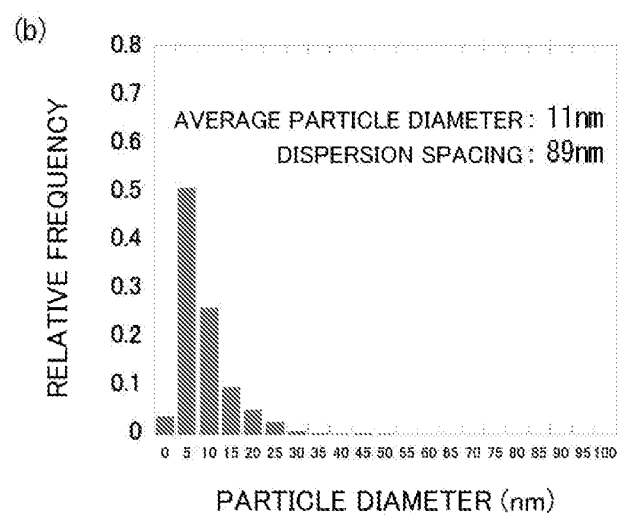


Fig. 13

(a) **Ni-4.5Al-5Hf-1Y₂O₃**

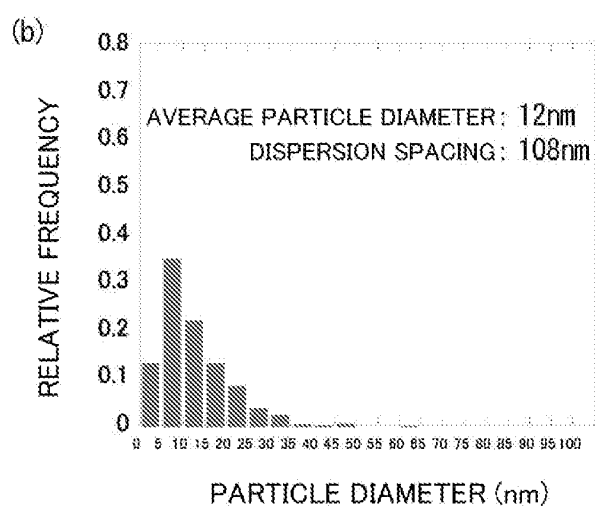
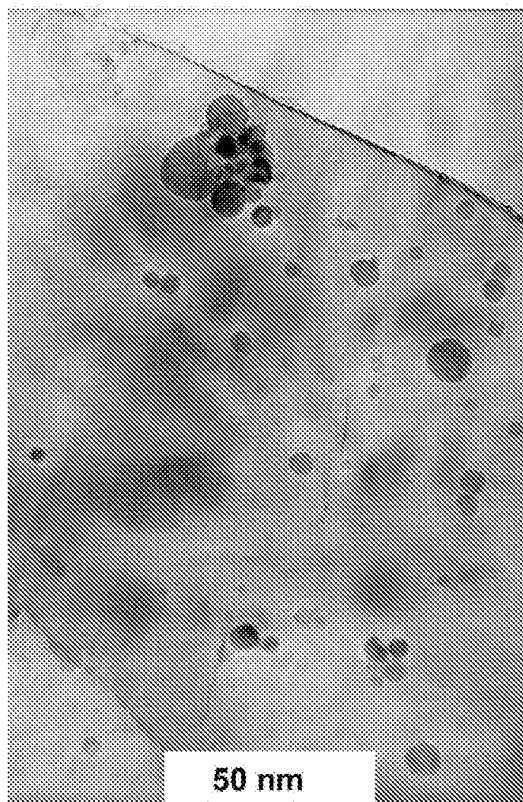


