

[54] ANODE COATED WITH MAGNETITE AND THE MANUFACTURE THEREOF

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[56] References Cited

UNITED STATES PATENTS

3,236,756 2/1966 Beer 204/290 F

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[57] ABSTRACT

An anode coated with magnetite is manufactured by electrodepositing iron on a metallic substrate consisting of titanium, zirconium, tantalum, or niobium and the like in an electrolyte containing ferrous sulfate, dipping said iron deposited substrate into a solution of ammonium ferric oxalate under a reduced pressure, and then heating said treated substrate in an atmosphere of a gaseous mixture of hydrogen and steam. The anode manufactured in this way is quite suitable for the production of chlorine, chlorates, and bromates, and, furthermore, it is also usable for electrolytic oxidation processes in general and as an anode for electro-winning of copper, for electrolysis of sodium sulphate, for cathodic protection, and for electro-dialysis.

4 Claims, No Drawings

ANODE COATED WITH MAGNETITE AND THE MANUFACTURE THEREOF

BACKGROUND OF THE INVENTION

A magnetite anode has hitherto been manufactured by casting as a hollow cylinder or a hollow plate, but disadvantages of the product were inferior workability, limited shapes available and inferior electric conductivity. An improved anode coated with magnetite was proposed in order to eliminate these disadvantages by allowing iron containing iron oxide to deposit electrically on a substrate consisting of iron or titanium, or by coating a solution containing iron compound which generates iron oxide on heating, followed by subjecting the treated substrate to heat treatment in a gaseous atmosphere consisting of a mixture of hydrogen and steam. Although the disadvantages limited in shapes and inferior electric conductivity of the product were eliminated by this improvement, other disadvantages due to coarse-grained and less durable magnetite coating which leads to an extremely short life of the product remained. Such a product, therefore, can not be accepted as a satisfactory product for industrial use.

SUMMARY OF THE INVENTION

An essential object of this invention is to provide a process for manufacturing an anode coated with magnetite with industrially advantageous performance.

Another object of this invention is to provide a process for forming a fine-grained and durable magnetite coating on a metallic substrate.

Still another object of this invention is to provide a process for manufacturing an anode coated with magnetite having an industrially advantageous life.

The aforementioned, objects, other objects and the merits of this invention will be made clear by the description hereunder.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention relates to a process for manufacturing an anode coated with magnetite which comprises electrodepositing iron on a metallic substrate of an electrically conductive, corrosion-resistant metal such as titanium, zirconium, tantalum, or niobium by using an electrolyte containing ferrous sulfate, then dipping said iron deposited substrate in a solution containing about 10 - 30 g/l of ammonium ferric oxalate under a reduced pressure of 10 - 30 mm Hg abs., further heating said treated substrate at a temperature of between 550° and 700°C in an atmosphere of a gaseous mixture of hydrogen and steam wherein the hydrogen content is 10 - 25 percent by volume and the steam content is 75 - 90 percent by volume. Any commercially available materials in the forms of a plate, wire, screen or rod of titanium, zirconium, tantalum, or niobium may be used as an electrically conductive, corrosion-resistant metallic substrate.

As an electrolyte for electrodepositing iron, a sulfate bath is preferable. When a chloride bath is used, although it is commonly used now in industry, close control of the temperature, pH, and the composition of the bath is necessary in order to obtain a fine-grained and firmly deposited metal bonded to the metallic substrate. When a sulfate bath in accordance with this invention is used, on the other hand, satisfactory results

of the electrodeposition can always be obtained under a wider range of the conditions of electrodeposition. In addition to this, the sulfate bath is less readily oxidized by the air than the chloride bath, and therefore said electro-deposition can be carried out in the absence of the ferric salt. The presence of a ferric salt accelerates, the generation of hydrogen on the electrodepositing surface, causing undesirable formation of pinholes, lowering the cathodic current efficiency and resulting in less adherent deposits, as is described in Japanese Pat. No. 219,829. The sulfate bath in accordance with this invention contains no ferric salt and gives an essentially high cathodic current efficiency, thus assuring a satisfactory deposit with few pinholes and a good adherence.

