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54 **BOILER ALLOY EXCELLENT IN MOLTEN-SALT CORROSION RESISTANCE.**57 A boiler alloy excellent in molten-salt corrosion resistance and workability, which contains Al, Co, Ni, Cr, and at least one of Mo and W, and further, if necessary, either at least one of Hf and Zr or at least one of Y, La and Ce, or alternatively both of at least one of Hf and Zr and at least one of Y, La and Ce, the balance consisting of Fe and inevitable impurities, and which satisfies the following conditions:  $0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65$ ,  $0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2$ .

## Technical Field

This invention relates to a steel tube for use in coal-fired boilers, garbage incinerators and the like and more particularly to a boiler alloy exhibiting excellent resistance in a molten-salt environment.

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## Background Art

Reflecting recent energy circumstances, such typical high-temperature energy equipment as fuel-fired boilers, fluid bed reactors, coal gasifiers and coal liquefiers have been receiving attention from the aspect of coal utilization technology and technology for effective utilization of garbage resources. As regards fuel-fired boilers, for example, while use has conventionally been made mainly of oil, an awareness of the current need to utilize alternative energy sources and to make effective utilization of garbage resources is today leading to a tendency toward increased use of coal and effective utilization of garbage incineration.

However, even such high-temperature energy equipment has been designed with oil utilization in mind and the problems when coal is used or garbage is incinerated have not been adequately overcome. For instance, coal-fired boilers are fabricated using the same materials as used in conventional oil-fired boilers. Differently from the oil-fired boiler, however, the coal-fired boiler experiences severe damage from high-temperature molten salt owing to the falling of clinkers formed by the solid ash component in the boiler and also to solid ash entrained in molten state as flyash by the combustion gas stream. Although these problems are well known among those in the industry, measures for overcoming them have not yet been worked out. Hardly any measures are available from the point of material, and the response has been limited to design countermeasures based on experience, such as reduction of stream velocity and the installation of protectors. In actual practice, however, such efforts to cope with the problem through design are often ineffective. Even when flow velocity is limited, local flow channels with higher-than-expected velocities arise, while when protectors are used, the protectors themselves are rapidly damaged.

On the other hand, from the viewpoint of materials, for the boiler tubes there are used SUS 304 steel, or 18-8 austenitic stainless steels such as SUS 321, 347 and 316, or alloys such as incoloy 800 and SUS 310. Moreover, for ordinary high-temperature members there are used various high-temperature austenitic stainless steels. However, these materials were adopted not in consideration of resistance to molten-salt corrosion but solely on the basis of experience with oil-fired boilers and the like.

While, as already pointed out, there are almost no material-related measures for preventing molten-salt corrosion under the present circumstances, if material-related measures should be available, this would to the contrary increase equipment design freedom and make it possible to expect such benefits as more compact and more heat efficient equipment.

The object of this invention is to provide a material having high resistance to molten-salt corrosion such as is observed in coal-fired boilers and garbage incinerator boilers and exhibiting excellent workability.

## Disclosure of the Invention

The gist of the present invention is as set out below.

1. A boiler alloy excellent in molten-salt corrosion resistance characterized in having a composition specified in weight % including not more than 0.1% C, not more than 2.5% Si, not more than 1.0% Mn, not more than 0.03% P, not more than 0.005% S, 0.01 - 0.03% Al, 25- 55% Co, 7 - 18% Cr and 10 - 40% Ni and including either or both of 2 - 4% Mo and not more than 8% W, the balance being Fe and unavoidable impurities, and satisfying the conditions of

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65, \text{ and} \\ 0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2.$$

2. A boiler alloy excellent in molten-salt corrosion resistance characterized in having a composition specified in weight % including not more than 0.1% C, not more than 2.5% Si, not more than 1.0% Mn, not more than 0.03% P, not more than 0.005% S, 0.01 - 0.03% Al, 25- 55% Co, 7 - 18% Cr and 10 - 40% Ni, including either or both of 2 - 4% Mo and not more than 8% W and further including either or both of not more than 0.2% Hf and not more than 0.2% Zr, the balance being Fe and unavoidable impurities, and satisfying the conditions of