Fig. 14

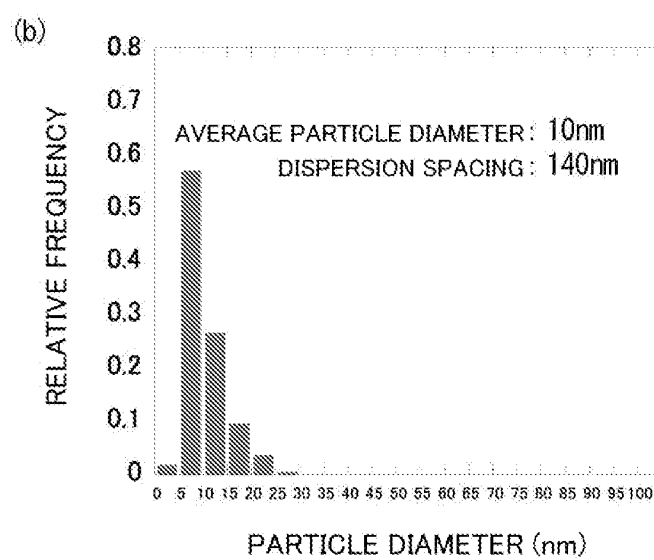
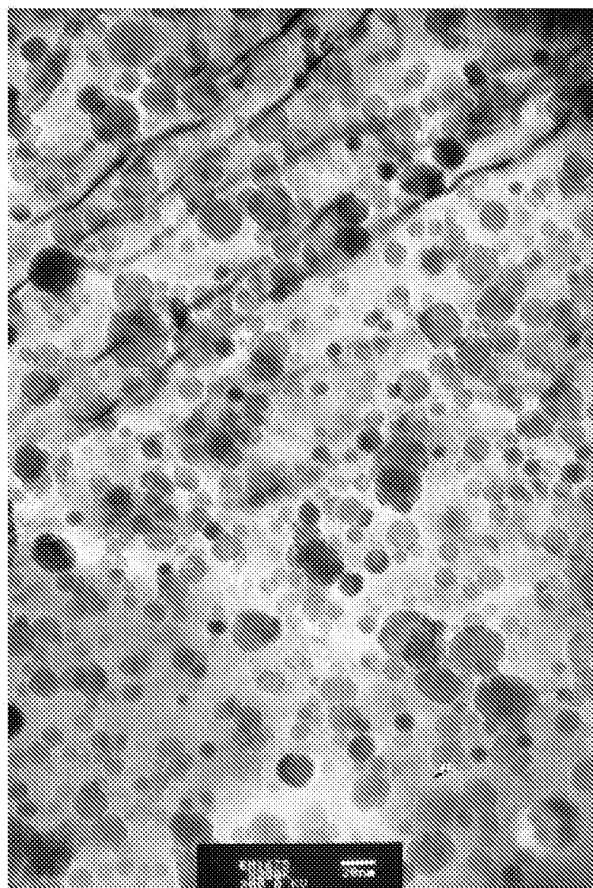
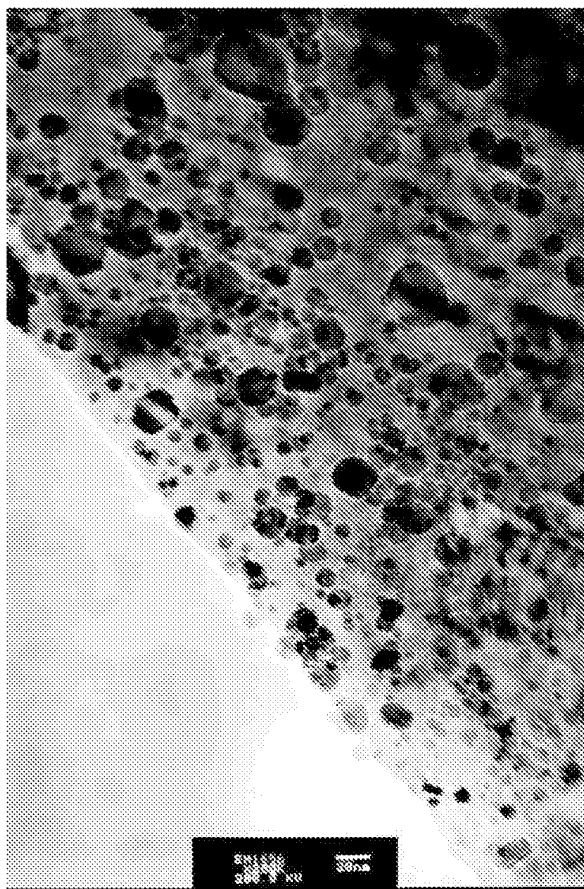
(a) **Ni-2Al-0.8Hf-1Y₂O₃**

