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(71) Applicants:
• **Chubu Electric Power Co., Inc.**
Nagoya-shi
Aichi-ken 461-8680 (JP)
• **Naigai Chemical Products Co., Ltd.**
Tokyo 140-0013 (JP)

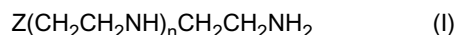
(72) Inventors:
• **ABE, Yoshiyuki**
Nagoya-shi
Aichi 461-8680 (JP)

• **MIYAJIMA, Masamichi**
Nagoya-shi
Aichi 461-8680 (JP)
• **MARUGAME, Kazuo**
Tokyo 140-0013 (JP)
• **YOSHIDA, Masaki**
Tokyo 140-0013 (JP)
• **SHIMIZU, Yuji**
Tokyo 140-0013 (JP)

(74) Representative: **Noel, Chantal Odile et al**
Cabinet Orès
36, rue de St Pétersbourg
75008 Paris (FR)

(54) **METHOD FOR TREATING IRON-BASED METAL SURFACE WHICH IS EXPOSED TO SUPERHEATED STEAM**

(57) The present invention provides a surface treatment method for suppressing the formation and growth of superheated steam oxide scale on an iron-based metal surface exposed to superheated steam, comprising treating said iron-based metal surface with a surface-treatment agent which comprises a polyoxy saturated aliphatic mono- or di-carboxylic acid or a salt thereof and an amine compound represented by the following formula (I):



wherein Z represents H or OH or NH₂ group, and n is an integer of 0-5.

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Description

Technical Field

[0001] The present invention relates to a method for treatment of an iron-based metal surface exposed to superheated steam. More particularly, the invention relates to a surface treatment method for suppressing the formation and growth of steam oxide scale on an iron-based metal surface exposed to superheated steam.

Background Art

[0002] The inner surfaces of steam pipes, such as superheater pipes, main steam pipes, reheater pipes, reheat steam pipes of thermal power plants and the like, are exposed to superheated steam, which is generated by superheating with superheaters or reheaters, saturated steam produced in boilers. Therefore, the inner surfaces are oxidized and coated with steam oxidation scale during a long period of operation. Since the steam pipe base materials (iron-based metals) are different in thermal expansion coefficient from steam oxide scale, thermal stress occurs between them by change in temperature at the start and the stop of the boilers, thereby exfoliating steam oxide scale from the steam pipe surfaces. Steam oxide scale is believed to be easily exfoliated when it grows more than approximately 200 μm thick.

[0003] The exfoliated steam oxide scale can be deposited at U-bent or other portions of the steam pipes to occlude them or can strike against turbine blades to damage them, thereby stopping the power plants irregularly and therefore reducing the generation efficiency or increasing the maintenance and repair costs. Thus, the formation and growth of steam oxide scale on the inner surfaces of steam or other pipes can cause problems relating to plant reliability or maintenance.

[0004] Conventionally, anticorrosion treatment of cooling water pipes' inner surfaces uses anticorrosion by a deposition coating of calcium phosphate, zinc phosphate, calcium carbonate or the like, or electric anticorrosion by using an oxidant such as sodium nitrite, sodium molybdate, sodium chromate, or others. For steam pipes supplying relatively low temperature steam at 450°C or less, anticorrosion is performed by using a neutralizing amine such as morpholine, cyclohexylamine or a film-forming amine such as octadecylamine, either alone or a combination thereof.

[0005] Formation and growth of steam oxide scale, which could be considered a corrosion phenomenon by high temperature steam, cannot be suppressed by conventional anticorrosion using a deposition coating, a neutralizing amine such as morpholine, cyclohexylamine or a film-forming amine. Steam oxide scales formed and grown on the inner surfaces of steam pipes carrying superheated steam at 450°C or more are usually removed by chemical cleaning in Japan and other countries. Chemical cleaning uses a cleaning agent containing an inorganic acid such as hydrochloric acid or hydrofluoric acid, an organic acid such as citric acid or oxalic acid, and a chelating agent such as an EDTA (ethylenediamine tetraacetic acid) salt.

[0006] However, for performing chemical cleaning, a large-scale work can be required in which only a steam piping system to be cleaned is once cut off from the other piping systems (which are adversely susceptible to cleaning agents) and after cleaning, they are welded to restore. In the case of cleaning the inner surface of a large-scale piping system used in a power plant for example, chemical cleaning requires a large amount of chemical cleaning solution and a large amount of the resultant drained cleaning solution must be cleaned up. In addition, even after once removing it from pipe inner surface by cleaning, steam oxide scale forms and grows again on the inner surface during use and therefore the surface must be re-cleaned. Thus, chemical cleaning has problems of very high costs and heavy burdens on the environment.

