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

(11) Publication number: **0 441 573 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **91300887.6**

(51) Int. Cl.5: **C22C 32/00**, F27D 3/02

(22) Date of filing: **04.02.91**

(30) Priority: **06.02.90 JP 26968/90**

(43) Date of publication of application: **14.08.91 Bulletin 91/33**

(84) Designated Contracting States: **AT BE CH DE FR GB IT LI SE**

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(54) **Heat-resistant alloy.**

(57) An oxide-dispersion strengthened type heat-resistant alloy is provided for use in preparing furnace members such as a skid rail. The alloy consists essentially of up to 0.2% C + N, up to 2.0% Si, up to 2.0% Mn, 25 to 35% Ni and 20 to 35% Cr, 5 to 50% Co; and one or more of 0.5 to 5% Mo, 0.5 to 5% W, and 0.2 to 4% Ta, and the balance of Fe, and contains 0.1 to 2% of fine particles of high melting point metal oxide such as Y_2O_3 dispersed in the austenite matrix.

The alloy exhibits excellent properties against hot deformation, also oxidation resistance, abrasion resistance and thermal shock resistance.

EP 0 441 573 A1

HEAT-RESISTANT ALLOY

The present invention concerns a heat-resistant alloy having good strength and anti-corrosion properties at high temperature. The alloy of this invention is suitable as the material for skid rails of furnaces used in, for example, steel industry for heating steel pieces.

Steel plates and steel wires are produced by rolling steel pieces called slabs or billets after uniformly heating them in a heating furnace such as a walking beam furnace or pusher furnace. If the temperature of the steel piece is lower at the position where the steel piece contacts the furnace bed than at the remaining positions, then uneven thickness of the rolled steel plate or even cracking may occur. In order to avoid these troubles, it is necessary to raise the temperature of the furnace bed at the position of contact with the heated piece to a temperature near the heating temperature. Thus, at the highest temperatures of use the furnace bed metal attains a temperature as high as 1300°C or more.

As a typical material for the furnace bed withstanding a high temperature of 1150°C or higher, there has been used a solid solution strengthened type heat-resistant casting alloy, which contains, in addition to Fe, 20-35% Cr, 15-35% Ni and 5-50% Co as the main components, and 0.5-5% Mo, 0.5-5% W and 0.2-4.0% Ta as the solid solution strengthening elements. However, skid rails in the soaking zone of a furnace are subjected to a high temperature such as 1200-1350°C, and suffer from heavy strain and abrasion. The above mentioned conventional heat-resistant casting alloy of the solid solution strengthened type is not satisfactory as the material of the skid rails.

It has been proposed to use ceramics having high heat-resistance and anti-abrasion properties as the material of the furnace bed metal (for example, Japanese Utility Model Publication No. 35326/1989). So-called fine ceramics materials such as SiC and Si_3N_4, preferable from the viewpoint of high shock-resistance which is one of the properties required for skid rails, are easily damaged by oxidation when used in a strongly oxidative atmosphere.

On the other hand, super alloys of the oxide-dispersion strengthened type, i.e., Ni-based super alloys in which fine particles of an oxide having a high melting point such as Y_2O_3 are dispersed, find application in gas-turbines and jet-engines (for example, Japanese Patent Publication No. 38665/1981). As to high temperature furnaces it has been proposed to use an oxide-dispersion strengthened type super alloy of the composition consisting of 12.5-20% Cr, up to 1% Al, up to 0.1% C and up to 0.5% (volume) Y_2O_3, the balance being Ni, as the material for mesh belts (Japanese Patent Publication No. 9610/1984).

One of these applicants attempted to use the oxide-dispersion strengthened type super alloys as the material of the skid member of a skid rail, and as the result of research, it was discovered that an oxide-dispersion strengthened type super alloy consisting of 18-40% Cr, up to 5% Ti, the balance being substantially Ni, and containing 0.1-2% of fine particles of a high melting point metal oxide dispersed in the austenite matrix thereof is useful as a material for a skid rail. The discovery has been disclosed (Japanese Patent Application No. 14044/1989).

In the furnaces using heavy oil as the fuel, however, Ni-based super alloys are easily corroded due to high temperature sulfidation attack by the sulfur in the heavy oil. The material having sufficient anti-corrosive properties is, for example, Fe-Ni-Cr-Co-W solid solution strengthened heat resistant cast alloy. If oxide-dispersion strengthened heat resistant alloy having the matrix composition similar thereto is obtained, then the alloy will be a material suitable for the furnace bed metal without the above drawback.