Fig. 15

(a) **Ni-4Al-0.8Hf-1Y₂O₃**

(b)

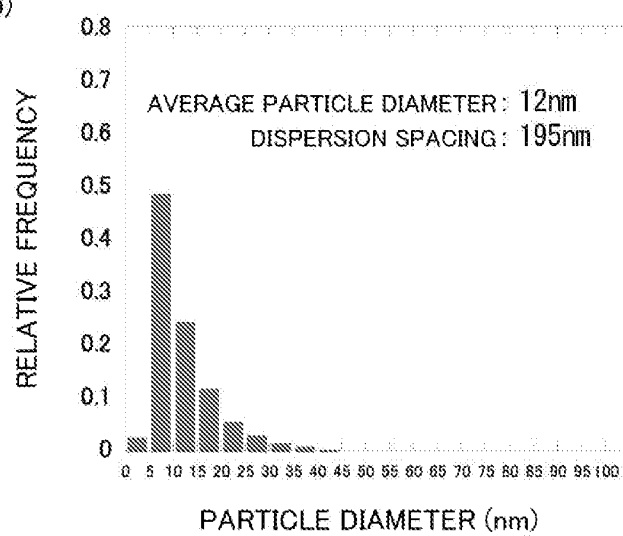


Fig. 16

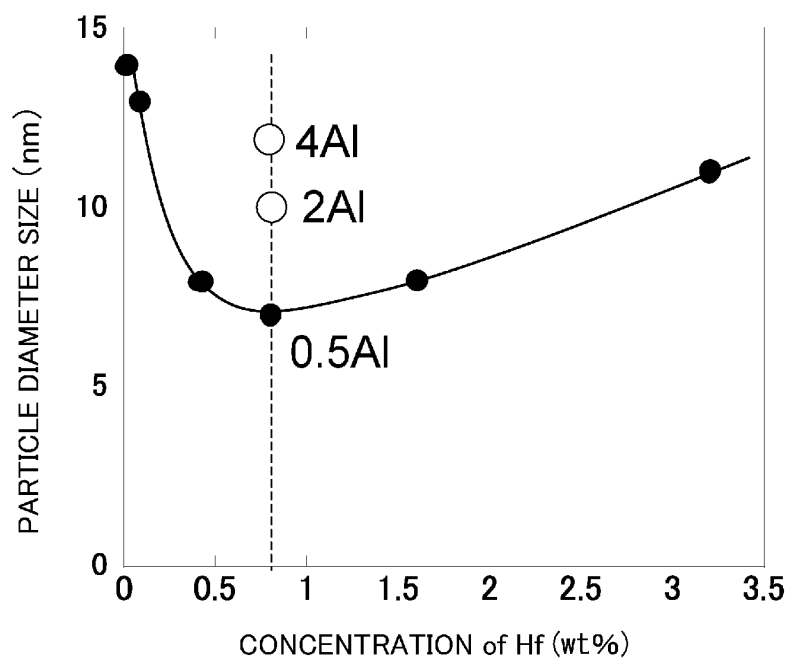