The composition of the electrolyte for electrodepositing iron consists of, for instance, 100 - 150 g/l of ferrous sulfate (heptahydrate), 100 g/l of ammonium sulphate and about 3 - 10 g/l of additives such as an ammonium salt of an organic acid, phenol, formalin, or hexamethylene tetramine, etc. Electrodeposition is carried out at a temperature of 10° - 40°C and at a cathodic current density of 1.0 - 2.5 A/dm² for about 7 - 20 min. Under these conditions the atmospheric oxidation of the ferrous salt in said electrolyte is retarded, and almost no hydrogen is generated at the electrodepositing surface, thus, a uniform and fine-grained deposit is obtained.

As a subsequent treatment following said electrodeposition, the iron deposited substrate is dipped into a solution of ammonium ferric oxalate ($(\text{NH}_4)_3\text{Fe}(\text{C}_2\text{O}_4)_3$). Although no such treatment to an electrodeposited surface with iron has hitherto been known, it is considered as a kind of sealing treatment which reinforces electrodeposits. It has been confirmed that by said treatment the durability of the final product as an anode is remarkably increased as compared to one to which said treatment is not applied. Said treatment is performed by dipping the iron deposited substrate in a sealing solution containing about 10 - 30 g/l of ammonium ferric oxalate, at about 10° - 25°C, then by allowing said iron deposited substrate to stand for about 20 min under a reduced pressure of 10 - 30 mm Hg abs. A concentration of ammonium ferric oxalate below 10 g/l is too dilute to be effective, and above 30 g/l, an undesirable deposition of crystals will occur. Further, if the pressure is higher than 30 mm Hg abs., the replacement of the air within pinholes with said solution is only imperfectly accomplished and only unsatisfactory results are obtained. The minimum pressure is limited by the saturated vapor pressure of the sealing solution.

Ammonium ferric oxalate permeated iron deposit is decomposed by a heat treatment as hereunder described, and generates gaseous ammonia and carbon dioxide, leaving only iron oxides. There are no particular difficulties in the subsequent operations.

A desired composition of magnetite and the best electric conductivity and the corrosion-resistant property of the product can be obtained by carrying out said heat treatment while maintaining conditions strictly within the range prescribed in the foregoing.

Said heat treatment is preferably carried out at a temperature ranging from 550° and 700°C. The reaction is very slow at a temperature below 550°C, requiring longer time for the operation. At a temperature higher than 700°C, more ferrous oxide forms and the desirable magnetite composition may not be obtained. The pref-

erable range of composition of the gaseous mixture in which said heat treatment is to be carried out is from 10 to 25 percent by volume of hydrogen and from 75 to 90 percent by volume of steam. In an atmosphere of a gaseous mixture containing less than 10 percent by volume of hydrogen and more than 90 percent by volume of steam, more ferric oxide will form, on the other hand, when the hydrogen content is higher than 25 percent by volume and the steam content lower than 75 percent by volume in said gaseous mixture, more ferrous oxide will form. In either of these cases, the desirable magnetite composition may not be or is difficult to be obtained. Moreover, when the hydrogen content is higher than 25 percent by volume, difficulties due to the hydrogen embrittlement of the metallic substrate may arise.

The gaseous hydrogen-steam mixture of this invention is prepared by saturating hydrogen with steam by passing hydrogen in water maintained at an appropriate temperature decided by taking the vapor pressure. Said gaseous mixture is introduced into a tube furnace to perform said heat treatment. The time required for said heat treatment is about 2 - 5 hr. Finally, a magnetite-coated layer of 3 - 20 μ in thickness is obtained.

By carrying out the treatment in accordance with the process of this invention a fine-grained magnetite-coated layer having desirable durability may be formed on the surface of a metallic substrate having high electric conductivity and sufficient corrosion-resistance. In particular, said sealing treatment of the iron deposit in an ammonium ferric oxalate solution produces a final product as anode having a life of one year, more than twice as that whereby no such treatment has been applied, thus offering a practical advantage.

