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METAL FIBER BODIES

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ABSTRACT OF THE DISCLOSURE

This invention relates to a method of manufacturing fiber bodies and materials and articles made from metal fibers, being of porous character and having improved surface properties. Said material is particularly suitable for use as catalysts in the after-burning of exhaust gases.

It is already known that metals can be provided with a surface protective coating of an alloy material by a process of gas-phase plating, aluminizing, or siliconising the basic metal or otherwise treating it with foreign metals, so that the foreign metals are caused to penetrate into the grain structure of the basic metal with the result that an alloyed layer is formed in the surface zone. An improvement in the surface zone is thereby achieved, for example in respect of its corrosion-resistance, its oxidation-resistance, its resistance to combustion, its hardness, and other similar properties. Although bodies which are protected in this manner are always an advantage when ready-made articles which require no further machining and which also are not subjected during use to any appreciable wear are required, such bodies show frequent disadvantages however if on account of a necessary finishing process the superficial alloy layer is removed here and there or if due to mechanical stresses and strains on the article cracks or scratches are formed on the surface or the surface is in some other way damaged. It is then impossible to prevent the basic metal which is no longer protected from being attacked, and undesirable corrosion of the article can no longer be prevented with certainty.

In order to overcome these disadvantages we have already (U.S. Patent No. 3,234,056) proposed the production of a material made from steel fibers which comprises steel fibers plated with additional alloying substances to provide the mechanical and chemical resistance, homogenised by diffusion annealing, and then possibly formed into shaped articles. Such a homogenously alloyed basic metal, which may consist, for example, of high-alloyed refined steel, ferritic or martensitic chromium steel, austenitic chrome-nickel steel, and which may have as the alloying substance practically any elements, such as, for example, chromium, aluminum, nickel, molybdenum, copper, vanadium, can be used for practically all purposes in a suitably adapted form.

In many cases however, besides good corrosion-resistance of the material over the whole cross-section thereof, certain mechanical, physical and chemical properties of the external surface and/or internal surface of any thickness covering layer are desired.

It is an object of the invention to provide a porous metallic fiber body having a surface layer of certain improved mechanical, physical and/or chemical properties.

It is a further object of the invention to provide a porous metallic fiber body with a surface layer embedded within the body and having a highly effective catalytic activity in the after-burning of exhaust gases.

Another object of the invention is a new method of producing fiber bodies consisting of metal alloys and having a surface layer at least partially consisting of compounds derived from the metal alloys in the body portion of said fiber body, by chemically converting said metal alloys.

Yet another object of the invention is the method of at least partially oxidising the metal alloys the fibers in the surface layer portion of a fiber body are consisting of, to form a fiber body the main inner portion consisting of metal alloys, and the outer layer at least partially consisting of oxides and/or mixed oxides of the metallic compounds of said metal alloys.

A further object is to provide a catalytically active material of skeleton-like structure having highly mechanical strength, good heat resistance and excellent shock and impact resistance, remaining unchanged and showing no friability with intense vibrations operating over long time.

Further and other objects and advantages of the present invention will appear from the following description.

It has now been discovered that one can produce such predetermined designed optimum combinations of properties for a special application, as desired, on a large or small portion of a body of homogenously alloyed metal fiber material, if, in the manufacture of the material which consists of metal fibers plated with additional alloying substances to provide the mechanical and chemical resistance, homogenised by diffusion annealing, and then possibly shaped into articles, the plating and diffusion annealing takes place so that elements which enter into easy combination with metals and/or metalloids, as well as non-metals, remain at least partially concentrated in the surface and by means of a suitable subsequent treatment are formed into a fiber coating which distinguishes itself by its special chemical and/or mechanical resistance or by special physical and/or chemical properties such as, for example, porosity or catalytic efficiency.

