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(54) **Ni-based alloys.**

(57) A Ni-based alloy consisting of, by weight :
(a) Cr 5 to 41%
(b) A1 8 to 16%
(c) Fe 5 to 30% (except that when both Cr is 28 to 31% and A1 is 10 to 11%, Fe is optionally present in an amount up to 30%)
(d) optionally, Ti up to 5%
(e) optionally, B up to 0.1%
(f) optionally, at least one element selected from the elements of Groups 2A and 3A of the Periodic Table, the lanthanoid elements (including Y), Zr, Hf and Si in an amount in the range 0.05 to 2.5%
(g) remainder Ni and unavoidable impurities.

This Ni-based alloy can have high-temperature strength, good oxidation resistance and excellent resistance to sulfate corrosion. It may also be hardly affected by the thermal history and have excellent strength stability and hardness stability. Furthermore, the alloy may have a relatively low specific gravity and be advantageous in specific strength.

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The present invention relates to a Ni-based alloy which can be superior in oxidation resistance, high-temperature strength, stability to thermal history, etc. and can have an improved resistance to sulfate corrosion.

Research and development are being made actively on alloys superior in high-temperature strength, oxidation resistance, etc. for their use as a material for gas turbines, engine parts, heaters, electric furnaces, etc. For example, a Fe-based alloy typified by Kanthal alloy (Fe- 21Cr-5.5Al) is known as an alloy having a higher oxidation resistance than stainless steel. Further, a Ni-based super alloy such as Inconel X-750 [Ni-15Cr-7Fe-0.7Al-2.5Ti-1(Nb+Ta)] is known as an alloy having a high strength at high temperatures. Furthermore, a Ni-Cr-Al alloy containing not more than 5% by weight of Al, typified by a Haynes 214 alloy (Ni-16Cr-4.5Al-2Fe) is known as an alloy having a high strength at high temperatures and an oxidation resistance. Also, Ni_3Al is known as an intermetallic compound having a high strength at high temperatures.

Further, in Japanese Patent Application Kokai (Laid-Open) No. 358037/1992 is disclosed, as a Ni-based heat-resistant alloy having an excellent high-temperature strength and an excellent corrosion resistance, a Ni-based heat-resistant alloy which comprises not more than 0.01% (by weight) of C, not more than 1.0% of Si, not more than 0.2% of Mn, more than 5% but not more than 18% of Cr, 4.5-12% of Al, at least one element selected from B (0.001-0.03%), Zr (0.01-0.3%), Hf (0.05-1.0%), Ti (0.05-1.0%) and Mg (0.001-0.02%), and the remainder of Ni or Ni, Fe (not more than 5%) and unavoidable impurities.

Further in Japanese Patent Application Kokai (Laid-Open) No. 86840/1988 is disclosed a Ni-Fe-Al alloy which has a high yield strength at high temperatures, a good ductility, a good oxidation resistance and good high-temperature processability.

Also in U.S. Patent No. 4,359,352 is disclosed a boron-containing Ni-based super alloy produced by rapid solidification.

The above alloys, however, have respective problems. That is, the Fe-based alloy (e.g. Kanthal alloy) has a relatively small strength and a relatively small hardness at high temperatures. The Ni-based super alloy such as Inconel X-750 contains Ta, Nb, W, Mo and Co for strength improvement; however, these elements are strategic elements and have problems of high cost and unstable supply, etc. In addition, while in such a super alloy, the oxidation resistance is exhibited by a Cr_2O_3 film formed on the surface, the Cr_2O_3 film has a high vapor pressure and does not act as a protective film at temperatures of 1,000°C or higher, resulting in insufficient oxidation resistance.

The Ni-Cr-Al alloy typified by Haynes 214 alloy, which is known as an alloy having a high-temperature strength and an oxidation resistance, contains Al in an amount of only 5% by weight or less and accordingly has an insufficient oxidation resistance. Further, the alloy has a problem of peeling-off of the oxide film, and is greatly affected by the thermal history because of the too small particles of the γ' phase precipitated and consequently has inferior stabilities in strength and hardness.

The Ni-based super alloy, the Haynes alloy, etc. moreover have a large specific gravity (8.05 g/cc) and resultantly have a small specific strength (specific strength = strength per unit weight), which poses a problem when they are used in the form of a rotor, etc.

Ni_3Al exhibits a high strength at high temperatures and has an excellent oxidation resistance. However, since the alloy shows brittle fracture, a special step such as quenching or the like is required in order for the alloy to have higher reliability, as described in, for example, Japanese Patent Application Kokai (Laid-Open) No. 76639/1986.