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65, \text{ and} \\ 0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2.$$

3. A boiler alloy excellent in molten-salt corrosion resistance characterized in having a composition specified in weight % including not more than 0.1% C, not more than 2.5% Si, not more than 1.0% Mn, not more than 0.03% P, not more than 0.005% S, 0.01 - 0.03% Al, 25- 55% Co, 7 - 18% Cr and 10 - 40% Ni, including either or both of 2 - 4% Mo and not more than 8% W and further including one or more of not more than 0.1% Y, not more than 0.1% La and not more than 0.1% Ce, the balance being Fe and unavoidable impurities, and satisfying the conditions of

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65, \text{ and}$$

$$0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2.$$

4. A boiler alloy excellent in molten-salt corrosion resistance characterized in having a composition specified in weight % including not more than 0.1% C, not more than 2.5% Si, not more than 1.0% Mn, not more than 0.03% P, not more than 0.005% S, 0.01 - 0.03% Al, 25- 55% Co, 7 - 18% Cr and 10 - 40% Ni, including either or both of 2 - 4% Mo and not more than 8% W and further including either or both of not more than 0.2% Hf and not more than 0.2% Zr and one or more of not more than 0.1% Y, not more than 0.1% La and not more than 0.1% Ce, the balance being Fe and unavoidable impurities, and satisfying the conditions of

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65, \text{ and}$$

$$0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2.$$

Best Mode for Carrying out the Invention

The invention will be explained in detail in the following.

The reason for limiting the component ranges in this invention in the foregoing manner will be explained first.

The upper limit of the C content is set at 0.1% because at a higher than 0.1% content C degrades workability and increases the probability of intergranular corrosion cracking.

The upper limit of the Si content is set at 2.5% because, while Si is required as a deoxidizing component, it degrades hot workability at a higher content than 2.5%.

The upper limit of the Mn content is set at 1.0% because, while it has a deoxidation effect similar to Si, it leads to brittleness when present in excess.

The upper limit of the P content is set at 0.03% because P, an unavoidable impurity, at a content higher than 0.03% produces pronounced intergranular segregation.

The upper limit of the S content is set at 0.005% because S, an unavoidable impurity, at a content higher than 0.005% markedly degrades the hot workability of the steel and makes production impossible.

While the effect of Al as a deoxidant does not require mentioning, it can reduce damage by molten salt by forming  $\text{Al}_2\text{O}_3$  on the alloy surface. However, the lower limit has to be set at 0.01% because no  $\text{Al}_2\text{O}_3$  film forms on the alloy surface at an added amount of less than 0.01%. On the other hand, the upper limit is specified as 0.03% because workability is degraded with addition exceeding 0.03%.

While Co, Ni, Cr, Mo and W improve molten-salt corrosion resistance and corrosion resistance, these effects of the elements are not manifested when they are added independently and are manifested only when they are added in combination. As a result of research conducted by the inventors for obtaining a material exhibiting excellent molten-salt corrosion resistance in a 500 °C high-temperature boiler environment postulated as the operating condition of an actual boiler, it was clarified that the properties of the alloying elements are manifested most effectively within the following content ranges when

(1) The amounts of Co, Ni and Cr satisfy the relation:

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65$$

and

(2) The amounts of Ni, Cr, Co, Mo and W satisfy the relation:

$$0.7 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2$$

Further, as a result of research conducted at a 600 °C high-temperature boiler environment, it was clarified that the properties of the alloying elements are manifested most effectively within the following

content ranges when

(3) The amounts of Co, Ni and Cr satisfy the relation:

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 55$$

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and

(2) The amounts of Ni, Cr, Co, Mo and W satisfy the relation:

$$0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 0.7$$

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Although Co is an element which improves molten-salt corrosion resistance when co-present with Ni, Cr, Mo and W, its lower limit is set at 25% because, at a content lower than 25% it does not have a pronounced effect in use at 500 °C and for obtaining the desired molten-salt corrosion resistance it is necessary to increase the amount of other alloying elements, which is uneconomical. On the other hand, its upper limit is set at 55% because the molten-salt corrosion resistance improvement effect in use at 600 °C decreases when the content thereof exceeds 55%.