In practice, it is preferably arranged that the basic fibers, which may consist of any metal or an alloy, are homogenously alloyed with such further alloying substances as will guarantee the necessary properties over the entire cross-section of the finished article. After this homogenous alloying process has been initiated or fully completed then, for the purpose of additionally improving the mechanical and/or chemical resistance, the completely homogenously alloyed fibrous material is treated with the same or further additional alloying substances. Under the heading of additional alloying substances are included, amongst other things, such additions which are introduced or extracted by carbonising, carbo-nitriding, boronising, siliconising, aluminising, or even oxidising, so that a more or less broad external region of the surface of the basic body is provided with these special properties. Thus, one can provide a material consisting of refined steel fibers homogenously alloyed with molybdenum with a particularly good resistance to combustion by subsequent siliconising, or one can manufacture a body with a high thermal resistance from a material which consists of chrome-nickel steel fibers homogenously alloyed with vanadium by forming a wear-resistant nitride layer thereon.

One particular advantage of the materials made from metal fibers and manufactured in accordance with the present invention resides in the fact that one can produce and prepare them for any special application with the least possible expense. The principle of present invention starts from the assumption that in order to achieve a sufficient corrosion-resistance in the central cores of the fibers only a limited amount of additional metal is necessary (for example, an unalloyed steel is extensively corrosion-resistant after the addition of approximately 14% of chromium), while a higher proportion of additional

metal is necessary on the surface of the fibers in order to induce predetermined physical or chemical effects.

It is possible by means of a suitable process step in the plating and diffusion treatments to increase the concentration of active additional metal at the surface to such a degree that, even after the diffusion out of a part of the metal or metal compound incorporated in the surface, the material has extremely good corrosion-resistance as well as, for example, a good catalytic efficiency.

In many cases, the same metal or the same metallic compound or other inorganic compound is not suitable for achieving both the corrosion-resistance on the one hand and the surface properties on the other hand. By the combination of several plating methods and diffusion treatments one after the other the necessary additional materials can be incorporated in or deposited on the fibers. Thus, one can with metal fibers of unalloyed steel improve their corrosion-resistance initially by a chromising process with subsequent diffusion annealing, and then, by gas-phase plating in a nickel carbonyl atmosphere, deposit nickel thereon in such proportions that after a further diffusion annealing treatment the corrosion-resistance is further improved since the steel has now been converted to a chrome-nickel steel. Due to the relatively slow diffusion velocity of nickel, there remains on the surface of the fibers a layer of pure nickel which is of use for many catalytic processes in chemical technology where the large surface area which is characteristic of the fiber structure is a further advantage.

It is known that in many applications the catalytically effective element must be activated, in other words, a further increase in the surface area must be achieved by some form of surface roughening. Even this process can be carried out by the method of the present invention in a simple manner. If during the final diffusion annealing the protective gas atmosphere changes alternately from reducing to oxidising and back to reducing, or if one introduces mercury vapour as an additional medium towards the end of the diffusion annealing treatment so that the mercury vapour is distilled off again from the amalgam which is formed, then due to the formation of nickel oxide or nickel amalgam, the nickel layer is loosened when it is reduced again, with the result that there is an increase in the active surface area and a rise in the catalytic efficiency. This is an advantage, for example, in the manufacture of very thin fiber-wool electrodes, such as are used in fuel cells.

It is known that the catalytic efficiency is not limited only to metallic materials and their surfaces, but that, on the contrary, oxides and mineral materials also display a considerable catalytic efficiency. The present invention includes the production of oxides and other metallic compounds on the fiber surfaces. If at any time the diffusion annealing treatment is switched over to a definite oxidising atmosphere and this atmosphere is maintained until the end of the treatment, then oxides of the desired degree of oxidation form on the surface of the fibers, the composition of the oxides corresponding to the amount of additional metal introduced and the length of the previous diffusion annealing treatment in the reducing atmosphere.