An alloy containing a large amount of boron, such as described in U.S. Patent No. 4,359,353 has an insufficient oxidation resistance.

The Ni-based heat-resistant alloy described in Japanese Patent Application Kokai (Laid-Open) No. 358037/1992 contains Fe in a small amount and has no sufficient resistance to sulfate corrosion. It is therefore difficult to use the alloy, for example, as a material for gas turbines, parts of automobile exhaust systems, etc. (these turbines and parts are exposed to the sulfur contained in the fuel used).

The Ni-based alloy described in Japanese Patent Application Kokai (Laid-Open) No. 86840/1988 contains no Cr and has insufficient resistances to sulfate corrosion and solution corrosion. Thus, the alloy has the same problem as the above Ni-based heat-resistant alloy.

The present invention has been completed in view of the above-mentioned problems of the prior art. The object of the present invention is to provide a Ni-based alloy which has a high-temperature strength, an oxidation resistance, an improved resistance to sulfate corrosion, a high specific strength and excellent stability to thermal history, or one or more of these properties.

In one aspect the invention is set out in claim 1.

According to the present invention there is provided a Ni-based alloy comprising 5-41% by weight of Cr, more than 8% by weight but not more than 16% by weight of Al, more than 5% by weight but not more than 30% by weight of Fe and the remainder of Ni and unavoidable impurities.

According to the present invention there is further provided a Ni-based alloy comprising 28-31% by weight of Cr, 10-11% by weight of Al, not more than 5% by weight of Fe and the remainder of Ni and unavoidable impurities.

According to the present invention there is furthermore provided a Ni-based alloy comprising, in addition to the components of the above alloy, not more than 5% by weight of Ti, or not more than 0.1% by weight of B, or 0.05-2.5% by weight of at least one element selected from the group consisting of the group 2A and group 3A elements of periodic table, the lanthanoid elements, Zr, Hf and Si.

Of the components contained in the Ni-based alloy of the present invention, Cr has an effect of allowing the alloy to have a large hardness at room temperature. The Cr content is limited to 5-41% by weight in the present alloy in view of the resistance to sulfate corrosion. When the Cr content is less than 5% by weight, no protective film against sulfate corrosion is formed. When the Cr content is more than 41% by weight, the Ni content is low correspondingly, resulting in low protectability. The Cr content is preferably as high as possible in view of the lightweightness (small specific gravity) of the alloy, but a preferable Cr content is 15-30% by weight in view of the resistance to sulfate corrosion. The Cr content is preferably not more than 20% by weight in view of the weight increase by oxidation, and is preferably not more than 10% by weight or not less than 25% by weight in view of the stability to thermal history.

Al is a source for formation of an alumina-based protective film and is an element effective for improvement in oxidation resistance. Al exhibits a striking effect when the content is more than 8% by weight. The Al content is preferably as high as possible in view of the lightweightness of the alloy but is limited to more than 8% by weight to 16% by weight in the present alloy because an Al content higher than 16% by weight gives a brittle alloy. The Al content of the present alloy is more preferably 10-13% by weight in view of the improvement in oxidation resistance and the prevention of brittleness.

Fe imparts an improved resistance to sulfate corrosion at a content higher than 5% by weight, and gives a more striking effect at a content of 8% by weight or more. The Fe content is preferably as high as possible in view of the lightweightness of the alloy but is limited to more than 5% by weight to 30% by weight in the present alloy because a Fe content higher than 30% by weight gives an alloy of low high-temperature hardness. The total content of Cr and Fe is preferably not more than 15% by weight in view of the high-temperature hardness. The Fe content is preferably not higher than 20% by weight in view of the weight increase by oxidation and is preferably not more than 10% by weight to reduce the peeling-off amount.

It was confirmed that even when the Fe content is zero or as low as 5% by weight or less, as long as the Cr content is 28-31% by weight and the Al content is 10-11% by weight, the resulting alloy has a satisfactory resistance to sulfate corrosion and exhibits good alloy properties, as compared with when the Fe content is 5-30% by weight. This is because the Al content is sufficient and the Cr content is appropriate, whereby a superior protective film is formed. Preferably Fe is at least 1%.

Ti has an effect of imparting improved hardness at room temperature and high temperatures to the present alloy. Hence, the present alloy may comprise Ti in an amount of not more than 5% by weight, in addition to the above-mentioned components. When the Ti content is higher than 5% by weight, the resulting alloy is brittle. Further, with the increase in Ti content, the melting point of the resulting alloy decreases. Preferably Ti is at least 0.1%.

The present alloy may comprise not more than 0.1% by weight of B for the purpose of increasing the ductility. With a B content of more than 0.1% by weight, the resulting alloy has inferior oxidation resistance. Preferably B is at least 0.01%.