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Ni has the effect of improving corrosion resistance. Its lower limit is set to 10% because at less than 10% it has no effect and for obtaining the desired corrosion resistance it is necessary to increase the amount of other alloying elements, which is uneconomical. On the other hand, since no appreciable effect is observed at a content exceeding 40%, its upper limit is set at 40% in consideration of economy.

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Cr is an element which markedly improves corrosion resistance when co-present with Ni, Mo and W. No effect is obtained when added at less than 7% and since no appreciable effect is observed at a content exceeding 18%, its upper limit is set at 18%.

Like Co, Mo also improves molten-salt corrosion resistance and in particular has an effect of improving molten-salt corrosion resistance by increasing hardness. However, its content range is set at 2 - 4% because at a content lower than 2% the hardness is insufficient and at a content higher than 4% the hardness becomes so high as to degrade workability.

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Like Mo, W also improves molten-salt corrosion resistance by increasing hardness. The upper limit is set at 8% because adding it to a higher content than 8% does not produce an appreciable improvement in molten-salt corrosion resistance, but only degrades workability.

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The upper limit of Hf content is set at 0.2% because addition of even a small amount improves strength at high temperature.

Zr acts as a deoxidizing element. Its upper limit is set at 0.2% because no appreciable improvement in effect is observed when the amount added exceeds 0.2%.

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As Y, La and Ce work to further improve the hot workability, they are added as required in cases where hot working is to be conducted under severe conditions. The upper limit of the content of each of these elements is set at 0.1% because addition in excess of 0.1% does not produce an appreciable improvement and may even have a degrading effect.

The inventors produced alloys with different amounts of Co, Ni and Cr, casted them, and hot rolled each into a 7 mm-thick plate. Next, each plate was heat treated by first holding it at 1050 °C for 30 minutes and then quenching it. A test specimen measuring 2 mm in thickness, 15 mm in width and 80 mm in length was then cut from the plate perpendicular to its rolling direction. The test specimens were bent, then held in an apparatus heated to 500 °C and 600 °C, coated with a mixed NaCl-KCl molten salt, and tested for 500 hr, whereafter the degree of change in appearance between before and after the test was observed. As a result of a scientific analysis of the results, the existence of the aforesaid condition among Co, Ni and Cr was clarified.

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#### Examples

One ton of each of the alloys of the compositions shown in Tables 1 - 6 was melted in a vacuum induction heating furnace, cleaned by ESR treatment, cast into an ingot measuring 500 mm x 250 mm in section and hot rolled into a 7 mm-thick plate. The plate was then heat treated by first holding it at 1050 °C for 30 minutes and then quenching it. A test specimen measuring 2 mm in thickness, 15 mm in width and 80 mm in length was cut from the plate perpendicular to its rolling direction. The test specimen was folded at its center in the longitudinal direction and evaluated for workability at that time, with the results shown in Table 2 (continued from Table 1), Table 4 (continued from Table 3) and Table 6 (continued from Table 5). It was then applied with a coat of mixed NaCl-KCl molten salt, held in an apparatus heated to 500 °C and 600 °C, tested for 500 hr, and examined for the result of measurement of degree of change in appearance.

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From the results indicated in Table 2, Table 4 and Table 6, it is clear that, contrary to the comparison alloys which did not have very good molten-salt corrosion resistance and workability, all of the materials of invention alloys 1 - 37, 38 -74 had excellent molten-salt corrosion resistance and workability properties.