The anode coated with magnetite manufactured in accordance with this invention is quite suitable for the manufacture of chlorine, chlorates, and bromates. Moreover, said anode can be used for any electrolytic oxidation processes in general, and as an anode for electro-winning of copper, as an insoluble anode for electrolyzing sodium sulphate, for cathodic protection, and for electro-dialysis.

The embodiment of this invention will be explained further in detail by the Examples and the Comparative Examples described hereunder.

EXAMPLE 1

A previously polished titanium plate 200 mm \times 50 mm and 1 mm thick was defatted in a boiling 10 percent NaOH solution, and was dipped into a 5 percent hydrofluoric acid solution at room temperature for 1 min, and then washed with water. Electro-deposition was carried out for 19 min in an electrolyte at 25°C consisting of 130 g/l of ferrous sulfate (heptahydrate), 100 g/l of ammonium sulfate and 6 g/l of formalin by using said titanium plate as a cathode (a cathodic current density = 2.5 A/dm²) and a low carbon steel as an anode. After the electrodeposition was completed, said iron deposited titanium plate was washed well with water, and then dipped into a solution of 20 g/l of ammonium ferric oxalate at 13°C, and was allowed to stand for 20 min under a reduced pressure of 15 mm Hg abs. produced by a vacuum pump and dried under the reduced pressure and was then subjected to heat treatment at 650°C for 2.5 hrs. in an atmosphere of a hydrogen/steam gaseous mixture consisting of 20 percent by volume of hydrogen and 80 percent by volume of

steam prepared by passing hydrogen into hot water at 94°C. On the surface of the product the formation of a magnetite-coated layer was clearly recognized. The thickness of said layer was confirmed to be 20 μ by weighing said product. The appearance of said product was uniformly black and fine-grained and no crack was observed therein.

EXAMPLE 2

A tantalum plate of 200 \times 50 mm and 2 mm in thickness was defatted in a boiling 10 percent NaOH solution and was dipped in an aqueous solution of 5 percent hydrofluoric acid for 1 min. It was then washed with water, and was electrodeposited for 10 min in an electrolyte at 20°C consisting of 100 g/l of ferrous sulfate (heptahydrate), 100 g/l of ammonium sulfate, 3 g/l of phenol, and 5 g/l of ammonium phthalate by using said tantalum plate as a cathode (cathodic current density = 1.0 A/dm²), with the use of a low carbon steel as an anode. After the electrodeposition was completed, said iron deposited tantalum plate was washed well with water, and was then dipped into a solution containing 30 g/l of ammonium ferric oxalate at 23°C, and was then allowed to stand for 25 min under a reduced pressure of 28 mm Hg abs. After said treatment was finished, it was dried in vacuum and was heat-treated at 580°C for 4 hrs. in an atmosphere of a hydrogen/steam gaseous mixture consisting of 15 percent by volume of hydrogen and 85 percent by volume of steam prepared by passing hydrogen into hot water maintained at 95° - 96°C. By this treatment a uniform and fine-grained magnetite-coated layer of 4.6 μ in thickness was obtained.

EXAMPLE 3

A 200 \times 50 mm titanium net having a wire diameter of 1 mm and mesh of 1 mm was defatted in a boiling 10 percent solution of NaOH, and was dipped into an aqueous solution of 5 percent hydrofluoric acid at room temperature for 1 min, and then washed. Electrodeposition was carried out for 15 min in an electrolyte maintained at 35°C consisting of 150 g/l of ferrous sulfate (heptahydrate), 100 g/l of ammonium sulfate and 10 g/l of ammonium citrate by using said titanium net as a cathode (cathodic current density = 2 A/dm²) and a low carbon steel as an anode. After said electrodeposition was completed, it was washed well with water, and was dipped into a solution containing 25 g/l of ammonium ferric oxalate at 10°C, and was allowed to stand for 20 min under a reduced pressure of 12 mm Hg abs. The treated substrate was then dried in vacuum and was heated at 670° C for 2 hrs. in an atmosphere of a hydrogen/steam gaseous mixture consisting of 20 percent by volume of hydrogen and 80 percent by volume of steam prepared by passing hydrogen into hot water at 94°C. By this treatment a magnetite-coated layer of about 13 μ in thickness was obtained.