Preferably, the Ni-based alloy of the present invention comprises 0.05-2.5% by weight of each of at least one element selected from the group 2A and group 3A elements of periodic table, the lanthanoid elements, Zr, Hf and Si. The total amount of these elements is preferably not more than 5%. More preferably, the present alloy comprises said amount of at least one element selected from the group consisting of Hf, Y, Zr, Nd, Ce, Ca and Si. With the presence of these elements, the oxide film of the alloy has higher adhesivity. The test conducted for the dependency of adhesivity on oxidation temperature indicates that the alloy of the present invention shows a good adhesivity at 1,050°C. In order to secure an adhesivity even at 1,150°C, it is preferable to add Si and Hf, Ca and/or Zr.

It is also preferable to allow the. Ni-based alloy of the present invention to comprise a γ' phase and a γ phase. The presence of γ' phase results in higher high-temperature hardness, and the presence of γ phase provides plastic fracture.

The present invention is hereinafter described in more detail by way of Example. However, the present invention is in no way restricted to the Example.

There were mixed electrolytic iron, electrolytic chromium, aluminum, nickel for casting (these are essential raw materials) and, as necessary, auxiliary raw materials such as Ti, B, Hf and the like. The mixture was subjected to induction melting in Ar, then kept at 1,150°C for 100 hours in Ar, and cooled slowly, whereby various alloy bars having the compositions shown in Tables 1-10 were obtained. Separately, there were prepared, for comparison with the present invention, various alloy bars or sheets (these are known alloys) having the compositions shown in Table 11. From each alloy bar or sheet were cut out test pieces to conduct various tests. The test items and test methods employed are shown below. The test results are shown in Tables 1-11.

Oxidation test

A test piece was placed in an alumina-based crucible with a lid. The crucible was kept at 1,150°C for 100 hours or at 1,050°C for 200 hours, in air. Then, the test piece was measured for weight change per unit area, and the weight change per unit area was taken as the "weight increase by oxidation" of the test piece. When there were present oxide scales (separated from the test piece by peeling-off) in the crucible, the weight of the oxide scales separated was measured to calculate the amount of scales separated per unit area. Then, the following formula was calculated to obtain an "adhesivity (%)".

$$\text{Adhesivity (\%)} = 100 \times [1 - (\text{amount of oxide film separated, mg/cm}^2)/(\text{total amount of oxide film, mg/cm}^2)] \quad (1)$$

Here, if "weight increase by oxidation" is assumed to be the amount of oxygen present in oxide film and the oxide film is assumed to consist of Al_2O_3 alone, the following is obtained.

$$\begin{aligned}\text{Total amount of oxide film} &= (\text{oxygen amount}) \times (Al_2O_3/3\text{xoxygen}) \\ &= (\text{weight increase by oxidation}) \times (26.98 \times 2+16 \times 3)/(3 \times 16) \\ &= (\text{weight increase by oxidation}) \times 2.1241 \quad (2)\end{aligned}$$

Hence, from the formulas (1) and (2), the following is obtained.

$$\begin{aligned}\text{Adhesivity (\%)} &= 100 - 100 \times (\text{amount of oxide film separated, mg/cm}^2)/[(\text{weight increase by oxidation, mg/cm}^2) \times 2.1241] \\ &= 100 - 47.1 \times (\text{amount of oxide film separated, mg/cm}^2)/(\text{weight increase by oxidation, mg/cm}^2)\end{aligned}$$

Test for evaluation of stability to thermal history

A test piece was measured for Vickers hardness at room temperature. Then, the test piece was heated to 800°C in Ar and measured for Vickers hardness at 800°C. The test piece was further heated to 1,000°C, after which the electric current was cut off and the test piece was allowed to cool to room temperature. The test piece was again measured for Vickers hardness at room temperature. The difference in Vickers hardness between two room temperatures, i.e. ΔHV was calculated to use it for evaluation of the stability to thermal history, of the test piece.

Crystalline phase(s)

The crystalline phase(s) of each test piece was (were) determined from both the X-ray diffraction and the structure observation.

Bulk specific gravity

Was measured by the Archimedes's method.

Test for resistance to sulfate corrosion

An aqueous solution containing NaCl and Na_2SO_4 at a weight ratio of 5:5 was coated on one side of a test piece so that the coated solution gave a solid content of 5 mg/cm^2. The resulting piece was placed in a crucible as in the oxidation test, and the crucible was kept at 850°C for 100 hours in air. Then, the test piece was washed with water and measured for weight change. The weight change was divided by the initial area. The resulting value was used for evaluation of the resistance to sulfate corrosion, of the test piece. A smaller value is better.