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Table 1 (wt %)

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No.	C	Si	Mn	P	S	Al	Co	Ni	Cr	Mo	W
1	0.06	1.38	0.23	0.02	0.002	0.023	39.5	15.6	16.4	2.4	-
2	0.02	2.44	0.67	0.01	0.001	0.015	38.6	16.3	17.7	3.1	-
3	0.04	1.86	0.05	0.01	0.003	0.029	31.8	19.8	12.5	2.2	-
4	0.06	1.35	0.38	0.02	0.002	0.011	33.9	17.4	16.5	2.3	-
5	0.04	0.75	0.91	0.03	0.003	0.024	30.2	20.5	13.1	2.8	-
6	0.08	2.22	0.32	0.01	0.004	0.018	29.8	23.5	12.2	3.5	-
7	0.01	1.43	0.15	0.01	0.004	0.016	30.1	15.3	13.9	-	7.7
8	0.06	1.67	0.48	0.03	0.005	0.012	26.7	15.2	17.4	-	5.6
9	0.07	1.05	0.53	0.03	0.003	0.027	34.9	24.0	15.7	-	6.8
10	0.05	0.55	0.06	0.01	0.001	0.029	39.7	22.9	12.8	-	5.1
11	0.09	1.95	0.86	0.02	0.002	0.026	34.1	17.8	16.5	-	6.4
12	0.04	1.87	0.97	0.01	0.003	0.018	39.9	16.4	13.9	-	7.0
13	0.02	0.95	0.31	0.01	0.001	0.016	38.4	24.3	14.2	3.9	1.3
14	0.03	2.35	0.72	0.02	0.002	0.022	29.8	18.7	17.3	2.7	1.9
15	0.04	0.32	0.58	0.03	0.003	0.023	35.1	24.1	15.7	2.2	2.5
16	0.06	0.91	0.77	0.01	0.001	0.027	31.5	21.7	12.4	3.3	0.7
17	0.04	1.76	0.68	0.02	0.002	0.019	37.7	20.7	13.6	2.6	2.1
18	0.02	1.89	0.91	0.01	0.003	0.011	28.7	20.4	16.3	3.4	1.2
19	0.03	0.22	0.51	0.01	0.002	0.026	35.7	22.2	12.6	2.5	2.7
20	0.08	0.27	0.34	0.02	0.001	0.023	32.0	21.2	16.7	2.3	3.1
21	0.03	0.91	0.29	0.03	0.002	0.024	35.9	20.9	14.5	-	6.3
22	0.04	0.87	0.54	0.02	0.003	0.028	38.1	16.3	15.3	2.5	2.2
23	0.08	2.42	0.31	0.02	0.003	0.011	38.7	13.8	17.8	3.2	-
24	0.09	1.76	0.66	0.02	0.005	0.012	33.1	22.1	12.2	-	5.8
25	0.09	2.38	0.38	0.03	0.002	0.017	34.6	19.5	16.9	-	7.3
26	0.01	1.58	0.25	0.02	0.003	0.016	35.8	15.7	17.8	3.4	-
27	0.05	0.96	0.13	0.01	0.002	0.020	37.9	18.7	12.4	3.6	-
28	0.07	1.63	0.91	0.03	0.003	0.019	30.3	16.4	18.0	2.5	-
29	0.03	1.52	0.61	0.02	0.003	0.016	38.1	16.1	15.0	2.4	-
30	0.08	2.18	0.88	0.02	0.004	0.024	35.4	20.9	12.9	2.8	2.8
31	0.05	0.39	0.52	0.01	0.002	0.028	38.0	18.4	14.1	3.3	-
32	0.03	1.68	0.41	0.02	0.001	0.018	33.4	15.1	17.2	2.6	-
33	0.02	0.72	0.07	0.01	0.001	0.022	32.1	18.8	13.3	-	5.5
34	0.07	2.28	0.76	0.02	0.003	0.026	36.4	17.2	16.3	2.3	-
35	0.04	1.61	0.80	0.01	0.002	0.022	33.3	22.8	14.8	2.8	2.2
36	0.06	2.47	0.68	0.03	0.004	0.027	34.8	18.6	17.1	2.4	2.2
37	0.08	1.93	0.41	0.02	0.003	0.029	38.8	13.9	17.9	3.7	1.3