The present invention is in no way limited to materials of ferrous metal. On the contrary, the method according to the present invention includes the treatment of many fibers and fibrous materials made of non-ferrous metals. If one selects an element such as copper for the basic fiber material and plates this according to any suitable process with chromium and nickel successively, then one can terminate the homogenisation by the diffusion annealing treatment at a time when the fiber cores consist of more or less low-alloyed copper and the surface zones consist of a highly-alloyed copper-nickel-chromium alloy. After the change over of the oven atmosphere from a reducing atmosphere to an oxidising atmosphere towards the end of the diffusion annealing treatment a mixed oxide of copper, chromium and nickel forms on the surface of the fibers, this oxide being particularly well able to withstand the catalytic after-burning of, for example, automobile exhaust gases, and being particularly suitable as the negative electrode in fuel cells. It is an advantage in the use of such a catalyst support manufactured in accordance with the present invention that the metallic core of the fibers has an extremely good thermal conductivity due to the high copper content, and thus the temperature in the catalyst bed need not be unnecessarily high, with the consequent result that the life of the whole unit is essentially increased. Sinmultaneously, the fibers are protected against excessively heavy oxidation due to the relatively favourable catalyst bed temperature. Moreover, the mixed oxide layer which slowly reforms itself ensures that new, unpoisoned, catalytically effective, contact material is always available.

Other properties which can be induced in the material fibers by the method of the present invention are oxidation-resistance, corrosion-resistance, thermal resistance, higher or lower co-efficients of expansion, and resistance to wear. All these properties may be either combined in any desired manner or separated from one another, the latter being of particular advantage when the metal fibers are made up into compound materials with other metallic, ceramic or other materials.

An number of examples of methods in accordance with the invention which represent a small selection from the large number of possibilities will now be set out in the following description. Unless otherwise indicated, the percentages referred to are percentages by weight.

EXAMPLE 1

Metal fibers of a chrome-nickel steel having the following composition:

	Percent
Carbon	0.08
Silicon	0.50
Manganese	1.00
Chromium	18.50
Nickel	9.00
Iron	Balance

are enriched with molybdenum in a process corresponding to gas chromising by the decomposition of molybdenum halides in a current of hydrogen. For homogenisation, a diffusion annealing treatment lasting for about 5 hours at 1400° C. was carried out in a hydrogen atmosphere and subsequently, sintering was performed by heating at about 1350° C.–1400° C. for a further 5 hours. After homogenisation and sintering, the material on average contains approximately 2% molybdenum. After a further reduction treatment in a hydrogen atmosphere at about 1000° C. for about half an hour, the material so obtained has all the properties, particularly the high corrosion-resistance, which are characteristic of known molybdenum-containing, austenitic chrome-nickel steels, which amongst other things are particularly suitable as filters.

EXAMPLE 2

Metal fibers formed from a chrome-nickel alloy as in Example 1 are provided with a molybdenum coating by electrolytic deposition from a solution containing aqueous tervalent molybdenum compounds. Thereafter, a similar homogenisation annealing is carried out at 1400° C. in a hydrogen atmosphere, but in this case the homogenisation and sintering processes are terminated earlier, after a period of treatment of about 3 hours, so that a molybdenum content of approximately 20% remains in the surface zone of the fibers. Finally, the fibers are siliconized in a known manner which results in fibers which are particularly oxidation-resistant and fire-resistant due to the formation of a coating of molybdenum disilicide in the surface zone.

EXAMPLE 3

Metal fibers which in the manner of U.S. Patent No. 3,234,056 are manufactured from a chrome-nickel steel having the composition as given in Example 1 are chromised in a chromising retort wherein ferro-vanadium is introduced in addition to the chromium or ferro-chromium used and chromising is carried out in a hydrogen stream containing hydrogen chloride at 1200° C. for about 30 minutes. Then, the fibers treated in this manner are subjected to a diffusion annealing treatment for about 3 hours at 1300° C. in a hydrogen atmosphere, and subsequently to a sintering treatment for 2 to 3 hours at 1300° C. Thereafter, the treatment is continued at 1300° C. in a hydrogen atmosphere which contains about 10% of ammonia and about 1% of hydrogen chloride for activation. The annealing time as well as the time at which the ammonia is added to the hydrogen can be selected so that 20 to 60% of the fiber cross-section, as desired, is nitrided, such a nitride coating providing good resistance to wear.