Tensile test

It is known that strength has a positive correlation to hardness. Therefore, tensile strength was measured only for representative alloys. A test piece was prepared, by cutting, so as to have 25 mm (length) x 2 mm x 6 mm and measured for tensile strength in accordance with JIS G 0567 (1978).

Table 1

Alloy No.	1	2	3	4	5	6
Alloy composition Ni(wt%)	84.2	79.5	74.7	64.8	55.1	43.2
Cr(wt%)	5.1	5.2	5.2	5.1	5.2	5.2
Fe(wt%)	0.0	4.7	9.4	19.4	29.5	41.3
Al(wt%)	10.6	10.6	10.7	10.7	10.2	10.3
Bulk specific gravity	7.69	7.59	7.54	7.42	7.32	7.26
Oxidation test(1,150°C × 100hr, in air)						
Weight increase by oxidation(mg/cm²)	1.1	1.1	1.1	1.2	1.6	2.2
Adhesivity(%)	4	7	12	11	12	12
Vickers hardness(HV)						
Room temperature(1st time)	134	160	191	292	281	286
800 °C	194	224	229	202	162	95
Room temperature(2nd time)	135	155	194	283	282	250
ΔHV	+1	-5	+3	-9	+1	-36
Tensile strength(kg/mm², at 1,000 °C)	—	—	—	—	—	—
Crystalline phase(s) (γ:fcc, α:bcc)	γ'	γ'	γ' + γ + α	γ' + γ + β_2	β_2 + γ	β_2 + γ
Resistance to sulfate corrosion	16.7	16.0	8.1	6.3	4.1	3.9

Table 2

Alloy No.	7	8	9	10	11	12
Alloy composition Ni (wt%)	79.5	74.7	70.1	60.5	50.5	49.9
Cr (wt%)	9.9	10.0	9.6	9.7	9.6	9.6
Fe (wt%)	0.0	4.6	9.9	19.7	29.4	40.2
Al (wt%)	10.6	10.7	10.4	10.1	10.5	10.3
Bulk specific gravity	7.58	7.52	7.45	7.38	7.28	7.16
Oxidation test (1,150°C × 100hr, in air)						
Weight increase by oxidation (mg/cm²)	1.1	1.1	1.2	1.3	1.7	2.1
Adhesivity (%)	4	<1	16	6	12	15
Vickers hardness (HV)						
Room temperature (1st time)	167	229	293	318	289	277
800 °C	236	257	220	190	115	89
Room temperature (2nd time)	174	235	296	310	279	234
ΔHV	+7	+6	+3	-8	-10	-43
Tensile strength (kg/mm², at 1,000 °C)	9.7	—	—	—	—	—
Crystalline phase(s) (γ: fcc, α: bcc)	γ'	γ' + γ + β_2	γ + β_2 + γ'	γ + β_2 + γ'	γ + β_2	γ + β_2
Resistance to sulfate corrosion	14.2	13.4	6.0	4.9	4.0	3.8

Table 3

Alloy No.	13	14	15	16'	17	18
Alloy composition Ni(wt%)	69.0	64.8	60.7	50.1	40.5	38.6
Cr(wt%)	20.3	20.4	19.8	19.4	19.4	20.1
Fe(wt%)	0.0	4.6	9.2	19.5	29.4	41.0
Al(wt%)	10.7	10.2	10.3	10.5	10.7	10.3
Bulk specific gravity	7.37	7.36	7.31	7.20	7.12	7.05
Oxidation test(1,150°C × 100hr, in air)						
Weight increase by oxidation(mg/cm^2)	1.2	1.1	1.2	1.2	1.3	2.4
Adhesivity(%)	<1	<1	8	10	8	11
Vickers hardness(HV)						
Room temperature(1st time)	353	352	339	326	292	269
800 °C	298	244	212	132	120	88
Room temperature(2nd time)	366	324	297	274	293	272
ΔHV	+13	-28	-42	-52	+1	+3
Tensile strength(kg/mm^2, at 1,000 °C)	—	—	—	—	—	—
Crystalline phase(s) (γ:fcc, α:bcc)	$\gamma' + \gamma + \beta_2$	$\gamma' + \gamma + \beta_2$	$\gamma + \beta_2 + \gamma'$	$\gamma + \beta_2$	$\alpha + \beta_2 + \gamma$	$\alpha + \beta_2 + \gamma$
Resistance to sulfate corrosion	10.4	10.2	4.3	3.2	2.9	2.9