Table 2 (continued from Table 1) (wt %)

No.	Other	A	B	Workability	Molten-salt corrosion resistance (500°C×500hr)
1		60.0	0.76	○	○
2		61.9	0.70	○	○
3	Hf:0.05	54.5	0.96	○	○
4	Hf:0.16, Zr:0.14	59.1	0.93	○	○
5	Zr:0.01	54.8	1.02	○	○
6		52.1	1.07	○	○
7	Hf:0.12, Zr:0.10	51.2	0.86	○	○
8	Hf:0.08	57.7	1.17	○	○
9	Zr:0.19	65.0	1.03	○	○
10		58.4	0.77	○	○
11		60.2	0.97	○	○
12		58.6	0.73	○	○
13	Hf:0.08	56.9	0.71	○	○
14	Zr:0.14	59.6	1.06	○	○
15	Hf:0.15, Zr:0.19	59.8	0.89	○	○
16		58.5	1.04	○	○
17		61.0	0.85	○	○
18		59.2	1.12	○	○
19		59.0	0.88	○	○
20		62.3	1.06	○	○
21	Zr:0.03	60.6	0.91	○	○
22	Hf:0.05	58.3	0.76	○	○
23	Hf:0.14, Zr:0.16	59.9	0.75	○	○
24	Hf:0.12, Zr:0.10	57.0	0.95	○	○
25	Hf:0.02	62.2	0.95	○	○
26	Hf:0.18	60.3	0.85	○	○
27	Zr:0.19	57.0	0.75	○	○
28	La:0.02, Y:0.07	58.6	1.05	○	○
29	La:0.03	58.3	0.76	○	○
30	Ce:0.09	58.0	0.83	○	○
31	Y:0.08, Ce:0.10	58.6	0.79	○	○
32	La:0.08, Y:0.05, Ce:0.04	57.6	0.90	○	○
33	Y:0.04	54.8	0.92	○	○
34	Hf:0.07, La:0.02, Y:0.08	59.9	0.87	○	○
35	Hf:0.13, Zr:0.10, La:0.08, Y:0.07	61.7	1.01	○	○
36	Hf:0.18, La:0.04, Ce:0.05	61.7	0.93	○	○
37	Zr:0.18, La:0.02, Y:0.01, Ce:0.08	60.2	0.74	○	○

$$A = 1/2Co + Ni + 3/2Cr$$

$$B = (Ni + Cr) / (Co + Mo + 1/2W)$$

Workability ○ : No cracking or pucker caused by working △ : Pucker × : Cracking

Molten-salt corrosion resistance } ○ : No surface pits × : Surface pits observed

Table 3

(wt %)

