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(54) Acidproof materials.

(57) An acidproof material is disclosed, comprising from 2 to 30% by weight of molybdenum or from 0.2 to 10% by weight of ruthenium, the remainder being substantially composed of chromium. An acidproof material is further disclosed, comprising from 2 to 30% by weight of molybdenum and from 0.1 to 10% by weight of at least one metallic element of ruthenium, platinum, and palladium, the remainder being substantially composed of chromium. These acidproof materials exhibit excellent corrosion resistance to various organic and inorganic acids even under high temperature and high acid concentration conditions while having satisfactory workability.

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ACIDPROOF MATERIALS

FIELD OF THE INVENTION

This invention relates to acidproof materials suitable as materials of equipment used, for example, for handling acid aqueous solutions. The acidproof materials of the invention are especially effective when used as basic materials, cladding materials or lining materials of distillation towers, reactors, heat exchangers, pipes, tanks, etc. in chemical plants or acid treatment plants.

BACKGROUND OF THE INVENTION

Conventional materials with which sulfuric acid, nitric acid, phosphoric acid, formic acid, acetic acid, hydrochloric acid, and various mixed acids are handled include stainless steel, high chromium alloys, zirconium, niobium, tantalum, titanium, and materials with rubber lining, resin lining, glass lining, or Teflon lining.

In handling reducing inorganic acid solutions such as sulfuric acid and phosphoric acid, Fe-Cr-Ni alloys including SUS 304 are generally used. These alloys, though satisfactory in workability, are poor in corrosion resistance in high temperature and highly concentrated acid solutions so that they are greatly corroded in the presence of hydrochloric acid, hydrofluoric acid, etc. Therefore, they are considerably limited in service conditions. Ti and Ti alloys, though sufficiently resistant to various acid solutions including nitric acid, are poor in corrosion resistance in halide-containing acids, e.g., hydrochloric acid and hydrofluoric acid, or reducing acid solutions, e.g., phosphoric acid and sulfuric acid. For those parts or in environments which permit of no use of metallic materials, rubber- or resin-lined materials are used. However, these lining materials are not resistant to a high temperature environment and poor in thermal conductivity. Zirconium, niobium and tantalum have sufficient resistance to corrosion in acid solutions of broad composition range but are difficult to apply to any of a rather wide range of large-sized equipment because of their expensiveness. High chromium alloys or Ni-Cr alloys lack workability and are therefore difficult to apply to structures having a complicated shape such as stirring blades. Moreover, these alloys are not sufficiently resistant to corrosion in the presence of impurities such as hydrochloric acid so that their use is restricted similarly to stainless steel.

Ti or high Cr alloys find their use in a plant handling high-temperature and high-concentration organic acids, e.g., formic acid and acetic acid. However, under a high-temperature and high-concentration condition as in a distillation tower, corrosion is so accelerated that the material will soon be wasted away to considerably reduce the life of a plant.

Further, Ta or Ni alloys have been used in a plant handling hydrochloric acid. From the economical-consideration, their use in large-sized equipment is under considerable restrictions, and cases are often met in which other materials such as high grade stainless steel are used instead. However, such materials are greatly corroded and wasted to remarkably reduce the life of a plant.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an acidproof material which is highly resistance to corrosion in high temperature and highly concentrated acid solutions while having satisfactory workability.

Another object of the present invention is to provide an acidproof material which is highly resistance to corrosion in acid solutions containing a halide, or reducing acid solutions.

A further object of the present invention is to provide an acidproof material which can be prepared at low cost.

The inventors have conducted extensive studies on chromium-based acidproof materials and, as a result, found that the above objects of the present invention are accomplished by certain chromium-based alloys having a novel and specific composition hereinafter described, and thus reached the present invention.

A first embodiment of the present invention relates to an acidproof material comprising from 2 to 30% by weight of molybdenum or from 0.2 to 10% by weight of ruthenium, the remainder being substantially composed of chromium.

A second embodiment of the present invention relates to an acidproof material comprising from 2 to 30% by weight of molybdenum and from 0.1 to 10% by weight of at least one metallic element of ruthenium, platinum, and palladium, the remainder being substantially composed of chromium.