Table 4

Alloy No.	19	20	21	22	23	24
Alloy composition Ni (wt%)	59.3	56.5	50.5	40.5	30.7	20.5
Cr (wt%)	30.4	28.6	28.9	29.7	30.0	30.0
Fe (wt%)	0.0	4.8	9.8	19.3	29.4	39.3
Al (wt%)	10.3	10.1	10.8	10.5	9.9	10.2
Bulk specific gravity	7.24	7.18	7.15	7.04	7.00	6.95
Oxidation test (1,150°C × 100hr, in air)						
Weight increase by oxidation (mg/cm^2)	1.7	1.7	1.7	1.8	1.9	3.2
Adhesivity (%)	2	6	9	11	17	20
Vickers hardness (HV)						
Room temperature (1st time)	379	408	385	460	423	430
800 °C	303	291	211	198	171	97
Room temperature (2nd time)	388	404	379	461	428	443
ΔHV	+9	-4	-6	+1	+5	+13
Tensile strength (kg/mm^2, at 1,000 °C)	—	—	—	—	—	—
Crystalline phase(s) (γ: fcc, α: bcc)	$\gamma' + \gamma + \beta_2$	$\gamma' + \gamma + \beta_2 + \alpha$	$\alpha + \beta_2 + \gamma$	$\alpha + \beta_2$	$\alpha + \beta_2$	$\alpha + \beta_2$
Resistance to sulfate corrosion	5.7	5.5	2.3	1.9	1.7	1.6

Table 5

Alloy No.	25	26	27	28	29	30	31	32
Alloy composition Ni (wt%)	48.7	44.7	38.6	36.7	20.3	23.3	76.5	34.2
Cr (wt%)	41.1	40.8	40.9	37.8	40.6	40.6	3.6	45.6
Fe (wt%)	0.1	4.4	10.3	18.5	29.0	36.0	9.8	10.0
Al (wt%)	10.1	10.1	10.2	9.2	10.1	10.1	10.1	10.2
Bulk specific gravity	7.12	7.05	7.05	6.98	6.84	6.81	—	—
Oxidation test (1,150℃ × 100hr, in air)								
Weight increase by oxidation (mg/cm^2)	1.8	1.9	1.9	1.9	1.9	2.6	1.3	4.6
Adhesivity (%)	30	22	29	24	36	44	1	47
Vickers hardness (HV)								
Room temperature (1st time)	421	459	492	505	430	381	—	—
800 ℃	312	292	290	267	226	110	—	—
Room temperature (2nd time)	423	463	494	510	431	344	—	—
ΔHV	+2	+4	+2	+5	+1	-37	—	—
Tensile strength (kg/mm^2, at 1,000 ℃)	—	—	—	—	—	—	—	—
Crystalline phase(s) (γ: fcc, α: bcc)	γ + γ' + α	γ + γ' + α	α	α	α	α	—	—
Resistance to sulfate corrosion	13.8	12.9	8.8	8.7	8.7	8.6	18.1	15.9

Table 6

Alloy No.	33	34	35	36	37
Alloy composition Ni (wt%)	79.35	64.95	63.45	56.70	46.75
Cr (wt%)	11.1	9.9	15.4	25.0	35.9
Fe (wt%)	5.3	5.1	5.1	5.1	5.0
Al (wt%)	4.1	14.9	15.8	8.1	12.2
B (wt%)	0.1	0.1	0.0	0.0	0.10
Ti (wt%)	0.0	5.0	0.0	4.9	0.0
Hf (wt%)	0.05	0.05	0.25	0.20	0.05
Bulk specific gravity	—	6.80	6.87	7.27	6.88
Oxidation test (1,150°C × 100hr, in air)					
Weight increase by oxidation (mg/cm^2)	5.8	0.8	0.5	1.1	0.6
Adhesivity (%)	29	89	81	79	86
Vickers hardness (HV)					
Room temperature (1st time)	—	499	397	458	442
800 °C	—	384	267	360	280
Room temperature (2nd time)	—	502	446	465	443
ΔHV	—	+3	+49	+7	+1
Tensile strength (kg/mm^2, at 1,000 °C)	—	—	—	14	—
Crystalline phase(s) (γ: fcc, α: bcc)	$\beta_2 + \gamma + \gamma'$	$\beta_2 + \gamma + \gamma'$	$\beta_2 + \gamma$	$\beta_2 + \gamma + \gamma'$	$\alpha + \gamma + \gamma'$
Resistance to sulfate corrosion	41.6	4.0	3.6	6.2	6.2

