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(54) Titre : PROCÉDE DE REDUCTION DE LA RESISTIVITE INHERENTE A LA COUCHE D'OXYDE DUE A LA
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 (54) Title: METHOD FOR REDUCING THE RESISTIVITY OF THE CORROSION-INDUCED OXIDE LAYER, AND
APPLICATIONS

(57) **Abrégé/Abstract:**

In order to reduce the resistivity of the corrosion-induced superficial oxide layer at the point where current passes to a chromium-plated steel component, said component is annealed and the oxide layer with which it may become covered during the annealing process is removed prior to the component being exposed to the current flow.



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<p>(21) Internationales Aktenzeichen: PCT/DE98/02538 (22) Internationales Anmeldedatum: 28. August 1998 (28.08.98) (30) Prioritätsdaten: 197 38 405.6 3. September 1997 (03.09.97) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): DAIM- LER-BENZ AKTIENGESELLSCHAFT [DE/DE]; Epplestrasse 225, D-70567 Stuttgart (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): WIND, Jörg [DE/DE]; Seestrasse West 36a, D-88090 Immenstaad (DE). NITSCHKE, Felix [LU/DE]; Thalkirchnerstrasse 278, D-81371 München (DE).</p>	<p>(81) Bestimmungsstaaten: CA, JP, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i></p>	
<p>(54) Title: METHOD FOR REDUCING THE RESISTIVITY OF THE CORROSION-INDUCED OXIDE LAYER, AND APPLICATIONS</p>		
<p>(54) Bezeichnung: VERFAHREN ZUR HERABSETZUNG KORROSIONSBEDINGTER OXIDWIDERSTÄNDE AUF CHROMSTAHL-BAUTEILEN UND ANWENDUNGEN DES VERFAHRENS</p>		
<p>(57) Abstract</p> <p>In order to reduce the resistivity of the corrosion-induced superficial oxide layer at the point where current passes to a chromium-plated steel component, said component is annealed and the oxide layer with which it may become covered during the annealing process is removed prior to the component being exposed to the current flow.</p>		
<p>(57) Zusammenfassung</p> <p>Um den elektrischen Widerstand durch eine korrosionsbedingte Oberflächenoxidschicht an dem stromführenden Übergang zu einem Chromstahl-Bauteil herabzusetzen, wird das Bauteil geglüht, wobei eine beim Glühen gegebenenfalls entstehende Oxidschicht vor dem Einsatz des Bauteils zur Stromführung entfernt wird.</p>		

Method for Reducing the Resistivity of the Corrosion-Induced
Oxide Layer, and Applications

The invention relates to a method for reducing the electrical resistance on the current-carrying transition to a component made of chromium steel due to a corrosion-caused surface layer of oxide on the component. It also has
5 applications of this method as its subject.

In many technical apparatus chromium steel is used for many kinds of components for reasons of strength and corrosion resistance. This material resists corrosion
10 attack by forming a protective chromium oxide coating. The chromium oxide coating is a good barrier against diffusion and thus prevents corrosion attack. Especially in high-temperature applications the chromium oxide coating leads to a great reduction of oxide growth and thus to a lasting
15 protection against the destruction of the material.

If chromium steel, however, is used for electric current carrying components in high-temperature applications in an oxidizing atmosphere, the necessary
20 formation of the chromium oxide coating causes an electrical resistance caused by this coating, which in turn leads to voltage losses and thus to a lowering of the efficiency of the apparatus in question.

25 An example of a component which is exposed to an oxidizing atmosphere at high temperatures is the cathode current collector of a molten carbonate fuel cell (MCFC).

Molten carbonate fuel cells consist essentially of a
30 porous cathode and a porous anode and a matrix which is imbibed with a molten electrolyte, namely a eutectic mixture containing a lithium carbonate and other alkali carbonates

which is in contact with the electrodes. To carry the electrochemically produced current, current collectors are in contact with the cathode and the anode, and they are usually corrugated in order also to form a gas transport space, and namely for carrying air or other oxygen-containing gas at the cathode and a fuel gas at the anode. The fuel cell is operated at a temperature of 500 to 800°C. The cathode current collector is exposed to severe corrosive influences by contact with the oxygen-containing gas and the molten carbonate as well as by the high temperature. In spite of the use of chromium steel, an oxide coating thus forms on the surface of the cathode current collector, which leads to a high resistance to transition between the cathode current collector and the cathode and thus to high power losses in the molten carbonate fuel cell.