	No.	C	Si	Mn	P	S	Al	Co	Ni	Cr	Mo	W
5	38	0.03	1.85	0.31	0.02	0.003	0.023	44.5	10.6	11.4	2.4	-
	39	0.02	2.25	0.58	0.01	0.002	0.016	43.6	10.3	11.7	3.2	-
	40	0.04	1.87	0.07	0.03	0.001	0.027	46.8	14.8	9.5	2.5	-
	41	0.08	2.26	0.36	0.02	0.003	0.015	48.7	12.4	10.5	2.3	-
	42	0.05	0.85	0.91	0.03	0.004	0.026	45.2	15.0	11.0	3.1	-
10	43	0.09	2.25	0.31	0.01	0.002	0.016	44.6	16.5	9.2	3.9	-
	44	0.01	2.33	0.08	0.03	0.002	0.022	44.8	10.3	9.9	-	7.6
	45	0.04	0.86	0.47	0.03	0.003	0.028	41.5	10.2	9.4	-	5.2
	46	0.03	1.23	0.51	0.02	0.004	0.022	49.8	11.8	11.7	-	6.4
	47	0.07	0.66	0.09	0.01	0.003	0.020	44.5	10.4	10.8	-	5.0
15	48	0.09	1.63	0.91	0.02	0.002	0.018	47.9	15.9	9.5	-	6.6
	49	0.08	1.95	0.88	0.03	0.003	0.015	44.7	10.8	10.9	-	7.0
	50	0.02	1.37	0.31	0.02	0.003	0.012	43.2	10.4	12.0	3.8	1.0
	51	0.01	2.43	0.71	0.02	0.002	0.011	44.8	18.3	9.3	3.4	2.4
	52	0.07	0.21	0.51	0.03	0.004	0.016	49.9	13.7	9.7	2.4	2.6
20	53	0.05	0.73	0.79	0.03	0.002	0.026	46.3	17.1	9.4	3.0	1.0
	54	0.04	2.05	0.98	0.01	0.003	0.023	42.5	11.7	10.6	2.4	2.4
	55	0.02	1.46	0.82	0.02	0.002	0.024	43.5	15.4	10.3	3.3	1.4
	56	0.09	0.50	0.59	0.03	0.001	0.028	40.5	11.2	11.6	2.6	2.4
	57	0.06	0.38	0.43	0.03	0.001	0.023	46.8	16.2	9.3	2.0	3.0
25	58	0.08	0.91	0.22	0.02	0.002	0.021	40.7	14.6	9.5	-	6.4
	59	0.03	0.78	0.50	0.02	0.003	0.020	42.9	11.3	11.3	2.2	2.4
	60	0.04	2.48	0.34	0.01	0.004	0.016	43.5	13.5	9.7	3.0	-
	61	0.09	1.78	0.69	0.02	0.002	0.022	47.9	15.1	8.8	-	6.0
	62	0.06	2.39	0.29	0.03	0.003	0.021	49.4	14.5	8.9	-	7.6
30	63	0.05	1.88	0.35	0.03	0.004	0.029	40.6	10.7	9.8	3.6	-
	64	0.06	1.06	0.14	0.01	0.002	0.017	42.7	15.7	7.4	3.5	-
	65	0.07	1.73	0.86	0.02	0.005	0.021	45.1	16.4	8.2	2.8	-
	66	0.02	0.62	0.58	0.01	0.003	0.015	43.1	11.5	12.1	2.1	-
	67	0.08	2.31	0.96	0.01	0.002	0.019	40.2	15.9	8.7	2.6	2.7
35	68	0.05	0.52	0.52	0.02	0.003	0.012	46.8	16.5	8.2	3.2	-
	69	0.03	1.66	0.44	0.02	0.004	0.024	47.9	10.1	10.7	2.7	-
	70	0.01	0.67	0.05	0.01	0.001	0.026	46.9	13.8	9.3	-	5.7
	71	0.02	2.08	0.81	0.03	0.003	0.015	41.2	12.2	9.3	2.5	-
	72	0.08	1.61	0.79	0.02	0.004	0.024	48.1	17.7	8.8	2.9	2.2
40	73	0.04	2.47	0.66	0.01	0.002	0.029	46.6	13.6	7.1	2.6	2.0
	74	0.06	1.93	0.41	0.03	0.001	0.021	41.3	14.7	9.7	3.8	1.4

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Table 4 (continued from Table 3) (wt %)