[0007] Boiler steel pipes having good steam oxidation resistance (e.g., Patent Literature 1) and a method for suppressing oxidation of a steam pipe inner surface by setting the electrical potential within a certain range at the inner surface of the pipe (Patent Literature 2) are under consideration, but are not yet widely applied due to high cost.

Citation List

[0008]

Patent Literatures

Patent Literature 1: The specification of Japanese Patent No. 4205921

Patent Literature 2: Japanese Unexamined Patent Publication No. 2007-56312

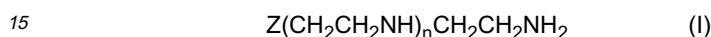
Summary of Invention

Technical Problem

5 **[0009]** Therefore, this invention aims to provide a surface treatment method capable of suppressing the formation and growth of steam oxide scale on an iron-based metal surface exposed to superheated steam.

Solution to Problem

10 **[0010]** The present invention provides a surface treatment method for suppressing the formation and growth of steam oxide scale on an iron-based metal surface exposed to superheated steam, comprising treating said iron-based metal surface with a surface-treatment agent, wherein said surface-treatment agent comprises a polyoxy saturated aliphatic mono- or di-carboxylic acid or a salt thereof and an aliphatic amine represented by the following formula (I):



wherein Z represents H, or OH or NH₂ group, and n is an integer of 0-5.

Advantageous Effects of Invention

20 **[0011]** By the treatment method according to the invention, the formation and growth of steam oxide scale is suppressed on an iron-based metal surface exposed to superheated steam. As the result, it is possible to reduce the frequencies of irregular stop and chemical cleaning of a plant (a power plant, for example) due to steam oxide scale exfoliation and therefore achieve the improvement in the reliability and operation efficiency and the reduction of the maintenance costs
25 of a plant equipped with pipes carrying superheated steam. It is also possible to reduce the burdens on the environment.

Brief Description of Drawings

[0012]

30 [Figure 1] This figure illustrates an experimental system used in order to apply the present method to a test specimen.

[Figure 2] This figure illustrates a system evaluating the formation and growth of steam oxide scale on the test specimens treated with the present method and the test specimen in a comparative example.
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[Figure 3] This figure shows the evaluation results by the evaluation system illustrated in Figure 2 (the relationship between the time of exposure to superheated steam and the mass gain of the test specimens).

Description of Embodiments

40 **[0013]** The treatment method according to the invention comprises treating an iron-based metal surface exposed to superheated steam with a surface-treatment agent comprising a polyoxy saturated aliphatic mono- or di-carboxylic acid or a salt thereof and an aliphatic amine represented by said formula (I).

[0014] The present treatment method is considered to suppress the formation and growth of steam oxide scale by high temperature superheated steam on an iron-based metal surface, though the mechanism described below. However, it is not intended to limit the invention by the following theory.
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[0015] Steam oxide scale forms and grows on an iron-based metal surface by contacting and oxidizing it with high temperature superheated steam, as shown in formula (1). The thickness T of steam oxide scale follows the parabola equation is represented as the one-half power of the product of oxidation rate constant Kp and time t, as shown in formula
50 (2). The oxidation rate constant Kp varies depending on materials.

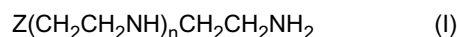


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$$T = (Kp \cdot t)^{0.5} \quad (2)$$

[0016] It is believed that by applying the present treatment method to an iron-based metal surface, a dense coating film is formed on the surface and prevents the inward diffusion of oxygen derived from high temperature superheated steam and the outward diffusion of iron from the surface (it makes oxidation rate constant K_p small), thereby suppressing the formation and growth of steam oxide scale on the iron-based metal surface.

[0017] In the present invention, "iron-based metal" refers to iron and alloys comprising iron as a main (50% or more) component such as carbon steels (e.g., STB410 and the like), stainless steels (e.g., SUS321THB and the like), alloy steels (for example, alloy steels with chromium, nickel, molybdenum and/or manganese; e.g., STBA24, STPA24 and the like). The iron-based metal surface, to which the present method is applied, is an inner surface of a pipe exposed to superheated steam (for example at 450°C, preferably at 450 to 700°C), and more preferably an inner surface of a main or reheat steam pipe of a power plant (especially a thermal power plant).