To lower this transition resistance, it is proposed according to DE 195 32 791 A1 to apply a noble metal, such as gold or platinum, to the cathode current collector at the points of contact with the cathode. Aside from the high costs of the noble metals, this method has the disadvantage that a diffusion barrier must still be placed between the thin noble metal coating and the chromium steel cathode current collector in order to prevent the diffusion of the noble metal into the chromium steel. Thus several coating steps are necessary.

The invention is addressed to the problem of offering a method whereby the electrical resistance at the transition to a current-carrying chromium steel component due to a surface oxide coating caused by corrosion on the component can be reduced in a simple manner.

This is achieved according to the invention with use of a Chromium steel component as cathode current collector for a molten carbonate fuel cell, wherein, in order to reduce the electrical resistance caused by a corrosion oxide layer growing in the oxidizing atmosphere of the fuel cell, the chromium steel component with a chromium content of 10 to 22 wt.-% is annealed at at least 950°C before use in the fuel cell, and wherein an oxide layer forming in some cases during the annealing is removed before the use of the component as a cathode current collector.

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By the method of the invention the chromium steel component in question is annealed. The annealing must be performed either with the absolute exclusion of oxygen, or any oxide coating formed by the annealing must be removed entirely at least at the current-carrying transition points, before the component is installed.

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A surface oxide coating is necessarily again formed on the current-carrying chromium steel component treated according to the invention when it is used in an oxidizing temperature, especially at high temperatures. Amazingly, however, this oxide coating has a substantially reduced electrical resistance, and indeed the transition resistance compared with a chromium steel component of the same composition, but one that has not been annealed by the method of the invention, is reduced approximately ten-fold.

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It is furthermore amazing that, despite the lowering of the electrical transition resistance the oxide coating formed on the component when used in an oxidizing atmosphere resists the attack of corrosion in the same manner as a chromium steel component of the same composition, but one which has not been annealed in an oxygen-free atmosphere according to the invention.

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The phenomenon that occurs in the practice of the invention, namely that the surface oxide coating formed when

the component is used in an oxidizing atmosphere has on the one hand a high corrosion resistance, but on the other hand a low electrical resistance, cannot be explained. It is true that the grain structure of the chromium steel changes in the annealing, so that it may be thought that less chromium diffuses out of the steel to the surface and thus the formation of chromium oxide at the surface is repressed. On the other hand, however, it is precisely an oxide coating containing chromium oxide on the surface is considered as a requirement for the anticorrosive properties of a chromium steel.

In other words, it has been found that, in comparison to oxide coatings forming on untreated chromium steel the electrical resistance is surprisingly lowered by the method of the invention by about one order of magnitude. Detailed studies by physical methods show a decided difference in the composition and structure of the oxide coatings formed and those of untreated chromium steel of the same composition. The chromium content in the case of the oxide coating that has grown on the steel treated according to the invention is decidedly lower through the entire coating than the oxide coating grown on the same but untreated steel. The chromium content of the untreated steel and the steel according to the invention itself is equal in volume, so that the cause of the combination of good corrosion resistance and low electrical resistant is not simply a lowering of the chromium content. For is simply the chromium content of the steel is lowered, a lowering of the electrical resistance is indeed obtained, but at the same time a definite deterioration of the corrosion resistance is found. If the treated chromium steel is a steel of the material number 1.4404 (AISI 316 L), the steel treated by the method of the

invention shows in comparison with untreated steel a coarse structure and a lowering of the chromium and magnesium content at the surface.

5 Preferably, a chromium steel with a chromium content of 10 to 22 wt.-%, especially 15 to 19 wt.-%, and with very special preference less than 17 wt.-%.