Fig. 17

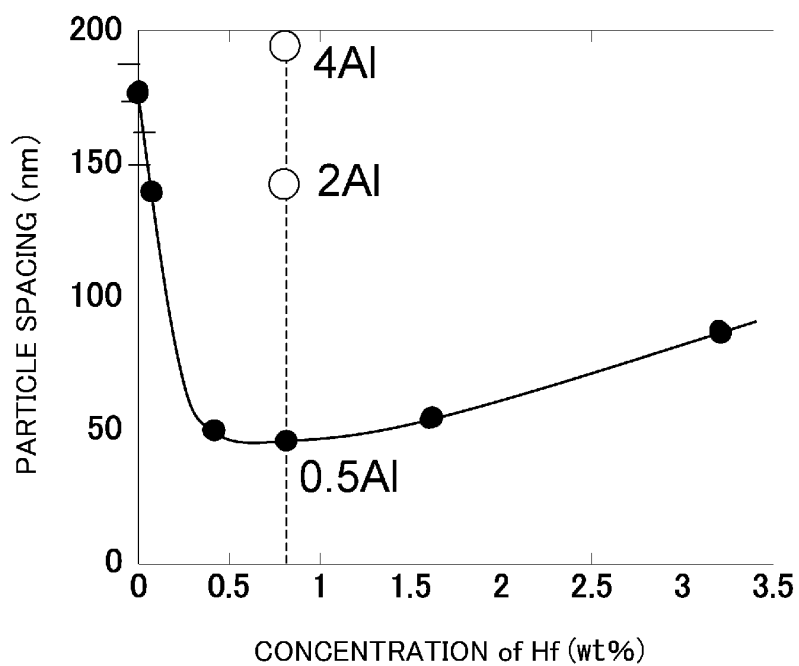


Fig. 18

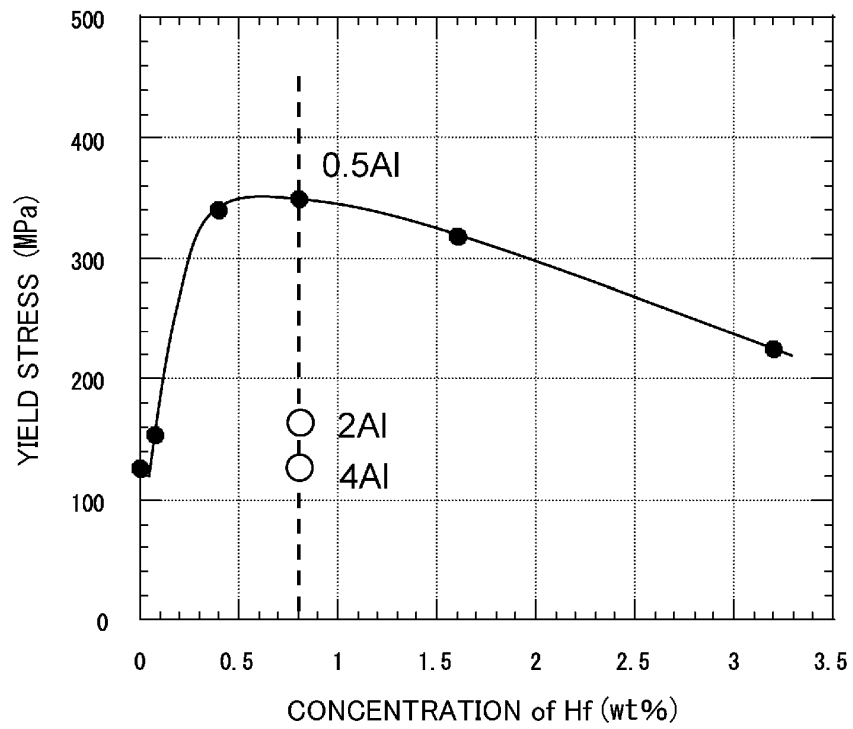


Fig. 19

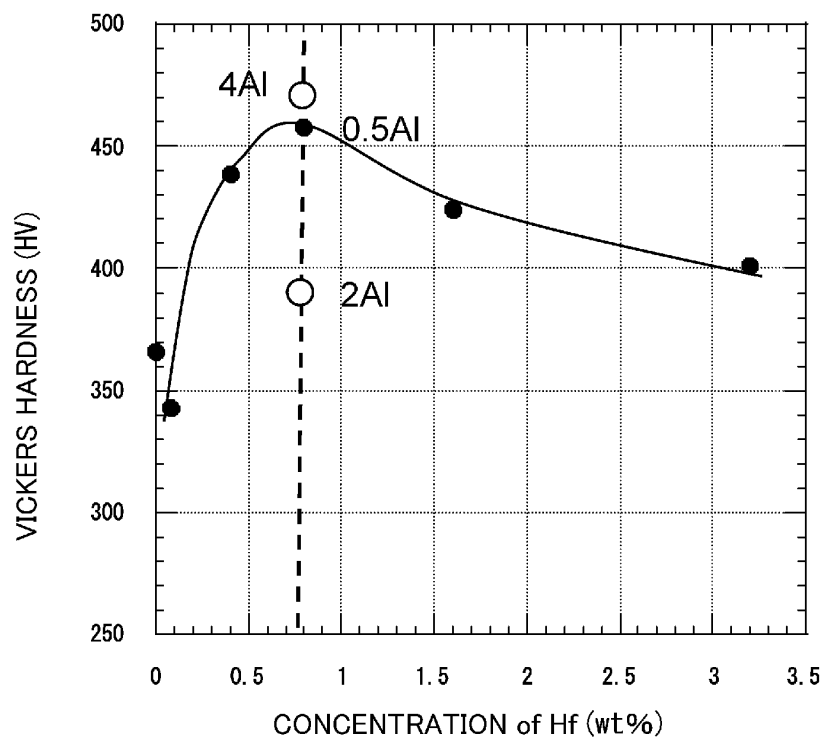