EXAMPLE 4

Metal fibers of the same composition as those of Example 1 are chromised and homogenised, but the homogenisation annealing treatment is terminated prematurely. This produces a concentration gradient from the outside to the inside of the metal fibers, the chromium content in the surface region being approximately 30 to 35%, and in the core being only approximately 15 to 20%. After the termination of this homogenisation process and after sintering, the metal fibers are oxidisingly annealed at 1000° C. in a moist hydrogen atmosphere (dew point approximately 0° C.). The oxide layer embedded securely in the surface consists essentially of chromic oxide and has catalytic properties. A porous body of metal fibers treated in the manner is particularly suitable for the catalytic after-burning of exhaust gases from automobiles.

EXAMPLE 5

Metal fibers are treated as described in Example 4 except that the composition differs from that of the fibers in Example 4 in that approximately 1 to 2% of copper is alloyed with the chromium-nickel-iron alloy. By means of this copper addition a mixed oxide of copper and chrominum forms during the oxidising final treatment, and this oxide embedded in the surface layer of the final product, has an improved catalytic efficiency for the afterburning of automobile exhaust gases, as shown in the following test report.

The catalyst materials made according to Examples 4 and 5, in which the catalytically active mixed oxide layer is embedded within the surface layer of the support material consisting of alloyed metal fibers, have the same excellent catalytic effectiveness, e.g. in catalytic waste gas combustion, as catalyst materials known for that purpose, in which the active substance is carried on an inert support of ceramic material.

The catalysts which can be made by the method of the invention have the advantage over the known catalysts that they are not sensitive to impact and remain unchanged and show no friability with intense vibrations operating over long times, such as occur for example in the after-burning of exhaust gases from vehicles.

This was established by comparison tests as described below.

Catalyst products which have been made as described in Examples 4 and 5 were used for waste gas consumption to test their catalytic effect in a combustion tube provided with means for measuring gas volumes and a trace detector device. The CO content of the gas serves as the criterion of effectiveness of the catalyst, since this represents a measure for advantageous waste gas consumption because of its extreme toxicity.

Also, the CO_2 content was determined analytically in the trace detector device. The catalyst material was introduced into the combustion tube at a temperature of 500° to 600° C., since this corresponds to the exhaust gas temperatures in a car in the region of the exhaust manifold.

As a comparison, a commercial catalyst for exhaust gas consumption with a ceramic support was tested in the same device under the same conditions. This was a Degussa catalyst RD–9509 (manufactured by Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, Frankfurt am Main) which has been specially developed for the catalytic after-burning of motor car exhaust gases. The results are summarised in the following Tables 1 and 2.

TABLE I

[Amount supplied (l./min.)]

Air	Gas	Catalyst temp., ° C.	CO vol. percent	CO_2 vol. percent
Degussa catalyst RD 9509:				
20	5	20	0.2	0.3
20	5	550	0.1	2.0
Catalyst made per Ex. 4:				
20	5	20	0.3	0.3
20	5	550	0.1	2.5

TABLE II

[Amount supplied (l./min.)]

Air	Gas	Catalyst temp., ° C.	CO vol. percent	CO_2 vol. percent
Degussa catalyst RD 9509:				
20	5	20	0.2	0.3
20	5	300	0.1	2.0
Catalyst made per Ex. 5:				
20	5	20	0.3	0.3
20	5	300	0.1	2.5

A shaking test at room temperature on a vibrator table produces a weight loss with the commercial catalyst carried on a ceramic support of several grams after 5 hours, whereas the catalyst manufactured according to the invention produces no residue due to friability under the same conditions.

What is claimed is:

1. A body of intertwined metal fibers consisting essentially of iron that extends out to and comprises the exposed surface of each fiber and throughout which a metal selected from the group consisting of chromium, aluminum, nickel, molybdenum, copper and vanadium is substantially uniformly distributed throughout the thickness of each fiber, and a member selected from the group consisting of carbon, nitrogen, boron, silicon, aluminum, nickel and oxygen but different from said metal and substantially uniformly distributed throughout a substantial depth of each fiber from said exposed surface of each fiber inwardly but only partially through the thickness of each fiber.

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