	No	Other	A	B	Workability	Molten-salt corrosion resistance (600°C×500hr)
5	38		50.0	0.47	○	○
	39		49.7	0.47	○	○
	40	Hf:0.05	52.5	0.49	○	○
	41	Hf:0.18, Zr:0.13	52.5	0.45	○	○
10	42	Zr:0.01	54.1	0.67	○	○
	43		52.3	0.66	○	○
	44	Hf:0.13, Zr:0.08	47.6	0.52	○	○
	45	Hf:0.09	45.1	0.57	○	○
	46	Zr:0.19	49.3	0.55	○	○
15	47		54.1	0.62	○	○
	48		49.1	0.64	○	○
	49		49.5	0.45	○	○
	50	Hf:0.17	50.0	0.47	○	○
	51	Zr:0.14	54.7	0.56	○	○
20	52	Hf:0.15, Zr:0.13	53.2	0.54	○	○
	53		49.4	0.67	○	○
	54		48.9	0.48	○	○
	55		52.6	0.68	○	○
	56		48.9	0.51	○	○
25	57		53.6	0.63	○	○
	58	Zr:0.07	49.9	0.57	○	○
	59	Hf:0.09	49.7	0.49	○	○
	60	Hf:0.11, Zr:0.18	49.8	0.50	○	○
	61	Hf:0.17, Zr:0.08	52.3	0.58	○	○
30	62	Hf:0.02	52.6	0.54	○	○
	63	Hf:0.17	45.7	0.47	○	○
	64	Zr:0.16	48.2	0.50	○	○
	65	La:0.04, Y:0.03	51.3	0.51	○	○
	66	La:0.03	49.8	0.43	○	○
35	67	Ce:0.07	53.9	0.63	○	○
	68	Y:0.05, Ce:0.08	55.0	0.61	○	○
	69	La:0.09, Y:0.07, Ce:0.02	50.1	0.41	○	○
	70	Y:0.08	51.2	0.46	○	○
	71	Hf:0.08, La:0.02, Y:0.09	46.8	0.49	○	○
40	72	Hf:0.10, Zr:0.11, La:0.07, Y:0.03	55.0	0.51	○	○
	73	Hf:0.16, La:0.06, Ce:0.05	47.6	0.41	○	○
	74	Zr:0.18, La:0.04, Y:0.01, Ce:0.08	49.9	0.55	○	○

$$A = 1/2Co + Ni + 3/2Cr$$

$$B = (Ni + Cr) / (Co + Mo + 1/2W)$$

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Table 5 (wt %)

	No.	C	Si	Mn	P	S	Cr	Ni	Mo	Co	W	Al
COMPARISON SUS STEELS	1	0.02	0.45	0.25	0.016	0.003	22.5	11.9	-	-	-	<0.05
	2	0.06	0.27	0.26	0.022	0.001	19.8	32.5	-	-	-	0.4
	3	0.08	0.36	0.22	0.018	0.002	15.4	42.4	3.2	-	-	1.0
	4	0.07	0.22	0.18	0.019	0.003	18.6	59.2	2.9	-	-	0.4
	5	0.03	0.19	0.27	0.021	0.004	-	95.6	-	0.1	-	-
	6	0.02	0.23	0.29	0.019	0.003	16.4	74.1	-	0.1	-	<0.05
	7	0.08	0.15	0.23	0.024	0.003	22.8	60.2	-	-	-	1.4
	8	0.04	0.16	0.19	0.017	0.003	16.8	66.5	-	-	-	0.8
	9	0.07	0.28	0.24	0.025	0.004	20.6	78.6	-	-	-	<0.05
	10	0.08	0.18	0.26	0.023	0.005	19.8	74.5	-	-	-	1.4

Table 6 (continued from Table 5) (wt %)

	No.	Fe	N	O	Other	A	B	Workability	Molten-salt corrosion resistance	
									500°C×500hr	600°C×500hr
COMPARISON SUS STEELS	1	bal	0.02	0.001		45.7	∞	△	×	×
	2	bal	0.02	0.001	Ti:0.4	62.2	∞	△	×	×
	3	bal	0.02	0.001	Ti:3.0	65.5	28.7	△	×	×
	4	18	0.02	0.001	Ti:1, Nb:5	87.1	26.8	×	×	×
	5	0.5	-	-		95.6	∞	△	×	×
	6	8	0.02	0.001		98.7	∞	×	×	×
	7	15	0.02	0.001		94.4	∞	×	×	×
	8	7.5	0.02	0.001	Nb:1.0	91.7	∞	△	×	×
	9	0.3	0.02	0.001	Ti:0.5	109.5	∞	×	×	×
	10	1.0	0.02	0.001	Ti:2.4	104.2	∞	×	×	×

$A = 1/2Co + Ni + 3/2Cr$

$B = (Ni + Cr) / (Co + Mo + 1/2W)$

Workability ○ : No cracking or pucker caused by working △ : Pucker × : Cracking

Molten-salt corrosion resistance } ○ : No surface pits × : Surface pits observed

Industrial Applicability

Since the present invention makes it possible to obtain an alloy with excellent resistance against a molten-salt corrosion environment and also excellent in workability, its contribution to practical application and wider utilization of the high-temperature energy equipment that has become the focus of attention in recent years is extremely large.