DETAILED DESCRIPTION OF THE INVENTION

The acidproof material according to the first embodiment of the present invention essentially contains at least 2% by weight of molybdenum or at least 0.2% by weight of ruthenium. It preferably contains from 2 to 30% by weight of molybdenum or from 0.2 to 10% by weight of ruthenium, and more preferably from 5 to 30% by weight of molybdenum or from 0.5 to 10% by weight of ruthenium. If the molybdenum content is less than 2% by weight or if the ruthenium content is less than 0.2% by weight, sufficient corrosion resistance cannot be obtained, failing to accomplish the object of the present invention. A molybdenum content exceeding 30% by weight or a ruthenium content exceeding 10% by weight brings about no further proportional improvement in performance properties, only resulting in an increase of cost, and rather adversely affects mechanical workability.

The acidproof material according to the second embodiment of the present invention essentially contains molybdenum and at least one metallic element of ruthenium, platinum and palladium for improving corrosion resistance. The molybdenum content ranges from 2 to 30% by weight, and preferably from 5 to 30% by weight. The total content of at least one of ruthenium, platinum and palladium ranges from 0.1 to 10% by weight, and preferably from 0.5 to 10% by weight. If the molybdenum content is less than 2% by weight or if the total content of at least one of ruthenium, platinum and palladium is less than 0.1% by weight, sufficient corrosion resistance cannot be obtained, failing to accomplish the object of the present invention. A molybdenum content exceeding 30% by weight or a total content of at least one of ruthenium, platinum and palladium exceeding 10% by weight brings about no further proportional improvement in performance properties, resulting in an increase of cost, and rather adversely affects mechanical workability.

For production of the acidproof materials of the first and second embodiments of the present invention, each of raw materials to be used, i.e., metallic chromium which is a basic material, molybdenum, ruthenium, palladium, and platinum preferably has a purity of 99.9% by weight or more. Alloys prepared from raw materials having extremely high contents of impurities have deteriorated workability and are liable to undergo material degradation on welding.

A metallic chromium powder having such a high purity can be obtained by grinding metallic chromium prepared by electrolysis of a chromium salt solution or metallic chromium prepared by purifying a chromium salt solution by solvent extraction, oxidizing the purified chromium salt solution or a chromium salt isolated therefrom, and reducing the resulting chromic acid by, for example, a hydrogen reduction process.

The acidproof material of the present invention can be prepared by mixing the thus prepared metallic chromium powder with prescribed amounts of molybdenum, ruthenium, palladium and/or platinum powder(s) and molding the mixed metal powder, for example, in a vacuum- and heat-resistant sealed vessel. The vessel to be used is not strictly limited in material and shape. From the economical consideration, a vessel made of stainless steel or copper is recommended. The shape of the vessel is appropriately decided according to a desired rolled shape. According to this molding method, after the mixed metal powder is sealed into a vessel, the sealed vessel is evacuated to a degree of vacuum of 10^{-5} mmHg or less, and the powder is subjected to hot rolling at a temperature of from 600° to 1000°C using a grooved roll. General-purpose grooved rolls may be used, and a two-stage rolling mill is usually employed. Under the above-specified rolling temperature condition, solid solubility of nitrogen in metallic chromium is so low as 3 to 17 ppm that recrystallization can be suppressed. With a rolling degree being controlled between 50% and 80%, a rolled shape having a dense structure can be obtained.

Cooling after hot rolling is preferably performed gradually because rapid cooling tends to impose non-uniform thermal stress to the inner chromium alloy structure to cause cracking.

The resulting rolled shape is then subjected to annealing at a temperature of from 800 to 1000°C to make the metallurgical structure uniform and soft. The time of annealing is not particularly limited and is usually at least 1 hour.

The above-described process of production is by no means limitative, and the acidproof materials of the present invention can also be produced by preparing an ingot by various melting methods using a high-frequency atmosphere furnace, a high-frequency arc furnace, etc. and subjecting the ingot to plastic working such as hot rolling.