Furthermore, Ni-based alloys are expensive, and therefore, it is desirable to construct the skid rails with a less expensive alloy, i.e. less Ni.

The general object of the present invention is to provide an alloy having not only high temperature deformation resistance, anti-abrasion property and shock resistance, but also a good oxidation resistance, which are of the same rank as those of the above noted oxide-dispersion strengthened type Ni-based super alloy.

A preferred object of the present invention is to provide a heat-resistant alloy of better performance by dispersing oxide particles in the matrix of the heat-resistant alloy of the composition giving the highest ranked high temperature strength and anti high temperature corrosion property as the solid solution strengthened type casting alloy so as to suppress plastic deformation of the matrix at high temperature with the oxide particles.

Another aspect of the present invention is to provide furnace metals, particularly, skid rails, of higher performance by using the above mentioned heat-resistant alloy.

The alloy according to the present invention is an oxide-dispersion strengthened type alloy consisting essentially of up to 0.2% C + N, up to 2.0% Si, up to 2.0% Mn, 15 to 35% Ni, 20-35% Cr, 5-50% Co, and one or more of 0.5 to 5% Mo, 0.5 to 5% W and 0.2 to 4% Ta; and the balance of Fe; and containing 0.1-

2% of fine particles of high melting point metal oxide dispersed in the austenite matrix of the alloy. Percentages are by weight.

The high melting point metal oxide may be one or more selected from Y_2O_3, ZrO_2 and Al_2O_3. Y_2O_3 gives the best results.

Figure 1 to Figure 3 illustrate a typical embodiment of a skid rail using an alloy according to the invention:

Figure 1 being a plan view;
Figure 2 a side elevation view; and
Figure 3 a cross-sectional view.

In order to produce the above mentioned oxide-dispersion strengthened type alloy, so-called mechanical alloying technology developed by INCO (The International Nickel Co., Inc.) is useful. The technology comprises subjecting powders of metal components and fine crystals of a high melting point metal oxide in a ball mill, for example, a high kinetic energy type ball mill, so as to produce by repeated welding and fracturing a granular product comprising an intimate and uniform mixture of very fine particles of the components. The product prepared by mechanical alloying is then compacted and sintered by hot extrusion or hot isostatic pressing and, if necessary, machined to produce the skid member.

A typical embodiment of a skid rail using an alloy of the present invention is, as shown in Figure 1 to Figure 3, a skid rail 1A made by welding metal saddles 3A on a water-cooled skid pipe 2, attaching skid members 4A made of the oxide-dispersion strengthened heat-resistant alloy to the saddles and covering all the members except for the skid members 4A with refractory insulator 5. As the material of the skid member, there is used the above oxide-dispersion strengthened type alloy.

The skid rails may be of other configurations. For example, a skid structure may use cylindrical saddles to attach button shaped skid members.

In general, nickel-basedoxide-dispersion strengthened type super alloys are stable even at a high temperature, and the above mentioned known nickel-base alloys have alloy compositions suitable for the use such as turbine blades (Japanese Patent Publication No. 56-38665) or mesh belts (Japanese Patent Publication No. 59-9610) and contain suitable amounts of oxide particles. However, these known nickel-base alloys do not have sufficient corrosion-resistance against the high temperature sulfidation attack occurring in furnaces having an atmosphere resulting from combustion of heavy oil.

By using the above described oxide-dispersion strengthened alloy according to the present invention, it is possible to achieve a high compresssion creep strength, as shown in the working example described later, in addition to the heat-resistance and oxidation-resistance. Thus, less expensive, but more durable heat-resistant alloy is provided.

The following factors are relevant in the selected alloy compositions:

In the heat-resistant alloy of the basic composition,

C + N: Up to 0.2%

Though C is useful for improving high temperature strength, a content of C + N higher than 0.2% lowers the melting point, and decreases the weldability and the toughness.

Si: Up to 2.0%

Si improves oxidation resistance of the alloy at high temperature. Too high a content causes precipitation of gamma-phase.

Mn: Up to 2.0%

Mn is also useful for high temperature oxidation resistance of the alloy, but an excess addition rather deteriorates the property.

Ni: 15 to 35%

Ni makes the austenite structure stable and enhances the heat-resistance, anti-carburization property and high temperature strength. Less than 15% gives little effect, and at more than 35% the effect saturates.