Table7

Alloy No.	38	39	40	41	42
Alloy composition Ni(wt%)	70.46	63.86	50.65	35.20	57.64
Cr(wt%)	10.0	15.0	25.7	36.1	14.9
Fe(wt%)	8.0	8.0	8.3	8.2	8.0
Al(wt%)	11.3	8.1	15.2	15.2	19.2
B (wt%)	0.0	0.09	0.10	0.0	0.0
Ti(wt%)	0.0	4.9	0.0	5.0	0.0
Hf(wt%)	0.24	0.05	0.05	0.30	0.26
Bulk specific gravity	7.28	7.41	6.71	6.48	Sample preparation was impossible.
Oxidation test(1,150°C × 100hr, in air)					
Weight increase by oxidation(mg/cm²)	0.5	1.2	0.5	4.2	
Adhesivity(%)	37	<1	83	100	
Vickers hardness(HV)					
Room temperature(1st time)	298	401	427	527	
800 °C	246	365	236	354	
Room temperature(2nd time)	307	430	435	523	
ΔHV	+9	+29	+8	-4	
Tensile strength(kg/mm², at 1,000 °C)	—	23	—	—	
Crystalline phase(s) (γ:fcc, α:bcc)	γ+γ' +β₂	γ+γ' +α	β₂ +α	β₂ +α +γ	
Resistance to sulfate corrosion	7.5	3.8	2.0	9.2	

Table 8

Alloy No.	43	44	45	46	47
Alloy composition Ni (wt%)	62.8	74.6	60.1	68.1	69.6
Cr (wt%)	10.2	9.7	19.8	10.1	10.0
Fe (wt%)	9.7	5.2	7.8	9.5	9.6
Al (wt%)	10.4	10.5	10.1	10.2	9.9
Ti (wt%)	6.9	4.8	2.0	2.1	0.9
Bulk specific gravity	Sample preparation was impossible.	7.30	7.18	7.29	7.35
Oxidation test (1,150°C × 100hr, in air)					
Weight increase by oxidation (mg/cm^2)		0.9	0.9	0.9	0.8
Adhesivity (%)		61	65	90	73
Vickers hardness (HV)					
Room temperature (1st time)		370	392	353	300
800 °C		378	348	282	221
Room temperature (2nd time)		415	459	362	296
ΔHV		+45	+67	+9	-4
Crystalline phase(s) (γ: fcc, α: bcc)		$\gamma' + \gamma + \beta_2$	$\gamma' + \gamma + \beta_2$	$\gamma' + \gamma + \beta_2$	$\gamma' + \gamma + \beta_2$
Resistance to sulfate corrosion		9.8	1.3	2.1	1.1

Table 9

Alloy No.	48	49	50	51	52	53	54	55	56
Alloy composition Ni (wt%)	68.4	68.3	68.4	66.9	67.2	69.3	68.5	68.6	67.9
Cr (wt%)	9.9	9.9	9.8	11.1	10.0	10.1	10.0	10.2	9.7
Fe (wt%)	9.4	9.9	9.5	9.6	9.6	10.3	10.2	10.2	9.9
Al (wt%)	9.9	10.1	10.0	10.2	10.3	10.2	11.0	10.5	10.2
Others (wt%)	Y 2.4	Ce 1.8	Hf 2.3	Nd 2.2	Ca 2.2	Zr 0.1	Zr 0.3	Zr 0.5	Zr 2.3
Bulk specific gravity	7.37	7.49	7.50	7.39	7.07	7.45	7.45	7.44	7.41
Oxidation test (1,150°C × 100hr, in air)									
Weight increase by oxidation (mg/cm^2)	0.7	14.2	2.8	4.2	13.5	1.4	3.0	3.9	16.0
Adhesivity (%)	45	96	100	70	97	76	92	98	99
Vickers hardness (HV)									
Room temperature (1st time)	306	310	294	319	240	282	281	276	314
800 °C	251	245	276	265	168	246	252	232	266
Room temperature (2nd time)	309	320	303	328	—	287	289	283	315
ΔHV	+3	+10	+9	+9	—	+5	+8	+7	+1
Crystalline phase(s) (γ:fcc, α:bcc)	γ' + γ + β_2+uk	γ' + γ + β_2+uk	γ' + γ + β_2	γ' + γ + β_2+uk	γ' + γ + β_2	γ' + γ + β_2	γ' + γ + β_2	γ' + γ + β_2+uk	γ' + γ + β_2+uk
Resistance to sulfate corrosion	0.4	0.6	1.2	0.8	37.8	3.9	2.3	2.0	0.9