The acidproof materials according to the present invention exhibit superior corrosion resistance to conventional materials, particularly sintered chromium and Ti or high Cr alloys, enabling one to make new designs of equipment and to enjoy an extended working life of equipment. An improvement in reliability of equipment brought about by the improved corrosion resistance makes it feasible to sufficiently cope with alterations of operating conditions attending increases in temperature and concentration, which leads to an improvement in reaction efficiency and a reduction in product cost. Further, the acidproof materials of the present invention are not only far cheaper than high grade metallic materials, e.g., tantalum, niobium, and zirconium but also capable of molding into a thin sheet unlike the conventional high chromium alloys or Ni-Cr alloys. Accordingly, use of the acidproof materials of the invention as a pressure welding material, a cladding material, or a lining material will allow great cost-cutting of materials of equipment. Combined use with other materials having high workability will satisfy both workability and corrosion resistance.

Since the acidproof materials of the present invention exhibit by themselves satisfactory thermal conductivity and markedly high corrosion resistance, they serve as such as various acidproof materials without requiring glass lining, Teflon lining, etc. Thus, the present invention provides materials extremely excellent as a plant material. The acidproof materials of the invention also find their applications, such as lining and flame spraying, to conventional acidproof materials.

The acidproof materials of the present invention have satisfactory workability as compared with already known metallic chromium or chromium-based alloys. They have very high corrosion resistance in various kinds of acids including inorganic acids containing halides, e.g., hydrochloric acid, and organic acids.

The acidproof materials of the present invention can be used in place of those conventionally employed in chemical plants handling various acid aqueous solutions, such as tanks, reactors, heat exchangers, and pipes. Not being limited to chemical plants, the acidproof materials are also applicable to parts or containers which are required to have acid resistance.

The present invention is now illustrated in greater detail with reference to the following Examples, but it should be understood that the present invention is not deemed to be limited thereto.

EXAMPLES 1 TO 5 AND COMPARATIVE EXAMPLES 1 TO 3

Cr alloys of the present invention and comparative materials each having the composition shown in Table 1 below were prepared as follows.

Chromium powder, ruthenium powder, and molybdenum powder each having a purity of 99.9% or higher were mixed to have the composition shown in Table 1. The mixed powder was sealed into a sealed vessel made of stainless steel, and the vessel was evacuated to 10^{-5} mmHg. The powder briquette was hot rolled by using a grooved roll at a temperature of 800°C and at a rolling degree of 70%. The resulting rolled mold was subjected to annealing at 1000°C for 1 hour and then cut to a test piece of 2 cm x 3 cm. The test piece was immersed in an aqueous solution of hydrochloric acid, acetic acid, phosphoric acid, sulfuric acid, or formic acid containing sodium chloride each having the concentration and temperature shown in Table 2 below, and an average rate of corrosion was determined. The results obtained are shown in Table 2.

TABLE 1

Example No.	Composition (wt%)		
	Ru	Mo	Cr
Example 1		3.0	97.0
Example 2	0.2		99.8
Example 3		15	85.0
Example 4	0.5		99.5
Example 5		20	80.0
Comparative Example 1			99.9
Comparative Example 2	0.1		99.9
Comparative Example 3		1.0	99.0

TABLE 2

Acid Solution:

Acid	Hydrochloric acid	Acetic acid	Phosphoric acid	Formic acid + NaCl	Sulfuric acid
Concn. (%)	5	100	85	90 + 5	50
Temp. (°C)	110	250	120	100	120
Example No.	Rate of Corrosion (mm/year)				
Example 1	<0.01	0.04	0.02	0.02	0.03
Example 2	<0.01	0.02	0.02	0.03	0.04
Example 3	<0.01	<0.01	<0.01	<0.01	<0.01
Example 4	<0.01	<0.01	<0.01	<0.01	<0.01
Example 5	<0.01	<0.01	<0.01	<0.01	<0.01
Comparative Example 1	>10	0.8	0.5	>10	1.9
Comparative Example 2	>10	0.9	1.2	>10	2.3
Comparative Example 3	>10	0.8	2.0	4.5	1.8

EXAMPLES 6 TO 10 AND COMPARATIVE EXAMPLES 4 TO 6

Cr alloys of the present invention and comparative materials each having the composition shown in Table 3 below were prepared as follows.