[0018] The surface-treatment agent used in the present treatment method comprises a polyoxy saturated aliphatic mono- or di-carboxylic acid or a salt thereof and an aliphatic amine represented by the following formula (I):



wherein Z represents H, or OH or NH_2 group, and n is an integer of 0-5, preferably 0-3.

[0019] The polyoxy saturated aliphatic mono- or di-carboxylic acid or the salt thereof is preferably selected from the group consisting of C_4 - C_6 polyoxy saturated aliphatic mono- or di-carboxylic acids and salts thereof and more preferably selected from the group consisting of gluconic acid, tartaric acid and salts of aforesaid acids. The polyoxy saturated aliphatic mono- or di-carboxylic acid can be any of the d-, 1- and dl-form optical isomers.

The salts of polyoxy saturated aliphatic mono- or di-carboxylic acids are preferably alkaline metal salts and more preferably sodium salts.

[0020] One or more polyoxy saturated aliphatic mono- or di-carboxylic acids or salts thereof may be used, alone or in combination.

The concentration of the polyoxy saturated aliphatic mono- or di-carboxylic acid(s) or salt(s) thereof in the surface-treatment agent can range for example from 20 to 6000 mg/L, preferably from 40 to 3000 mg/L, and more preferably from 200 to 600 mg/L.

[0021] The aliphatic amine represented by the formula (I) includes ethylamine, ethylenediamine, monoethanolamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine (TEPA) and the like. Among them, more preferable are mono ethanolamine and TEPA, and still more preferable is TEPA.

A single amine may be used alone, or two or more amines may be used in combination.

[0022] The concentration of the aliphatic amine represented by the formula (I) in the surface-treatment agent may range for example from 3 to 15000 mg/L, preferably from 6 to 7500 mg/L, and more preferably from 30 to 1500 mg/L.

The ratio by weight of said carboxylic acid(s) or salt(s) thereof to said aliphatic amine in the surface-treatment agent may range for example from 1:800 to 2000:1, preferably from 1:200 to 500:1, and more preferably from 1:8 to 20:1.

[0023] The surface-treatment agent may comprise an additional component such as an alkali metal hydroxide, such as sodium hydroxide and potassium hydroxide, and an aliphatic cyclic amine (or non-aromatic cyclic amine), such as morpholine and cyclohexyl gamine. The additional component may be present in the surface-treatment agent at for example 5 to 5000 mg/L, preferably 10 to 2500 mg/L, and more preferably 50 to 500 mg/L.

[0024] The surface-treatment agent can be an aqueous solution. Water as a solvent may be demineralized water, soft water, tap water, industrial water, groundwater or the like. Demineralized water is preferable, in which less causal components of corrosion and scale remain.

The present method is more effective if it applies to an iron-based metal surface when it is clean (e.g., before initial use or after removal of steam oxide scale (at the time of performing regular maintenance, for example)).

[0025] The treatment of an iron-based metal surface with the surface-treatment agent can be carried out at a temperature of 120°C to 380°C for example. In view of costs, efficiency and easiness, it is preferably carried out at a temperature of 120°C to 250°C. For the treatment at a temperature mentioned above, the surface-treatment agent can be heated directly by e.g. an electric heater, or indirectly via heating of the iron-based metal to be treated by e.g. an electric heater or steam.

[0026] The treatment time is not limited specifically, but the lower limit may be for example 10 hours or more, preferably 24 hours or more and the upper limit may be for example 100 hours in view of costs and efficiency.

The treatment of the iron-based metal surface with the surface-treatment agent can be carried out by contacting the agent with the surface. If the iron-based metal surface to be treated is an inner surface of a pipe, it is preferable to circulate the surface-treatment agent into a pipe so as to make the reaction conditions constant.

[0027] In view of another aspect, the present invention provides a surface treatment method for suppressing the formation and growth of steam oxide scale on an inner surface of a main or reheat steam pipe of a power plant, comprising treating said inner surface with a surface-treatment agent at a temperature of 120°C to 250°C for 10 to 100 hours, wherein said surface-treatment agent comprises gluconic acid, tartaric acid or a salt of aforesaid acids and tetraethyl-

enepentamine and said inner surface is an iron-based metal surface exposed to superheated steam.