Cr: 20 to 35%

Cr is included at a content of 20% or more to improve high temperature oxidation resistance. Excess addition will make the austenite unstable and lower the toughness.

Co: 5 to 50%

Co is an austenite enstabling element, which dissolves in the matrix to decrease the stacking fault energy, and thus improves the creep strength at a temperature of 1150°C or higher. For this purpose, addition of at least 5% is necessary. At 50% or more the effect saturates, and it becomes disadvantageous from the economic viewpoint.

One or More of Mo: 0.5 to 5%, W: 0.5 to 5.0% and Ta: 0.2 to 4.0%

These elements dissolve in austenite and strongly increase the high temperature strength and creep strength at a temperature higher than 1000°C.

High Melting Point Metal Oxide: 0.1-2%
The most preferred metal oxide is, as noted above,Y_2O_3. In the material for skid rails used in furnaces heated to relatively low temperature (up to about 1200°C), the whole or a portion of the Y_2O_3 may be replaced with ZrO_2 or Al_2O_3. Of course, combined use of two or three of Y_2O_3, ZrO_2 and Al_2O_3 is possible. Contents of the high melting point metal oxide should be 0.1% or more. Otherwise, the effect of stabilizing the alloy at a high temperature will not be satisfactory. As the content increases, the effect slows down at about 1% and saturates at 2%, and therefore, a suitable content in this range should be chosen. It should be noted that during processing, originally added Y_2O_3 may convert to various yttria-alumina compounds (e.g., YAG) if alumina is copresent.

Alloys embodying the invention have been found to show, when used as the material of the skid rails or other skid surfaces in various furnaces such as heating furnaces for hot processing of steel, excellent properties against hot deformation, oxidation resistance, abrasion resistance and thermal shock resistance, and therefore, can be used for a long period of time. This will decrease maintenance labor of the heating furnaces and facilitates continuous operation thereof. Decreased costs for energy and maintenance result in lowering production costs in the hot processing of steel.

Oxide-dispersion strengthened type alloys of the composition as shown in Table 1 were prepared by the above mechanical alloying process, and the alloys were hot extruded and machined to give test samples.

Test samples were subjected to compressive creep test and high temperature oxidation at very high temperature, and the durability and oxidation resistance thereof were compared with those of a conventional material for skid rails, TH101 (0.1C-32Cr-21Ni-23Co-2.5W, Bal. Fe).

The compression creep test is carried out by cramping a columnar test piece of 3mm in diameter and 6.5mm in height between a fitting plate and a receiving plate, and applying compressing load at a high temperature. After a certain period of time, the height of the test piece is measured, and the deformation is calculated as the percentage of decrease in height.

The deformations(%) at the testing temperatures are as shown in Table 2. The oxidation losses per unit area of the materials after the high temperature oxidation test for various periods are as shown in Table 3.

From reference to the case of alloy No. 4, temperature 1300°C, and testing period 150 hours, it is seen that the oxidation loss of the conventional material reached 356.2 mg/cm^2, while the loss of the material embodying the present invention was only 17.54 mg/cm^2. The improvement by the present invention was thus ascertained.

Table 1

No.	C	Si	Mn	Ni	Cr	Co	Mo	W	Ta	N	Oxide	
1	0.12	1.2	1.2	21.0	20.0	23.9	1.5	2.5	1.5	0.015	Y_2O_3	0.6
2	0.12	1.2	1.2	21.0	15.0	23.9	1.5	2.5	1.5	0.015	Y_2O_3	0.8
3	0.07	1.4	0.91	16.7	27.1	40.5	1.0	2.5	1.5	0.015	Y_2O_3	0.7
											ZrO_2	0.3
4	0.12	1.2	1.2	21.0	32.0	23.9	1.5	2.5	1.5	0.015	Y_2O_3	0.7
											Al_2O_3	0.3

Table 2

Alloy	Testing Conditions	Period (Hrs)			
		20	40	60	80
TH101	1200oC	3.63	6.94	9.95	13.2
No. 1	0.9 kgf/cm2	0.04	0.11	0.18	0.25
TH101	1250°C	4.72	7.21	9.83	
No. 1	0.6 kgf/mm^2	0.10	0.22	0.33	

		Period (Hrs)		
		10	20	30
TH101		2.31	4.43	6.14
No. 1		0.08	0.18	0.27
No. 2	1300°C	0.06	0.14	0.22
No. 3	0.4 kgf/mm^2	0.06	0.14	0.21
No. 4		0.08	0.17	0.25