Table10

Alloy No.	57	58	59	60	61	62	63	64	65	66
Alloy composition Ni(wt%)	62.14	62.54	62.63	61.35	60.56	62.02	61.8	68.1	63.91	68.5(61.1atm%)
Cr(wt%)	15.2	15.0	15.0	15.6	15.3	15.3	15.0	9.7	15.1	10.2(10.3atm%)
Fe(wt%)	8.3	8.0	8.0	8.4	8.3	8.3	8.0	9.8	8.0	9.9(9.3atm%)
Al(wt%)	8.1	8.3	8.0	8.1	8.1	8.0	8.2	10.2	8.0	9.9(19.2atm%)
B (wt%)	0.09	0.10	0.10	0.08	0.09	0.08	0.10	—	0.09	1.0
Ti(wt%)	4.9	4.9	4.8	5.0	5.0	4.8	4.8	—	4.9	
Si(wt%)	0.8	1.1	1.0	0.9	2.1	1.2	1.3	2.2		
Hf(wt%)	0.47		0.42	0.52	0.55		0.50			0.5(0.15atm%)
Ca(wt%)		0.06	0.05							
Others(wt%)				Zr 0.05		Y 0.30	Y 0.30			
Oxidation test(1,150°C×100hr, in air)										
Weight increase by oxidation(mg/cm²)	1.6	1.1	1.4	1.6	2.5	1.8	4.6	0.9	1.5	11.4
Adhesivity(%)	94	93	94	96	95	52	79	0	0	20
Oxidation test(1,050°C×200hr, in air)										
Weight increase by oxidation(mg/cm²)	0.9	0.4	0.8	1.0	0.7	1.2	2.3	0.6	0.8	6.8
Adhesivity(%)	95	93	90	95	88	86	89	77	91	41
Vickers hardness(HV)										
Room temperature(1st time)	471	424	445	435	510	474	480	330	385	
800 °C	397	347	361	358	316	400	401	265	405	
Room temperature(2nd time)	500	445	469	460	537	494	489	338	413	
ΔHV	+29	+21	+24	+25	+27	+20	+8	+8	+28	
Tensile strength(kg/mm², at 1,000 °C)	11	15	13						22	
Crystalline phase(s) (γ:fcc, α:bcc)	γ+γ' +β_2	γ+γ' +β_2	γ+γ' +β_2	γ+γ' +β_2	γ+γ' +β_2	γ+γ' +β_2	γ+γ' +β_2	γ' +γ +β_2	γ+γ' +α	γ' +γ +β_2

Table 11

	Known alloys					
	SUS304	Fe-Cr-Al	Kanthal	Inconel 600	Haynes 214	Ni_3Al
Alloy composition Ni(wt%)	8.0		—	77.0	76.8	87.9
Cr(wt%)	18.0	15.1	21.2	16.0	16.1	
Fe(wt%)	74.0	77.3	73.2	7.0	2.7	(B:0.1)
Al(wt%)	—	7.6	5.6	—	4.4	13.0
Bulk specific gravity	8.03	—	7.80	8.43	8.05	7.47
Oxidation test (1,150°C × 100hr, in air)						
Weight increase by oxidation (mg/cm²)	—	2.6	1.7	-5	1.7	1.3
Adhesivity (%)	—	11	50	0	53	49
Vickers hardness (HV)						
Room temperature (1st time)	<211	191	211	—	268	173
800 °C	—	84	79	—	223	268
Room temperature (2nd time)	—	204	216	—	298	181
Δ HV	—	+13	+5	—	+30	+8
Tensile strength (kg/mm², at 1,000 °C)	—	—	1.5	5.9	7.0	8.9
Crystalline phase(s) (γ :fcc, α :bcc)	—	α	α	—	γ	γ'
Resistance to sulfate corrosion	134	114	17.9	19.8	15.5	22.9

The above test results indicate that the alloy of the present invention has good properties, as explained in detail below.

Firstly, in Tables 1-5, there can be confirmed the improvement in resistance to sulfate corrosion, imparted by Fe and the improvement in room temperature hardness, imparted by Cr. Alloy Nos. 1, 7 and 13 (each containing no Fe) and alloy Nos. 2, 8, 14 and 25 (each containing not more than 5% by weight of Fe) are inferior in resistance to sulfate corrosion. Alloy Nos. 6, 12, 18, 24 and 30, which contain more than 30% by weight of

Fe, have good resistances to sulfate corrosion but show large weight increase by oxidation. However, alloy Nos. 19 and 20, which contain no Fe or only 5% by weight or less of Fe, show good properties because they contain 28-31% by weight of Cr and 10-11% by weight of Al. Alloy No. 31, which contains less than 5% by weight of Cr, has an insufficient hardness at room temperature and an inferior resistance to sulfate corrosion. Alloy Nos. 25 and 32, which contain more than 41% by weight of Cr, have relatively high hardnesses at room temperature but inferior resistances to sulfate corrosion.