Examples

[0028] The invention will be specifically described with reference to the following examples, which are not intended to limit the scope of the invention in any way.

[0029] In the following working and comparative examples, a pipe alloy steel STPA24 (chromium-molybdenum steel) was cut into pieces of 7 x 100 x 1 mm, which were used as (iron-based metal) test specimens after polishing with a coated abrasives up to number 400 and defatting with acetone.

The surface-treatment agents and the treatment conditions used in the examples are given in Tables 1 and 2, respectively.

[0030]

[Table 1]

Surface-treatment agents	Components and concentrations
A	In a demineralized water
	Gluconic acid 270 mg/ L
	Monoethanolamine 450 mg/L
	Morpholine 300 mg/ L
B	In a demineralized water
	Tartaric acid 300 mg/L
	Monoethanolamine 1500 mg/L
C	In a demineralized water
	Sodium tartrate dihydrate 600 mg/L
	Tetraethylenepentamine 30 mg/ L
	Sodium hydroxide 200 mg/L

[0031]

[Table 2]

Treatment conditions			
Condition No.	Surface-treatment agent	Treatment temperature (°C)	Treatment time (hours)
1	A	250	24
2	B	212	24
3	B	180	48
4	C	150	24

[0032] The test specimens were treated under the above-listed conditions 1-4 as Examples 1-4 respectively.

The surface treatments were carried out in the autoclave illustrated in Figure 1. Briefly, into a pressure vessel 1 of the autoclave was feed 2400 mL of a surface-treatment agent 5, in which a test specimen 6 attached to the front end of the rotating shaft of a stirrer 2 was immersed and surface-treated while rotating at 100 rpm. The surface-treatment agent 5 was heated and maintained at a predetermined temperature by an electric heater 3 fit on the outer wall of the vessel 1. The temperature was monitored with a thermocouple 4.

An untreated test specimen was used as a Comparative Example.

[0033] Next, the formation and growth of steam oxide scale was evaluated on the surfaces of the test specimens of Examples 1-4 and Comparative Example in the evaluation system illustrated in Figure 2.

[0034] Briefly, boiler water actually used in a thermal power plant was introduced into a steam generator 11 (which was actually the autoclave illustrated in Figure 1) and heated to 250°C to generate saturated steam. The generated saturated steam was feed to an electric superheater furnace 12 and further superheated into superheated steam at a temperature of 550°C. Then, the superheated steam at 550°C was feed from the electric superheater furnace to a specimen-holder tube 15, in which a test specimen 17 had been previously held and was exposed to the superheated steam. In order not to lower the temperature of the superheated steam in the specimen-holder tube 15, it was kept at

550°C by an electric heater furnace 14.

[0035] After passing through the specimen-holder tube 15, the superheated steam was cooled by an air-cooling device 16 to form into condensed water, which was then returned to the steam generator 11. The evaluation system is a closed circulatory system, wherein a cycle of water → saturated steam → superheated steam → water was repeated.

[0036] The test specimen 17 was brought into contact with the superheated steam for a predetermined period of time (830, 3,830, 7,680 or 10,000 hours) and the mass was then measured. The oxidation rate constant K_p was calculated from the mass gain. In calculating the oxidation rate constant, it was assumed that the thickness of steam oxide scale follows the parabola equation represented by the above-described formula (2), and the thickness [in μm] of steam oxidation scale is 0.75 times of the mass gain [in g/m^2] of the test specimen based on the relationship of the oxidation mass gain with the scale thickness described in "A study on steam oxidation behavior of Cr-Mo steel pipe for boilers" (Sumitomo Metal Industries, Ltd., Catalogue No. JB04806).

After 10,000 hours, the appearance of the test specimen was also inspected.

[0037] The changes in mass of the test specimens over time were shown in Figure 3.

The calculated oxidation rate constant K_p based on mass gain and the number of exfoliations determined by the appearance inspection after 10,000 hours are given in Table 3.

[0038]

[Table 3]

Test specimens	Oxidization rate constant K_p ($\text{cm}^2/\text{sec} \times 10^{15}$)	Number of exfoliations
Example 1	6.5	0*1
Example 2	6.3	0*1
Example 3	6.7	1
Example 4	6.3	0
Comparative example 1	15	7
*1: minor exfoliations in which the test specimen base materials were not exposed.		