10 The other components of the alloy steel can be in weight-percent:

0 to 2% of at least one of carbon, silicon, phosphorus or sulfur

0 to 20% manganese

0 to 10% molybdenum

15 0 to 20% nickel

0 to 15% cobalt

less than 0.5% aluminum, yttrium, titanium or cerium.

20 In particular the content of aluminum, yttrium, titanium and/or cerium should be less than 0.05%, for these elements form oxides with a very high electrical resistance on the surface of the component.

25 Especially, steel of the material number 1.4404 has proven suitable for the method of the invention. This steel has the following composition in weight-percent:

C ≤ 0.030

Si ≤ 1.00

30 Mn ≤ 2.00

P ≤ 0.045

S ≤ 0.030

Cr 16.5 - 18.5

Mo 2.00 - 2.50

Ni 11.0 - 14.0

5 Remainder iron and impurities caused in production, or

C \leq 0.03

Si \leq 1.50

Mn \leq 1.50

10 P \leq 0.035

S \leq 0.020

Cr 17.0 - 20.0

Mo 2.00 - 3.00

Ni 9.00 - 13.0

15 Remainder iron and impurities caused in production.

20 The annealing of the chromium steel component is performed in the method of the invention at a temperature of at least 950°C, preferably in a temperature range between 1050 and 1400°C, annealing for at least one hour.

25 To prevent a thick oxide coating from forming during the annealing process, the annealing process must be performed in vacuo or in an oxygen-free atmosphere, for example in pure hydrogen. It is not sufficient to anneal under a common shielding gas, i.e., noble gas, nitrogen or forming gas, because at the annealing temperature the oxygen present, even though in extremely small amounts, leads in any case to the formation of an oxide coating which does not
30 have the desired properties.

 Also it is possible to anneal in other atmospheres, or even air, if after this annealing treatment the oxide

coating is carefully removed again, at least from the current-carrying transition points on the component.

5 If the chromium steel components thus treated are used in a temperature range of 500 to 800°C in an oxidizing atmosphere, an oxide coating forms which is composed of several phases. In this case it is a mixture of many different iron oxides, nickel chromium oxides, and spinels.

10 Since, as mentioned above, especially the cathode current collectors of molten carbonate fuel cells are exposed to severe corrosive attack, but on the other hand must have a low electrical transition resistance at the points of contact with the cathode, the method of the
15 invention is appropriate, for example, for the production of cathode current collectors of chromium steel for molten carbonate fuel cells.

Claims

1. Use of a Chromium steel component as cathode current collector for a molten carbonate fuel cell, wherein, in order to reduce the electrical resistance caused by a corrosion oxide layer growing in the oxidizing atmosphere of the fuel cell, the chromium steel component with a chromium content of 10 to 22 wt.-% is annealed at at least 950°C before use in the fuel cell, and wherein an oxide layer forming in some cases during the annealing is removed before the use of the component as a cathode current collector.
2. Use according to claim 1, wherein the chromium content of the chromium steel amounts to 15 to 19 wt.-%.
3. Use according to claim 1 or 2, wherein the chromium steel contains, in weight-percent:
- 0 to 2% of at least one of carbon, silicon, phosphorus or sulfur,
 - 0 to 20% manganese
 - 0 to 10% molybdenum
 - 0 to 20% nickel
 - 0 to 15% cobalt, and
 - less than 0.5% aluminum, yttrium, titanium or cerium.
4. Use according to any one of claims 1 to 3, wherein a chromium steel of the material number 1.4404 is used.
5. Use according to any one of claims 1 to 4, wherein the annealing is performed at a temperature between 1050 and 1400°C.
6. Use according to any one of claims 1 to 5, wherein the annealing treatment is performed for at least one hour.

7. Use according to any one of claims 1 to 6, wherein to prevent the formation of an oxide coating during annealing, the annealing is performed in vacuo or in an oxygen-free atmosphere.

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8. Use according to claim 7, wherein hydrogen is used as the oxygen-free atmosphere.