Next, in Tables 6 and 7, the improvement in oxidation resistance, etc., imparted by Al can be confirmed. Alloy No. 33, which contains less than 8% by weight of Al, shows a large weight increase by oxidation and is very low in resistance to sulfate corrosion. Alloy No. 42, which contains more than 16% by weight of Al, was fragile and allowed for no sample preparation.

In Table 8, the improvement in hardness, imparted by Ti can be confirmed. However, alloy No. 43, which contained more than 5% of Ti, allowed for no sample preparation.

In Table 9, there can be confirmed the improvement in adhesivity of oxide film, imparted by Hf, Y, Zr, Nd, Ce and Ca.

In Table 10, the comparison of alloy Nos. 57-64 with alloy No. 65 indicates that sufficient adhesivity is obtained at 1,050°C even if none of Hf, Y, Zr, Nd, Ce, Ca, Si, etc. is present. The comparison of alloy Nos. 57-61 with alloy Nos. 62-65 indicates that good adhesivity is obtained even at 1,150°C when Si and Hf, Ca and/or Zr are added. The comparison of alloy No. 66 with alloy Nos. 65, 9, 34, 37, 39 and 40 indicates that the inclusion of B in a large amount gives a significantly large weight increase by oxidation.

Table 11 shows the test results of various known alloys. These alloys, when compared with the Ni-based alloys of the present invention, are generally inferior in resistance to sulfate corrosion and, except for Ni_3Al, have large specific gravities.

In tensile test, alloy No. 7 and Ni_3Al each containing a γ' phase alone gave elongations of 1% or less and showed brittle fracture, while alloy Nos. 36 and 39 each containing a γ' phase and a γ phase gave elongations of 34% and 18%, respectively, and showed plastic deformation.

As described above, Ni-based alloys of the present invention have high-temperature strength, good oxidation resistance and an excellent resistance to sulfate corrosion. Further, the alloy may be hardly affected by the thermal history and be superior also in strength and hardness. Furthermore, the alloy can have a relatively small specific gravity and be advantageous in specific strength.

Claims

1. A Ni-based alloy consisting of, by weight:
   (a) Cr 5 to 41%
   (b) Al 8 to 16%
   (c) Fe 5 to 30% (except that when both Cr is 28 to 31% and Al is 10 to 11%, Fe is optionally present in an amount up to 30%)
   (d) optionally, Ti up to 5%
   (e) optionally, B up to 0.1%
   (f) optionally, at least one element selected from the elements of Groups 2A and 3A of the Periodic Table, the lanthanoid elements (including Y), Zr, Hf and Si in an amount in the range 0.05 to 2.5%
   (g) remainder Ni and unavoidable impurities.

2. A Ni-based alloy according to claim 1 wherein Ti, if present, is in an amount of at least 0.1%.

3. A Ni-based alloy according to claim 1 or claim 2 when B, if present, is in an amount of at least 0.01%.

4. A Ni-based alloy according to any one of claims 1 to 3 wherein Cr is 28-31% and Al is 10-11% and Fe is present in an amount of at least 1%.

5. Use of a Ni-based alloy according to any one of claims 1 to 4 in a location where it is subjected to hot gas containing components liable to cause sulfate corrosion.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 5546

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-4 054 469 (GENERAL ELECTRIC CO.) 18 October 1977 *Table I, Alloys 4-7 and claims 2,4,5,9 and 10* ---	1,3,5	C22C19/05 C22C19/00
X	US-A-4 731 221 (UNITED STATES DEP. OF ENERGY) 15 March 1988 *Table V, Alloys IC-199, IC-206 and IC-168* ---	1,3,5	
X	US-A-4 214 042 (UNITED TECHNOLOGIES CORP.) 22 July 1980 * Claims* ---	1,2,5	
A	JOURNAL OF METALS vol. 35, no. 11 , November 1983 pages 16 - 22 HERCHENROEDER, LAI AND RAO. 'A new, wrought, heat resistant Ni-Cr-Al-FeY alloy' ---	1-5	
A	JOURNAL OF MATERIALS SCIENCE vol. 28, no. 2 , 15 January 1993 pages 561 - 568 TAWANCY 'Development of Al2O3 scale during oxidation of a wrought nickel-base alloy.' ---	1-5	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** C22C
A	DE-A-25 28 241 (CABOT CORP.) 13 January 1977 *Claims, p.3, middle para., Tables 1-5* ---	1-5	
A	US-A-3 795 510 (FORD MOTOR CO.) 5 March 1974 *Tables 1 and 2* -----	1-5	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	30 November 1994	Badcock, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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