[0039] As shown in Figure 3, the mass gain by contact with superheated steam was suppressed in the test specimens of Examples 1-4 as compared to the test specimen of Comparative Example. Since the mass gain is due to oxidation of the test specimen surface, it is considered that the formation and growth of steam oxide scale on the surfaces of the test specimens of Examples 1-4 was suppressed by applying the present method to the specimens.

[0040] In addition, the oxidation rate constants, K_p values, which are calculated from the mass gains, of the test specimens of Examples 1-4 are found to be half or less of that of the test specimen of Comparative Example. Therefore, one can understand that the growth rate of steam oxide scale in an iron-based metal surface treated by the present method is half or less of that in an untreated surface and therefore after the treatment by the present method, the interval of chemical cleanings to remove steam oxide scales is around two times longer than the interval after the conventional surface treatment.

[0041] By the appearance inspection of the test specimens, 7 exfoliations were detected in Comparative Example 1 whereas no exfoliations were found in the test specimen of Example 4, minor exfoliations, in which the base materials were not exposed, in the test specimens of Examples 1 and 2, and only one exfoliation in the test specimen of Example 3. Thus, it is understood that the treatment of an iron-based metal surface by the present method can reduce the frequency of steam oxide scale exfoliation from the surface. Hence, the application of the present method to an inner surface of a superheated steam piping system of a power plant for example can prevent occlusion of the piping system and damages of a steam turbine by exfoliated steam oxide scale.

[0042] As described above, it was confirmed that the treatment method according to the present invention can suppress the formation and growth of steam oxide scale on an iron-based metal surface by superheated steam.

Thus, the present treatment method is especially suitable for the application to a piping system, such as a superheated steam piping system of a power plant, which cannot frequently be cleaned (in particular, by chemical cleaning) and in which an anti-corrosion agent or the like cannot be constantly circulated, and therefore can contribute to the improvement in reliability and operating efficiency and the reduction in administrative and maintenance costs of a plant equipped with such a piping system.

[0043] This application is related to Japanese Patent Application No. 2009-159887 filed on July 6, 2009.

All of the patents, patent applications and other publications cited in the present specification are incorporated herein in its entirety by reference, as if specifically set forth herein, to the fullest extent permitted by applicable law.

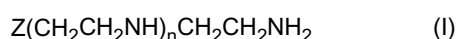
Reference Signs List

[0044]

- 5 1 Pressure Vessel
- 2 Stirrer
- 3 Electric Heater
- 4 Thermocouple
- 5 Surface-Treatment Agent
- 10 6 Test Specimen
- 11 Steam Generator
- 12 Electric Superheat Furnace
- 13 Thermometer
- 14 Electric Heater Furnace
- 15 15 Specimen-Holder Tube
- 16 Air-cooling Device
- 17 Test Specimen

20 **Claims**

1. A surface treatment method for suppressing the formation and growth of steam oxide scale on an iron-based metal surface exposed to superheated steam, comprising treating said iron-based metal surface with a surface-treatment agent, wherein said surface-treatment agent comprises a polyoxy saturated aliphatic mono- or di-carboxylic acid or a salt thereof and an aliphatic amine represented by the following formula (I):



wherein Z represents H, or OH or NH₂ group, and n is an integer of 0-5.

- 30 2. The method of claim 1, wherein said amine is an amine represented by the formula (I) wherein n is an integer of 0-3.
- 3. The method of claim 1, wherein said amine is monoethanolamine or tetraethylenepentamine.
- 35 4. The method of claim 1, wherein said amine is tetraethylenepentamine.
- 5. The method of claim 1, wherein said polyoxy saturated aliphatic mono- or di-carboxylic acid or said salt thereof is selected from the group consisting of gluconic acid, tartaric acid and a salt thereof.
- 40 6. The method of claim 1, wherein said surface-treatment agent further comprises an alkali metal hydroxide or an aliphatic cyclic amine.
- 7. The method of claim 1, wherein said treatment is carried out at a temperature of 120°C to 380°C.
- 45 8. The method of claim 1, wherein said treatment is carried out at a temperature of 120°C to 250°C.
- 9. The method of claim 1, wherein said treatment is carried out for a period of from 10 to 100 hours.
- 50 10. The method of claim 1, wherein said iron-based metal surface is an inner surface of a main or reheating steam pipe of a power plant.
- 11. The method of claim 1, wherein said amine is tetraethylenepentamine, said polyoxy saturated aliphatic mono- or di-carboxylic acid or said salt thereof is selected from the group consisting of gluconic acid, tartaric acid and a salt thereof, said treatment is carried out at a temperature of 120°C to 250°C for a period of from 10 to 100 hours, and said iron-based metal surface is an inner surface of a main or reheating steam pipe of a power plant.
- 55 12. A surface treatment method for suppressing the formation and growth of steam oxidation scale on an inner surface of a main or reheating steam pipe of a power plant, comprising treating said inner surface with a surface-treatment