Table 3

Alloy	Temperature	Oxidation Loss (mg/cm2) 50 (Hrs)	100 (Hrs)	150 (Hrs)
TH101		5.53	12.3	19.1
No. 3	1200°C	4.32	9.10	13.8
No. 4		4.10	8.52	13.2
TH101		6.15	57.3	250
No. 3	1250°C	5.31	9.42	13.82
No. 4		5.12	9.38	13.26
TH101		40.5	175.2	356.2
No. 3	1300°C	12.8	15.31	18.10
No. 4		12.3	14.92	17.54

Claims

1. An oxide-dispersion strengthened type heat-resistant alloy, characterized in that the alloy consists essentially of up to 0.2% C + N, up to 2.0% Si, up to 2.0% Mn, 15 to 35% Ni, 20 to 35% Cr, 5 to 50% Co; and one or more of 0.5 to 5% Mo, 0.5 to 5% W and 0.2 to 4% Ta; and the balance of Fe, and that the alloy further contains 0.1-2% of fine particles of high melting point metal oxide dispersed in the austenite matrix.

2. A heat-resistant alloy according to claim 1, wherein the high melting point metal oxide is Y_2O_3.

3. A skid rail using the heat-resistant alloy according to one of claims 1 and 2.

4. A skid rail according to claim 3 comprising skid members (4A) of said alloy secured by saddles (3A) along a skid pipe (2).

5. Use of an article formed of an alloy in accordance with claim 1 or claim 2 as a member subject to heat and abrasion in a high-temperature furnace.