EXAMPLE 4

An electrolyte consisting of 250 g/l sodium chloride, 70 g/l of sodium chlorate, and 2 g/l of sodium bichromate was electrolyzed at 60°C for 11 months with an anodic current density of 10 A/dm² by using an anode coated with magnetite prepared as described in Example 1 as an anode with the use of a mild steel plate as a cathode. The current efficiency was 85 percent and the average cell voltage was 3.38 V. The required en-

ergy per ton sodium chlorate was 6,000 kwh. During this period almost no change was observed on the surface of the anode.

Comparative Example

2. A process for manufacturing an anode coated with magnetite according to claim 1 wherein said composition of the electrolyte containing ferrous sulfate consisting of 100 - 150 g/l of ferrous sulfate (heptahy-

Table I

Anode	Time of the Electrolysis*	The State of the Surface of the Anode
An anode prepared by the process of this invention (Example 1).	11 months	Almost no change was observed.
An anode prepared by the process of this invention except that dipping in an aqueous solution of ammonium ferric oxalate was omitted.	4.5 months	A stripping off of the magnetite-coated layer was distinctly observed, and the substrate was laid bare.
An anode prepared by the process of this invention except that the heat treatment was carried out at 800°C.	2 months	The stripping off of the magnetite-coated layer was slightly observed, but the surface was colored brown.
An anode prepared by the process of this invention except that heat treatment was carried out at 450°C.	3 months	Same as above.

* Same conditions of electrolysis as in Example 4.

EXAMPLE 5

Sea water having a sodium chloride concentration of 27 g/l, pH = 8, and 25°C in temperature, was electrolyzed by an anodic current density of 3 A/dm², using an anode coated with magnetite prepared by the process described in Example 3 with the use of a mild steel as a cathode. A solution containing 0.5 g/l of sodium hypochlorite was continuously obtained. Even after 6 months no abnormalities were observed on said coated anode.

What is claimed is:

1. A process for manufacturing an anode coated with magnetite comprising electrodepositing iron onto an electric conductive corrosion-resistant metallic substrate, such as titanium, zirconium, tantalum, niobium, and the like in an electrolyte containing ferrous sulfate, dipping said iron deposited substrate into a solution containing about 10 - 30 g/l ammonium ferric oxalate for about 20 min under a reduced pressure of 10 - 30 mm Hg abs., and then heating said treated substrate at 550° - 700°C for about 2 - 5 hrs. in an atmosphere of a hydrogen/steam gaseous mixture consisting of hydrogen of a content in a range of 10 - 25 percent by volume and steam of a content in a range of 75 - 90 percent by volume.

drate), 100 g/l of ammonium sulfate, and about 3 - 10 g/l of an additive selected from a group consisting of ammonium salts of an organic acid, phenol, formalin and hexamethylene tetramine, and mixtures thereof.

30 3. A process for manufacturing an anode coated with magnetite according to claim 1 wherein said electrodeposition is carried out under a bath temperature in a range of 10° - 40°C, a cathodic current density of 1.0 - 2.5 A/dm², and the electrodeposition time being about 7 - 20 min.

35 4. An anode coated with magnetite, manufactured by a process which comprises electrodepositing iron onto an electric conductive corrosion-resistant metallic substrate, such as titanium, zirconium, tantalum, niobium, and the like in an electrolyte containing ferrous sulfate, dipping said iron deposited substrate into a solution containing about 10 - 30 g/l ammonium ferric oxalate for about 20 min. under a reduced pressure of 10 - 30 mm Hg abs., and then heating the treated substrate at 550° - 700°C for about 2 - 5 hrs. in an atmosphere of a hydrogen/steam gaseous mixture consisting of hydrogen of a content in a range of 10 - 25 percent by volume and steam of a content in a range of 75 - 90 percent by volume.

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