Chromium powder, ruthenium powder, palladium powder, platinum powder, and molybdenum powder each having a purity of 99.9% or higher were mixed to have the composition shown in Table 3. The mixed powder was put into a sealed vessel made of stainless steel, and the vessel was evacuated to 10^{-5} mmHg. The powder briquette was hot rolled by using a grooved roll at a temperature of 800°C and at a rolling degree of 70%. The resulting rolled mold was subjected to annealing at 1000°C for 1 hour and then cut to a test piece of 2 cm x 3 cm. The test piece was immersed in an aqueous solution of hydrochloric acid, formic acid, phosphoric acid, or sulfuric acid each having the concentration and temperature shown in Table 4 below, and an average rate of corrosion was determined. The results obtained are shown in Table 4.

TABLE 3

Example No.	Composition (wt%)				
	Ru	Pd	Pt	Mo	Cr
Example 6		1.5		10.0	Remainder
Example 7	3.0			10.0	"
Example 8		0.3		5.0	"
Example 9			0.5	15.0	"
Example 10	1.0	0.2		20.0	"
Comparative Example 4					99.93
Comparative Example 5			0.2	1.0	Remainder
Comparative Example 6		0.4			Remainder

TABLE 4

Acid Solution:

Acid	Hydrochloric acid	Formic acid	Phosphoric acid	Sulfuric acid	Sulfuric acid
Concn. (%)	10	90	90	70	50
Temp. (°C)	110	150	150	170	140
Example No.	Rate of Corrosion (mm/year)				
Example 6	<0.01	<0.01	0.01	0.02	0.01
Example 7	<0.01	<0.01	<0.01	<0.01	<0.01
Example 8	0.13	0.04	0.03	0.11	0.02
Example 9	0.08	0.03	0.02	0.05	0.02
Example 10	<0.01	<0.01	<0.01	0.01	<0.01
Comparative Example 4	>10	>10	4.2	>10	>10
Comparative Example 5	>10	>10	1.8	>10	>10
Comparaitve Example 6	>10	7.5	1.2	>10	>10

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. An acidproof material comprising from 2 to 30% by weight of molybdenum or from 0.2 to 10% by weight of ruthenium, the remainder being substantially composed of chromium.

2. An acidproof material as claimed in Claim 1, wherein molybdenum is present in an amount of from 5 to 30% by weight.

3. An acidproof material as claimed in Claim 1, wherein ruthenium is present in an amount of from 0.5 to 10% by weight.

4. An acidproof material comprising from 2 to 30% by weight of molybdenum and from 0.1 to 10% by weight of at least one metallic element of ruthenium, platinum, and palladium, the remainder being substantially composed of chromium.

5. An acidproof material as claimed in Claim 4, wherein molybdenum is present in an amount of from 5 to 30% by wight, and the metallic element or elements of ruthenium, platinum, and palladium is/are present in a total amount of from 0.5 to 10% by weight.

6. Use of an acid-resistant material as claimed in any preceding claim to provide a container or flow path for one of the following solutions:
   (a) highly concentrated acid;
   (b) highly concentrated acid at high temperature;
   (c) an acidic solution containing a halide;
   (d) a reducing acid solution.

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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 1795

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)
X	US-A-3 246 980 (STERN) * Claims 1-5; table I: example Cr-10MO-0,5Pt * & GB-A-903 679, & LU-A-38 827 ---	1	C 22 C 27/06
X	FR-A-2 011 421 (GENERAL ELECTRIC AND ENGLISH ELECTRIC CO., LTD) * Claims 1,2; table: pages 9-11, examples 16 (70Cr-22Mo-8Pd) and 17(80Cr-12Mo-8Pd) * & GB-A-1 231 432, & DE-A-1 931 345 -----	1,2,4,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 22 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-05-1991	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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D : document cited in the application
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