FIG.1

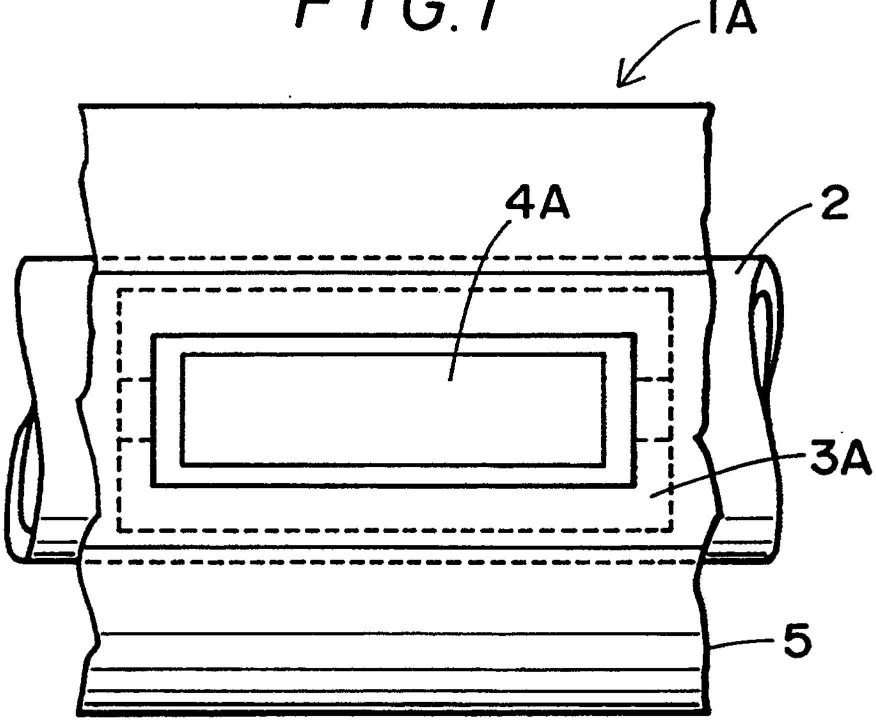


FIG.2

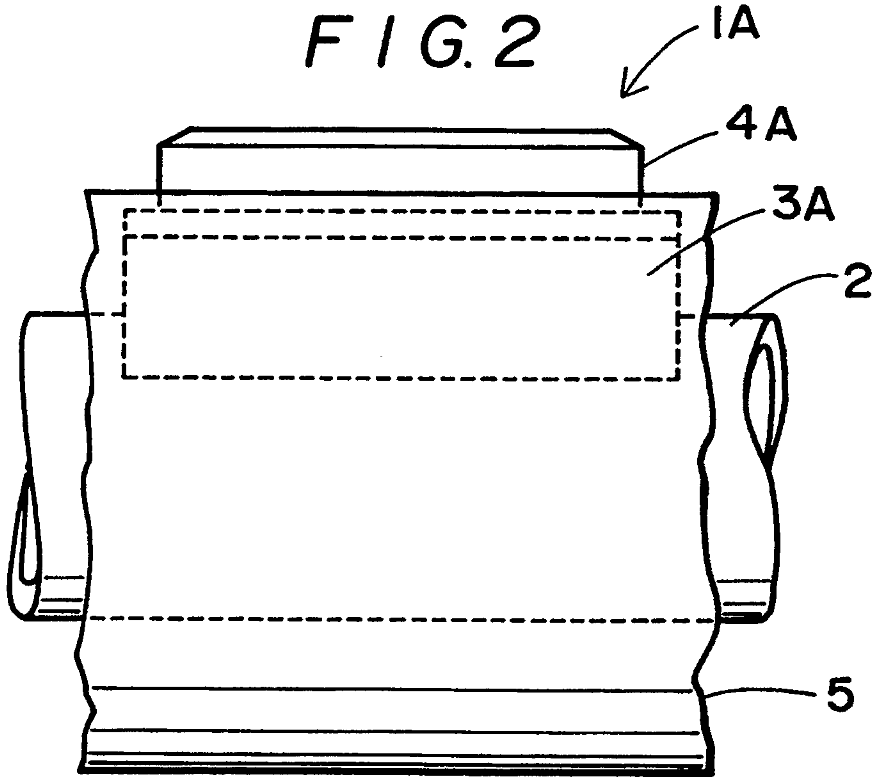
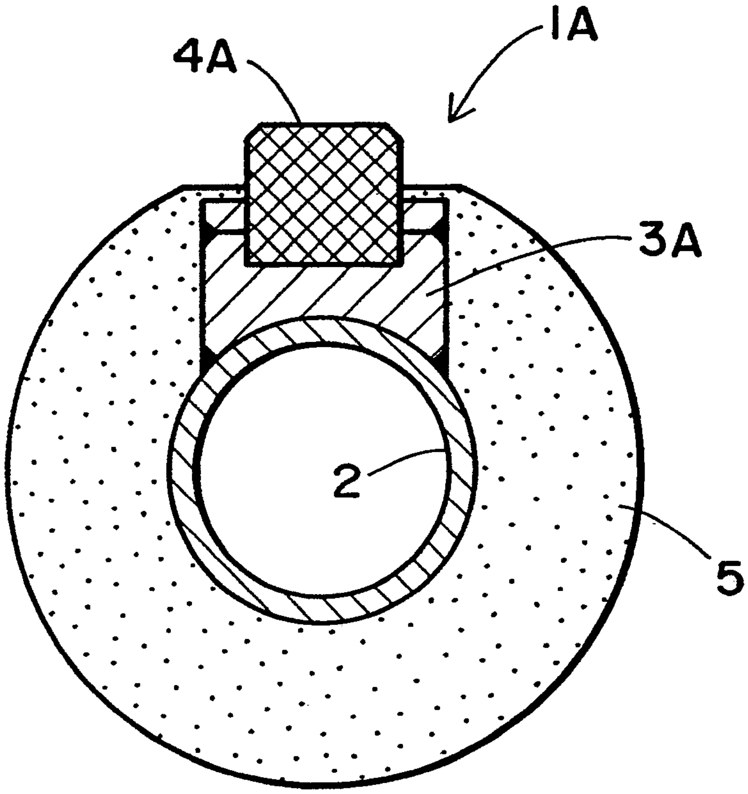


FIG. 3



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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 0887

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.5)
A	EP-A-0 326 371 (DAIDO TOKUSHUKO K.K.) * Claims 1-5 *	1-5	C 22 C 32/00 F 27 D 3/02
A	FR-A-2 370 103 (SPECIAL METALS CORP.) * Claims 1,2,4-6; page 2, lines 4-6 *	1,2	
X	CHEMICAL ABSTRACTS, vol. 109, no. 22, 28th November 1988, page 331, abstract no. 195479n, Columbus, Ohio, US; & JP-A-63 157 827 (SUMITOMO METAL INDUSTRIES) 30-06-1988 *Abstract; JP-A-63 157 827, page 144, table 1, examples E,F,G,H	1,3	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 22 C
F 27 D

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	16 May 91	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

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