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agent at a temperature of 120°C to 250°C for a period of 10 to 100 hours, wherein said surface-treatment agent comprises gluconic acid, tartaric acid or a salt thereof and tetraethylenepentamine and said inner surface is an iron-based metal surface exposed to superheated steam.

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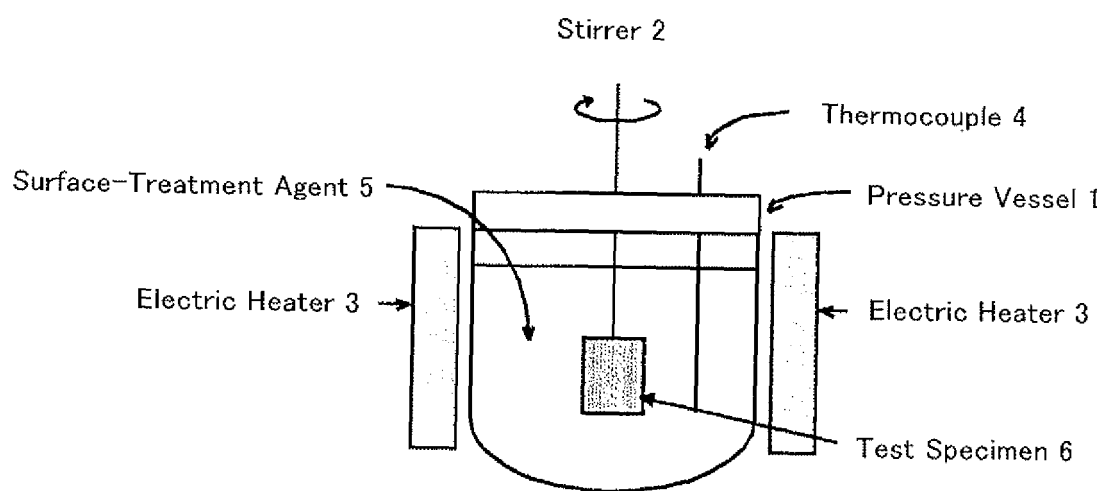