Fig. 20

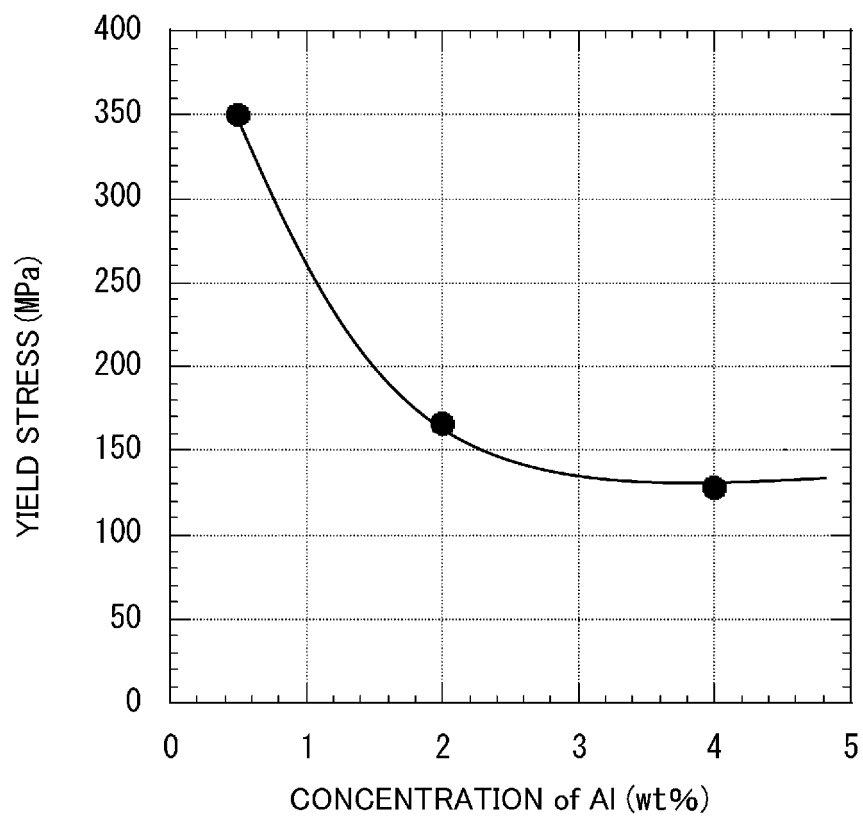
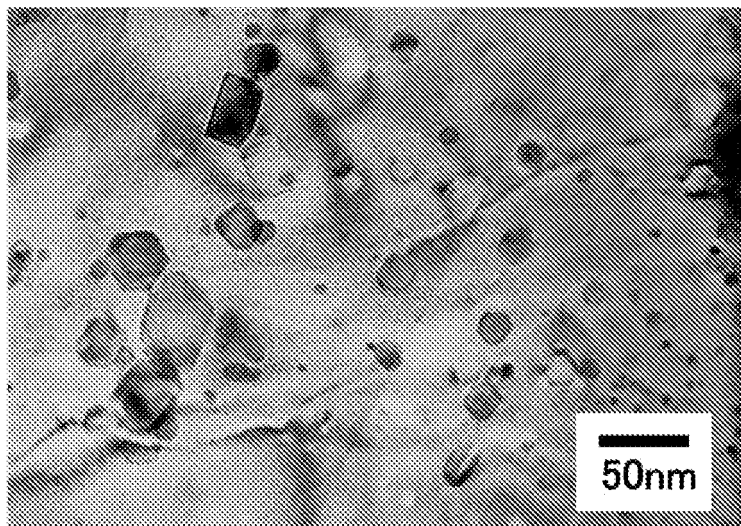


Fig. 21

(a)



(b)