## Claims

1. A boiler alloy excellent in molten-salt corrosion resistance characterized in having a composition specified in weight % including not more than 0.1% C, not more than 2.5% Si, not more than 1.0% Mn, not more than 0.03% P, not more than 0.005% S, 0.01 - 0.03% Al, 25- 55% Co, 7 - 18% Cr and 10 - 40% Ni and including either or both of 2 - 4% Mo and not more than 8% W, the balance being Fe and unavoidable impurities, and satisfying the conditions of

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65, \text{ and}$$

$$0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2.$$

2. A boiler alloy excellent in molten-salt corrosion resistance characterized in having a composition specified in weight % including not more than 0.1% C, not more than 2.5% Si, not more than 1.0% Mn, not more than 0.03% P, not more than 0.005% S, 0.01 - 0.03% Al, 25- 55% Co, 7 - 18% Cr and 10 - 40% Ni, including either or both of 2 - 4% Mo and not more than 8% W and further including either or both of not more than 0.2% Hf and not more than 0.2% Zr, the balance being Fe and unavoidable impurities, and satisfying the conditions of

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65, \text{ and}$$

$$0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2.$$

3. A boiler alloy excellent in molten-salt corrosion resistance characterized in having a composition specified in weight % including not more than 0.1% C, not more than 2.5% Si, not more than 1.0% Mn, not more than 0.03% P, not more than 0.005% S, 0.01 - 0.03% Al, 25- 55% Co, 7 - 18% Cr and 10 - 40% Ni, including either or both of 2 - 4% Mo and not more than 8% W and further including one or more of not more than 0.1% Y, not more than 0.1% La and not more than 0.1% Ce, the balance being Fe and unavoidable impurities, and satisfying the conditions of

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65, \text{ and}$$

$$0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2.$$

4. A boiler alloy excellent in molten-salt corrosion resistance characterized in having a composition specified in weight % including not more than 0.1% C, not more than 2.5% Si, not more than 1.0% Mn, not more than 0.03% P, not more than 0.005% S, 0.01 - 0.03% Al, 25- 55% Co, 7 - 18% Cr and 10 - 40% Ni, including either or both of 2 - 4% Mo and not more than 8% W and further including either or both of not more than 0.2% Hf and not more than 0.2% Zr and one or more of not more than 0.1% Y, not more than 0.1% La and not more than 0.1% Ce, the balance being Fe and unavoidable impurities, and satisfying the conditions of

$$0.5 \text{ Co} + \text{Ni} + 1.5 \text{ Cr} \leq 65, \text{ and}$$

$$0.4 \leq (\text{Ni} + \text{Cr})/(\text{Co} + \text{Mo} + 0.5 \text{ W}) \leq 1.2.$$

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/JP93/01604

**A. CLASSIFICATION OF SUBJECT MATTER**

Int. Cl<sup>5</sup> C22C19/00, 30/00

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>5</sup> C22C19/00-19/07, 30/00

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

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, B2, 2-43812 (Mitsubishi Metal Corp.), October 1, 1990 (01. 10. 90), Columns 1 to 4, (Family: none)	1-4
A	JP, B2, 62-54179 (Daido Steel Co., Ltd.), November 13, 1987 (13. 11. 87), Columns 1 to 2, (Family: none)	1-4

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search  
January 17, 1994 (17. 01. 94)

Date of mailing of the international search report  
February 1, 1994 (01. 02. 94)

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