Figure 1

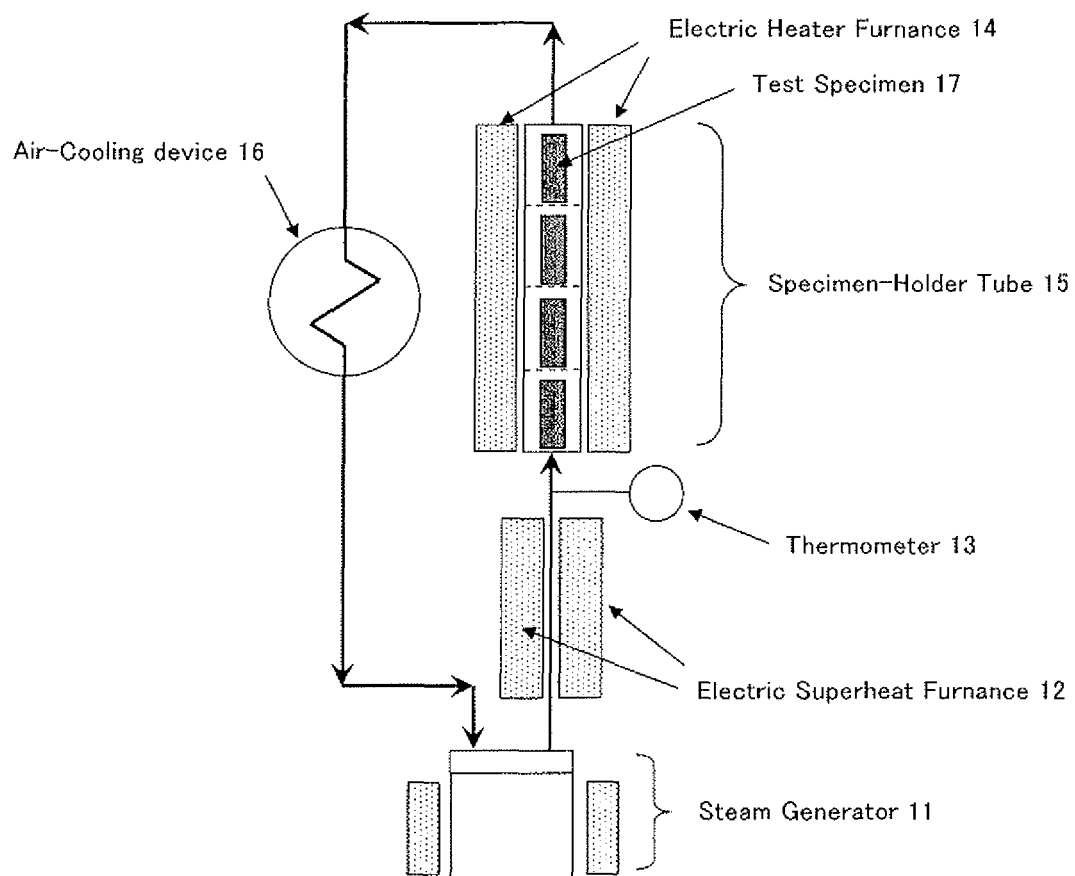
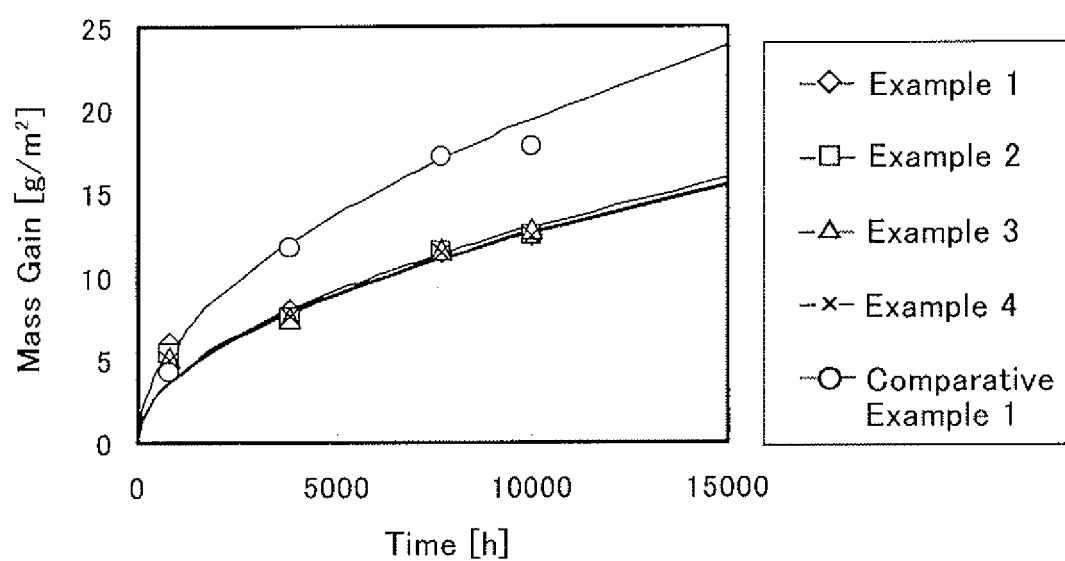


Figure 2

*Figure 3*

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/061264

A. CLASSIFICATION OF SUBJECT MATTER

C23F14/02 (2006.01) i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23F14/02

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	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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 2007-056312 A (Chubu Electric Power Co., Inc.), 08 March 2007 (08.03.2007), entire text (Family: none)	1-12
A	JP 01-159388 A (Mitsubishi Heavy Industries, Ltd.), 22 June 1989 (22.06.1989), entire text & EP 299166 A1	1-12
A	JP 2001-070986 A (Fujisawa Pharmaceutical Co., Ltd.), 21 March 2001 (21.03.2001), entire text (Family: none)	1-12

☒ 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

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

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"&" document member of the same patent family

Date of the actual completion of the international search
23 July, 2010 (23.07.10)Date of mailing of the international search report
03 August, 2010 (03.08.10)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/061264

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 03-056681 A (Katayama Chemical, Inc.), 12 March 1991 (12.03.1991), entire text (Family: none)	1-12

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 4205921 B [0008]
- JP 2007056312 A [0008]
- JP 2009159887 A [0043]