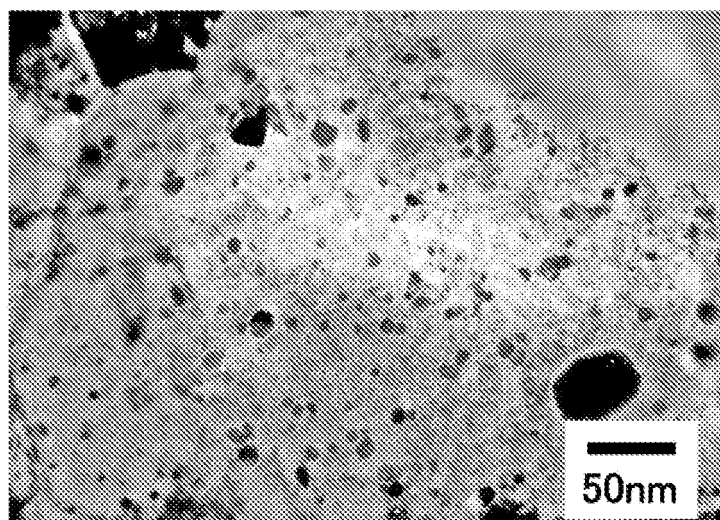
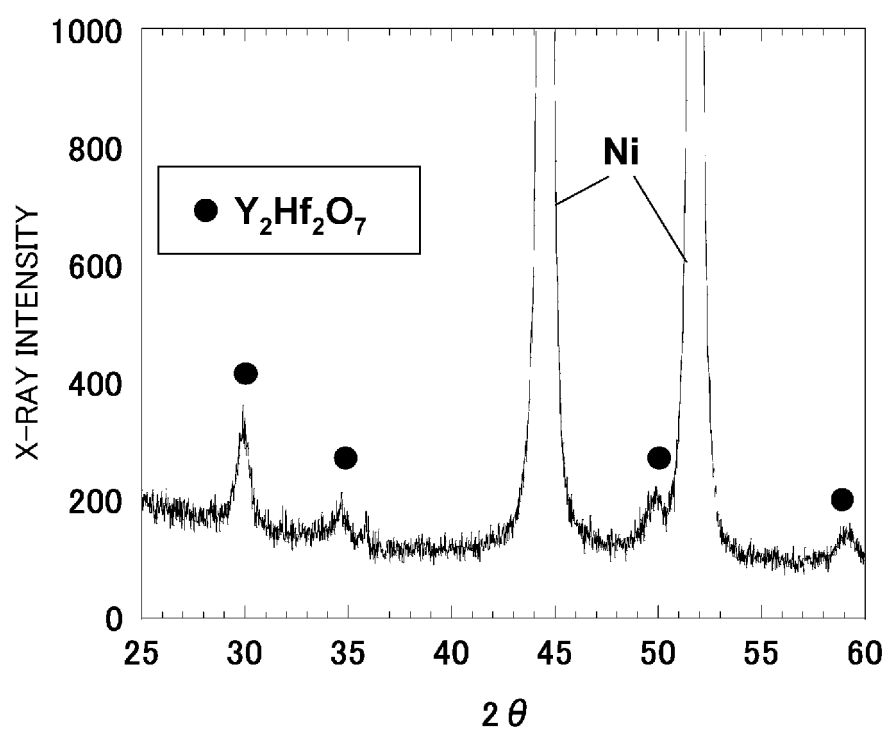


Fig. 22



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/064410

A. CLASSIFICATION OF SUBJECT MATTER

C22C19/03(2006.01) i, C22C1/05(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)

C22C19/03, C22C1/05

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	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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.
X Y A	JP 62-33737 A (Hitachi, Ltd.), 13 February 1987 (13.02.1987), Embodiments (Family: none)	1, 2, 7 3 4-6
Y	JP 61-264147 A (Inco Alloys International, Inc.), 22 November 1986 (22.11.1986), table 1 & EP 196513 A1	3
A	JP 2001-152208 A (Daido Steel Co., Ltd.), 05 June 2001 (05.06.2001), examples (Family: none)	1-7

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

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search
30 October, 2009 (30.10.09)Date of mailing of the international search report
10 November, 2009 (10.11.09)Name and mailing address of the ISA/
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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